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(54) **Title:** THERMALLY CONDUCTIVE TWO COMPONENT ADHESIVES

(57) **Abstract:** The present invention relates to a process for the production of a thermal conductive polyure- thane adhesive wherein an isocyanate reactive component (A) and an isocyanate component (B) are mixed at an isocyanate index in the range of 80 to 130 to form a reaction mixture and the reaction mixture is allowed to cure, wherein the polyisocyanate reactive component (A) comprises at least one polyol (a1), at least one catalyst (a2), optionally at least one surface modified aluminum tri-hydroxide (Al(OH)3) (a3), and the isocyanate component (B) comprises at least one aliphatic polyisocyanate (b1) and at least one surface modified aluminum tri-hydroxide (Al(OH)3) (b2), wherein the content of the at least one surface modified aluminum tri-hydroxide (a3) is from 70 to 95 % by weight, based on the total weight of the isocyanate reactive compo- nent (A) and the content of the at least one surface modified aluminum tri-hydroxide (b2) is from 70 to 95 % by weight, based on the total weight of the isocyanate component (B) and wherein the at least one polyol (a1) comprises at least one polymeric compound with at least two hydro- gen atoms reactive towards isocyanate (a1a) and the at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least one polyeth- erpolyol (a1a1), obtainable from alkoxylation of a starter molecule selected from aliphatic alco- hols having 2 to 6, preferably 2 to 4 alcohol groups, aliphatic amines, water and mixtures of at least two starter molecules thereof. The present invention further relates to a two component polyurethane composition comprising an isocyanate reactive component (A) and an isocyanate component (B) according to the invention, a thermal conductive adhesive obtained by a process according to the invention and a battery module comprising a module case having a top plate, a bottom plate and sidewalls, wherein an inner space is formed by the top plate, the bottom plate, and the sidewalls; a plurality of battery cells existing in the inner space of the module case; and a resin layer formed by a process according to the present invention, wherein the reaction mix- ture is cured in contact with the plurality of battery cells.

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Thermally conductive two component adhesives

The present invention relates to a process for the production of a thermal conductive polyurethane adhesive wherein an isocyanate reactive component (A) and an isocyanate component (B) are mixed at an isocyanate index in the range of 80 to 130 to form a reaction mixture and the reaction mixture is allowed to cure, wherein the polyisocyanate reactive component (A) comprises at least one polyol (a1), optionally at least one catalyst (a2), at least one surface modified aluminum tri-hydroxide, (a3), and the isocyanate component (B) comprises at least one aliphatic polyisocyanate (b1) and at least one surface modified aluminum tri-hydroxide (b2), wherein the content of the at least one surface modified aluminum tri-hydroxide (a3) is from 70 to 95 % by weight, based on the total weight of the isocyanate reactive component (A) and the content of the at least one surface modified aluminum tri-hydroxide (b2) is from 70 to 95 % by weight, based on the total weight of the isocyanate component (B) and wherein the at least one polyol (a1) comprises at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) and the at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least one polyetherpolyol (a1a1), obtainable from alkoxylation of a starter molecule selected from aliphatic alcohols having 2 to 6, preferably 2 to 4 alcohol groups, aliphatic amines, water and mixtures of at least two starter molecules thereof. The present invention further relates to a two component polyurethane composition comprising an isocyanate reactive component (A) and an isocyanate component (B) according to the invention, a thermal conductive adhesive obtained by a process according to the invention and a battery module comprising a module case having a top plate, a bottom plate and sidewalls, wherein an inner space is formed by the top plate, the bottom plate, and the sidewalls; a plurality of battery cells existing in the inner space of the module case; and a resin layer formed by a process according to the present invention, wherein the reaction mixture is cured in contact with the plurality of battery cells.

If power storage systems are used in medium and large devices, such as cars, battery modules in which a large number of battery cells are electrically connected to each other are used for reasons of capacity and performance, or a battery pack in which several such battery modules are connected. In order to design the battery module or the battery pack, various fasteners, cooling devices and the like are needed, wherein the cooling device is intended to dissipate the heat generated during charging and discharging operations. It is important that the heat is quickly transferred from the individual battery cells to the cooling device. This is usually done by attaching the battery cells to the cooling device with the help of a thermally conductive adhesive. In particular, when the battery module is used in a car or the like, it is also exposed to external shocks, such as shocks or vibrations, as well as high temperature differences, for example from less than 0 ° C to more than 100 ° C and must ensure excellent durability under these

conditions. In addition, the thermally conductive adhesive has to show a high thermal conductivity, a low electric conductivity, a low flammability and a low viscosity during application.

As described by Frauenhofer et al. (Frauenhofer, M., Gormanns, M., Simon, M., Rütters, M., & Fricke, H. Optimized heat dissipation of energy storage systems. adhesion ADHESIVES+ SEALANTS, 17, 12-17 (2020)), for the assembly of the battery, the thermally conductive adhesive is applied on the cooling plate. Afterwards, the battery cells / modules are inserted into the adhesive. During this movement, the adhesive is effectively pressed against the surface to be wetted, and great care must be taken not to damage the pressure-sensitive battery cells. Therefore, the flow properties and the resulting pressing forces of the adhesive have to be adjusted to prevent any damage to the battery and the cooling plate. This is even more challenging since the adhesives have a high filler load. It is aimed to formulate adhesives which can be easily compressed also to ensure a good wetting, pumpability, and put less strain on the application equipment. In this regard, the squeeze flow (SQF) is a well-known topic in bonding technology, which occurs when joining substrates. The pressure in the adhesive can increase unexpectedly when squeezing small gap heights. Thus, low SQF pressure forces are desired. The SQF is well accepted to simulate the forces when battery cells / modules are pressed into the adhesive on the cooling plate.

Thermal conductive adhesives are disclosed for example in EP 3670558, EP 3835332, WO 2019120924 and WO2022056096. The solutions according to the state of the art often are a tradeoff between thermal conductivity and mechanical properties as well as flammability, electric conductivity and viscosity during application. Reason for this is that on the one hand a high content of the thermal conductive filler material generally results in good thermal conductivity, a low flammability and a low electric conductivity but reduces mechanical properties and makes it more difficult to process due to high viscosity of the reaction mixture.

US20220213249 discloses thermal conductive materials using a combination of fillers wherein the filler has a broad particle size distribution and the thermal conductive material can be obtained by reaction of a phenol blocked isocyanate and a carbamate reactive compound such as an amine. In the examples section in a comparative example HDI polyether prepolymers, aluminum trihydroxide, a methyl ester of an unsaturated fatty acid and silane surface modifier are mixed to produce an isocyanate component. In contrast to the phenol blocked isocyanate, the isocyanate component obtained from the isocyanate prepolymer has poor shelf stability and solidifies after 3 days.

In example 1 of CN113999643, a reaction is disclosed involving a polyol obtained through the propoxylation of bisphenol A, with a molecular weight ranging from 300 to 800 g/mol, castor oil,

and a H12MDI-based prepolymer. This reaction takes place in the presence of silane-treated aluminum hydroxide. However, the resulting mixture has a very high viscosity, making it difficult to work with, especially at a filler content above 70 % by weight.

It has been object of the present invention to increase thermal conductivity and flame retardancy while having a high isolating resistance (low electric conductivity) of a thermal conductive adhesive to avoid an electronical short circuit and at the same time at least maintaining mechanical properties as shear strength and adhesive properties and maintaining or lowering viscosity of the reaction mixture, especially maintaining or lowering squeeze flow. It has been especially object of the present invention to achieve these goals by using standard raw materials with good availability and low price.

This object has been solved by a process for the production of a thermal conductive polyurethane adhesive wherein an isocyanate reactive component (A) and an isocyanate component (B) are mixed at an isocyanate index in the range of 80 to 130 to form a reaction mixture and the reaction mixture is allowed to cure, wherein the polyisocyanate reactive component (A) comprises at least one polyol (a1), optionally at least one catalyst (a2), at least one surface modified aluminum tri-hydroxide, (a3), and the isocyanate component (B) comprises at least one aliphatic polyisocyanate (b1) and at least one surface modified aluminum tri-hydroxide (b2), wherein the content of the at least one surface modified aluminum tri-hydroxide (a3) is from 70 to 95 % by weight, based on the total weight of the isocyanate reactive component (A) and the content of the at least one surface modified aluminum tri-hydroxide (b2) is from 70 to 95 % by weight, based on the total weight of the isocyanate component (B) and wherein the at least one polyol (a1) comprises at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) and the at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least one polyetherpolyol (a1a1), obtainable from alkoxylation of a starter molecule selected from aliphatic alcohols having 2 to 6, preferably 2 to 4 alcohol groups, aliphatic amines, water and mixtures of at least two starter molecules thereof.

The present invention further relates to a two component polyurethane composition comprising an isocyanate reactive component (A) and an isocyanate component (B) according to the invention, a thermal conductive adhesive obtained by a process according to the invention and a battery module comprising a module case having a top plate, a bottom plate and sidewalls, wherein an inner space is formed by the top plate, the bottom plate, and the sidewalls; a plurality of battery cells existing in the inner space of the module case; and a resin layer formed by a process according to the present invention, wherein the reaction mixture is cured in contact with the plurality of battery cells.

In a preferred embodiment the cured adhesive according to the present invention has a thermal conductivity of at least 0.8 W/mK, preferably 1.0 to 3.0 W/mK, determined according to ISO 22007-2 at 25°C, a lap shear strength of preferably at least 0.5 MPa, more preferred at least 1.0 MPa and especially preferred > 1.5 MPa, determined according to the method as described in the Examples section, and a flame retardance of V0 tested according to UL-94. The reaction mixture according to the present invention preferably has a squeeze flow <300 N, preferably <200 N determined according to the method as described in the Examples section

The isocyanate reactive component (A) comprises at least one polyol (a1), optionally at least one catalyst (a2), at least one surface modified aluminum tri-hydroxide, (a3).

It is possible to use, as polyols (a1), any of the known compounds having at least two hydrogen atoms reactive toward isocyanates, for example those with functionality from 2 to 8 and with number-average molar mass from 62 to 15 000 g/mol. Polyols preferably comprise polymeric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a). Polymeric compounds with at least two hydrogen atoms reactive towards isocyanate usually have a functionality from 2 to 8 and number-average molar mass from 200 to 15 000 g/mol. By way of example it is possible to use compounds selected from the group of the polyether polyols (a1a1), fatty acid based polyols (a1a2), polybutadiene based polyols (a1a3), polyester polyols (a1a4), and mixtures thereof as polymeric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a).

Polyetherpolyols (a1a1) are by way of example produced from epoxides; for example, propylene oxide and/or ethylene oxide, or from tetrahydrofuran, with starter compounds exhibiting hydrogen-activity containing 1 to 8, preferably 2 to 6 and more preferably 2 to 4 reactive hydrogen atoms bound, or a starter molecule mixture which contains 1.5 to 8, preferably 1.8 to 6 and more preferably 1.9 to 3.5 reactive hydrogen atoms bound in the presence of catalysts. As starter molecules for example aliphatic alcohols, phenols, amines, carboxylic acids, water, or compounds based on natural substances, for example sucrose, sorbitol or mannitol can be applied. Preferred starter molecules are aliphatic alcohols having 2 to 6, preferably 2 to 4 alcohol groups, aliphatic amines and water. In a preferred embodiment Polyetherols (a1a1) comprise molecules produced from starter molecules selected from the group, consisting of aliphatic alcohols having 2 to 6, preferably 2 to 4 alcohol groups, aliphatic amines and water, more preferred from the group consisting of aliphatic alcohols having 2 to 4 alcohol groups and water. In a preferred embodiment, polyetherols (a1a1) consist of molecules produced from starter molecules selected from the group, consisting of aliphatic alcohols having 2 to 6, preferably 2 to 4 alcohol groups, aliphatic amines and water. According to the present invention aliphatic alcohols are not only compounds where the alcohol group is bound to an aliphatic carbon atom but a

compound free of aromatic structures. If mixtures of starter molecules with different functionalities are used, fractional functionalities can be obtained. Influences on the functionality, for example through side reactions, are not considered in the nominal functionality. Examples for suitable catalysts are basic catalysts and double-metal cyanide catalysts, as described by way of example in PCT/EP2005/010124, EP 90444, or WO 05/090440.

Polyesterpolyols are by way of example produced from aliphatic or aromatic dicarboxylic acids and polyhydric alcohols, polythioether polyols, polyesteramides, hydroxylated polyacetals, and/or hydroxylated aliphatic polycarbonates, preferably in the presence of an esterification catalyst. Other possible polyols are mentioned by way of example in " Polyurethane Handbook, 2nd edition 1993, editor Guether Oertel, Carl Hanser Verlag Munich, Chapter chapter 3.1.

In a particularly preferred embodiment of the present invention, component (a1a) comprises polyetherols (a1a1), and more preferably comprises no polyesterpolyols (a1a3). In an especially preferred embodiment component (a1a) consists of polyetherols (a1a1).

In a preferred embodiment, the polymeric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least one polyether polyol (a1a1) obtainable by reacting at least one starter molecule, selected from the group consisting of aliphatic alcohols having 2 to 6, preferably 2 to 4 and more preferred 2 to 3 alcohol groups, aliphatic amines, water and mixtures comprising a combination of at least two thereof, with alkylene oxides. In one preferred embodiment the polyetherpolyol (a1a1) comprises a polyetherpolyol (a1a1a) obtainable by reacting at least one starter molecule having a functionality of 2, selected from aliphatic alcohols, water and a combination of at least one aliphatic alcohol and water, with alkylene oxide wherein the alkylene oxides comprise preferably at least 70 mol-%, more preferred at least 85 mol-% and especially preferred 100 mol.-% propylene oxide, and having a hydroxyl value of preferably 50 to 500 mg KOH/g, more preferred 100 to 400 mg KOH/g and especially preferred 200 to 300 mg KOH/g. In a more preferred embodiment, the polyetherpolyol (a1a1) comprises in addition to the polyetherpolyol (a1a1a) a polyetherpolyol (a1a1b) obtainable by reacting at least one starter molecule having a functionality of 3, preferably at least one aliphatic alcohol having a functionality of 3, with alkylene oxide wherein the alkylene oxides comprise preferably at least 50 mol-%, more preferred at least 70 mol-% and especially at least 80 mol-% propylene oxide, and having a hydroxyl value of preferably 20 to 200 mg KOH/g, more preferred 25 to 100 mg KOH/g and especially preferred 30 to 50 mg KOH/g. Preferably polyetherols (a1a1a) and ((a1a1b) are used in a mass ratio of 5:1 to 1:3, more preferred 3:1 to 1:2 and especially preferred 2:1 to 1:1.5. In a preferred embodiment, polymeric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least 80 % by weight, more preferred by at least 90 % by weight and especially preferred by 100 % by weight, each based on the total amount of poly-

meric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a), of polyetherols, selected from the group, consisting of polyetherpolyols (a1a1) and polyetherpolyols (a1a2) and mixtures thereof.

In a further preferred embodiment of the invention the polymeric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least one fatty acid-based polyol (a1a2). Suitable fatty acid-based polyols are preferably those having a hydroxyl value of greater than 50 to less than 500 mg KOH / g, more preferably 100 to 300 mg KOH / g and in particular 100 to 200 mg KOH / g, and a functionality of at least 2. The OH functionality of the fatty acid-based polyols is preferably in the range of 2 to 3. Particularly preferably, the OH functionality of the fatty acid-based polyols is 2.3 to 3 and most preferably 2.6 to 3.

A faty acid-based polyol (a1a2) may be a fat, oil, fatty acid or fatty acid derivative or obtained from the aforementioned compounds by physical or chemical modification. Fat-based polyols according to the above definition are known in the art per se or can be obtained by methods known per se.

Suitable fat-based polyol are, for example, vegetable oils or derivatives thereof. As a fat-based polyol can also be used generally known fatty acids, preferably natural fatty acids, particularly preferably vegetable fatty acids, in particular unsaturated vegetable fatty acids, and derivatives thereof such as the esters with mono-, di- and / or trialcohols, provided that the further properties in terms of molecular weight and OH functionality are met.

As fat-based polyol, however, for example, ring-opened epoxidized or oxidized fatty acid compounds and / or adducts of fatty acid compounds and alkylene oxides can be used. Hydroxylated fatty acids and / or hydroxylated fatty acid derivatives are preferred, which are obtainable by the aforementioned methods.

The adducts of OH-functional fat-based compounds, for example castor oil or hydroxylated vegetable oils, and alkylene oxides can be prepared by generally known alkoxylation of the compounds with, for example, ethylene oxide, propylene oxide and / or butylene oxide at temperatures of 80 to 130 °C and pressures of 0.1 to 1 MPa, optionally in the presence of customary catalysts such as alkali metal hydroxides or alkali metal alcoholates.

As fat-based polyol, hydroxylated fatty acid compounds based on rapeseed oil, soybean oil, rapeseed oil, olive oil and / or sunflower oil and / or those based on oleic and / or linoleic acid can also be used. As fat-based polyols, polyols based on hydroxylated soybean oil are particularly suitable. Also preferred are triglycerides of fatty acids having an OH functionality of 2 to 3.

Particularly preferred are the triglyceride of ricinoleic acid, optionally in a mixture with triglycerides containing other natural fatty acids, for example linoleic acid and / or palmitic acid.

Particularly preferably, however, a vegetable oil without chemical modification is used as fat-based polyol. Particularly preferred is castor oil or the alkoxylation product of castor oil, in particular castor oil.

In a particularly preferred embodiment, polyol (a1a) comprises at least 70 % by weight of polypropylene glycol, more preferably 85 to 100 % polyetherpolyol and especially preferred the polyol consists of polypropylene glycol.

Besides polymeric compounds having at least two hydrogen atoms reactive towards isocyanate, the polyol (a1) preferably comprises chain extenders (a1b) and/or crosslinking agents (a1c).

Chain extenders (a1b) used here can be compounds of molar mass less than 200 g/mol, preferably less than 150 g/mol and more preferred 62 to 150 g/mol, which have two groups reactive toward isocyanates as for example -SH or NH_2-groups and preferably OH-groups. According to the present invention, if chain extenders (a1b) are used, they are preferably used in an amount of 0.1 to 20 wt.-%, more preferred 1-10 and especially preferred 1 to 5 wt.-%, each based on the total weight of components (a1). As chain extenders (a1c), use may be made of the chain extenders known in the production of polyurethanes. These are preferably low-molecular-weight compounds having two functional groups reactive toward isocyanates, for example monoethylene glycol, diethylene glycol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,3-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, tetraethylene glycol, dipropylene glycol, cyclohexane diol and aliphatic or aromatic amine based chain extenders as aliphatic or aromatic diamines like ethylene diamine, triethylene diamine and/or diethyl toluene diamine (DETDA). In a preferred embodiment the chain extender is selected from the group, consisting of monoethylene glycol, diethylene glycol, dipropylene glycol, 1,2-propane diol, 1,3 propane diol, 1,4 butane diol, 1,6 hexane diol or mixtures thereof. Other possible low-molecular-weight chain extenders are mentioned by way of example in "Polyurethane Handbook", Carl Hanser Verlag, 2nd edition 1994, chapter 3.2 and 3.3.2.

In addition to chain extenders (a1b) or instead of chain extenders (a1b) crosslinking agents (a1c) may be added to the mixture. As crosslinking agents used in the invention are compounds of molar mass less than 200 g/mol preferably less than 150 g/mol which have at least three groups reactive toward isocyanates. Examples for crosslinking agents are glycerine, trimethylolpropane, pentaerythritol and triethanolamine, in a preferred embodiment glycerine is used as crosslinking agent. Other possible low-molecular-weight crosslinking agents are mentioned

by way of example in "Polyurethane Handbook", Carl Hanser Verlag, 2nd edition 1994, chapter 3.2 and 3.3.2. According to the present invention, if chain extenders (a1b) and /or crosslinking agents (a1c) are used, they are used in an amount of 0.1 to 10 wt.-%, preferably 0.5-10 and especially preferred ably 1 to 5 wt.-%, each based on the total weight of components (a1).

Catalysts (a2) greatly accelerate the reaction of the polyols (a1) with the polyisocyanates (b1). As catalysts (a2) any catalyst known in the field of polyurethane catalysts may be used. These comprise basic amine catalysts and metal-based catalysts. In a preferred embodiment the catalysts comprise incorporable amine catalysts. In a further preferred embodiment the catalysts comprise delayed action catalysts. Delayed action catalysts are well known in the art and provide a long open time of the reaction mixture at room temperature and a fast curing at elevated temperatures. Examples for delayed action catalysts are metal based catalysts.

Incorporable amine catalysts have at least one, preferably from 1 to 8, and particularly preferably from 1 to 2, groups reactive toward isocyanates, for example primary amine groups, secondary amine groups, hydroxy groups, amides, or urea groups, preferably primary amine groups, secondary amine groups, or hydroxy groups. Incorporable amine catalysts are used mostly for the production of low-emission polyurethanes which are in particular used in the automobile-interior sector. These catalysts are known and are described by way of example in EP1888664. These comprise compounds which preferably comprise, alongside the group(s) reactive toward isocyanates, one or more tertiary amino groups. It is preferable that at least one tertiary amino groups of the incorporable catalysts bear at least two aliphatic hydrocarbon moieties, preferably having from 1 to 10 carbon atoms per moiety, particularly preferably having from 1 to 6 carbon atoms per moiety. It is particularly preferable that the tertiary amino groups bear two moieties selected mutually independently from methyl and ethyl moiety, and bear another organic moiety.

Suitable metal based catalysts comprise organometallic compounds, preferably organotin compounds, such as tin(II) salts of organic carboxylic acids, e.g. tin(II) acetate, tin(II) octoate, tin(II) ethylhexoate, and tin(II) laurate, and the dialkyltin(IV) salts of organic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate, and dioctyltin diacetate, and also bismuth carboxylates, such as bismuth(III) neodecanoate, bismuth 2-ethylhexanoate, and bismuth octanoate, or a mixture thereof. The organometallic compounds can be used alone or in combination with strongly basic amines. A preferred metal based catalyst is dioctyltin diacetate. In a particularly preferred embodiment, catalysts (a2) used comprise or consist of at least one metal based catalysts.

Catalysts (a2) can by way of example be used at a concentration of from 0.001 to 5% by weight, in particular from 0.05 to 2% by weight, as catalyst or, respectively, catalyst combination, based on the weight of component (a1).

The at least one surface modified aluminum tri-hydroxide (a3) preferably is an alkyl-silane treated aluminium trihydroxide. Such surface modified aluminum tri-hydroxide (a3) are known and for example disclosed in WO9932554. Preferably the surface modification can be obtained by reacting a silicon compound and aluminum trihydroxide (also abbreviated as “ATH”). Preferably the silane content of the surface modified ATH (a3) is in the range of 0.01 to 0.5 parts by weight, more preferred 0.05 to 0.4 parts by weight, based on the total weight of the surface modified ATH (a3). In a preferred embodiment the silane molecule of the surface modified ATH does not comprise isocyanate reactive groups, i.e. hydroxyl groups are coordinated and not available for a reaction with isocyanate groups.

Preferably ATH is a coarse ATH. The size distribution of the surface modified ATH (a3) may be monomodal, bimodal or multimodal. In a preferred embodiment the size distribution of the ATH (a3) is bimodal or trimodal to allow a dense packing of the filler in the binder matrix. Preferably the surface modified ATH (a3) has a particle size D90 of preferably 50 to 200 µm, more preferable 60 to 150 µm and especially preferred 80 to 120 µm. In an especially preferred embodiment the surface modified ATH (a3) has at least a bimodal size distribution of 30 to 70 wt.-% of a surface modified ATH having a size of 1-20 µm and 30 to 70 wt.-% of a surface modified ATH having a D90 size of 40 bis 200 µm, each based on the total weight of the surface modified ATH (a3).

The term “particles” in connection with thermal conductive filler (a3) of the invention relates to ATH having a particular particle size DX, based on a particle size distribution where X % of the particles have a diameter less than the DX, value. The D50 particle size is the median value of the particle size distribution. According to the present invention, the D90 value relates to the numerical distribution, where 90 % of the total number of particles has a smaller diameter. Particle sizes, such as D10, D50 and D90 values and particle size distributions of powders and powdery materials can be measured, using a wide variety of measurement methods known per se to the person skilled in the art, for example via sieve analyses according to DIN 66165-2:2016-08, sedimentation or light scattering, e.g. laser diffraction in accordance with DIN ISO 13321:2004-10. Particle size can be measured by dispersing the powder in a suitable solvent and to perform laser diffraction in accordance with ISO 13320:2009 or dynamic light scattering in accordance with ISO 22412:2008.

The particle size distribution can be reported as intensity distribution, volume distribution, surface distribution or numerical distribution. In the present case, given particle sizes of the fillers are determined by dispersing the powder in 2-isopropanol using laser diffraction in accordance with ISO 13320:2009.

Preferably to the isocyanate reactive component (A) no blowing agent as for example water is added. In a more preferred embodiment the isocyanate reactive component (A) comprises a water scavenger. Generally, all water scavengers known in the field of polyurethanes are suitable. Examples for water scavengers are zeolites, especially in form of zeolithe pastes. One example is the zeolite paste Baylith® L-Paste 3A. Water scavengers are generally used in an amount of 1 to 10 % by weight, preferably 3 to 8 % by weight, based on the total weight of the polyol (a1).

In addition, the isocyanate reactive component (a) and/or the isocyanate component (b) may comprise flame retardants. Preferably the flame retardants are liquid at 25 °C. An example of a liquid flame retardant is TCPP. If flame retardants are present, thex may be present in any amount, typically in amounts from preferably 2 to 30 % by weight, more preferred 3 to 20 % by weight, bease on the total weight of components (a) and(b).

As aliphatic polyisocyanate (b1), all commonly used aliphatic isocyanates can be used. These may be unmodified or modified, wherein by a modification, the reaction of these isocyanates to isocyanate-terminated polyisocyanate prepolymer and / or the reaction to biuret, allophanat, uretdione, and / or isocyanurate-containing isocyanates, preferably allophanate and / or isocyanurate containing isocyanates as well as their prepolymers is understood. These isocyanates can be used individually or in mixtures. Preferably, the aliphatic isocyanate contains less than 15 wt .-%, particularly preferably less than 7.5 wt .-% and in particular less than 1 wt .-%, based on the total weight of the aliphatic isocyanate, of monomeric aliphatic isocyanate. The remaining amount of aliphatic isocyanate is present as modified aliphatic isocyanate. Examples of unmodified aliphatic isocyanates which can be used as basis for modification are tetramethylene diisocyanate, hexamethylene diisocyanate (HDI) isophorone diisocyanate (IPDI) or 4,4´-diisocyanatodicyclohexylmethn (H12MDI). Preferably, modified isocyanates based on HDI are used, for example allophanate modified hexamethylene diisocyanate, carbodiimide modified hexamethylene diisocyanate and / or isocyanurate modified hexamethylene diisocyanate. In particular, allophanate and simultaneously isocyanurate-modified hexamethylene diisocyanate is used as isocyanate (b1).

In addition to the aliphatic isocyanates (b1) are preferably less than 20 wt .-%, especially preferably less than 9 wt.-%, more preferred less than 5 wt. -% and in particular no other isocyanates, such as aromatic isocyanates used.

The at least one surface modified aluminum tri-hydroxide (b2) preferably is an alkyl-silane treated aluminium trihydroxide. Such surface modified aluminum tri-hydroxide (b2) are known and for example disclosed in WO9932554. As surface modified aluminum tri-hydroxide (b2) the same material as disclosed under (a3) may be used. In a preferred embodiment, the surface modified aluminum tri-hydroxide (b2) is identical to the surface modified ATH (a3).

In addition, the isocyanate component (B) preferably comprises water scavenger.

Preferably, the isocyanate reactive component (A) and an isocyanate component (B) comprise less than 20 % by weight of unmodified filler and more preferably is free of unmodified filler. Unmodified filler might be unmodified ATH or other filler as for example unmodified aluminium oxide.

Isocyanate reactive component (A) and isocyanate component (B) are preferably mixed at temperatures of 5 to 60 °C, more preferred 10 to 50 °C and especially preferred 15 to 35 °C at an isocyanate index in the range of 80 to 130 , preferably 90 to 120, more preferred 95 to 115 and especially preferred 100 to 110 to form a reaction mixture and the reaction mixture is allowed to cure to form the thermal conductive polyurethane adhesive.

The thermal conductive adhesive is preferably used to attach the battery cells to the cooling device in a battery module. Therefore, a further aspect of the present invention is a battery module comprising a module case having a top plate, a bottom plate and sidewalls, wherein an inner space is formed by the top plate, the bottom plate, and the sidewalls; a plurality of battery cells existing in the inner space of the module case; and a resin layer formed by a process according to the invention, wherein the reaction mixture is cured in contact with the plurality of battery cells.

An additional aspect of the present invention is a two component polyurethane adhesive composition comprising an isocyanate reactive component (A) and an isocyanate component (B), each as defined in any of the claims 1 to 9.

The thermal adhesive according to the invention has a high thermal conductivity, a good flame retardancy and low electrical conductivity as well as good mechanical properties such as shear strength, adhesion, elasticity and a low and temperature independent modulus in the range from

-20 °C to 80 °C with simultaneous good processability due to low abrasiveness, low viscosity and a low squeeze flow. In addition, even at the low viscosity, the polyol component (A) according to the invention and the polyisocyanate component (B) according to the invention show a long shelf life and low sedimentation tendency. These advantages are achieved by using cost-effective standard raw materials.

The invention will be illustrated below with reference to examples.

Examples:

Raw materials:

Polyol 1:	polypropylene glycol obtained by propoxylation of propylene oxide having an OH-Number of 250 mgKOH/g.
Polyol 2:	polyalkylene glycol obtained by alkoxylation of glycerine having an OH-Number of 35 mgKOH/g and a propylene oxide content of 80 to 90 % by weight based on the total weight of the alkylene oxide.
Polyol 3:	Bisphenol-A initiated polypropylene oxide, having an OH-number of 249 mg KOH/g.
Polyol 4:	castor oil based polyether/-ester polyol having an OH-number of 170 mgKOH/g.
Additive 1:	silane-based adhesion promoter
Plasticizer:	non-reactive diluent which is a natural-oil based fatty acid polyol.
Filler 1:	AEROSIL® R 202 is a fumed silica after-treated with polydimethylsiloxane from Evonik.
TC filler 1:	alkyl-silane treated aluminium trihydroxide having a particle size D90 of about 100 µm
TC filler 2:	spherical aluminium oxide filler having a particle size D90 of about 20 µm, sold under the trademark Bestry BAK® 10
TC filler 3:	spherical aluminium oxide filler having a particle size D90 of about 130 µm, sold under the trademark Bestry BAK® 90
TC filler 4:	aluminium trihydroxide without surface modification having a particle size D90 of about 100 µm and a comparable size distribution to the TC filler 1
Chain extender:	1,2-propylene glycol
Cross-linker:	glycerine (97.7%)
Drying agent 1:	alkali aluminosilicate
Drying agent 2:	water scavenger for isocyanates (Luna PTSI)
Catalyst 1:	dioctyltin mercaptide catalyst
Iso 1:	isocyanurate modified hexamethylene diisocyanate, NCO content 22 wt.-%
Iso 2:	allophanate modified hexamethylene diisocyanate, NCO content 20 wt.-%

Iso 3: polymeric MDI with an average functionality of 2.7 and an NCO-value of 31.5

Iso 4: diphenylmethane diisocyanate with an NCO-value of 33.5

Iso 5: polyether-MDI prepolymer, NCO content 11 wt.-%, functionality: 2

Iso 6: polyether-MDI prepolymer, NCO content 20 wt.-%, functionality: 2

Iso 7: polyether-HDI prepolymer, NCO content 13,0%, obtained from reaction of isocyanate 2 and polypropylene glycol

Methods:

Squeeze flow:

To measure the SQF, a rotationally symmetrical cylinder with diameter D is mounted such to be axially movable. The gap between the underside of the cylinder and a plane surface is filled with the thermally conductive adhesive. In tests where the cylinder has been lowered at a linear speed v, the force F(h) occurring during the axial movement of the cylinder and the height of the gap h(t) are simultaneously measured. The movement of the cylinder causes a radial squeezing of the adhesive out of the gap. The maximum hydrostatic pressure in the adhesive occurs on the rotational axis (r=0). The exact parallelism of the cylinder and the plane surface are decisive for the measuring quality, as are the speed control and the very precise measurement of the gap height h(t).

For the patent experiments, the following measurement setup was used:

- Test speed: v = 1 mm/s
- Diameter D of the cylinder = 40 mm; diameter of the plane surface = 60 mm
- Initial gap of 5 mm was lowered to a final gap of 0.3 mm
- The SQF force was evaluated at a gap of 0.5 mm
- Apparatus: Table-top testing machine Zwicki Z2.5 (ZwickRoell) with PC and measurement and control software (testXpert III and testControl II).

The measurement of the SQF took place at room temperature immediately after mixing the A and B components or after an incubation time of 10 min. Some measurements were repeated after aging of the A and B components after one week.

Lap shear strength:

For lap shear strength measurements, the samples are prepared by forming a layer of the adhesive between two 100 mm X 25 mm isopropanol cleaned Al-specimen (5005A from Rocholl for Table 1 with 2 mm thickness, AA6060 with Gardobond 4707 treatment for Table 2 with 1 mm thickness), that overlap to form a bond area of about 14 mm X 25 mm. The adhesive layer is 1.0 mm thick. The adhesive is applied, and the test samples were assembled at room temperature and cured for 16 h at 60 °C (Table 1) or for 7 d at room temperature, followed by 1 h at 85 °C

(Table 2). The measurement was performed at room temperature with a pulling speed of 5 mm/min and the resulting lab shear strength is recorded in MPa.

Storage modulus G':

Temperature dependent viscoelastic properties of the samples were characterized via dynamic mechanical thermal analysis (DMTA) in accordance with the standard DIN EN ISO 6721-2 by using the ARES-G2 from TA Instruments. Used software was TRIOS from TA Instruments. Rectangular samples with the dimensions of 50 x 10 mm² (length x width), thickness between 3.5 and 4.5 mm, were prepared from test-plates and tested.

The dynamic mechanical loading was applied under torsion mode. The viscoelastic properties were determined at the linear viscoelastic region. The temperature was varied from - 80 to 120 °C with the heating rate corresponding to 2 K/min. The frequency was fixed and set to 1 Hz. Finally, the storage, loss modulus and the tan delta of the samples as a function of temperature at 1 Hz were evaluated.

According to the formulations as given in Table 1

The composition composed of component A and the component B are shown in Table 1. Polyol and isocyanate component were obtained as follows:

Polyol components: in a speed blender cup all liquid components and on top of them the fillers are added (in total 500 g). These ingredients are then stirred with a speed mixer for 1 min at 800 rpm and another minute at 1600 rpm. Then the mixing is continued for 10 minutes under vacuum at 800 rpm.

Isocyanate component: in a speed blender cup all liquid components and on top of them the fillers are added (in total 200 g). These ingredients are then stirred with a speed mixer for 1 min at 800 rpm and another minute at 1600 rpm. Then the mixing is continued for 10 minutes under vacuum at 800 rpm.

To ensure comparability, the mixtures of these components were adjusted to an index of 105 and were mixed under the same conditions. All workable mixtures showed a lap shear strength of >0.6 MPa (Ex. 1 to 3 and Ref. Ex. 1 to 5 and 15 to 18). Further, all ATH-based workable mixtures fulfill the V0 classification according to UL-94.

The influence of different isocyanates and TC fillers on the workability, especially the squeeze flow (SQF) was investigated. Here, a low SQF which stays constant over 10 minutes is preferred. This might be important, if there is a delay in assembling the battery module in the process street. An indication of the storage stability is given when both components (A and B) are stored for one week at RT and nearly the same SQF values are obtained by repeating the SQF measurements direct after mixing and after mixing plus an incubation time of 10 minutes at room temperature (RT). Interestingly, only in case of using inventive mixtures of aliphatic isocy-

anates in combination with alkyl-silane modified aluminium trihydroxide, the SQF is low, and the value remains almost constant after 10 minute and after aging.

In reference examples 6-14 (Ref. Ex. 6-14 not shown in Table 1), the silane modified ATH in the examples: Ex. 1 to 3 and Ref. Ex. 1 to 5 was substituted (1:1) against an ATH filler without surface modification. Both ATH types have comparable particle size distributions. The resulting mixtures were unworkable crumbly pastes. Therefore, the SQF is too high and was not measurable. This indicates the importance of surface modification of the ATH filler according to the invention.

Table 1: Composition of component A and the component B of the examples (x.) and reference examples (Ref. Ex.) and the resulting SQF-values.

	Ex. 1	**Ex. 2**	**Ref. Ex. 1**	**Ref. Ex. 2**	**Ref. Ex. 3**	**Ref. Ex. 4**	**Ex. 3**	**Ref. Ex. 5**	**Ref. Ex. 15**	**Ref. Ex. 16**	**Ref. Ex. 17**	**Ref. Ex. 18**
Component A												
Drying agent 1	1	1	1	1	1	1	1	1	1	1	1	1
Catalyst 1	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
TC filler 1	81	81	81	81	81	81	81	81				
TC filler 2									23.1	23.1	37.9	37.9
TC filler 3									57.9	57.9	95.1	95.1
Chain extender	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Cross-linker	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Polyol 1	17.085	17.085	17.085	17.085	17.085	17.085	17.085	17.085	17.085	17.085	17.085	17.085
Component B												
Drying agent 2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TC filler 1	81	81	81	81	81	81	81	81				
TC filler 2									23.1	23.1	37.9	37.9
TC filler 3									57.9	57.9	95.1	95.1
Iso 1		18.5					9.25					
Iso 2	18.5						9.25		18.5		18.5	
Iso 3			18.5							18.5		18.5
Iso 4				18.5		9						
Iso 5					18.5	9.5						
Iso 6								18.5				
SQF (AB) [N]	30	67	112	34	227	98	47	185	20	30	31	120
SQF (AB) 10 min [N]	28	70	253	1417	677	736	46	1225	13	n.m.	41	n.m.
After 1 week:												
SQF (AB) [N]	33	89	146	46	433	152	50	399	10	23	33	95
SQF (AB) 10 min [N]	32	94	1459	733	950	780	52	1591	16	n.m.	55	n.m.
Flammability	V0	V0	V0	V0	V0	V0	V0	V0	Not V0	Not V0	Not V0	Not V0

Abbreviations: n.m. = not measurable; X = not measured; Not V0 means that the V0-classification was not fulfilled.

Inventive example 4 and 5 in Table 2 show a low and less temperature dependent modulus especially in the range from -20 °C to 80 °C with Iso 2, but also in the range of 20 °C to 80 °C with Iso 1, while in comparative example 19 where an aromatic isocyanate is used instead of an aliphatic isocyanate, the modulus is not constant at all. Especially in the automotive sector, where temperatures in the range of -20 °C and 80 °C are common, a low and less temperature dependent modulus is desirable. It can also be desirable to have a high lap shear strength. Inventive example 6 shows an increased lap shear strength compared to inventive example 4, and the modulus has a low temperature dependency between 20 °C and 80 °C, but not between -20 °C and 80 °C anymore. In addition, the absolute values increased. Inventive examples 7 and 8 show that the combination of a difunctional polypropylene glycol and a trifunctional alkylene glycol leads to increased lap shear strength compared to example 4 but can keep the absolute modulus values and the temperature dependency low. Iso 7 was used to keep the volume mixing ratio constant. With an increased amount of polyol 2 the modulus can even be further decreased while keeping the lap shear strength constant.

Table 2: Composition of component A and the component B of the examples (Ex.) and reference examples (Ref. Ex.).

	Ex. 4	Ex. 5	Ref. Ex. 19	Ex. 6	Ex. 7	Ex. 8	Ref. Ex 20	Ref. Ex 21	Ref. Ex 22
Component A									
Drying agent 1	1	1	1	1	1	1	1	1	1
Catalyst 1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TC filler 1	84	84	84	85.5	84	83	84	84	84
Cross-linker				0.5					
Polyol 1	12	12	12	9.6	9	7			
Polyol 2	2.45	2.45	2.45	2.85	5.45	8.45	2.45		
Polyol 3							12	12	4.45
Polyol 4								2.45	10
Additive 1	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Component B									
Drying agent 2	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TC filler 1	82.5	82.5	82.5	81	82.5	81.5	82.5	82.5	82.5
Filler 1	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Plasticizer	3.5	3.5	3.5		3.5	3.5	3.5	3.5	3.5
Iso 1		12.8		9.8					
Iso 2	12.8			8	5.8		12.8	12.8	12.8
Iso 4			12.8						
Iso 7					7	13			

SQF (AB) [N]	78	-	-	-	-	-	>800	>800	>800
Lap shear strength	1.38	-	-	2.61	1.56	1.55			
G' at -20 °C	73.3	654.5	439.5	1811.3	56.6	41.8	825.3	2642,0	2472,5
G' at +20 °C	18.9	68.0	12.8	47.9	19.8	14.2	26.6	47.6	35,4
G' at +80 °C	14.9	59.6	0.1	33.8	16.1	12.0	18.9	28.7	19,7

Abbreviations: -. = not measured

Aromatic-based polyols, such as polyol 3, exhibit a temperature-dependent modulus within the operating temperature range (ranging from -20 °C to 80 °C), which is disadvantageous for maintaining constant mechanical properties within this temperature range.

Claims

1. A process for the production of a thermally conductive polyurethane adhesive obtained by mixing an isocyanate reactive component (A) and an isocyanate component (B) at an isocyanate index in the range of 80 to 130 to form a reaction mixture and allowing the reaction mixture to cure, wherein the polyisocyanate reactive component (A) comprises
(a1) at least one polyol
(a2) optionally at least one catalyst,
(a3) at least one surface modified aluminum tri-hydroxide,

and the isocyanate component (B) comprises

(b1) at least one aliphatic polyisocyanate and
(b2) at least one surface modified aluminum tri-hydroxide,

wherein the content of the at least one surface modified aluminum tri-hydroxide (a3) is from 70 to 95 % by weight, based on the total weight of the isocyanate reactive component (A) and the content of the at least one surface modified aluminum tri-hydroxide (b2) is from 70 to 95 % by weight, based on the total weight of the isocyanate component (B) and
wherein the at least one polyol (a1) comprises at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) and the at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least one polyetherpolyol (a1a1), obtainable from alkoxylation of a starter molecule selected from aliphatic alcohols having 2 to 6, preferably 2 to 4 alcohol groups, aliphatic amines, water and mixtures of at least two starter molecules thereof.

2. A process according to claim 1 wherein the at least one aliphatic isocyanate (b1) comprises at least one allophanate structure.

3. A process according to claim 1 or claim 2, wherein the at least one aliphatic isocyanate (b1) comprises at least one isocyanurate structure.

4. A process according to any of claims 1 to 3, wherein the isocyanate (b1) comprises a carbodiimide structure.

5. A process according to any of claims 1 to 4, wherein the isocyanate (b1) comprises hexamethylene diisocyanate or hexamethylene diisocyanate based prepolymer.

6. A process according to any of claims 1 to 5, whereinthe at least one polymeric compound with at least two hydrogen atoms reactive towards isocyanate (a1a) consists of at least one polyetherol (a1a1) .

7. A process according to any of claim 1 to 6, wherein the polyether polyol (a1a1) comprises at least one polyether polyol (a1a1a) having a hydroxyl value of 50 to 500 mg KOH/g obtainable by reacting at least one a starter molecule having a functionality of 2 selected from aliphatic alcohols, water and a combination of at least one aliphatic alcohol and water, with alkylene oxide wherein the alkylene oxides comprise at least 70 mol-% propylene oxide.

8. A process according to claim 7, wherein the polyether polyol (a1a1) comprises in addition to polyetherpolyol (a1a1a) at least one polyether polyol (a1a1b) having a hydroxyl value of preferably 50 to 500 mg KOH/g, obtainable by reacting at least one a starter molecule having a functionality of 3, selected from at least one aliphatic alcohol having a functionality of 3, with alkylene oxide wherein the alkylene oxides comprise at least 70 mol-% propylene oxide.

9. A process according to any of claim 8, wherein ratio by weight of the at least one polyether polyol (a1a1a) and at least one polyether polyol (a1a1b) is 5:1 to 1:3.

10. A process according to any of claims 1 to 9, wherein polymeric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a) comprises at least 80 % by weight, based on the total amount of polymeric compounds with at least two hydrogen atoms reactive towards isocyanate (a1a), of polyetherols, selected from the group, consisting of polyetherpolyols (a1a1) and polyetherpolyols (a1a2) and mixtures thereof.

11. A process according to any of claims 1 to 10, wherein the polyol (a1) comprises at least one chain extender (a1b) and/or at least one crosslinker (a1c).

12. A process according to any of claims 1 to 11, wherein the at least one surface modified aluminum tri-hydroxide (a3) and (b2) are each alkyl-silane treated aluminium trihydroxide having a particle size D90 of 50 to 200 µm.

13. A process according to any of claims 1 to 12, wherein the isocyanate reactive component (A) comprises at least one drying agent.

14. A two component polyurethane adhesive composition comprising an isocyanate reactive component (A) and an isocyanate component (B), each as defined in any of the claims 1 to 13.

15. A thermal conductive adhesive obtained by a process according to any of claims 1 to 13.

16. A battery module comprising a module case having a top plate, a bottom plate and side-walls, wherein an inner space is formed by the top plate, the bottom plate, and the side-walls;
a plurality of battery cells existing in the inner space of the module case; and
a resin layer formed by a process according to any of claims 1 to 13, wherein the reaction mixture is cured in contact with the plurality of battery cells.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/066105

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/10 C08G18/24 C08G18/32 C08G18/48 C08G18/73
C08G18/78 C08G18/79

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)

C08K 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	US 2022/213249 A1 (GRUNDER SERGIO [CH] ET AL) 7 July 2022 (2022-07-07) tables 3,5,11 paragraph [0008]; claim 10 paragraph [0085] -----	1-16
X	CN 113 999 643 A (HUITIAN NEW MAT CO LTD; GUANGZHOU HUITIAN NEW MAT CO LTD ET AL.) 1 February 2022 (2022-02-01) Comparative Example 1; example 1; table 1 -----	1-16

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
26 August 2024	10/09/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/066105

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		EP 3973571 A1	30-03-2022
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