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(54) Title: METHOD OF PREPARING LAMINATE AND LAMINATE

(57) Abstract: Provided are a method of preparing a laminate and a laminate prepared therefrom.

METHOD OF PREPARING LAMINATE AND LAMINATE

TECHNICAL FIELD

[1] The present disclosure relates to a method of preparing a laminate and a laminate.

BACKGROUND

[2] Artificial leathers are of various types and getting applied in many products such as home furniture, car interiors, and garments. One of the most frequently used artificial leather is laminates containing a layer of polyurethane foam due to its low production costs and tunable performances.

[3] In traditional process of preparing a polyurethane-based laminate, a polyurethane forming composition is spread over a release paper and then cured and foamed under elevated temperature.

[4] US 4,102,719 A disclosed a process for producing an artificial leather. The process comprises coating a composition comprising an urethane prepolymer, a combination of catalysts and a foam stabilizer and including a plurality of extremely fine cells of an inert gas, onto a release paper or a layer of a surface treating agent coated on a release paper in a specified thickness; subjecting the resultant to a steam treatment under a specified atmosphere; laminating a base sheet onto the coating layer under pressure; subjecting the laminated product to a heat treatment at a specified temperature, and then peeling off the release paper, and optionally further treating the product with a surface treating agent.

[5] CN 102505518 A disclosed a method of preparing a 100 % solid content polyurethane intermediate layer of synthetic leather. A non-reactive gas is introduced into a polyurethane material in a spraying device before the polyurethane material is heated.

[6] There has been a need of simple processes of preparing a polyurethane-based laminate.

BRIEF SUMMARY

[7] According to one aspect of the present disclosure, provided is a method of preparing a laminate including, (a) preparing an aerated blend from a solvent-free polyurethane forming composition and a gas, wherein the gas is dispersed in the aerated blend in a form of bubbles; (b) spreading and heating the aerated blend on a surface of a substrate to form a polyurethane composite; (c) attaching a fabric layer on a surface of the polyurethane composite and forming a laminate preform; (d) heating the laminate preform; and (e) detaching at least part of the substrate from the laminate preform and forming a laminate. The solvent-free polyure-

thane forming composition includes a polyol component and a polyisocyanate component. The polyol component includes a polyol; a catalyst; and a foam stabilizer. The solvent-free polyurethane forming composition has an isocyanate index within a range of 1.05 to 3.8.

[8] According to another aspect of the present disclosure, provided is a laminate including a fabric layer and a polyurethane foam prepared by the method.

BRIEF DESCRIPTION OF THE DRAWINGS

[9] To easily identify the discussion of any particular element or act, the most significant digit or digits in a reference number refer to the figure number in which that element is first introduced.

[10] FIG. 1 illustrates a flow chart of exemplary process for preparing a laminate in accordance with one embodiment.

[11] FIG. 2 illustrates a flow chart of exemplary process for preparing an aerated blend from solvent-free polyurethane forming composition and a gas in accordance with one embodiment.

[12] FIG. 3 illustrates an exemplary system for preparing a synthetic leather from a solvent-free polyurethane forming composition and a gas in accordance with one embodiment.

[13] FIG. 4 illustrates a cross-section of an exemplary synthetic leather in accordance with one embodiment.

DETAILED DESCRIPTION

[14] Unless defined otherwise, all technical and scientific terms used herein have the meaning commonly understood by a person skilled in the art to which the present disclosure belongs. As used herein, the following terms have the meanings ascribed to them below, unless specified otherwise.

[15] As used herein, the articles "a" and "an" refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

[16] Unless otherwise identified, all percentages (%) are “percent by weight".

[17] "Hydroxyl number", also known as “OH value”, refers to the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize the acetic acid taken up on acetylation of one gram of a polyol or a blend of polyols. It is determined in accordance with Deutsches Institut für Normung (DIN) 53240 from 2012 and refers to mgKOH/g.

[18] "Functionality" of an alcohol (be it a small molecule alcohol or polyol) refers to the number of hydroxyl groups per molecule. Average functionality of a blend of several alcohols refers to the molar average of the functionality of all the components.

[19] "Isocyanate index" or index in short of a polyurethane forming composition refers to the ratio of number of NCO groups over number of isocyanate-reactive hydrogen atoms present in the polyurethane system, given as a percentage

[20]

[21] $$Isocyanate\ index\ =\ \frac{[NCO]}{[Isocyanate-reactive\ hydrogen]} \times 100\%$$

[22]

[23] [NCO] is the number of NCO groups.

[24] [isocyanate-reactive hydrogen] is the number of isocyanate-reactive hydrogen atoms.

[25] In other words, the isocyanate index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation.

[26] "Isocyanate content" refers to a content of isocyanate groups in a formulation and calculated as a ratio of the mass of isocyanate groups (NCO) to the mass of the formulation. It is determined in accordance with ISO 14896 Method A and refers to wt.%.

[27] FIG. 1 illustrates a flow chart of exemplary process for preparing a laminate. The laminate comprises a layer of polyurethane foam and a layer of fabric. The laminate may serve as a semi-product or a final product of synthetic leather. Although the example routine depicts a particular sequence of operations, the sequence may be altered without departing from the scope of the present disclosure. For example, some of the operations depicted may be performed in parallel or in a different sequence that does not materially affect the function of the routine. In other examples, different components of an example device or system that implements the routine may perform functions at substantially the same time or in a specific sequence.

[28] According to some examples, the method includes preparing an aerated blend from solvent-free polyurethane forming composition and a gas at block 102.

[29] The gas is dispersed in the aerated blend in a form of bubbles. The gas may be ambient air, nitrogen, carbon dioxide, or the like.

[30] The solvent-free polyurethane forming composition comprises a polyol component and a polyisocyanate component. The polyol component comprises a polyol; a catalyst; and a

foam stabilizer. the solvent-free polyurethane forming composition has an isocyanate index within a range of 1.05 to 3.8.

[31] In some embodiments, the polyol component and the polyisocyanate component is mixed before being aerated. In some embodiments, the polyol component is aerated before mixing with polyisocyanate component. In some embodiments, the polyisocyanate component is aerated before mixing with polyol component. In some embodiments, both polyol component and polyisocyanate component are aerated separately and mixed subsequently. The aeration may be achieved by using a vigorous stirrer, optionally a vigorous stirrer that is able to introduce bubbles of the gas into a liquid phase, be it the polyol component, the polyisocyanate component, or the mixture thereof.

[32] After the aeration, the blend expands in volume. The volume of the aerated blend is more than two times and less than five times of the volume of the solvent-free polyurethane forming composition. Preferably, the volume of the aerated blend is more than three times and less than four times of the volume of the solvent-free polyurethane forming composition. The volume of the aerated blend and the volume of the solvent-free polyurethane forming composition can be determined by pouring them into a measuring cup or a measuring cylinder. After block 102, the aerated solvent-free polyurethane forming composition may appear like a slurry.

[33] According to some examples, the method includes spreading and heating the aerated blend on a surface of a substrate to form a polyurethane composite at block 104.

[34] Spreading of the aerated blend may be achieved by using a sprayer, a knife, a brush, or a roller, for example. Heating may take place within an oven or an enclosed space with preset temperature. The heating may cause the hydroxyl groups in the polyol component to react with the isocyanate groups in the polyisocyanate component. In such a way, urethane bonds are formed. Under the heating condition, the aerated blend may further expand in volume, due to expansion of the gas bubbles. As the viscosity of the aerated blend increases dramatically, at least part of the gas bubbles may be kept in the aerated blend. During the process of heating, the aerated blend gelatinizes but is not fully cured. After the block 104, the polyurethane composite may include two layers, namely, a substrate and a layer of gelatinized polyurethane on top of the substrate.

[35] Preferably, the aerated blend on the surface of the substrate is heated for a duration of 60 to 300 seconds, preferably a duration of 90 to 180 seconds.

[36] In some embodiments, the substrate is a release paper, as typically known in the pertinent art. Examples of suitable substrates are foils of metal, plastic, or paper. In one preferred embodiment, the substrate used is a release paper optionally coated with a polymeric

composition. Preferably, the release paper here is coated with a polyolefin, preferably polypropylene. Alternatively, the release paper is preferably coated with silicone. In an alternative preferred embodiment, the substrate used is a polyethylene terephthalate (PET) layer optionally coated with a polymeric composition. Preferably, the PET layer here is coated with a polyolefin, preferably polypropylene. Alternatively, the PET layer is preferably coated with silicone.

[37] Alternatively, the substrate includes a release paper and a topcoat contacting with the release paper. The release paper contacts the topcoat. The release paper can be separated from the topcoat without great efforts. When the aerated blend is spread on the surface of the substrate, the aerated blend is in contact with the topcoat. Thus, from up to down, there are three layers, namely, the aerated blend, the topcoat, and the release paper.

[38] Release papers are commercially available. Examples of renowned manufacturers in the pertinent art include Warren (Sappi, USA), Binda (Italy), Arjo Wiggins (UK/USA) and Lintec (Japan).

[39] The topcoat used herein preferably is based on polyurethane chemistry, which is known in the art.

[40] According to some examples, the method includes attaching a fabric layer on a surface of the polyurethane composite and forming a laminate preform at block 106.

[41] The laminate preform formed at block 106 includes three layers, namely, a fabric layer, a layer of gelatinized polyurethane, and a substrate.

[42] The fabric layer may be attached to the polyurethane composite by hot pressing. As the gelatinized polyurethane is not fully cured, it can permeate into tiny pores and channels inside the fabric layer under the elevated temperature and pressure and form a strong bonding.

[43] The fabric layer may be woven, knitted or non-woven. The following materials will be particularly suitable to produce the fabric layer: cotton, linen, cashmere, wool, silk, hair, hemp, polyester, polyamide, polyurethane, or any combination thereof.

[44] According to some examples, the method includes heating the laminate preform at block 108.

[45] The heating may cause the chemical bonds in the gelatinized polyurethane to further crosslink and the bubbles to enlarge in volume. As a result, the gelatinized polyurethane solidifies and forms a polyurethane foam. The heating may happen in an oven.

[46] Preferably, the laminate preform is heated for a duration of 180 to 900 seconds, more preferably a duration of 300 to 780 seconds.

[47] According to some examples, the method includes detaching at least part of the substrate from the laminate preform and forming a laminate at block 110.

[48] The detachment of at least part of the substrate may be achieved by dragging part of or the whole substrate from the laminate preform.

[49] When the substrate only includes only a release paper, the whole release paper is detached from the laminate preform. The laminate obtained after step at block 110 includes the layer of polyurethane foam and the layer of fabric. The laminate can serve as a semi-product for producing a synthetic leather. In some scenarios, the laminate may be attached to an additional topcoat and then be made into a consumer product, for example, a handbag.

[50] When the substrate includes a release paper and a topcoat, only the release paper of the substrate is detached from the laminate preform. In that case, the obtained laminate includes a layer of topcoat, a layer of polyurethane foam, and a layer of fabric. The laminate may serve, directly or after post-treatment, as a final product of synthetic leather. The laminate may be made into consumer products, for example, a handbag.

[51] The detached part of the substrate after step at block 110 is then rolled and recycled for another cycle of production. For example, the release paper can be re-used for several times for the sake of material saving. Alternatively, the release paper is coated with a polymeric material being a precursor of the topcoat and then heated to form a substrate including the topcoat and the release paper.

[52] FIG. 2 illustrates a flow chart of an exemplary process for preparing an aerated blend from solvent-free polyurethane forming composition and a gas. The exemplary process may serve as step at block 102 of FIG. 1. Although the example routine depicts a particular sequence of operations, the sequence may be altered without departing from the scope of the present disclosure. For example, some of the operations depicted may be performed in parallel or in a different sequence that does not materially affect the function of the routine. In other examples, different components of an example device or system that implements the routine may perform functions at substantially the same time or in a specific sequence.

[53] According to some examples, the method includes mixing the polyol component and the polyisocyanate component to form a solvent-free polyurethane forming composition at block 202.

[54] In some embodiments, the mixing is achieved through a stirrer in operation. The stirrer may be in any form or shape. The stirrer may be a mechanical stirrer or a magnetic stirrer.

[55] According to some examples, the method includes entrapping the gas into the solvent-free polyurethane forming composition at block 204.

[56] In some embodiments, the gas is entrapped into the mixture through a stirrer in operation. The stirrer may be in any form or shape. The stirrer may be a mechanical stirrer or a magnetic stirrer. The stirrer brings a plurality of bubbles of the gas to the mixture.

[57] In some embodiments, the step mixing the polyol component and the polyisocyanate component at block 202 and the step entrapping the gas into the solvent-free polyurethane forming composition at block 204 are concurrent, i.e., the gas is entrapped while the polyol component and the polyisocyanate component are being mixed to form the solvent-free polyurethane forming composition.

[58] In some embodiments, the step at block 202 precedes the step at block 204.

[59] FIG. 3 illustrates an exemplary system for preparing a synthetic leather from a solvent-free polyurethane forming composition and a gas. The exemplary system may perform the steps of FIG. 1.

[60] The system comprises a release paper roller 302, a release paper 304a, a roller 306a, a roller 306b, a release paper 304b, a polyurethane tank 308, a pipeline 310, a knife 312, a polyurethane composite 314, a curing oven 316, a fabric roller 318, a fabric 320, a roller 322a, a roller 322b, a post-curing oven 326, a roller 328a, a roller 328b, a release paper winder 330, a recycled release paper 332, a laminate 334, and a laminate winder 336. The system can be used to prepare a laminate containing a polyurethane foam layer and a fabric layer.

[61] The release paper roller 302 rotates and unrolls release paper 304a. The release paper 304a is pressed by rollers 306a and 306b to form a release paper 304b. The release paper 304b is flat and serves as a substrate.

[62] The polyurethane tank 308, through pipeline 310, delivers an aerated blend to the release paper 304b. The aerated blend is prepared from a solvent-free polyurethane forming composition comprising a polyol component and a polyisocyanate component and a gas. The polyurethane composite 314 is obtained. The polyurethane composite 314 contains a layer of the aerated blend and a layer of release paper 304b. Knife 312 helps to spread the aerated blend with a roughly even thickness on the surface of the release paper 304b.

[63] The polyurethane composite 314 then proceeds and enters a curing oven 316. The curing oven 316 heats the polyurethane composite 314. The aerated blend undergoes a urethane forming process accompanied by a foaming process. The aerated blend gelatinizes and expands in volume. Its viscosity increases. Still, the solvent-free polyurethane forming composition does not solidify yet.

[64] The fabric roller 318 rotates and supplies a fabric 320. The fabric 320 is attached to the polyurethane composite 314 through pressing of roller 322a and roller 322b. The laminate preform 324 is formed, which includes a layer of release paper 304b, a layer of aerated

blend (not shown in FIG. 3) and a layer of fabric 320. As the solvent-free polyurethane forming composition in the polyurethane composite 314 is not solidified, it permeates into tiny pores and channels inside the fabric 320 as a consequence of the pressing. The permeation allows enhanced bonding between the polyurethane foam formed later and the fabric 320.

[65] The laminate preform 324 enters post-curing oven 326 and is heated by the same. The heating causes the solvent-free polyurethane forming composition in the laminate preform 324 to foam, cure, and crosslink. In the post-curing oven 326, the layer of aerated blend is converted to a layer of polyurethane foam.

[66] The laminate preform 324 is then pressed by roller 328a and roller 328b. The release paper layer is split from the polyurethane foam and the fabric 320 and forms a recycled release paper 332. The recycled release paper 332 is wound by a release paper winder 330. The recycled release paper 332 is reusable and can re-enter the whole process as depicted by FIG. 3.

[67] After splitting of recycled release paper 332, a laminate 334 is formed. It then is wound and collected by a laminate winder 336 for storage or transportation.

[68] FIG. 4 shows a cross-section of an exemplary synthetic leather. The synthetic leather comprises in sequence a layer of topcoat 402, a layer of polyurethane foam 404, and a fabric layer 406. The layer of polyurethane foam 404 can be part of the laminate preform 324 or part of the laminate 334 in FIG. 3. The layer of polyurethane foam 404 comprises a polyurethane matrix 408, a pore 410a, a pore 410b, a pore 410c, a pore 410d, a pore 410e, a pore 410f, a pore 410g, a pore 410h, a pore 410i, and a pore 410j. The pores 410a through 410j are distributed inside the polyurethane matrix 408. The polyurethane matrix 408 is prepared from the solvent-free polyurethane forming composition.

Solvent-free polyurethane forming composition

[69] The solvent-free polyurethane forming composition is a system comprising a polyol component and a polyisocyanate component.

[70] Within the polyurethane forming composition, no or negligible amount of solvent or diluent such as water, dimethylformamide, or toluene is included. Solvent-free polyurethane forming composition reduces environmental impact as well as safety and health hazards to the labor.

[71] The isocyanate index of the solvent-free polyurethane forming composition is within a range of 1.05 to 3.8, preferably within a range of 1.7 to 3.2. When the isocyanate index is too low, the curing or hardening of the polyurethane forming composition may be an issue. When the isocyanate index is too high, the polyisocyanate component may be highly excessive and the composition may remain liquid after being heated. The following steps such as attaching

a fabric layer will be left insufficient time, further causing difficulties for process and/or leading to product quality issues.

[72] Preferably, the solvent-free polyurethane forming composition comprises no or less than 0.3 wt.% of a chemical blowing agent, based on the total weight of the solvent-free polyurethane forming composition. The chemical blowing agent may be selected from water, a gas-releasing compound, a carboxylic acid, a salt of the carboxylic acid, and any combination thereof. The gas-releasing compound refers to a chemical compound that is able to release a gas such as CO_2, NH_3, N_2, or mixture thereof, under a temperature less than 180 °C. Examples of gas-releasing agent include without limitation to alkali bicarbonate, alkali carbonate, ammonium bicarbonate, combination of alkali carbonate and an ammonium salt, azocarbonamide, azodicarbonamide, 4,4'-oxybis(benzenesulfonyl hydrazide), p-toluenesulfonyl hydrazide, or combinations thereof. The carboxylic acid includes formic acid, acetic acid, citric acid, or the similar.

[73] Normally, presence of water in the polyurethane forming composition, especially in the polyol component, can initiate foaming of the polyurethane forming composition as water reacts with isocyanate groups and releases CO_2. It was believed that inclusion of water in the polyurethane forming composition helps formation of polyurethane foam.

[74] Surprisingly, it is found that the polyurethane foam in the laminate expresses a low density even when chemical blowing agents used in conventional polyurethane chemistry are essentially absent from the polyurethane forming composition.

[75] Preferably, the solvent-free polyurethane forming composition further comprises a filler in a content of 0.5 to 50 wt.%, more preferably 20 to 40 wt.%, based on a total weight the polyurethane forming composition. The filler is preferably selected from calcium carbonate, aluminum hydroxide, barium sulfate, magnesium oxide, talcum, diatomite, zinc oxide, titanium dioxide, aluminosilicate, and a combination thereof. The filler may help to tune the mechanical strength and other performances of the polyurethane foam and the laminate.

Polyol component

[76] In the present disclosure, the polyol component comprises a polyol, a catalyst, and a foam stabilizer.

[77] Preferably, the polyol component has an average functionality of 2.0 to 2.6.

[78] The polyol preferably is selected from a polyether polyol, a polycarbonate polyol, a polyester polyol, and any combination thereof. These are commonly known in the pertinent art.

[79] When polyether polyols are employed, these are generally obtained by known methods, for example by anionic polymerization using alkali metal hydroxides as catalysts and with addition of a starter molecule comprising multiple reactive hydrogen atoms in attachment, from one or more alkylene oxides selected from propylene oxide (PO) and ethylene oxide (EO), butylene oxide and tetrahydrofuran. Useful polyether polyols further include so-called low unsaturation polyetherols. Low-unsaturation polyols for the purposes of the present disclosure are more particularly polyether polyols comprising less than 0.02 meq/g and preferably less than 0.01 meq/g of unsaturated compounds. Polyether polyols of this type are obtained via addition of ethylene oxide and/or propylene oxide and mixtures thereof onto at least difunctional alcohols in the presence of so-called double metal cyanide catalysts.

[80] The alkylene oxides may be used individually, alternatingly in succession or as mixtures. The use of an EO-PO mixture leads to a polyether polyol having randomly distributed PO/EO units. It is possible to begin by using a PO-EO mixture and then, prior to termination of the polymerization, continue use of just PO or EO, the product then being a polyether polyol having a PO endcap or, respectively, an EO endcap.

[81] Starter molecules used are typically NH- or OH-functional compounds such as water, amines, or alcohols. Preference is given to using di- to hexahydric alcohols, such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, and/or sorbitol.

[82] It is further preferable to use polyetherols obtained by ring-opening polymerization of tetrahydrofuran. These polytetrahydrofuran (pTHF) polyols preferably have a functionality of about 2 and often termed polytetrahydrofuran diols. They preferably further have a number average molecular weight in the range from 500 to 4,000 g/mol, preferably in the range from 700 to 3,000 g/mol and more preferably in the range from 900 to 2,500 g/mol. The pTHF polyols are also known in the pertinent art under the designations poly(tetramethylene) glycols (PTMGs), poly(tetramethylene ether) glycols (PTMEGs), or polytetramethylene oxides (PTMOs).

[83] When polyester polyols are employed, these are typically obtained by condensation of polyfunctional alcohols having from 2 to 12 carbon atoms, preferably from 2 to 6 carbon atoms, with polyfunctional carboxylic acids having from 2 to 12 carbon atoms, examples being succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid and preferably phthalic acid, isophthalic acid, terephthalic acid and the isomeric naphthalenedicarboxylic acids.

[84] Preferably, the polyol component comprises a chain extender selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, dipropylene glycol, and a combination thereof.

[85] Preferably, the content of the chain extender is 0.1 to 10 wt.%, based on a total weight of the polyol component.

[86] Preferably, the polyol component comprises a polytetrahydrofuran diol.

[87] As catalyst, it is possible to use compounds which accelerate the isocyanate-polyol reaction. These comprise amine-based catalysts and catalysts based on organic metal compounds, or the mixture of thereof. As catalysts based on organic metal compounds, it is possible to use, for example, organic tin compounds such as tin(II) salts of organic carboxylic acids, e.g., tin(II) acetate, tin(II) octoate, tin(II) ethylhexanoate 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 Zn salts or Bi salts, e.g., zinc octoate, bismuth(III) neodecanoate, bismuth 2-ethylhexanoate and bismuth octanoate, or alkali metal salts of carboxylic acids, e.g., potassium acetate or potassium formate.

[88] As amine-based catalysts, it is possible to use, for example, strongly basic amines such as N,N,N-triethylaminoethoxyethanol, bis(N,N-dimethylaminoethyl)ether, dimethyl cyclohexylamine, trimethyl hydroxyethyl ethylenediamine, dimethylbenzylamine, triethylamine, triethylenediamine, pentamethyldipropylenetriamine, dimethylethanolamine, N-methylimidazole, N ethylimidazole, tetramethylhexamethylenediamine, tris(dimethylaminopropyl)hexahydrotriazine, dimethylaminopropylamine, N- ethylmorpholine, diazabicycloundecene, diazabicyclononene, diazabicyclooctane, preferably triethylenediamine or bis(N,N-dimethylaminoethyl)ether.

[89] The catalyst used in the present disclosure can be commercially available, such as Haptex CC 6945/92 C-CC from BASF.

[90] Preferably, the catalyst has a content of from 0.05 to 5 wt.%, more preferably from 0.1 to 1.5 wt.%, based on the total weight of polyol component.

[91] The foam stabilizer can stabilize the aerated blend and prevent the dispersed gas bubbles from breaking and releasing the gas. Without the foam stabilizer, the aerated blend may be unstable and release a portion of or even essentially all of the gas in the following steps, for example, when the aerated blend is heated.

[92] The foam stabilizer preferably is selected from a siloxane-oxyalkylene copolymer, an organosiloxane, an ethoxylated alkylphenol, an ethoxylated fatty alcohol, a paraffin oil, a castor oil ester, a ricinoleic ester, Turkey red oil, peanut oil, and a combination thereof.

[93] The foam stabilizer preferably has a content of from 0.1 to 5 wt.%, more preferably from 0.5 to 3 wt.%, based on the total weight of polyol component.

Polyisocyanate component

[94] The polyisocyanate component is selected from a diisocyanate, an oligomeric form of diisocyanate, a carbodiimide-modified diisocyanate, an isocyanate-terminated prepolymer, and a combination thereof. The diisocyanate may be an aliphatic diisocyanate such as hexamethylene diisocyanate, a cycloaliphatic diisocyanate such as isophorone diisocyanate or 4,4'-methylenedi(cyclohexyl isocyanate), or an aromatic diisocyanate such as toluene diisocyanate or methylene diphenyl diisocyanate. The polycarbodiimide-modified diisocyanate is a polyisocyanate in which at least part of isocyanate groups have been modified to carbodiimide structure.

[95] Preferably, the polyisocyanate component is an isocyanate-terminated prepolymer formed by reacting an excessive diisocyanate or an excessive oligomeric form of diisocyanate with an active-hydrogen containing compound. Due to insufficient number of the active-hydrogen groups respective to the isocyanate groups, all or substantially all of active-hydrogen groups in the compound are annihilated. The isocyanate-terminated prepolymer contains a plurality of urethane, urea, or thiocarbamate linkages and a plurality of terminal isocyanate groups. The active-hydrogen containing compound may include an alcohol, an amine, an aminoalcohol, a thiol, or a combination thereof. Preferably the active-hydrogen containing compound is a polyester polyol, a polyether polyol, a polycarbonate polyol, or a combination thereof.

[96] Preferably, the polyisocyanate component is essentially free of carbodiimide modification. “Being essentially free of carbodiimide modification” means that there are minimal (due to trace impurities) to no carbodiimide functionality in the polyisocyanate component, which is under detection limit of characterization method.

[97] Preferably, the polyisocyanate component has an isocyanate content of 7 to 22 wt.%, preferably an isocyanate content of 10 to 19 wt.%, determined in accordance with ISO 14896 Method A.

Laminate

[98] The present disclosure also provides a laminate including a fabric layer and a polyurethane foam. Preferably, the laminate further includes a topcoat in contact with the polyurethane foam.

[99] Preferably, the polyurethane foam has a density of 0.3 to 0.5 g/cm^3.

[100] Preferably, the laminate has a peeling strength of more than 30 N/3cm, more preferably more than 45 N/3cm.

[101] Besides the high peeling strength and lightweight, the laminate also has a good flexibility.

[102] The laminate may be used as synthetic leathers, which find applications in various scenarios including without limitation to, interior decoration of transportation vehicles, furniture, handbags, garments, or shoes.

Examples

[103] The following examples are intended to illustrate the present disclosure, but not to limit its scope.

[104] The materials used in the examples are as follows.

[105] Polyether polyol 1, an ethylene oxide-propylene oxide polymer polyol with a diol as starter, functionality 2, hydroxyl number 29.5 mgKOH/g.

[106] Polyether polyol 2, an ethylene oxide-propylene oxide polymer polyol with a triol as starter, functionality 3, hydroxyl number 35 mgKOH/g.

[107] Polytetrahydrofuran diol (pTHF diol), from BASF, functionality 2, hydroxyl number 56 mgKOH/g.

[108] 1,4-butanediol ("BDO"), used as chain extender in polyol component, from BASF, CAS No. 110-63-4.

[109] Diphenylmethane diisocyanate (MDI) from BASF, CAS No. 101-68-8.

[110] Lupranat® MM 103, a carbodiimide-modified isocyanate, from BASF, isocyanate content 29.5 wt.%.

[111] Zinc carboxylate and N,N-dimethylcyclohexylamine mixed in a 1:1 weight ratio was used as catalyst.

[112] VORASURF™ DC 193 silicone surfactant from Dow, used as foam stabilizer.

[113] Water and sodium bicarbonate used as chemical blowing agent.

[114] Calcium carbonate, used as filler.

[115] The polyol mixtures A1 through A7 used for preparing the polyurethane forming compositions are shown in Table 1.

[116] Table 1

	A1	A2	A3	A4	A5
Polyether polyol 1, g	50	50	10	70	30
Polyether polyol 2, g	55	55	5	35	75
pTHF diol, g	-	-	90	-	-
BDO, g	1	-	1	1	1
pTHF diol, wt.%	-	-	85.8	-	-
Overall functionality	2.52	2.52	2.05	2.33	2.71
OH value, mgKOH/g	44.4	33.2	110.9	43.4	45.4

[117] The isocyanate-terminated prepolymers for preparing the polyurethane forming compositions are shown in Table 2.

[118] Table 2

	B1	B2
Polyether polyol 1, g	63	-
pTHF, g	-	40
MDI, g	37	53
Carbodiimide modified MDI, g	-	7
Isocyanate content, %	11.0	18.1

[119] For preparing the polyurethane forming composition F1 through F12 and cF1 to cF2, first the mixed polyol, the catalysts, the foam stabilizer, and the filler were mixed thoroughly.

The mixture was agitated with a hand mixer which introduced air bubbles into the liquid phase. The aerated liquid phase was then mixed with the isocyanate component to form a polyurethane forming system. The polyurethane forming system was then stirred and further aerated with air bubbles by the hand mixer. With a measuring cup, the final aerated polyurethane forming system was found to have a volume approximately three times of the sum of volumes of its constituents except the air bubbles. The aerated polyurethane forming system was applied to the release paper during the process of preparing synthetic leathers.

[120] For preparing the polyurethane forming composition cF3 to cF4, the mixed polyol, the catalysts, the foam stabilizer, the filler, and the chemical blowing agent were mixed thoroughly. The liquid phase was then mixed with the isocyanate component to form a polyurethane forming system. No aeration was performed. The polyurethane forming system was applied to the release paper during the process of preparing synthetic leathers.

[121] Synthetic leathers L1 through L12 and cL1 through cL4 were made according to the following protocol.

[122] A commercial release paper with a PU topcoat travelled at a speed of 1 m/min across a continuous rig for synthetic leather preparation. The topcoat layer was about 50 micrometers in thickness. Thereafter, an approximately 400-micrometer thick layer of the non-solvent polyurethane forming system was applied with hand mixer with whisky. The material was subsequently led through an oven temperature controlled to 140 °C. The material reemerged out of the oven after about 90 seconds. Thereafter, a textile substrate was applied under slight pressure to the still incompletely cured polyurethane. A laminate preform was produced. Subsequently the laminate preform was pressed and cured in the oven at 140°C. The laminate preform exited from the oven after 10 minutes. Thereafter, a final synthetic leather was obtained by peeling off the release paper from the laminate preform. Hereinafter, processability of a solvent-free polyurethane forming composition refers to successful or failed preparation of the synthetic leather by processing it according to the above protocol. Successful preparation of synthetic leather after the protocol is indicated in Table 5 as “G” and failed preparation of synthetic leather as “B”.

[123] The polyurethane forming compositions used for preparing synthetic leathers are shown in Table 3, in which “CBA” refers to chemical blowing agent. Polyurethane forming compositions F1 through F12 are working examples while polyurethane forming compositions cF1 through cF4 are comparative examples. cF3 and cF4 comprised a layer of chemically blown polyurethane foam.

[124] The synthetic leathers (L1 through L12 and cL1 through cL4) prepared from the polyurethane forming compositions had their properties or performances tested according to standards listed in Table 4.

[125] Density here refers to the density of foamed layer within the synthetic leather that was tested. Peeling strength (shortened as "PS" in the tables) refers to the strength of adhesion between two adjacent layers of a laminate.

[126] Measurement of peeling strength followed the standard GB/T 8949-2008 and was conducted as below. Synthetic leather specimen was cut into a dimension of 15cm×3cm, which was adhered with a TPU hot melt tape on the outmost surface of the topcoat layer. Then it was pressed in 150 °C for several minutes, then cooled at room temperature. Then T-peel test was conducted on a ZwickRoell tensile machine with a speed of 100 mm/min.

[127] Flexing resistance tests of dry synthetic leather specimen were conducted under room temperature (RT) for 300,000 cycles; under -20 °C for 30,000 cycles; and -30 °C for 30,000 cycles. The test followed the standard ISO 5402-1 2017. The synthetic leather specimen either failed (indicated in Table 5 as "F") or passed (indicated in Table 5 as "P") the test without crack.

[128] The testing results of synthetic leathers are listed in Table 5.

[129] Table 3

Example	F1	F2	F3	F4	F5	F6	cF1	cF2	cF3	cF4	F7	F8	F9	F10	F11	F12
A1, g	106	106	106	106	106	106	106	106	106	106	-	-	-	-	-	-
A2, g	-	-	-	-	-	-	-	-	-	-	106	-	-	-	-	-
A3, g	-	-	-	-	-	-	-	-	-	-		106	106	106	-	-
A4, g	-	-	-	-	-	-	-	-	-	-	-	-	-	-	106	-
A5, g	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	106
Catalyst, g	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5
Surfactant, g	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$NaHCO_3$, g	-	-	-	-	-	-	-	-	3	-	-	-	-	-	-	-
H_2O, g	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-
CBA, wt.%	-	-	-	-	-	-	-	-	1.0	.3	-	-	-	-	-	-
$CaCO_3$, g	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
B1, g	97.5	78	58.5	-	-	-	130	32.5	97.5	97.5	73	193	146	100	97.5	97.5
B2, g	-	-	-	60	47	35.5	-	-	-	-	-	-	-	-	-	-
Index	3.0	2.4	1.8	3.0	2.4	1.8	4.0	1.0	3.0	3.0	3.0	2.4	1.8	1.25	3.0	3.0

Table 4

Performance	Unit	Testing standard
Density	g/cm^3	-
Peeling strength	N/3cm	GB/T 8808-1988B
Flexing resistance	-	ISO 5402-1 2017

[130] Table 5

Example	L1	L2	L3	L4	L5	L6	cL1	cL2	cL3	cL4	L7	L8	L9	L10	L11	L12
Formulation	F1	F2	F3	F4	F5	F6	cF1	cF2	cF3	cF4	F7	F8	F9	F10	F11	F12
Processability	G	G	G	G	G	G	B	B	G	G	G	G	G	G	G	G
Density, g/cm^3	.37	.38	.37	.38	.40	.38	N.A.	N.A.	.90	.90	.38	.40	.40	.35	.30	.35
PS, N/3cm	45	30	45	27	15	12	N.A.	N.A.	N.A.	N.A.	18	60	45	45	36	24
RT flexing	P	P	P	P	P	P	N.A.	N.A.	N.A.	N.A.	P	P	P	P	P	P
-20°C flexing	P	P	P	P	P	P	N.A.	N.A.	N.A.	N.A.	P	P	P	P	P	P
-30°C flexing	P	P	P	P	P	P	N.A.	N.A.	N.A.	N.A.	P	P	P	P	P	P

[131] "N.A." indicates non-availability of data, which may be due to unsuccessful preparation of synthetic leather or abandonment of performance testing. For comparative synthetic leathers cL1 and cL2, the compositions failed to cure and thus no useful synthetic leathers were obtained. For comparative synthetic leathers cL3 and cL4 based on polyurethane forming compositions containing significant amount of chemically blowing agents, synthetic leathers with high-density foamed layer were obtained, which were of little practicality for synthetic leather. Therefore, the testing was abandoned.

[132] Normally, for the test pieces used in the present disclosure, passing the room temperature flexing and the -20 °C temperature flexing indicates a good flexibility under an ordinary environment. Passing the -30 °C temperature flexing indicates an excellent flexibility even under an extremely cold environment.

[133] From Table 5, all the solvent-free polyurethane forming composition can be processed into a synthetic leather except the examples cL1 and cL2, which had isocyanate indexes of 4.0 and 1.0, respectively.

[134] Compared with examples L1, L2, or L3, examples L4, L5, or L6 had a much lower peeling strength respectively. The main difference between F1 and F4, between F2 and F5, or between F3 and F6, was whether a carbodiimide-modified polyisocyanate was included in the polyisocyanate component. The solvent-free polyurethane forming compositions free of carbodiimide modification were able to produce strong synthetic leathers.

[135] Comparing example L1 and comparative example cL3 or cL4, it is suggested that synthetic leathers prepared from the composition with no chemical blowing agent by mechanical foaming process can achieve a lower density of foamed layer.

[136] Compared with synthetic leather L7 made from composition F7 containing no small diol as chain extender, synthetic leather L1 expressed a much higher peeling strength. Synthetic leather L1 was made from composition F1 with similar formulation to F7 except 1,4-butanediol as chain extender was included in the polyol component. A peeling strength within the range of 30 to 80 N/3cm was achieved for synthetic leather L1.

CLAIMS

1. A method of preparing a laminate comprising,

(a) preparing an aerated blend from a solvent-free polyurethane forming composition and a gas;

(b) spreading and heating the aerated blend on a surface of a substrate to form a polyurethane composite;

(c) attaching a fabric layer on a surface of the polyurethane composite and forming a laminate preform;

(d) heating the laminate preform; and

(e) detaching at least part of the substrate from the laminate preform and forming a laminate,

wherein the gas is dispersed in the aerated blend in a form of bubbles, the solvent-free polyurethane forming composition comprises a polyol component and a polyisocyanate component, the polyol component comprises a polyol; a catalyst; and a foam stabilizer, and the solvent-free polyurethane forming composition has an isocyanate index within a range of 1.05 to 3.8.

2. The method of claim 1, wherein the isocyanate index of the solvent-free polyurethane forming composition is within a range of 1.7 to 3.2.

3. The method of claim 1, wherein the solvent-free polyurethane forming composition comprises no or less than 0.3 wt.% of a chemical blowing agent, based on the total weight of the solvent-free polyurethane forming composition.

4. The method of claim 1, wherein the polyurethane forming composition further comprises a filler in a content of 0.5 to 50 wt.%, preferably 20 to 40 wt.%, based on a total weight of the polyurethane forming composition.

5. The method of claim 1, wherein the polyol component has an average functionality of 2.0 to 2.6.

6. The method of claim 1, wherein the polyol component comprises a chain extender selected from ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, dipropylene glycol, and a combination thereof.

7. The method of claim 1, wherein the polyol component comprises a polytetrahydrofuran diol.

8. The method of claim 1, wherein the polyisocyanate component is an isocyanate-terminated prepolymer formed by reacting an excessive diisocyanate or an excessive oligomeric form of diisocyanate with an active-hydrogen containing compound.

9. The method of claim 1, wherein the polyisocyanate component is essentially free of carbodiimide modification.

10. The method of claim 1, wherein step (a) comprises,

(a1) mixing the polyol component and the polyisocyanate component to form the solvent-free polyurethane forming composition; and

(a2) entrapping the gas into the solvent-free polyurethane forming composition.

11. The method of claim 1, wherein the aerated blend on the surface of the substrate is heated for a duration of 60 to 300 seconds, preferably a duration of 90 to 180 seconds.

12. The method of claim 1, wherein the laminate preform is heated for a duration of 180 to 900 seconds, preferably a duration of 300 to 780 seconds.

13. A laminate comprising a fabric layer and a polyurethane foam prepared by the method of any one of claims 1 to 12.

14. The laminate of claim 13, wherein the polyurethane foam has a density of 0.3 g/cm^3 to 0.5 g/cm^3.

15. The laminate of claim 14 having a peeling strength of more than 30 N/3cm, preferably more than 45 N/3cm.

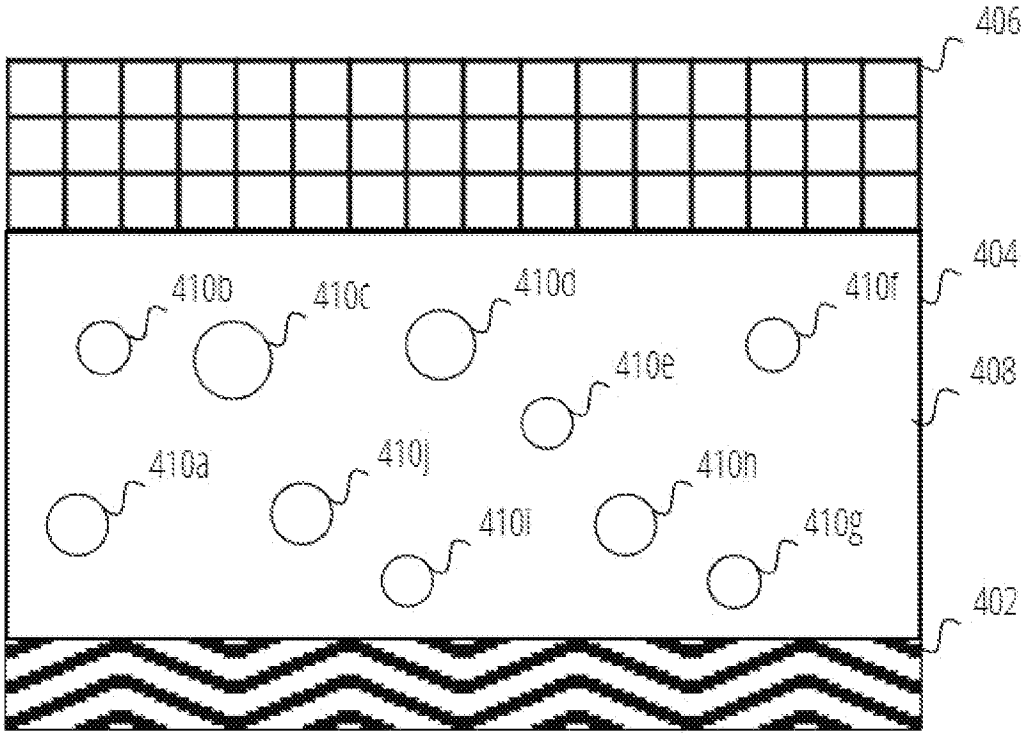
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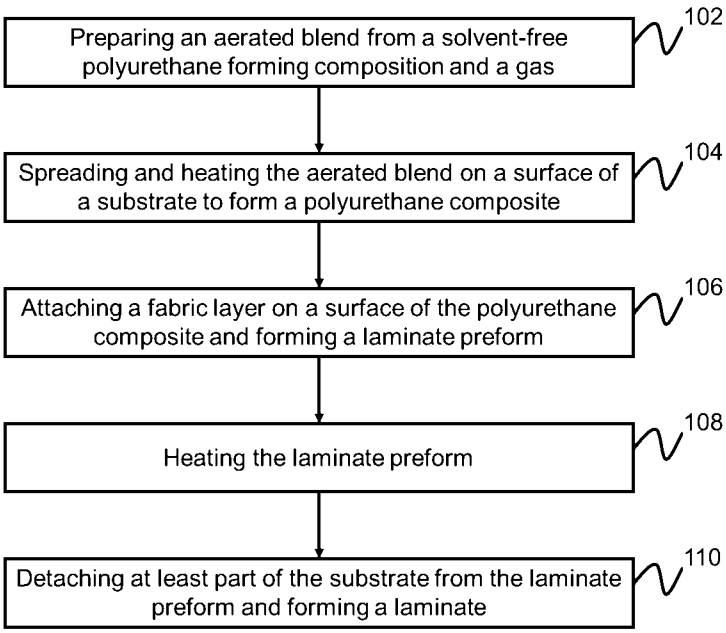
FIG. 4


Preparing an aerated blend from a solvent-free polyurethane forming composition and a gas
102
Spreading and heating the aerated blend on a surface of a substrate to form a polyurethane composite
104
Attaching a fabric layer on a surface of the polyurethane composite and forming a laminate preform
106
Heating the laminate preform
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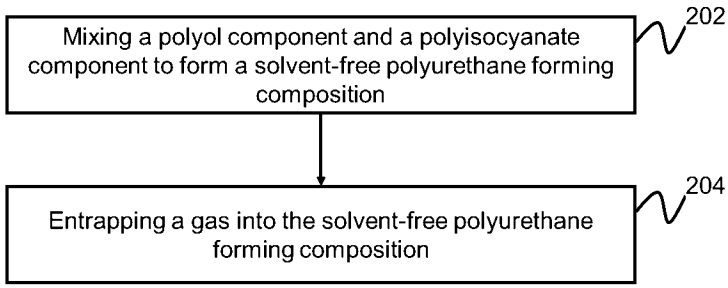
Detaching at least part of the substrate from the laminate preform and forming a laminate
110

FIG. 1


Mixing a polyol component and a polyisocyanate component to form a solvent-free polyurethane forming composition
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Entrapping a gas into the solvent-free polyurethane forming composition
204

FIG. 2

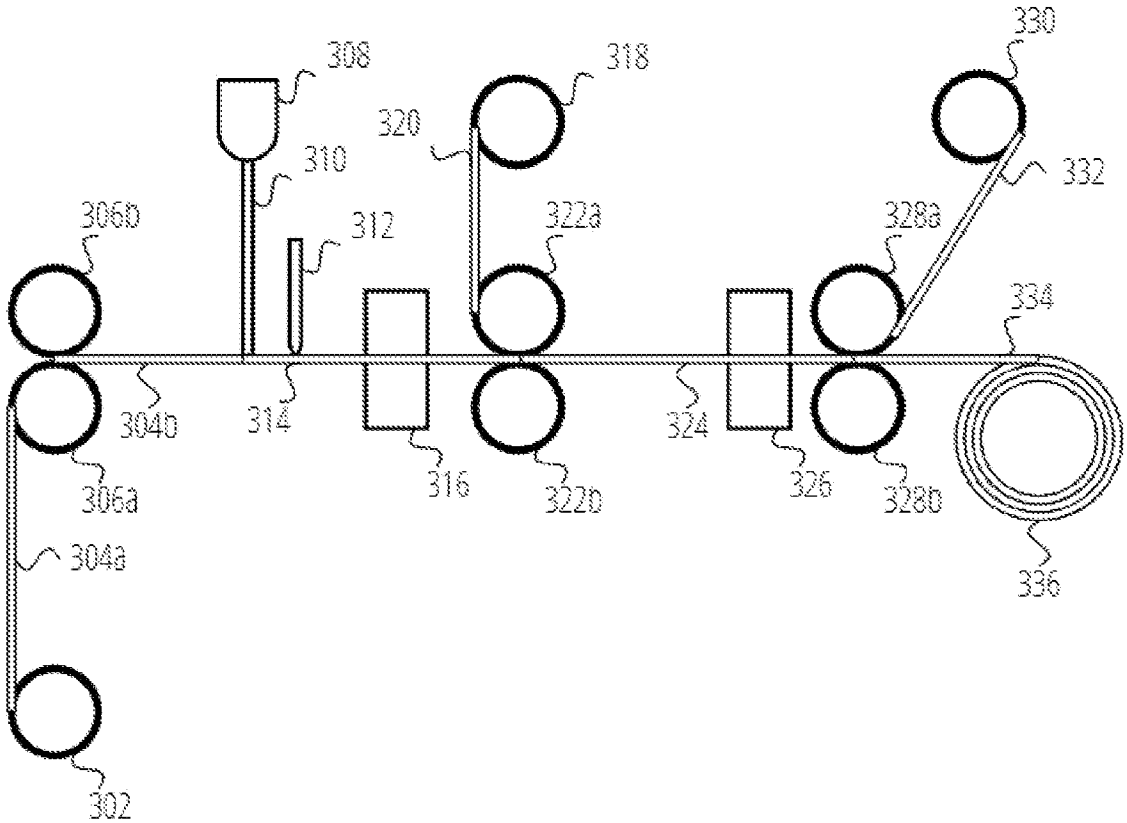
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FIG. 3

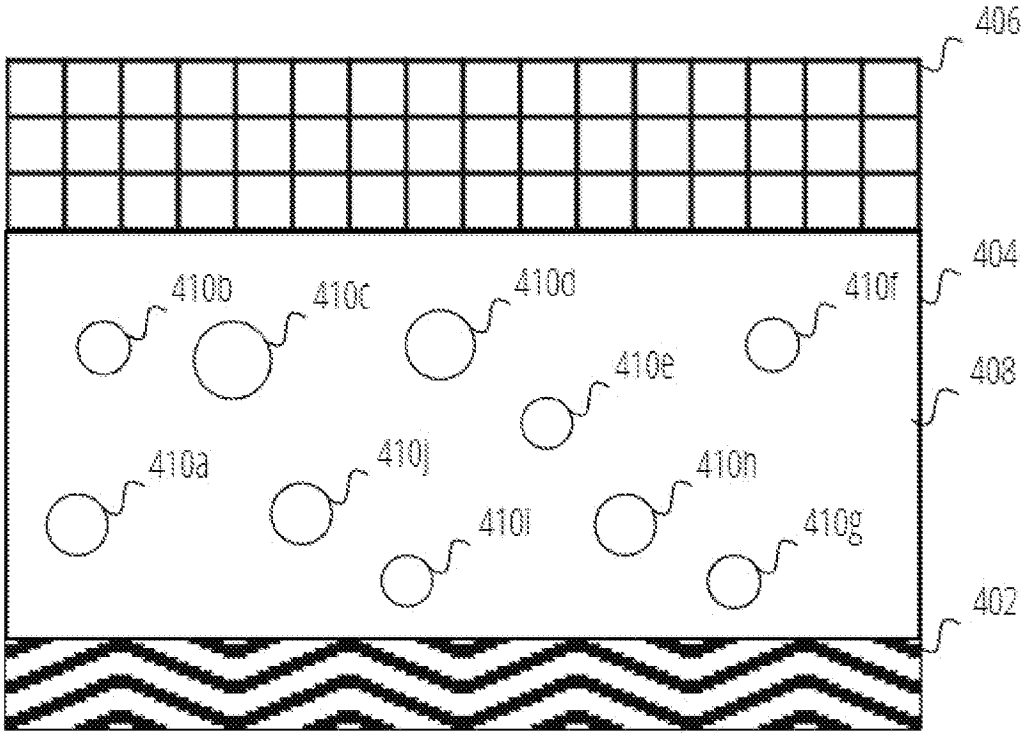
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FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/CN2024/090556

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/12 B32B5/18 C08G18/16 C08G18/48 C08G18/66
C08G18/72 C08G18/76 C08G18/79 C08J9/00 D06N3/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08J B32B D06Q D06N

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 4 102 719 A (FUJII SADAO ET AL) 25 July 1978 (1978-07-25) claims 1-8; examples 1-2 -----	1-15
A	CN 102 505 518 A (WENZHOU HONGDELI RESIN CO LTD) 20 June 2012 (2012-06-20) claims 1-7 -----	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 August 2024	26/08/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Scheuer, Sylvie

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CN2024/090556

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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