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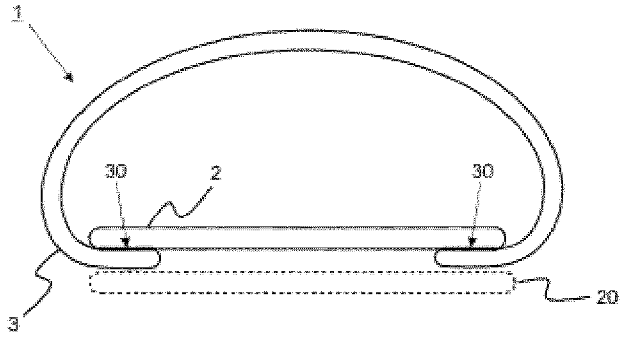

FIG. 2

**(57) Abstract:** The present invention pertains to a new shoe comprising a sole of a thermoplastic material adhered to an upper shoe with a hot melt adhesive that is applied between the sole and the upper shoe, wherein the hot melt adhesive is fused with the thermoplastic material. Advantageously, the fusion is brought about by heating the hot melt adhesive to a temperature THM such that it softens, heating the second body such that the thermoplastic material that has a melting temperature TM obtains a temperature $T_{SUB}$ below $T_M$ while making sure that $(T_{HM} + T_{SUB})/2$ is equal to or higher than $(T_M$-10°C).

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# A SHOE COMPRISING A SOLE OF A THERMOPLASTIC MATERIAL AND A METHOD FOR USE IN MANUFACTURING SUCH A SHOE

## GENERAL FIELD OF THE INVENTION

The present invention pertains to shoes and the manufacturing thereof. More particularly the invention pertains to shoes with a sole of a thermoplastic material and a method for making a workpiece that can be used in the manufacturing of such shoes.

## BACKGROUND OF THE INVENTION

Contemporary shoes comprise the same basic parts. All shoes have a sole, which is the bottom of a shoe, in contact with the ground. Soles can be made from a variety of materials, although most modern shoes have soles made from natural rubber, polyurethane, polyvinyl chloride (PVC) or ethylene-vinyl acetate copolymer (EVA). Soles can be simple, a single material in a single layer, but most often they are more complex, with multiple structures or layers and materials. When various layers are used, soles may consist of an insole (also known as a sock liner), a midsole, and an outsole (i.e. the layer in direct contact with the ground). The midsole is the layer in between the outsole and the insole, typically there for shock absorption.

Another common part to all shoes is the upper shoe. The upper shoe helps hold the shoe onto the foot. In the simplest cases, such as sandals or flip-flops, this may be nothing more than a few straps for holding the sole in place. Closed shoes, such as boots, trainers and most men's shoes, will have a more complex upper. This part is often decorated or is made in a certain style to look attractive. The upper may be connected to the sole by a strip of leather, rubber, or plastic that is stitched between it and the sole, or it may be glued to the sole by using an adhesive. In the manufacture of athletic shoes, the upper shoe is in most cases glued to the midsole (the latter being an important item for such shoes) using a solvent based adhesive, either using an aqueous solvent (such as water based PUD’s, polyurethane adhesives) or a non-aqueous solvent (such as polychloroprene or styrene-isoprene-styrene adhesives). Although solvent-based adhesives are relatively expensive, inherently require a long processing time and also, despite the fact that special care may need to be taken to prevent environmental damage and deleterious health effects (caused by many non-aqueous solvents), such adhesives are preferred over hot melt adhesives. Hot melt adhesives have the advantage of being (almost) solvent free and allowing very short processing times without any foaming tendency during processing, but the adhering properties on the relatively smooth soles are relatively bad. This is in particular true when adhering an upper shoe to a sole of a thermoplastic material. The latter type of material would in principle be preferred over the commonly used EVA (that is typically used for mid-soles) because of its easy recyclability when compared to EVA, the finished foam of which has thermoset properties that prevent recycling by simply melting the material and reprocessing it. Still, due to the difficulty of gluing an upper shoe to a thermoplastic sole, EVA is still the polymer of choice, using solvent based adhesives to adhere the upper shoe.

The problem of low quality adherence of an upper shoe to a thermoplastic sole, especially when using a hot melt adhesive, has been known since decades.

GB 1247855 (filed 1967, published 1971) describes the problem of using a hot melt adhesive to bond the upper shoe to a sole of plasticised polyvinyl chloride. The solution proposed in this patent is to use a polyester hot melt adhesive that includes a quantity of a nitrogen containing organic compound having a polar group, such as N-Butyl-Benzenesulphonamide or N-Ethyl-P-tolylsulphonamide. Such compounds however are associated with health hazards. N-Butyl-Benzenesulphonamide is neurotoxic and has been found to induce spastic myelopathy in rabbits. N-Ethyl-P-tolylsulphonamide is toxic and highly irritating.

US 3,168,754 (filed 1961, published 1965) also mentions the problem of using a hot melt adhesive for adhering an upper shoe to a sole, despite the fact that in other fields than sole attaching, hot melt adhesives have been found very useful towards the end of the 1950's. The '754 patent states (column1, lines 28-30) that "attempts to bond outsoles to uppers using the known hot melt adhesive processes gave inadequate bonds, apparently because of unsatisfactory penetration and/or wetting of the surfaces to be bonded." The solution proposed aimed at increasing the penetration and wetting properties of the hot melt adhesive by using a process of repeated heating and cooling. This increases process time and still may not provide adequate bonding, in particular when adhering to a thermoplastic sole.

US 3,212,115 (filed 1959, published 1965) confirms that the use of hot melt adhesives in the manufacturing of shoes leads to several disadvantages, not the least of which is failure of the bond at temperatures involved in the treatment or use of the bonded structures in practice. The solution proposed is a complicated method involving depositing a relatively thick body of a molten, crystallisable hot melt adhesive on a surface, supercooling the adhesive to a temperature below its crystallization temperature but above its second order transition temperature, pressing said body of supercooled adhesive between said surface and a second surface to distort the body of adhesive, wherein the distortion should induce crystallisation and effecting orientation of the molecules of the deposited adhesive to increase the tensile strength and toughness of the adhesive.

GB 2048897 (filed 1979, published 1980) states (page 1, lines 14-16) that it is known that the receptiveness of elastomeric soling material towards adhesives and to thermoplastic materials is often unsatisfactory. The solution proposed is to use aggressive primers comprising an organic halogen donor, like mixtures of isocyanuric chloride and a sulphonamide such as, for example, p-toluene sulphonamide, for promoting adhesion. These primers are toxic, irritating and environmentally unfriendly.

US 6,497,786 (filed 1997, published 2002) describes the potential advantages of using solvent less adhesives, but indicates that the need to heat the adhesives to be able and apply them is a disadvantage, in particular since present-day sole materials may deform at high temperatures. The ‘786 patent proposes to use microwaves to locally heat the adhesive while keeping the sole at a low temperature. The solution however needs a very complicated device for specifically heating the adhesive. Next to this, the problem of inadequate adherence when using a hot melt adhesive is neither addressed nor solved.

## OBJECT OF THE INVENTION

It is an object of the invention to provide a new shoe and method of assembling a workpiece that can be used in manufacturing such a shoe that mitigates the prior art disadvantages.

## SUMMARY OF THE INVENTION

In order to meet the object of the invention a new shoe has been devised, the shoe comprising a sole composed of a thermoplastic material adhered to an upper shoe with a hot melt adhesive that is applied between the sole and the upper shoe, wherein the hot melt adhesive is fused with the thermoplastic material.

The inventors surprisingly found that a good adherence using a standard hot melt adhesive can be obtained, even when adhering to a body of a thermoplastic material that has a very smooth surface, when the method provides for a fusion of the hot melt adhesive with the thermoplastic material. This finding was based on the recognition that although a thermoplastic material per se is less receptive for adhering to another material, in particular a hot melt adhesive, it provides the option of melting an upper region of the body (i.e. a region that has a thickness beyond molecular scale, at least being at a micrometer level or beyond, i.e. 1 µm or thicker, e.g. 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100 or more µm's), which on its turn may provide the option of the molecules in the molten hot melt adhesive and the molten upper region of the thermoplastic body to fuse, i.e. to mix and form a new material that acts as a bridge between the hot melt adhesive on the one hand and the thermoplastic body on the other hand.

The invention also relates to a method of assembling a workpiece for use in the manufacturing of the shoe, comprising heating the hot melt adhesive to a temperature $T_{HM}$ such that it softens and can be applied, heating the thermoplastic body such that the thermoplastic material obtains a temperature $T_{SUB}$ below its melting temperature, such that $(T_{HM} + T_{SUB})/2$ is equal to or higher than the said melting temperature of the thermoplastic material minus 10°C ($T_M$-10°C). When applying these specific temperatures, the total heat available is sufficient to melt the upper region of the thermoplastic body upon contact with the hot met adhesive, and fusing the two molten substances is allowed, in particular when applying pressure, e.g. when applying the upper shoe (wherein the molten hot melt adhesive may have been applied as such to the sole before applying the upper shoe, or may have been pre-applied to this upper shoe and kept at a sufficient temperature while in contact with this upper shoe alone). Although the melting of a thin upper region of the thermoplastic body could be accomplished in various ways (using e.g. convection of hot air or a liquid, radiation, etc.)

it was found that a very simple way is to use the heat capacity of the hot melt adhesive and the body themselves to provide the heat for melting the upper region of the thermoplastic body.

In any case, by providing the fusion between the hot melt adhesive and the thermoplastic body, a very strong mechanical connection may be obtained, without the need for applying special organic molecules, primers or using complicated heating procedures and equipment.

## DEFINITIONS

A *shoe* is an outer covering for the human foot typically having a thick or stiff sole with an attached heel and an upper part (also denoted as the upper shoe) of lighter material, such as a textile or leather sheeting.

A *hot melt adhesive* is a thermoplastic adhesive with no (less than 1 or 2 wt%) solvent. Upon heating the adhesive softens in order to be applied to a substrate. Preferably the hot melt adhesive undergoes a first order phase transition when being heated and transformed from a solid into a liquid.

A *thermoplastic* material is a material (typically a synthetic polymer material) that becomes plastic, e.g. shapeable, upon heating and hardens upon cooling to retain desired shape and is able to reversibly undergo this process repeatedly. The melting temperature ($T_M$) of the thermoplastic material is the peak melting temperature as defined in ASTM D3418 measured during the second heating step in a Differential Scanning Calorimetry (DSC) experiment conducted at 10°C/min heating rate. If multiple peaks are present, then the first peak (e.g. lowest temperature) corresponding to the melting of the hard block of the thermoplastic elastomer should be taken.

A *first order phase transition temperature* of a material is the temperature at which the material undergoes a discontinuous change in density. Examples of first order transitions are melting (solid to liquid conversion) and evaporating (liquid to gas conversion). A glass-transition is a second order transition since there is no discontinuous change in density.

A *body* is a solid 3-dimensional object having predetermined dimensions.

To be *fused* means to unite to form a single entity by melting or as if by melting, in particular which results in the absence of a borderline and/or distinct boundary between materials in Scanning Electronic Microscopy (SEM) pictures at an enlargement of 500 to 1000 times.

A *textile material* is a material that is consists in essence (for more than 50%, for example more than 55%, 60%, 65%, 70%, 75%, 80%, 85%, or even more than 90%) of fibrous material such as polymeric yarns.

A body being *composed* of a thermoplastic material means that the basic structure of the body consists of a thermoplastic material, the material typically containing over 50% (on a weight basis), preferably over 60%, 70%, 80%, 85%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99% or even up to 100% of a thermoplastic polymer.

A *workpiece* is an assembly of materials that is used in manufacturing an end product.

A *smooth* surface is a surface not having a regular or irregular pattern of protrusions that are tactually perceived as “rough” by man, i.e. not having a pattern of protrusions with an average height above 100μm, preferably not above 90μm, 80μm, 70μm, 60μm, 50μm, 40μm, 30μm, 20μm, 10μm, 9μm, 8μm, 7μm, 6μm, 5μm, 4μm, 3μm, 2μm or even 1 μm, and a surface not having a regular or irregular pattern of indentations or cavities that are visually perceived as the inverse of such protrusions, i.e. not having a pattern of indentations with an average depth of more than 100μm, preferably not more than 90μm, 80μm, 70μm, 60μm, 50μm, 40μm, 30μm, 20μm, 10μm, 9μm, 8μm, 7μm, 6μm, 5μm, 4μm, 3μm, 2μm or even 1 μm.

## EMBODIMENTS OF THE INVENTION

A thermoplastic material specifically suitable for the sole of the shoe according to the present invention is thermoplastic elastomers. Thermoplastic elastomers (TPE), sometimes referred to as thermoplastic rubbers, are a class of copolymers or a physical mix of polymers which consist of materials with both thermoplastic and elastomeric properties. Six generic classes of commercial TPEs can be distinguished: styrenic block

copolymers, thermoplastic olefins, elastomeric alloys, thermoplastic polyurethanes, thermoplastic copolyester and thermoplastic polyamides.
In an embodiment the shoe according to the invention has a sole that comprises a foamed composition comprising a thermoplastic copolyester elastomer in an amount of 70 to 99wt% based on the total amount of the foamed composition. In another embodiment, the foamed composition comprises a thermoplastic copolyester elastomer in an amount of 70 to 99wt% and a plasticizer in an amount of 1 to 30wt% based on the total amount of the foamed composition. Such compositions are disclosed in WO2018134166. Surprisingly, the inventors have found that the presence of a plasticizer in combination with a thermoplastic copolyester elastomer results in the possibility to achieve low density foams which exhibit less cracks, which are ideally suitable as a sole material in shoes. Lower density crack-free foams are very attractive as it is an important feature in applications where light-weight is favorable, in particular in athletic shoes. A foamed composition is herein understood to be known to a person skilled in the art. Preferably a foamed composition has a density of between 0.1 and 0.7 g/cm$^3$, typically between 0.2 and 0.3 g/cm$^3$, especially for use in athletic shoes. A thermoplastic copolyester elastomer is herein understood to be a copolymer comprising hard segments built up from polyester repeating units, and soft segments chosen from another type of polymer.

In a further embodiment, the thermoplastic copolyester elastomer comprises hard segments built up from polyester repeating units derived from at least one aliphatic diol and at least one aromatic dicarboxylic acid or an ester thereof, and soft segments chosen from the group consisting of aliphatic polyether, aliphatic polyester, aliphatic polycarbonate, dimer fatty acids and dimer fatty diols and combinations thereof.

Aliphatic diols contain generally 2-10 C-atoms, preferably 2-6 C-atoms. Examples thereof include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, butylene glycol, 1,2-hexane diol, 1,6-hexamethylene diol, 1,4-butanediol, 1,4-cyclohexane diol, 1,4-cyclohexane dimethanol, and mixtures thereof. Preferably, 1,4-butanediol is used. Suitable aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, phthalic acid, 2,6-naphthalenedicarboxylic acid and 4,4'-diphenyldicarboxylic acid, and mixtures thereof. Also very suitable is a mixture of 4,4’-diphenyldicarboxylic acid and 2,6-naphthalenedicarboxylic acid or a mixture of 4,4’-diphenyldicarboxylic acid and terephthalic acid. The mixing ratio between 4,4’-diphenyldicarboxylic acid and 2,6-naphthalenedicarboxylic acid or 4,4’-diphenyldicarboxylic acid and terephthalic acid is preferably chosen between 40:60 – 60:40 on weight basis in order to optimize the melting temperature of the thermoplastic copolyester.

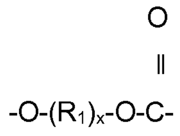
The hard segment preferably has as repeating unit chosen from the group consisting of ethylene terephthalate (PET), propylene terephthalate (PPT), butylene terephthalate (PBT), polyethylene bibenzoate, polyethylene naphthalate, polybutylene bibenzoate, polybutylene naphthalate, polypropylene bibenzoate and polypropylene naphthalate and combinations thereof. Preferably, the hard segment is butylene terephthalate (PBT), as thermoplastic copolyester elastomers comprising hard segments of PBT exhibit favourable crystallisation behaviour and a high melting point, resulting in thermoplastic copolyester elastomer with good processing properties and excellent thermal and chemical resistance.

Soft segments chosen from aliphatic polyesters have repeating units derived from an aliphatic diol, and an aliphatic dicarboxylic acid or repeating units derived from a lactone. Suitable aliphatic diols contain generally 2-20 C-atoms, preferably 3-15 C-atoms in the chain and an aliphatic dicarboxylic acid containing 2 - 20 C atoms, preferably 4 - 15 C atoms. Examples thereof include ethylene glycol, propylene glycol, butylene glycol, 1,2-hexane diol, 1,6-hexamethylene diol, 1,4-butanediol, cyclohexane diol, cyclohexane dimethanol, and mixtures thereof. Preferably, 1,4-butanediol is used. Suitable aliphatic dicarboxylic acids include sebacic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, adipic acid, glutaric acid, 2-ethylsuberic acid, cyclopentanedicarboxylic acid, decahydro-1,5-naphtylene dicarboxylic acid, 4,4’-bicyclohexyl dicarboxylic acid, decahydro-2,6-naphthylene dicarboxylic acid, 4,4’-methylenebis (cyclohexyl)carboxylic acid and 2,5-furan dicarboxylic acid. Preferred acids are sebacic acid, adipic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid. Most preferred is adipic acid. Preferably, the soft segment is polybutylene adipate (PBA) which may be obtained from 1,4 butanediol and adipic acid.

The soft segment may be aliphatic polyethers, which may comprise units of polyalkylene oxides, such as polyethylene oxide and polypropylene oxide and polytetramethylene oxide and combinations thereof, either as individual segment or combined in one segment. A combination is for example ethylene oxide-capped polypropylene oxide.

A preferred soft segment is polytetramethylene oxide (PTMO). Also soft segments comprising a block copolymer in which two types of glycols are reacted to form a soft segment such as based on polyethylene oxide (PEO) and polypropylene oxide (PPO) can be used. The latter is also referred to as PEO-PPO-PEO, as the PEO blocks are at the ends of a soft segment as PEO reacts best with a hard segment. PTMO, PPO and PEO based soft segments allow for foams having a lower density.

The soft segment may be an aliphatic polycarbonate and is made up of repeating units from at least one alkylene carbonate. Preferably as alkylene carbonate repeating unit is represented by the formula:



$$-O-(R_1)_x-O-\overset{\overset{O}{\|}}{C}-$$

where $R_1$= alkyl and X= 2 – 20.

Preferably $R_1$ = CH2 and x = 6 and the alkylene carbonate is therefore hexamethylene carbonate, as this provides high heat resistance to the article and is readily available.

The soft segment may be dimer fatty acids or dimer fatty diols and combinations thereof. The dimerised fatty acids may contain from 32 up to 44 carbon atoms. Preferably the dimerised fatty acids contain 36 carbon atoms. Also suitable are dimer fatty diols which may be derived from the dimer fatty acids as disclosed above. For example a dimerised fatty diol may be obtained as a derivative of the dimerised fatty acid by hydrogenation of the carboxylic acid groups of the dimerised fatty acid, or of an ester group made thereof. Further derivatives may be obtained by converting the carboxylic acid groups, or the ester groups made thereof, into an amide group, a nitril group, an amine group or an isocyanate group.

In a preferred embodiment the foamed composition comprises a thermoplastic copolyester elastomer having hard and soft segments, wherein the hard segment is chosen from PBT or PET, preferably PBT, and the soft segment is chosen from the group consisting of polybutylene adipate (PBA) polyethylene oxide (PEO), polypropylene oxide (PPO), polytetramethylene oxide (PTMO), PEO-PPO-PEO and combinations thereof, preferably PTMO, as this provided an article exhibiting low densities. In a further preferred embodiment the foamed composition comprises a thermoplastic copolyether-ester elastomer composed of PBT and PTMO.

Plasticizers are known substances to a person skilled in the art per se, and for example lower the hardness and/or increases the strain at break of the composition as compared to the elastomer itself. Plasticizers are present in an amount of between 1 to 30 wt% based on the total amount of the foamed composition, preferably between 5 to 25 wt% and even more preferred between 8 to 20 wt%. Plasticizers include for example phthalate esters, dibasic acid esters, mellitates and esters thereof, cyclohexanoate esters, citrate esters, phosphate esters, modified vegetable oil esters, benzoate esters, and petroleum oils, and combinations thereof. Preferably, the plasticizer is chosen from the group consisting of Triphenyl phosphate (TPP), tert-Butylphenyl diphenyl phosphate (Mono-t-but-TPP), di-tert-butylphenyl phenyl phosphate (bis-t-but-TPP), Tris(p-tert-butylphenyl) phosphate (tri-t-but-TPP), Resorcinol bis (Diphenyl Phosphate) (RDP), dichloropropyl phosphate, Bisphenol A bis-(Diphenyl Phosphate) (BDP), tricresyl phosphate (TCP), triethyl phosphate, tributyl phosphate (TBP), tri-2-ethylhexyl phosphate, trimethyl phosphate, epoxidized soybean oil (ESO), epoxidized palm oil (EPO), epoxidized linseed oil (ELO), argan oil and combinations thereof.

To the alternative, the shoe according to the invention comprises a sole of a thermoplastic material adhered to an upper shoe with a hot melt adhesive that is applied between the sole and the upper shoe, wherein the hot melt adhesive is fused with the thermoplastic material and wherein the sole comprises thermoplastic polyurethane (TPU). Beneficially, the sole comprises TPU in an amount of 70 to 100 wt% based on the total amount of the sole composition. Advantageously, the sole may comprise expanded, i.e. foamed TPU, such as disclosed in WO94/20568 or US2010/0222442. Thermoplastic polyurethanes and processes for their production are well known. TPU is a block copolymer consisting of alternating sequences of hard and soft segments or domains formed by the reaction of (1) diisocyanates with short-chain diols (so-called chain extenders) and (2) diisocyanates with long-chain diols. By varying the ratio, structure and/or moleculair weight of the reaction compounds, a large variety of different TPUs can be produced. Preferably, polyester-based TPUs are used for soles, for example those derived from adipic acid esters.

In another embodiment the upper shoe comprises a layer of textile material that is contiguous with the sole. A textile material appears to be ideally suitable to be connected to the sole via a hot melt adhesive without any special measures being needed, probably due to the irregular surface that is provided by the constituting yarns. The textile material may comprise polymeric yarns, such as yarns made from polyester polymer. This is particularly advantageous when the sole is also made from a polyester material, allowing easy recycling of the assembly of the upper shoe and sole. Insoles, midsoles and outsoles are all considered a sole in the context of this invention.

In an embodiment the hot melt adhesive comprises as a main constituent (i.e. in an amount of at least 50% by weight of the adhesive composition) a polymer selected from the group consisting of (co)polyurethane(s), (co)polycarbonate(s), (co)polyester(s), (co)polyamide(s), (co)poly(ester-amide(s), mixtures thereof and/or copolymers thereof. Preferably the hot melt adhesive comprises a (co)polyester as a main constituent. The (co) polyester may be built up from an acid selected from terephthalic acid, isophthalic acid, succinic acid, suberic acid, pimelic acid, adipic acid, fumaric acid, maleic acid, itaconic acid, dimer fatty acid, sebacic acid, azelaic acid, sulfoisophthallic acid or its metal salt, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, furane dicarboxylic acid, trimellitic anhydride and/or dialkyl esters thereof, mixtures thereof together with an alcohol selected from: ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,5-pentanediol, neopentyl glycol, diethylene glycol, triethylene glycol, 1,8-octanediol, 2,2,4-trimethyl-1,3-pentanediol, polyethylene glycol, polypropylene glycol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-isobutyl-1,3-propanediol, 1,3-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-butanediol, dimer fatty acid diol, glycerol, pentaerythrithol, di-pentaerythritol and/or mixtures thereof. Dimer fatty acids, dimer fatty diols and/or dimer fatty diamines (e.g. available from Croda) may also be used as potential building blocks to obtain the polymer.
Preferably, the (co)polyester is obtained and/or obtainable from reacting at least one acid selected from terephthalic acid, 2,5-furanedicarboxylic acid, adipic acid, fumaric acid, dimer fatty acid, sebacic acid, azelaic acid, succinic acid, and/or combinations thereof with at least one alcohol selected from ethylene glycol, 1,6-hexandediol, 1,4-butanediol, dimer fatty acid diol and/or combinations thereof.

The esterification polymerisation processes for making the polyester for use in the invention composition are well known in the art and need not be described here in detail. Suffice to say that they are normally carried out in the melt optionally using catalysts such as titanium- or tin-based catalysts and with the provision for removing any water (or alcohol) formed from the condensation reaction. Preferably if the polyester resin comprises carboxylic acid functionalities, they are derived from a polyacid and or anhydride.

In yet another embodiment, the upper shoe, the hot melt adhesive and the sole are made from a polyester material.

In again another embodiment of the shoe according to the invention the hot melt adhesive is semi-crystalline (i.e. it at least partly transforms into crystals when solidifying under equilibrium conditions), preferably having a melting enthalpy between 1 and 80 J/g, more preferably between 5 and 60 J/g and even more preferably between 10 and 40 J/g. The determination of the melting enthalpy is based on ASTM standard D3418 ("Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry") using a Mettler STARe differential scanning calorimeter. For the actual measurement an adhesive sample of approximately 10 mg is placed in a sample cup. This sample is kept in an oven for 15 minutes at 150°C. After this, the sample is cooled to 50°C and then heated to 250°C at a speed of 5°C/min. The sample is kept at 250°C for 1 minute and thereafter directly cooled to 25°C at a speed of 5°C/min. From the obtained DSC data the melting enthalpy of the sample polymer is obtained.

As indicated here above, the present invention is also embodied in a method of assembling a workpiece that can be used to manufacture a shoe according to the invention, which workpiece comprises a first body (*i.c.* the upper shoe) mechanically connected to a second body (*i.c.* the sole) by adhering the first body to a surface of the second body, the second body being composed of a thermoplastic material that has a melting temperature $T_M$, the method comprising:

- Heating a hot melt adhesive to a temperature $T_{HM}$ such that it softens;
- Heating the second body such that the thermoplastic material obtains a temperature $T_{SUB}$ below $T_M$;
- Applying the heated hot melt adhesive to the surface of the heated second body;
- Applying the first body to the second body to form the workpiece;
- Cooling the workpiece such that the hot melt adhesive hardens;
- Wherein the temperatures are chosen such that $(T_{HM} + T_{SUB})/2$ is equal to or higher than ($T_M$-10°C).

The technical features of any of the above described specific embodiments of the shoe according to the invention can also be combined with this method.

In another embodiment of the method of assembling a workpiece the second body is heated in its entirety. Such heating can for example be established by warming the whole second body in an oven or microwave or in a heated mold. Such heating thus differs from partial heating of the upper region, which can be achieved by external radiation or convection, i.e. heating only the outer side of the second body.

Particularly, in this method the temperatures are chosen such that ($T_{HM}$ + $T_{SUB}$)/2 differs from $T_M$ by a number of degrees chosen from the group consisting of -10, -9, -8, -7, -6, -5, -4, -3, -2, -1, 0, +1, +2, +3, +4, +5, +6, +7, +8, +9, +10, +11, +12, +13, +14, +15, +16, +17, +18, +19 or +20°C. A higher number leads to a larger part of the upper region of the thermoplastic body to be melted. However, advantageously, this part should not become too thick, since it will not increase the bonding strength, but may negatively influence the shape and mechanical properties of the thermoplastic body. Hence the preferred upper limit of 20°C.

In yet a further embodiment, the second body is heated such that the thermoplastic material obtains a temperature $T_{SUB}$ that is at most X °C less than $T_M$, X being chosen from the group that consists of 100, 90, 80, 70, 60, 55, 50, 45, 40, 35 and 30. It was found that the thermoplastic body preferably is not heated to temperature too close to its melting temperature.

The invention will now be further explained using the following non limiting examples.

## EXAMPLES

Figure 1 schematically shows the interaction between hot melt adhesive and various substrates.
Figure 2 schematically shows the constituting parts of a workpiece for use in the manufacture of a shoe.
Figure 3 schematically shows a cross section of a material used for an upper shoe of an athletic shoe.
Figure 4 schematically shows a test set-up for measuring the strength of a mechanical connection brought about by a hot melt adhesive.
Figure 5 is the SEM picture from the connected thermoplastic bodies of example 1.

Example 1 describes the connection of two thermoplastic bodies using a hot melt adhesive.

***Figure 1***

Figure 1 schematically shows the interaction between hot melt adhesive 4 and various substrates (200, 200’ and 200”). In figure 1A, the interaction between a layer 4 of hot melt adhesive in its hardened form (thus after application in liquid form and subsequent cooling down to below its solidification temperature) and a non-smooth surface of a body 200 is depicted. The surface of the body has various protrusions (201) and indentations (202) which serve as anchoring point for the hardened hot melt adhesive. This brings about a good mechanical connection between the hot melt adhesive 4 and the body 200.

In figure 1B, a situation is depicted wherein the body 200’ has a smooth surface, leading to the absence of anchoring points for the hot melt adhesive 4. This means that the mechanical connection, if any, between the layer of hot melt adhesive 4 and the body 200’ is very weak. The layers can be easily separated by using a slight pulling force to either of the layers.

In figure 1C the situation is depicted where body 200” is made of a thermoplastic material and the hot melt adhesive is heated sufficiently just before application thereof, to make sure that the upper region of the body 200“ is heated to above its melting temperature. This way, the molecules of the molten hot melt adhesive and the molten body 200” may be able to mix and unite (to fuse) to form one new intermediate material 204, which material may ultimately (after solidification of all molten material) serve as a mechanical bridge between the layer of hot melt adhesive 4 and the body 200”. Although indicated in the schematic representation of figure 1C as individually identifiable layers, in practice the layers 4 and 200” gradually change from one pure material to another with the mixed material of a gradually changing composition in between.

***Figure 2***

Figure 2 schematically shows in a cross section the constituting parts of a workpiece 1 for use in the manufacture of a shoe (which need not be more than the workpiece itself).

In the figure, part 2 is the (mid-)sole of the shoe, in this case consisting of a foamed composition comprising a copolyether-ester elastomer (55wt% PTMO and 45wt% PBT with respect to the amount of copolyether-ester elastomer) in an amount of 85wt%, and 15wt% epoxidised soybean oil as a plasticizer with respect to the total amount of foamed composition, leading to a foam having a density of 0.24 g/cm$^3$ and having $T_M$ of 160°C. The upper shoe 3 consists of a textile base layer and a top coat of polyurethane (see figure 3). Part 30 is a segment of the upper shoe 3 that is used for adhering the upper shoe 3 to the sole 2 using a hot melt adhesive (see Example 1). In dotted lines an outer sole 20 is depicted.

### *Figure 3*

Figure 3 schematically shows a cross section of a material used for an upper shoe 3 of an athletic shoe. The upper shoe 3 consists of a textile base layer 31 and a top coat of polyurethane (32). The textile layer 31 is the layer that will be used to make the connection with the sole as indicated in Figure 2.

### *Figure 4*

Figure 4 schematically shows a test set-up for measuring the strength of a mechanical connection brought about by a hot melt adhesive (in line with standardised method ASTM D3936). In this set-up, two bodies 2 and 3 having a width L are mechanically connected with a layer of hot melt adhesive 4. These layers are separated at one of the ends, exerting a separating force F. To make adequate shoes, F/L should be larger than 30 Newton per inch (larger than 11.8 Newton per cm).

### *Example 1*

Example 1 describes the connection of a thermoplastic body using a hot melt adhesive. In order to assess whether a hot melt adhesive could be used to adhere a first body to a thermoplastic body, two thermoplastic bodies were chosen, in this case foamed thermoplastic bodies as described in connection with figure 2. The melting temperature $T_M$ of these bodies is 160°C (determined with ASTM D3418-03 as described in this patent application). In a first attempt, a polyester hot melt adhesive having a melting enthalpy of 27±3 J/g was used (the determination of which is based on ASTM standard D3418 using a Mettler STARe differential scanning calorimeter), showing a first order transition temperature (solid to liquid) around 110°C. The hot melt was heated to a temperature of 180°C, thus well above its melting temperature and at a level that is common for using this hot melt to obtain strong connections. The thermoplastic bodies were preheated to various temperatures, ranging from 80°C to 100°C before the hot melt adhesive was applied, meaning that $(T_{HM} + T_{SUB})/2$ varied from 130 to 140°C, i.e. 30° to 20° below $T_M$. Directly after application of the adhesive, both bodies were pressed together. In none of the cases a good mechanical connection could be obtained. F/L was less than 5 N/inch value for each workpiece. This confirmed the common knowledge that thermoplastic materials cannot be adequately connected using a hot melt adhesive.

In a second attempt, the hot melt adhesive was heated to 210°C (i.e. still well below the temperature at which the polyester hot melt adhesive would (start to) degrade, i.e. around 250°C) and the thermoplastic bodies to a temperature ranging from 120 to 130°C, meaning that $(T_{HM} + T_{SUB})/2$ varied from 165 to 170°C, i.e. 5° to 10° over $T_M$. Either one or both sides of the bodies were provided with the melted adhesive. In addition to the type of polyester adhesive used in the first experiment (“Type 1”), another type was used (“Type 2”). Keeping all other variables the same as in the first experiment, this way a very good mechanical connection between the two thermoplastic bodies could be obtained. The data are indicated in table 1 below. In figure 5 a Scanning Electronic Microscopy (SEM) picture is shown, which demonstrates that at an enlargement of 650 times no boundary between the thermoplastic bodies can be distinguished for the example with the Type 2 adhesive. In figure 5 the upper shoe 3 is connected to midsole 2 in the same way as is schematically depicted in figure 2.

This makes clear that the provision of a connection with a (very) high mechanical strength can be obtained for various hot melt adhesives, without relying on particular organic binding molecules, primers or complicated heat-cool cycles, simply by choosing the temperatures such that $(T_{HM} + T_{SUB})/2$ is equal to or higher than $(T_M\text{-}10°C)$.

***Table 1*** Strength of mechanical connection using various hot melt adhesives

| Hot melt application | Adhesive | Load at failure (N/inch) | Comment |
|---|---|---|---|
| One sided | Type 1 | 49.1 | - |
| One sided | Type 1 | 47.3 | - |
| Two sided | Type 1 | 40.6 | - |
| Two sided | Type 1 | 44.0 | |
| Two sided | Type 1 | n.a. | Foam rupture* |

| | | | |
|---|---|---|---|
| Two sided | Type 2 | 98.2 | - |
| Two sided | Type 2 | n.a. | Foam rupture* |
| Two sided | Type 2 | n.a. | Foam rupture* |

**Foam rupture means that the bond was stronger than the intrinsic tear strength of the thermoplastic foam.*

Above experiments were also conducted using thermoplastic bodies consisting of a foamed composition comprising TPU. Similar results were obtained and connections with high mechanical strengths were provided accordingly.

# CLAIMS

1. A shoe comprising a sole composed of a thermoplastic material adhered to an upper shoe with a hot melt adhesive that is applied between the sole and the upper shoe, characterised in that the hot melt adhesive is fused with the thermoplastic material.

2. A shoe according to claim 1, characterised in that the sole comprises a foamed composition comprising a thermoplastic copolyester elastomer in an amount of 70 to 99 wt% based on the total amount of the foamed composition.

3. A shoe according to claim 2, characterised in that the foamed composition comprises a thermoplastic copolyester elastomer in an amount of 70 to 99 wt% and a plasticizer in an amount of 1 to 30 wt% based on the total amount of the foamed composition.

4. A shoe according to claim 2 or 3, characterised in that the thermoplastic copolyester elastomer comprises hard segments built up from polyester repeating units derived from at least one aliphatic diol and at least one aromatic dicarboxylic acid or an ester thereof, and soft segments chosen from the group consisting of aliphatic polyether, aliphatic polyester, aliphatic polycarbonate, dimer fatty acids and dimer fatty diols and combinations thereof.

5. A shoe according to claim 4, characterised in that the hard segments are chosen from the group consisting of ethylene terephthalate (PET), propylene terephthalate (PPT), butylene terephthalate (PBT), polyethylene bibenzoate, polyethylene naphtalate (PEN), polybutylene bibenzoate, polybutylene naphtalate, polypropylene bibenzoate and polypropylene naphtalate and combinations thereof and the soft segments are chosen from the group consisting of aliphatic polyether, aliphatic polyester, aliphatic polycarbonate, dimer fatty acids and dimer fatty diols and combinations thereof.

6. A shoe according to claim 5, characterised in that the hard segment is chosen from PBT or PET and the soft segment is chosen from the group consisting of polybutylene adipate (PBA), polyethylene oxide (PEO), polypropylene oxide (PPO), polytetramethylene oxide (PTMO), PEO-PPO-PEO and combinations thereof.

7. A shoe according to any of the preceding claims, characterized in that the upper shoe comprises a layer of textile material that is contiguous with the sole.

8. A shoe according to claim 7, characterized in that textile material comprises polymeric yarns.

9. A shoe according to claim 8, characterized in that polymeric yarns comprise polyester polymer.

10. A shoe according to any of the preceding claims, characterised in that the hot melt adhesive comprises a polymer selected from the group consisting of (co)polyurethane(s), (co)polycarbonate(s), (co)polyester(s), (co)polyamide(s), (co)poly(ester-amide(s)), mixtures thereof and/or copolymers thereof.

11. A shoe according to claim 10, characterised in that the hot melt adhesive comprises a (co)polyester.

12. A shoe according to any of the preceding claims, characterised in that the hot melt adhesive is semi-crystalline, preferably having a melting enthalpy between 1 and 80 J/g.

13. A method of assembling a workpiece comprising a first body mechanically connected to a second body by adhering the first body to a surface of the second body, the second body being composed of a thermoplastic material that has a melting temperature $T_M$, the method comprising:

- Heating a hot melt adhesive to a temperature $T_{HM}$ such that it softens;
- Heating the second body such that the thermoplastic material obtains a surface temperature $T_{SUB}$ below $T_M$;
- Applying the heated hot melt adhesive to the surface of the heated second body;
- Applying the first body to the second body to form the workpiece;
- Cooling the workpiece such that the hot melt adhesive hardens;
- Wherein the temperatures are chosen such that $(T_{HM} + T_{SUB})/2$ is equal to or higher than $(T_M\text{-}10°C)$.

14. A method according to claim 13, characterised in that temperatures are chosen such that $(T_{HM} + T_{SUB})/2$ differs from $T_M$ by a number of degrees chosen from the group consisting of -10, -9, -8, -7, -6, -5, -4, -3, -2, -1, 0, +1, +2, +3, +4, +5, +6, +7, +8, +9,

+10, +11, +12, +13, +14, +15, +16, +17, +18, +19 or +20°C.

15. A method according to any of the claims 13 or 14, characterised in that the second body is heated such that the thermoplastic material obtains a temperature $T_{SUB}$ that is at most X °C less than $T_M$, X being chosen from the group that consists of 100, 90, 80, 70, 60, 55, 50, 45, 40, 35 and 30.

16. A method according to any of claims 13 to 15, characterised in that the second body is heated in its entirety.

17. A workpiece obtainable by a method according to any of the claims 13 to 16.

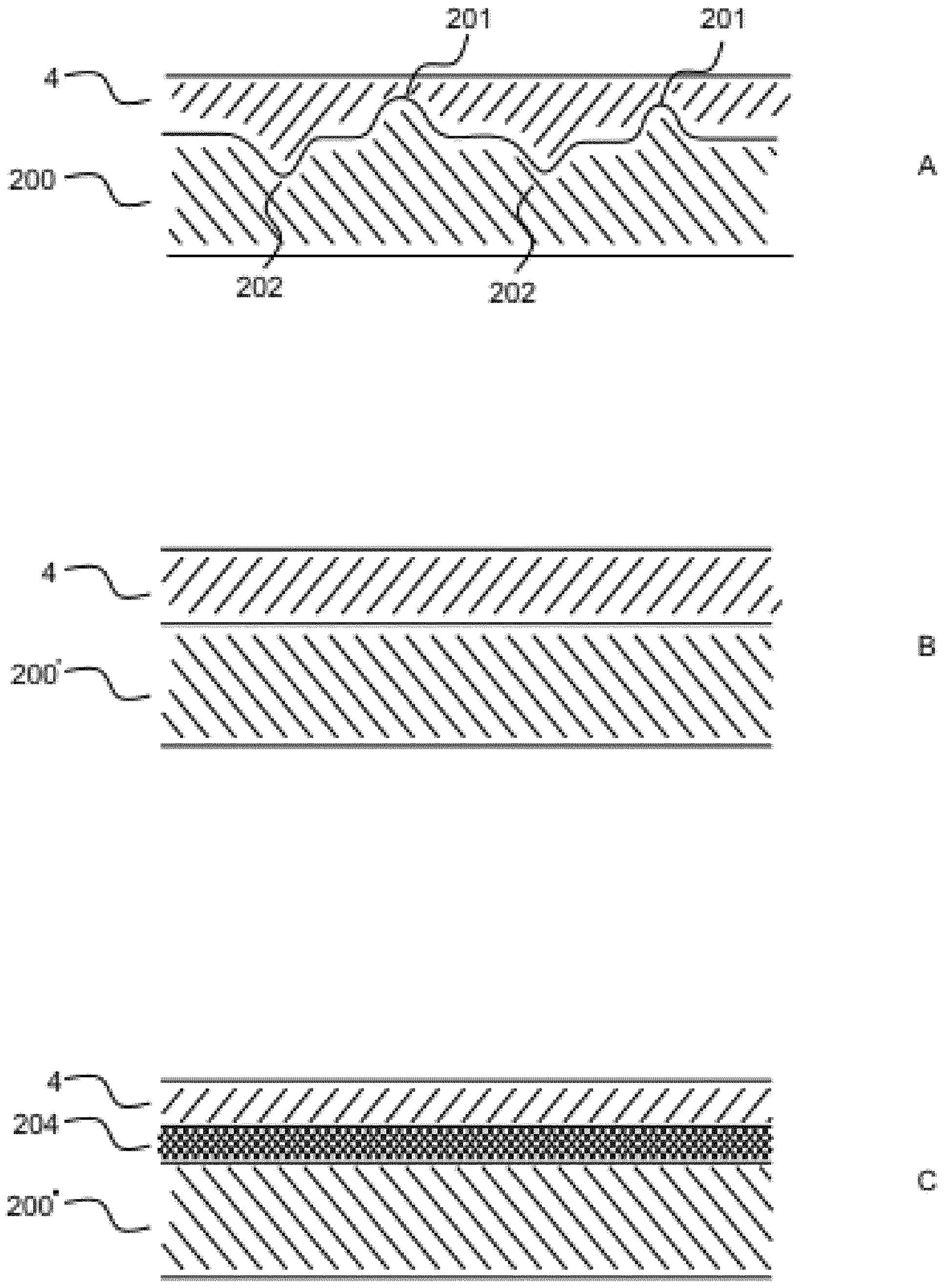


Fig. 1

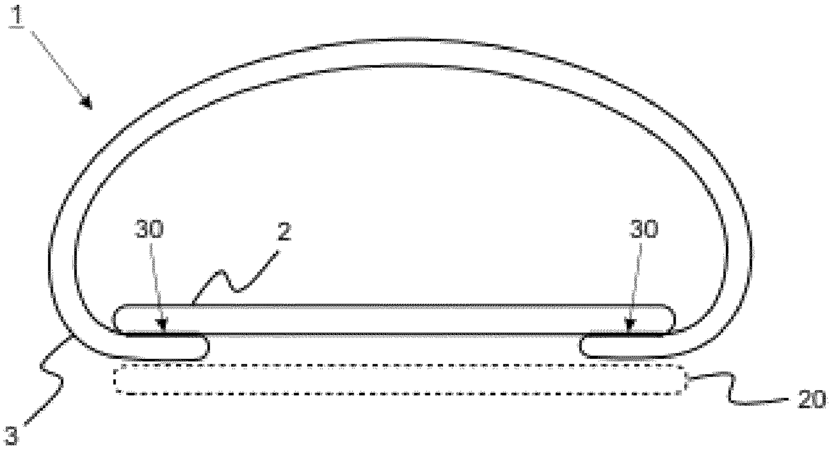


FIG. 2

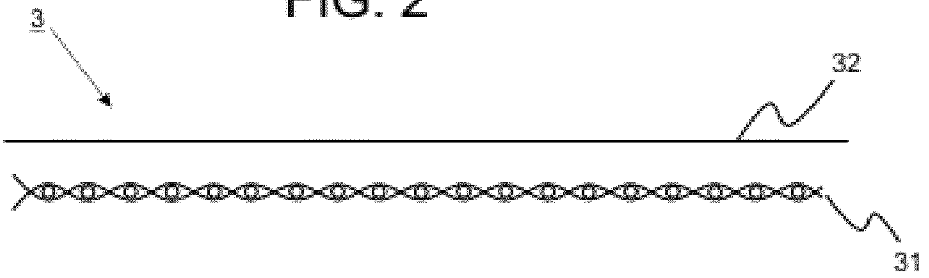


FIG. 3

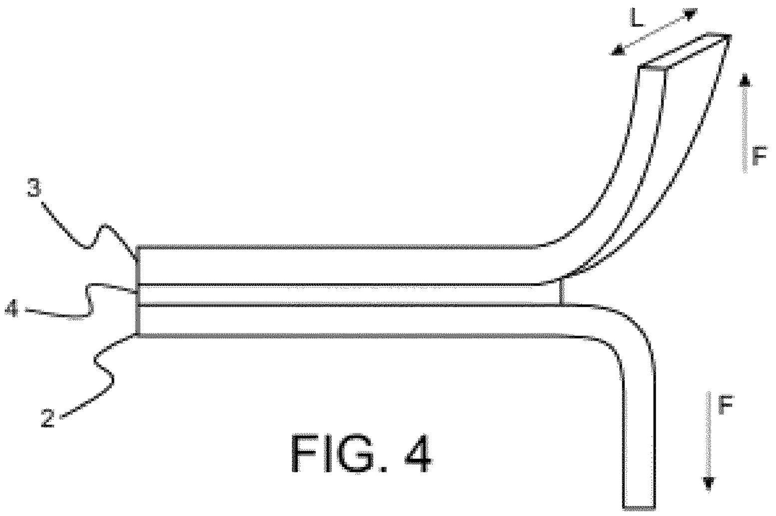


FIG. 4

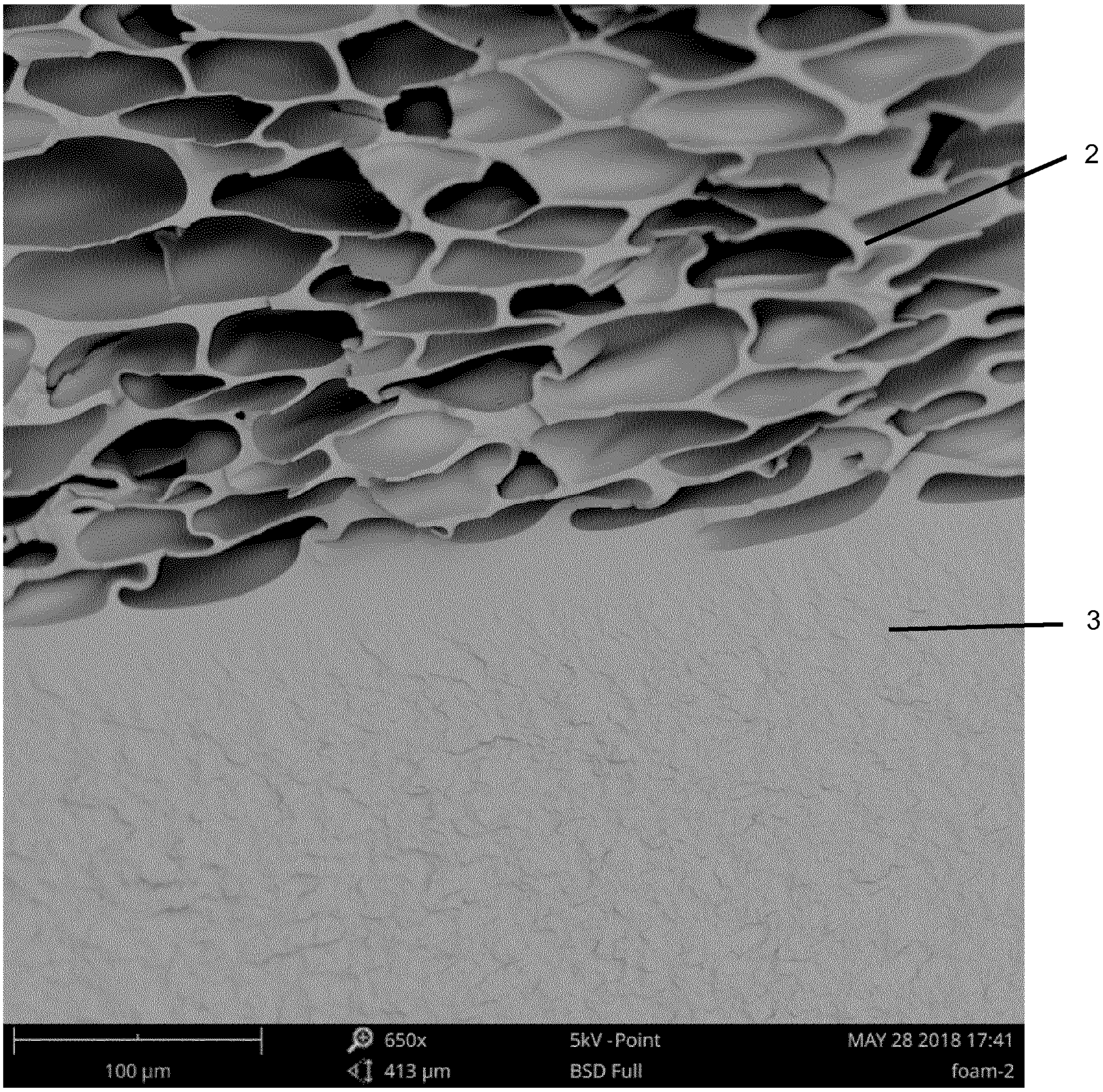


FIG. 5

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/073475

A. CLASSIFICATION OF SUBJECT MATTER
INV. A43B9/12 A43D25/20 A43B13/04
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)
A43B A43D

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. |
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| A | US 3 309 724 A (SPRAGUE JR GORDON V ET AL)<br>21 March 1967 (1967-03-21)<br>the whole document<br>----- | 1-17 |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 16 October 2019 | 23/10/2019 |

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

1

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