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(54) **Clean room shoe sole**

(57) The present invention relates to a shoe sole (1), in particular for a clean room shoe, the shoe sole (1) comprising a base (2) with a ground contacting face (3) and an inner face (4) facing the interior of the shoe. The ground contacting face (3) comprises at least one ground contacting protrusion (5, 15) which extends from the ground contacting face (3) of the sole in a ground contacting direction. The at least one ground contacting protrusion (5) extends towards and into the inner face (4) of the shoe sole. The at least one ground contacting protrusion (5) is located in a heel part (7) of the ground contacting face and is dimensioned to contact a walking surface during normal use of the clean room shoe. The at least one ground contacting protrusion (5) is made of a plastic material comprising a vulcanized thermoplastic material and at least one anti-static agent.

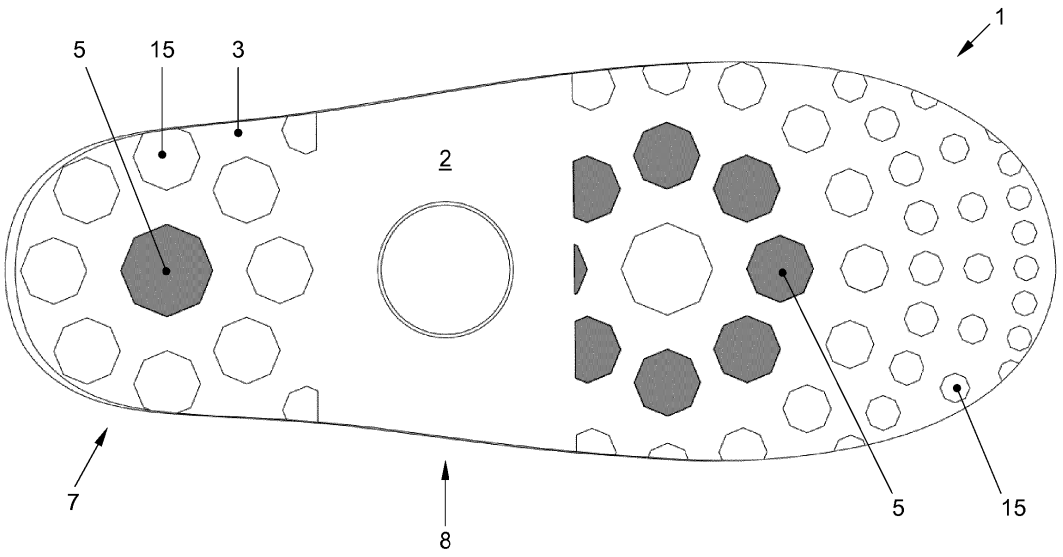


Fig. 1

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Description

[0001] The present invention relates to a shoe sole, in particular for a clean room shoe, the shoe sole comprising a base with a ground contacting face and an inner face facing the interior of the shoe, according to the preamble of the first claim.

[0002] Clean rooms find application in a wide variety of activities, such as the production of micro-electronic parts and optical parts. Clean rooms may be used for precision measurements, in aerospace centers, in scientific biotechnological or medical research etc. Clean rooms seek to control the level of contamination present in the room by controlling the number of dust particles of a specified particle size, present per cubic meter of room volume. Stringent construction requirements, and room entrance and leaving protocols seek to control contamination levels. Contamination of the clean room during use by staff working in it, is minimized by the use of adequate clothing. Particular clothing includes a.o. an overall, a head cap and adequate shoes and/or shoe covers. Nowadays, proper usage of clean room clothing is becoming more significant, as the clean rooms themselves operate at high levels of performance.

[0003] Shoes or disposable shoe covers form an important part of the clean room clothing. They may be made of a variety of plastic materials. Shoe covers made of non-woven spun-bond polypropylene (SBPP), though they prevent contaminants from a shoe worn outside from getting out into the clean room, constitute a well known source of unwanted contamination, as they shed particles and tear easily, thereby further increasing the shed particles contamination. The ability of SBBP shoe covers to absorb moisture on the floor increases the risk to tearing apart of the material and creates a slip hazard. Coating of the polypropylene clean room shoe cover with a PVC sole, although it makes the clean room shoe cover anti-skid even on wet floors, is a clean and durable, but expensive option for a shoe cover which is to be disposed. SBBP shoe covers are autoclavable and can be worn for up to a week. Shoe covers made of cross-linked polyethylene (CPE) proved to be cleaner. They last longer, as they are less prone to tearing than SBPP.

[0004] Disposable garments tend to digest a significant part of the clean room budget. Re-usable clean room shoes provide a solution when looking to cut down on the waste produced by the disposable clean room garments. They usually have slip-resistant soles and can be easily washed and wiped. Since clean room shoes are meant to be worn all day, comfort is an important parameter.

[0005] However, since most plastic materials are insulators, static charge will generally build up or accumulate on such materials. This gives rise to numerous problems in industrial applications. Not only will static build up and its sudden discharge annoy those wearing plastic clean room shoes, but sudden discharge of static charges may cause damage to sensitive electronic components - only a few hundred volts suffice.

[0006] DE3830744 discloses that clean room shoes having an outer sole made of a plastic material, in particular polyurethane, are known in the art. Other soles of this type however are highly anti-static, they have an electrical resistance of more than 10 MegaOhm which is much higher than the resistance of the human skin, and as a consequence provide weak dissipation of static charges, which is disadvantageous.

[0007] DE3830744 discloses to produce clean room shoe soles using a blend B of emulsion PVC, suspension PVC, plasticizers, stabilizers, and blowing agents, which is conventionally used for the production of shoe soles. By mixing this blend B with a further blend A comprising stabilizers, lubricants, and electrically conductive members, a material with a reduced electrical resistance may be obtained which is suitable for producing shoe soles capable of dissipating electrical charges. The electrical resistance of blend B and of the shoe sole may be controlled by correspondingly adapting the amount of blowing agent incorporated into blend B. In order to improve the electrically conductive contact between a human foot and the shoe sole used in clean rooms, it is advised to have a plurality of local electrical conductive parts over the entire surface area of the sole, which provide electrical conductivity between the upper and lower side of the shoe. This may be achieved by providing in the inner part of the shoe, on top of the running sole, a contact sole which contacts the foot. The contact sole may be rendered electrically conductive, by incorporation of an electrically conductive seam on the sole or by incorporation in the sole of electrically conductive bodies.

[0008] DE3830744 however shows the disadvantage that electrical conductivity is provided by the presence of the metallic parts, which may bring discomfort when wearing the shoe. Also, insertion of the metallic parts stands in the way of a more automated production of the clean room shoe.

[0009] The present invention therefore seeks to provide a sole for a clean room shoe, which is capable of providing the adequate dissipate of static electrical charges and which may be produced in large series in an automated manner.

[0010] This is achieved according to the present invention with a shoe sole showing the technical features of the characterizing portion of the first claim.

[0011] Thereto the clean room shoe sole of this invention is **characterized in that** the ground contacting face comprises at least one ground contacting protrusion, which extends from the ground contacting face of the sole in a ground contacting direction, in that the ground contacting protrusion extends towards and into the inner face of the shoe sole, in that the ground contacting protrusion is located in a heel part of the ground contacting face and is dimensioned to contact a walking surface during normal use of the clean room shoe, and in that the ground contacting protrusion is made of a material comprising a vulcanized thermoplastic material and an

anti-static agent.

[0012] The presence of the anti-static agent in the vulcanized thermoplastic material provides a protrusion with anti-static properties. One side of the anti-static protrusion contacts the person wearing the shoe, another side of the anti-static protrusion contacts the walking surface and thereby ensures that electrical charges may be dissipated from the person wearing the shoe to the walking surface. The positioning of this protrusion in a heel part of the clean room sole, permits to ensure that the protrusion providing the anti-static properties always contacts the walking surface during normal use, and ensures that an effective and continuous dissipation of electric charges from the person wearing the shoe towards the walking surface or the ground may take place. The inventors have namely observed that in the course of activities such as walking, standing or walking back and forth, the heel part of a shoe always contacts the walking surface. As a result, the risk to building of electrostatic charges in the shoe sole may be reduced to a minimum.

[0013] According to a first preferred embodiment, the shoe sole and the at least one ground contacting protrusion are made of the same plastic material, comprising a vulcanized thermoplastic material and at least one anti-static agent. This permits producing the at least one anti-static protrusion in one part with the remainder of the shoe sole, in one single production step, thereby significantly reducing manual handling and production costs. Thus, both the anti-static ground contacting protrusion and the remainder of the shoe sole are made of a vulcanized thermoplastic material comprising an anti-static agent. This way also, optimum binding of the anti-static protrusion to the remainder of the sole may be guaranteed and a shoe sole is provided which may be recycled as one part. With anti-static protrusion or anti-static ground contacting protrusion is meant any ground contracting protrusion made of a plastic material comprising a vulcanized thermoplastic material and an anti-static agent.

[0014] According to a second embodiment of this invention, the at least one anti-static protrusion and the remainder of the shoe sole are made of different plastic materials. This may for example be achieved in that the at least one ground contacting protrusion and the remainder of the shoe sole comprise different thermoplastic materials, or in that the at least one ground contacting protrusion and the remainder of the shoe sole comprise a different anti-static agent.

[0015] In order to improve the contact with the person wearing the shoe sole, the at least one protrusion is extended so as to extend along at least part of the inner face of the sole. This is achieved by extending the protrusion to provide a sole part.

[0016] In particular, in the embodiment where the at least one anti-static protrusion and the remainder of the shoe sole are made of different plastic materials, the anti-static protrusion is made of a plastic material comprising a vulcanized thermoplastic material and at least one anti-static agent, and the remainder of the shoe sole is made of a plastic material which comprises a vulcanized thermoplastic material, but does not comprise an anti-static agent. The production of the anti-static protrusion and the remainder of the sole of different materials, permits selecting the optimum material for each of the parts taking into account the function of the part in question. The material for the anti-static protrusion may thus be optimized for its anti-static properties, thermal stability and wearing resistance, whereas the material for the remainder of the sole may be optimized for its comfort, its wearing resistance, thermal stability and costs.

[0017] Because both the anti-static protrusion and the remainder of the shoe sole are made of a plastic material comprising a vulcanized thermoplastic material, both parts may be produced using the same process of injection molding. In particular, the anti-static protrusion may be produced so as to form one part with the remainder of the sole. This may be achieved by first forming the remainder of the shoe sole, followed by forming the anti-static protrusion in a stage where the remainder of the plastic material of the sole is still in a molten state, thereby enabling that both materials adhere to each other in the molten phase and optimum adhesion of the anti-static protrusion to the remainder of the material of the shoe sole may be achieved. Moreover, where the anti-static protrusion and the remainder of the sole are made of a material comprising the same vulcanized thermoplastic material, the shoe sole may be recycled as one part.

[0018] Often the presence of a single anti-static protrusion will suffice to provide anti-static properties to the shoe sole. Depending on the dimensions of the anti-static protrusion, the nature and charge dissipating properties of the anti-static material and the charges to be dissipated, a single anti-static protrusion or a plurality of such protrusions may be provided in the shoe sole.

[0019] With this embodiment material costs for the sole may be kept within acceptable limits, since the anti-static material is the material cost determining factor. It appears that some, but an acceptable increase of production costs for incorporation of the anti-static protrusion may occur, in case the anti-static protrusion and the remainder of the shoe sole are made of different plastic materials.

[0020] Within the present invention a wide range of vulcanized thermoplastic materials may be used. The preferred vulcanized thermoplastic material has a sufficient Shore A hardness, preferably a Shore A hardness of between 35 and 95, more preferably between 50 and 95, most preferably between 60 and 80, particularly between 60 and 75, more particularly between 60 and 70. The Shore A hardness may be measured according to ISO 868. The vulcanized thermoplastic material preferably has a Shore D hardness of between 30 and 60. Thus a shoe sole is provided which shows a good wearing comfort with sufficient flexibility and a good resistance against wearing, thereby minimizing the risk to dust formation.

[0021] To minimize the risk to contamination, the at least one ground contacting protrusion is fastened to the

sole in a seamless manner.

[0022] The shoe sole of the present invention is suitable for use in a wide variety of applications. The shoe sole of this invention may be used as shoe sole for clean room shoes, it may be used as the shoe sole part of a clean room jump suit. The shoe sole of the present invention is however also suitable for use in sports shoes, safety shoes etc. The shoe sole may be used as such, or it may be painted or covered or coated with a suitable material, as long as the anti-static properties are not adversely affected.

[0023] The vulcanized thermoplastic material used with the present invention will usually comprise a rubber material and a thermoplastic material. The vulcanized thermoplastic material may further comprise the usual ingredients.

RUBBER MATERIAL.

[0024] Within the scope of this invention a wide variety of rubber materials may be used. The rubber material may for example comprise natural rubber, nitrile rubber, acrylic rubber, styrene butadiene rubber, styrene-butadiene-styrene rubber (SBS), nitrile butadiene rubber, isobutene-isoprene rubber, polybutadiene, polyisoprene, polychloroprene, ethylene-propylene copolymers, hereinafter called EPM, ethylene-propylene-diene terpolymers, hereinafter called EPDM, styrene-ethylene-butylene-styrene block copolymers (SEBS), butyl rubber, isobutylene-p-methylstyrene copolymers or brominated isobutylene-p-methylstyrene copolymers, alpha-olefins in particular those having 3-8 carbon atoms, or a blend of two or more of the afore mentioned materials. Examples of alpha-olefins having 3 to 8 carbon atoms are propene, 1-butene, 1-pentene, 1-hexene, and 1-octene. Commercially available copolymers are for example EXACT™ or ENGAGE™.

[0025] The vulcanized thermoplastic material used in this invention may comprise a single rubber material or a mixture of two or more different rubber materials.

[0026] The vulcanized thermoplastic material used in this invention may comprise at least one unsaturated diene elastomer as rubber material, in particular it may comprise one single elastomer, or a mixture of two or more different elastomers. The diene monomers may be conjugated or unconjugated monomers bearing two double carbon-carbon bonds. The diene elastomer may be a homopolymer or copolymer.

[0027] Preferably, use is made of a diene elastomer which is at least in part obtained from conjugated diene monomers including:

a) homopolymers obtained by homopolymerization of a conjugated diene monomer, in particular a diene monomer having 4-12 carbon atoms, for example 1,3-butadiene, 2-methyl-1,3-butadiene (or isoprene), a 2,3-di(C1 to C5 alkyl)-1,3-butadiene, for example 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, and phenyl-1,3-butadiene;

b) copolymers obtained by copolymerization of one or more conjugated dienes with each other or with one or more vinyl aromatic compounds, in particular a diene monomer having 4-12 carbon atoms and one or more vinyl aromatic compounds having from 8 to 20 carbon atoms such as for example styrene, ortho-, para- or meta-methylstyrene. Examples of copolymers suitable for use with the present invention include butadiene-styrene copolymers and butadiene-isoprene copolymers.

[0028] In a first preferred embodiment EPDM or EPM is used as rubber, more preferably EPDM. The preferred EPDM contains 40-80 parts by weight of ethylene monomer units, 58-18 parts by weight of monomer units originating from an alpha-olefin and 2-12 parts by weight of monomer units originating from a non-conjugated diene whereby the total weight of the ethylene monomer units, the alpha-olefin and the non- conjugated diene is 100. The preferred alpha-olefin is propylene. The preferred non- conjugated diene use is dicyclopentadiene (DCPD), 5-ethylidene-2-norbornene (ENB) or vinylnorbomene (VNB) or mixtures thereof.

[0029] Both EPDM and EPM are capable of providing a vulcanized material with a good temperature stability at temperatures of about 135°C which are usually employed to sterilise clean room clothing, where the material appears to be capable of the withstanding repeated sterilisation at high temperature or by irradiation with γ-radiation, at minimal risk to damaging of the material.

[0030] In a second preferred embodiment use is made of nitrile rubber, as this is an advantageous material from an economic point of view, but also because of its haptic, and temperature stability, which is important since the sole may be subjected to repeated autoclaving at 135°C or higher or to irradiation with γ-radiation. Nitrile rubber provides an advantageous combination of properties, by providing sufficient flexibility and wearing comfort and good resistance against wearing and particle loss.

THERMOPLASTIC MATERIALS.

[0031] Within the scope of the present invention a wide variety of thermoplastic materials may be used. The vulcanised thermoplastic material may comprise one single type of thermoplastic material or a mixture of two or more different thermoplastic materials. Suitable thermoplastic materials for use in the vulcanized thermoplastic material include polyolefins, polyamides and polycarbonates, in particular co-polyetheresters, polymers containing polyamide blocks and polyether blocks, and mixtures of two or more of the afore mentioned materials, in particular mixtures of polyamide and of polyolefins. The thermoplastic material may for example comprise a thermoplastic polyethylene or polypropylene or a mixture thereof, a

preferred embodiment uses thermoplastic polypropylene.

[0032] Within the scope of this invention, preferably use is made of a polyolefin based thermoplastic material. Polyolefins are understood to mean polymers comprising olefin units, such as, for example, ethylene, propylene or 1-butene units and the like. Examples of the polyolefin thermoplastic suitable for use with this invention are homo-polymers of ethylene or propylene, copolymers of ethylene or propylene, copolymers of ethylene and an alpha-olefin co-monomer with 4-20 carbon atoms or copolymers of propylene and an alpha-olefin co-monomer with 4-20 carbon atoms. The polyolefin homo- and copolymers may be prepared with a Ziegler-Natta catalyst, a metallocene catalyst or with any other single site catalyst. Preferably, polypropylene, polyethylene or mixtures thereof are used as a polyolefin based thermoplastic, more preferably polypropylene is used as polyolefin. The polypropylene may be linear or branched. Preferably a linear polypropylene is used. The melt flow index (MFI) of the polypropylene preferably is between 0.1 and 100; more preferably between 0.1 and 50; most preferably 0.3-20, measured according to ISO standard 1133 (230^0C; 2.16 kg load).

[0033] If so desired, the thermoplastic material may comprise copolymers of ethylene/of an alkyl (meth)acrylate, copolymers of ethylene/of an alkyl (meth)acrylate/of maleic anhydride, the maleic anhydride being grafted or copolymerized, copolymers of ethylene/of an alkyl (meth)acrylate/of glycidyl methacrylate, the glycidyl methacrylate being grafted or copolymerized, polypropylene.

[0034] If so desired these products may be grafted with functional groups, for example they may be grafted with unsaturated carboxylic acid anhydrides, such as maleic anhydride or unsaturated epoxides, such as glycidyl methacrylate, copolymers of ethylene with at least one product chosen from (i) unsaturated carboxylic acids, their salts or their esters, (ii) vinyl esters of saturated carboxylic acids, (iii) unsaturated dicarboxylic acids, their salts, their esters, their half-ester, or their anhydrides, or (iv) unsaturated dicarboxylic acid anhydrides or unsaturated epoxides, styrene/ethylene-butene/styrene (SEBS) copolymers which are optionally modified with maleic acid functionalities.

[0035] Suitable polyamides include a single polyamide or mixtures of two or more different polyamides. Polyamide is understood to mean the condensation products of one or a number of amino acids, for example aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids, from one or a number of lactams, such as caprolactam, oenantholactam and lauryl lactam; of one or a number of salts or mixtures of diamines, such as hexamethylenediamine, dodecamethylenediamine, meta-xylylenediamine, bis(p-aminocyclohexyl)methane and trimethylhexamethylenediamine, with diacids, such as isophthalic, terephthalic, adipic, azelaic, suberic, sebacic and dodecanedicarboxylic acids; or of the mixtures of some of these monomers which results in copolyamides. Polyamide mixtures can be used. Use is advantageously made of PA-11, PA-12 and the copolyamide containing 6 units and 12 units (PA-6/12).

[0036] Co-polyetheresters are copolymers having polyether units derived from polyetherdiols, such as polyethylene glycol (PEG), polypropylene glycol (PPG) or polytetramethylene glycol (PTMG), dicarboxylic acid units, such as terephthalic acid, and glycol (ethanediol) or 1, 4-butanediol units. The linking of the polyethers and the diacids forms flexible segments whereas the linking of glycol or of butanediol with the diacids forms rigid segments of the copolyetherester. Such copolyetheresters are well known and are fore example described in EP 402,883 and EP 405,227.

[0037] Other examples of suitable thermoplastic materials include polymers containing polyamide blocks and polyether blocks. The polymers containing polyamide blocks and polyether blocks result from the co-polycondensation of polyamide sequences containing reactive ends with polyether sequences containing reactive ends, such as, inter alia:

1) Polyamide sequences containing diamine chain ends with polyoxyalkylene sequences containing dicarboxyl chain ends.
2) Polyamide sequences containing dicarboxyl chain ends with polyoxy-alkylene sequences containing diamine chain ends obtained by cyanoethylation and hydrogenation of alpha, omega-dihydroxylated aliphatic polyoxyalkylene sequences known as polyetherdiols.
3) Polyamide sequences containing dicarboxyl chain ends with polyetherdiols, the products obtained being, in this specific case, polyetheresteramides.

[0038] The polyether can be, for example, a polyethylene glycol (PEG), a polypropylene glycol (PPG) or a polytetramethylene glycol (PTMG) also known as polytetrahydrofuran (PTHF). Whether the polyether blocks are in the chain of the polymer containing polyamide blocks and polybther blocks in the form of diols or of diamines, they are known for simplicity as PEG blocks or PPG blocks or alternatively PTMG blocks and polymers containing PA-6 blocks and PTMG blocks.

[0039] The use of thermoplastic polyetherurethanes is preferably to be minimized as they are prone to absorbing water, which may accelerate wearing of the material and unwanted release of particles.

[0040] The amount of thermoplastic material incorporated in the vulcanized thermoplastic material may vary within wide ranges, but will usually vary from 5-90% by weight relative to the total weight of the vulcanized thermoplastic material. Preferably the amount of thermoplastic material is between 5-50% by weight, more preferably between 10-30% by weight relative to the total weight of the vulcanized thermoplastic material.

ANTI-STATIC AGENT.

[0041] Within the scope of the present invention a wide variety of anti-static agents generally known to the skilled person may be used, in particular migrating anti-static agents, permanent anti-static agents, conductive particles/fibres and nanomaterials. Suitable examples include anti-static plastic materials (inherently dissipative polymer), carbon black, carbon nanotubes, graphene, conductive fibres, including graphite and metal fibres for example stainless steel fibers.

[0042] Migrating anti-static agents diffuse to polymer surface over time and activated by water molecules. Surface resistivity of 10^{10} - 10^{12} Ohms/sq. can be achieved wherein the compound can be classified as 'anti-static'. Examples of migrating anti-static agents include long chain alkyl phenols, ethoxylated amines and glycerol esters (such as glycerol monostearate).

[0043] Permanent anti-static agents function by forming a conductive matrix or interpenetrating network throughout the polymer. With this faster charge decay rate and surface resistivity of 10^{8} - 10^{12} Ohms/sq. are achievable, giving an 'electrostatically dissipative' polymer. Examples of permanent anti-static agents are polyamide/polyether block amides, polyether block amides based on PA6 or PA12 chemistry, ethylene ionomers, polyaniline polymer additives and liquid organic PEG-carboxylate esters. Commercial polymeric grades include Pebax (Arkema), Irgastat P (BASF), Entira (Dupont), Pelestat (Sanyo Chemical). Non-poylmeric, Kenstat (Kenrich Petrochemicals) Organometallic additives.

[0044] Conductive particles and fibres can be used to achieve a 'conductive' polymer with surface resistivity of 10^{1} - 10^{6} Ohms/sq. Examples of conductive particles or fibres are carbon blacks and conductive fibres, both graphite and metals, and high surface area graphite particles.

[0045] Nano-material can also be used to achieve 'anti-static' or 'electrostatically dissipative' polymers. Examples of these are carbon nanotubes, single and multi-wall carbon nanotubes, carbon nanofibres, fullerene nanotubes, grapheme sheets, Inorganic salts and silicon dioxide.

[0046] The amount of anti-static agent to be incorporated in the thermoplastic rubber composition of this invention will often depends on the type of agent used and the level of electrostatic conductivity required. The concentration of the anti-static agent will usually vary between 0.1-20% by weight, preferably between 1-15% by weight relative to the total weight of the vulcanized thermoplastic rubber. Surface and volume resistivity of a polymer can be determined by testing methods according to ISO 14309:2011.

[0047] The amount of anti-static agent is preferably chosen such that it affects the essential characteristics of the plastic material of the present invention to the smallest possible extent, such as hardness, tensile strength, elongation, modulus at 100% elongation, abrasion resistance and electrical properties. Tensile strength can be determined according to methods described under ISO 37 and abrasion resistance can be determined using methods described in DIN 53516.

OTHER COMPONENTS.

[0048] The plastic material, in particular the rubber and/or thermoplastic material may contain the usual ingredients, known to the skilled person. Examples of such additives are reinforcing and non- reinforcing fillers, plasticizers, antioxidants, stabilizers, oil, waxes, foaming agents, pigments, flame retardants, antiblocking agents and other known agents and are described in the Rubber World Magazine Blue Book, and in Gaether et al., Plastics Additives Handbook (Hanser 1990). Examples of suitable fillers are calcium carbonate, clay, silica, talc, titanium dioxide, and carbon. Other examples of suitable fillers are alumina (Al_2O_3), such as high dispersibility aluminas, described in European Patent Specification EP-A-810 258 and aluminium hydroxides, such as those disclosed in WO-A-99/28376. Examples suitable oils are paraffinic oil, naphthenic oil, aromatic oil obtained from petroleum fractions.

[0049] Highly hydrogenated oil in which the concentration of aromatic compounds is preferably less than 4 wt.% and the concentration of polar compounds is less than 0.3 wt.% may be present as well. The oil/rubber ratio in the thermoplastic elastomer will usually be chosen to be between 0.5-3, preferably between 0.8-2.5, more preferably between 1.0-1.6.

[0050] Examples of antiblocking agents suitable for use with this invention are natural silica, fluoropolymers, silicon oil, stearates for example zinc stearate or calcium stearate or fatty acid amides.

[0051] Other additives for that can optionally be added is a Lewis base such as for instance a metal oxide, a metal hydroxide, a metal carbonate or hydrotalcite. The additives can be added during compounding.

[0052] The vulcanised thermoplastic material may be used in its original colour, or pigments or colourants may be added to give the entire sole, or if so desired the anti-static protrusions only, a desired colour.

[0053] The quantity of additive to be added is generally known to the person skilled in the art. Preferably the quantity of additives is chosen in that way that it does not impair the properties of the vulcanized thermoplastic material.

VULCANIZATION.

[0054] The rubber in the vulcanized thermoplastic elastomer is vulcanized in the presence of a vulcanization agent. Vulcanization systems suitable for achieving vulcanization of the above-described mixtures of rubber and thermoplastic are known per se, and a wide variety of vulcanization systems may be used with the present invention.

[0055] The rubber is preferably dynamically vulcanized in the presence of curing agents such as for example sulfur, sulfurous compounds, metal oxides, maleimides, phenol resins or peroxides which are all generally known to the skilled person. It is also possible to use siloxane compounds as curing agent, for example hydrosilanes or vinylalkoxysilanes. Within the scope of this invention however, it is preferred to use a peroxide vulcanization agent or a phenol resin curing agent.

[0056] Examples of suitable peroxide vulcanization agents are organic peroxides for example, alkyl-aralkyl peroxides, diaralkyl peroxides, peroxy-ketales and peroxyesters. Particularly suitable vulcanization agents are dicumyl peroxide, di-tert-butylperoxide, 2,5-dimethyl-(2,5-di-tert-butylperoxy)hexane, 1 ,3 - bis(tert-butylperoxyisopropyl)benzene, 1 ,1-bis(tert-butylperoxy)-2,3,5-trimethylcyclohexane, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropylcarbonate, diacetyl peroxide, lauroyl peroxide, tert-butyl cumyl peroxide. The skilled person is capable of selecting the most appropriate vulcanization system taking into account the nature of the rubber and the vulcanization kinetics desired at the temperatures of use.

[0057] The vulcanization system may comprise a co-vulcanization agent. Examples of suitable co-vulcanization agents are divinyl benzene, sulphur, p- quinondioxime, nitrobenzene, diphenylguanidine, triarylcyanurate, trimethylolpropane- N, N-m-phenylenedimaleimide, ethyleneglycol dimethacrylate, polyethylene dimethacrylate, trimethylolpropane trimethacrylate, arylmethacrylate, vinylbutylate and vinylstearate. The amount of co-vulcanization agent is preferably between 0-2% by weight of the total weight of the thermoplastic elastomer composition.

[0058] Alternatively a phenolic curing system may be used to cure the EPDM rubber, these systems are generally known to the skilled person. The phenolic curing resin may be produced by condensation of halogen substituted phenol, C_1-C_{12} alkyl phenol or un-substituted phenol with an aldehyde, preferably, formaldehyde, in an alkaline medium or by condensation of bi-functional phenoldialcohols. Dimethylol phenols substitution in the para-position with C_5-C_{10} alkyl groups are preferred. Halogenated alkyl substituted phenol curing resins prepared by halogenation of alkyl substituted phenol curing resin are also especially suitable. Phenolic curative systems comprising methylol phenolic resin, halogen donor and metal compound are especially recommended. Non-halogenated phenol curing resins are used in conjunction with halogen donors, preferably, along with a hydrogen halide scavenger. Conventional, halogenated, preferably brominated, phenolic resins containing 2-10 weight bromine, generally do not require a halogen donor but are used in conjunction with a hydrogen halide scavenger such as metal oxides such as iron oxide, titanium oxide, magnesium oxide, magnesium silicate, silicon dioxide and preferably zinc oxide, the presence of which promotes the cross-linking function of the phenolic resin, however, with rubbers which do not readily cure with phenolic resins or have slow cure rates, the conjoint use of a halogen donor and zinc oxide is recommended. Examples of suitable halogen donors are stannous chloride, ferric chloride, or halogen donating polymers such as chlorinated paraffin, chlorinated polyethylene, chlorosulphonated polyethylene, and polychlorobutadiene (neoprene rubber).

[0059] The aforementioned phenolic resins may be prepared in solid or liquid form. In solid form they may be of 100% purity or may comprise compositions with appropriate carrying medium. The phenolic resin may also be used in a liquid preparation by pre-suspension of the phenolic resin in an appropriate oil based medium to aid incorporation of said resin during the compounding process. Halogen donors and metal halides may also be used in their pure forms or alternatively in pre-dispersions in thermoplastic resins again to aid incorporation.

[0060] The amount of phenol resin is preferably between 0.02-5% by weight and more preferably between 0.05-2% by weight relative to the total weight of the thermoplastic rubber mixture to be vulcanized. The amount of halogen donor and metal halide can be adjusted according to the TPV properties required.

[0061] The degree of vulcanization of the rubber can be expressed in terms of a gel content. Gel content is the ratio of the amount of non-soluble rubber and the total amount of rubber (in weight) of a specimen soaked in an organic solvent for the rubber. Gel content, reported as percent gel is measured by a procedure which comprises determining the amount of insoluble polymer by soaking the specimen for 48 hours in organic solvent at room temperature and weighing the dried residue and making suitable corrections based upon knowledge of the composition. Thus, corrected initial and final weights are obtained by subtracting from the initial weight, the weight of soluble components, other than the rubber to be vulcanized, such as extender oils, plasticizers and components of the compositions soluble in organic solvent, as well as that rubber component of the DVA which it is not intended to cure. Any insoluble pigments, fillers, etc., are subtracted from both the initial and final weights. Herein a specimen is soaked for 48 hours in an organic solvent for the rubber at room temperature. After weighing of both the specimen before soaking and its residue, the amount of non-soluble elastomer and total elastomer can be calculated, based on knowledge of the relative amounts of all components in the thermoplastic elastomer composition. The rubber in the dynamically vulcanized polyolefin based thermoplastic elastomer according to the present invention is at least partly vulcanized and for instance has a gel content between 60 and 100%.

[0062] Preferably the rubber is vulcanized to a gel content higher than 70%. More preferably to a gel content higher than 90%, most preferably the rubber is vulcanized to a gel content of at least 95%.

[0063] The above-described combination of materials provides a shoe sole with good temperature stability, so that the shoe sole may be cleaned and sterilized using the conventional process in an autoclave at elevated pressure and temperature of at least 130°C, or using gamma irradiation. Since the temperature stability of the sole is such that it is capable of withstanding exposure to repeated heating cycles of the cleaning / sterilization process, a shoe sole with a prolonged life-time is provided, which may be used and re-used a large number of times.

PROCESSING.

[0064] The vulcanized thermoplastic material can be prepared by melt mixing and kneading the rubber, the anti-static agent and optional additives customarily employed by one skilled in the art. Thus, the thermoplastic may be incorporated into the rubber material at a temperature which is sufficient for it to be in the molten state. Mixing is carried out until a desired dispersion of the thermoplastic material in the rubber matrix is obtained. The thermoplastic is preferably chosen so that its melting temperature is similar to that of the non-formulated rubber or to the compounding temperature of the formulated rubber. It is also possible to proceed via an intermediate stage of rubber/thermoplastic non-vulcanized masterbatches, which are subsequently incorporated in the remainder of the rubber.

[0065] Melt mixing and kneading may be carried out in conventional mixing equipment for example roll mills, Banbury mixers, Brabender mixers, continuous mixers for example a single screw extruder, a twin screw extruder, multi-screw extruders (i.e. more than 2 screws) and the like. Preferably, melt mixing is carried out in a twin-screw extruder. After the rubber, the thermoplastic, the anti-static agent and optionally additives have been properly dispersed, the vulcanization agent is added to initiate dynamic vulcanization.

[0066] The vulcanized thermoplastic rubber in the present invention may also be prepared by melt mixing the rubber, the thermoplastic, the anti-static agent, the vulcanizing agent and optional additives in one step. By one step is meant that the rubber, the thermoplastic, the curing agent, anti-static agent and optionally other additives are simultaneously fed to a continuous mixer.

[0067] Where the plastic material also contains a polyolefin, part of the polyolefin may be added before the vulcanization, the other part may be added after the vulcanization. An oil may for example be added before, during or after the vulcanization. The oil may however also be added partly before and partially after the vulcanization. The anti-static agent may be added in whole or partly before, during or after the vulcanization.

[0068] The shoe sole according to the present invention may be produced by a conventional method for example injection moulding or compression moulding.

[0069] The present invention is further elucidated in the appending figures which show preferred embodiments of this invention, and description of the figures below.

Figure 1 shows a view to a bottom side of the shoe sole.

Figure 2 shows a view to the inside of a shoe sole of the present invention.

Figure 3 shows a sideways view to a shoe sole of this invention.

[0070] The preferred embodiment of the shoe sole 1 for a clean room shoe of the present invention shown in figure 2 and 3, comprises a base 2. The base 2 comprises a ground contacting face 3 which is provided to contact a walking surface, and an inner face 4 which faces the interior of the clean room shoe.

[0071] The ground contacting face 3 of the sole comprises at least one ground contacting protrusion 5, 15 which extends from the ground contacting face 3 of the sole 1 in a ground contacting direction. Preferably however, the ground contacting face 3 of the sole 1 comprises a plurality of such protrusions 5, 15. The plurality of protrusions may be randomly distributed over the ground contacting face 3, they may however also be ordered along a geometric pattern in case a particular application so requires.

[0072] In the preferred embodiment shown in fig. 3, protrusions 5, 15 in a heel area 7 of the sole are arranged in a circle, a central protrusion 5, made of a plastic material with anti-static properties being provided in the centre of the circle. A similar pattern of protrusions may be applied in a middle area 8 of the sole shifted towards a front part of the sole, with which the mid foot rests on the walking surface. The number of protrusions 5, 15 is not essential to the invention and may be selected by the skilled person taking into account the envisaged use of the shoe sole, the comfort to be provided to it, and any other relevant parameters. Similarly, the dimensions and shape of the protrusions 5, 15 are not essential to the invention. Usually they will be dimensioned such that at least part of them contacts the walking surface during normal use of a shoe comprising the sole 1.

[0073] At least one of the protrusions 5 has anti-static properties and is made of an anti-static plastic material comprising a vulcanized thermoplastic material and an anti-static agent. Preferably, this protrusion 5 is located in a heel part 7 of the sole 1. The inventors have namely observed that in the course of activities such as walking, standing or walking back and forth, the heel part of a shoe and sole always contacts the walking surface. By providing a protrusion comprising an anti-static plastic material in a heel part of the sole, the risk to building of electrostatic charges in the shoe sole may be reduced to a minimum. Although it may be sufficient that only one ground contacting protrusion 5 is made of an anti-static material, the present invention does not exclude that two or more protrusions are made of an anti-static plastic

material. Thereby the anti-static protrusions 5 may exclusively be located in a heel part 7 of the sole 1. The present invention however also provides a sole having anti-static protrusions in a middle or front area of the sole 1.

[0074] In order to ensure efficient deflection of any electrostatic charges from the person wearing the sole 1 towards the walking surface, the at least one protrusion 5 preferably extends towards and into a position on the inner face 4 of the sole 1, which faces the interior of the sole or the shoe comprising the sole (fig.2). The at least one protrusion 5 preferably extends towards and into a position on the inner face 4 of the sole 1 in such a way that the material of the at least one protrusion 5 contacts a part of a foot of the person wearing the shoe. In other words, the ground contacting protrusion is provided to contact a part of a foot of the person wearing the shoe.

[0075] The at least one protrusion 5, providing anti-static properties, may be made as a separate part, which is fitted into a corresponding hole in the sole 1 after the sole has been produced. Possible disadvantages of this method may comprise the formation a circumferential slit around the protrusion since complete fitting may be difficult to achieve, and loosening of the part. Preferably the at least one anti-static protrusion 5 is incorporated into the sole when producing the sole, in particular the at least one anti-static protrusion 5 is produced in the sole 1 in the molten state of the vulcanized thermoplastic material from which the sole 1 is made. This way adhesion of the two materials in the molten state may be achieved.

[0076] The at least one anti-static protrusion 5 is preferably extended in such a way that part of it 10 extends along part of the inner face 4 of the sole 1. Therewith the contact area and the adhesive area between the anti-static material 5 and the remainder of the material of the sole 1 may be enlarged, thereby enlarging the decreasing the risk to detaching of the two materials as a result of shearing forces occurring when the shoe sole is worn by a user. The anti-static protrusion 5 may extend along a substantial part of the inner face 4, or along virtually all of the inner face 4 as well. This may however increase material costs for producing the sole 1. As is shown in the preferred embodiment of fig. 3, a part of the at least one ground contacting protrusion 5 is extended towards an edge part of the sole, to provide an upright rim part 11,forming part of or extending along at least part of an upright rim 6 extending along at least part of a circumferential edge of the shoe sole.

[0077] Preferably the protrusion is fastened to the sole in a seamless manner, to minimize the risk to accumulation of dirt in the seam or slit and minimize the risk to particle loosening along the slit.

[0078] According to another preferred embodiment of this invention (not shown), the at least one protrusion, providing anti-static properties, and the remainder of the sole may be made in one part. In that case, the sole and the anti-static protrusion will generally be made of the same vulcanised thermoplastic material. The design of the sole will generally remain the same, and may be exemplified by figure 2.

[0079] The sole 1 preferably comprises an upright rim 6. The upright rim 6 extends from the base 2 in upright direction, in a direction pointing away from the ground contacting face. The upright rim 6 provides a connecting area for the shoe vamp, or a connecting area for connecting the sole to the shoe part of an overall. The upright rim 6 may extend along the entire circumference of the base 2, or along a part of it only. The upright rim may be made in one part or in a plurality of pieces. To facilitate cleaning and sterilization of the shoe sole, to minimize the accumulation of dirt and to minimize the number of accessible edges that may give rise to the release of material particles, the upright rim 6 is preferably made in one part with the base 2.

Claims

1. A shoe sole (1), in particular for a clean room shoe, the shoe sole (1) comprising a base (2) with a ground contacting face (3) and an inner face (4) facing the interior of the shoe, **characterized in that** the ground contacting face (3) comprises at least one ground contacting protrusion (5, 15) which extends from the ground contacting face (3) of the sole in a ground contacting direction, **in that** the at least one ground contacting protrusion (5) extends towards and into the inner face (4) of the shoe sole, **in that** the at least one ground contacting protrusion (5) is located in a heel part (7) of the ground contacting face and is dimensioned to contact a walking surface during normal use of the clean room shoe, and **in that** the at least one ground contacting protrusion (5) is made of a plastic material comprising a vulcanized thermoplastic material and at least one anti-static agent.

2. A shoe sole as claimed in claim 1, wherein the at least one ground contacting protrusion and the remainder of the shoe sole are made of the same plastic material.

3. A shoe sole according to claim 1, wherein the at least one ground contacting protrusion (5) and the remainder of the shoe sole are made of different materials, wherein the at least one ground contacting protrusion (5) is made of a plastic material comprising a vulcanized thermoplastic material and at least one anti-static agent and the remainder of the shoe sole is made of a vulcanized thermoplastic material.

4. A shoe sole according to claim 3, wherein the at least one anti-static protrusion and the remainder of the sole are produced of a plastic material comprising the same vulcanised thermoplastic material.

5. A shoe sole as claimed in any of the previous claims,

wherein the vulcanized thermoplastic material has a Shore A hardness of between 35 and 95, more preferably between 50 and 95, most preferably between 60 and 80, particularly between 60 and 75, more particularly between 60 and 70.

6. A shoe sole as claimed in any one of the previous claims, wherein the anti-static agent is selected from the group of migrating antistatic agents, permanent antistatic agents, conductive particles/fibres and nanomaterials, in particular anti-static plastic materials, more particularly inherently dissipative polymers, carbon black, carbon nanotubes, graphene, conductive fibres, including graphite and metal fibres for example stainless steel fibers, or mixtures of two or more of the afore mentioned compounds.

7. A shoe sole as claimed in any of the previous claims, wherein the rubber material is a nitrile rubber, an EPDM or an EPM rubber.

8. A shoe sole s claimed in any of the previous claims, wherein the thermoplastic material is selected from the group of polyolefins, polyamides, polycarbonates, polymers containing polyamide blocks and polyether blocks and mixtures of two or more of the afore mentioned materials, preferably polypropylene or polyethylene or a mixture thereof, more preferably polypropylene, wherein preferably the amount of thermoplastic material is 5-90 wt % with respect to the weight of the vulcanised thermoplastic.

9. A shoe sole as claimed in claim 8, wherein the polypropylene thermoplastic material is a linear polypropylene.

10. A shoe sole as claimed in claim 9, wherein the polypropylene has a melt flow index (MFI) of between 0.1 and 100, preferably between 0.1 and 50, more preferably 0.3-20, measured according to ISO standard 1133, at 230^0C and 2.16 kg load.

11. A shoe sole as claimed in any one of the previous claims, wherein the rubber is vulcanised using a peroxide or phenolic resin curing agent.

12. A shoe sole as claimed in any one of the previous claims, wherein the rubber is vulcanized to a gel content of at least 70%, preferably at least 90%, more preferably at least 95%.

13. A shoe sole according to any one of claims 3-12, wherein the at least one ground contacting protrusion (5) is extended to as to comprise a shoe sole part (10) which extends along at least part of the inner face (4) of the sole (1).

14. A shoe sole according to claim 13, wherein a part of the at least one ground contacting protrusion (5) is extended towards an edge part of the sole, to provide an upright rim part (11), which extends along at least part of an upright rim (6) extending along at least part of a circumferential edge of the shoe sole.

15. A shoe sole as claimed in any one of claims 3-14, wherein the at least one ground contacting protrusion is fastened to the sole in a seamless manner.

16. A shoe sole as claimed in any one of the previous claims, wherein the sole comprises a circumferential upright rim (6) which extends along at least part of a circumferential edge of the shoe sole, from at least part of the base (2), the upright rim being provided to provide a connecting area for a vamp part of a shoe.

17. A clean room shoe comprising the shoe sole according to any one of claims 1-16.

18. A shoe comprising the shoe sole according to any one of claims 1-17, in particular a safety shoe.

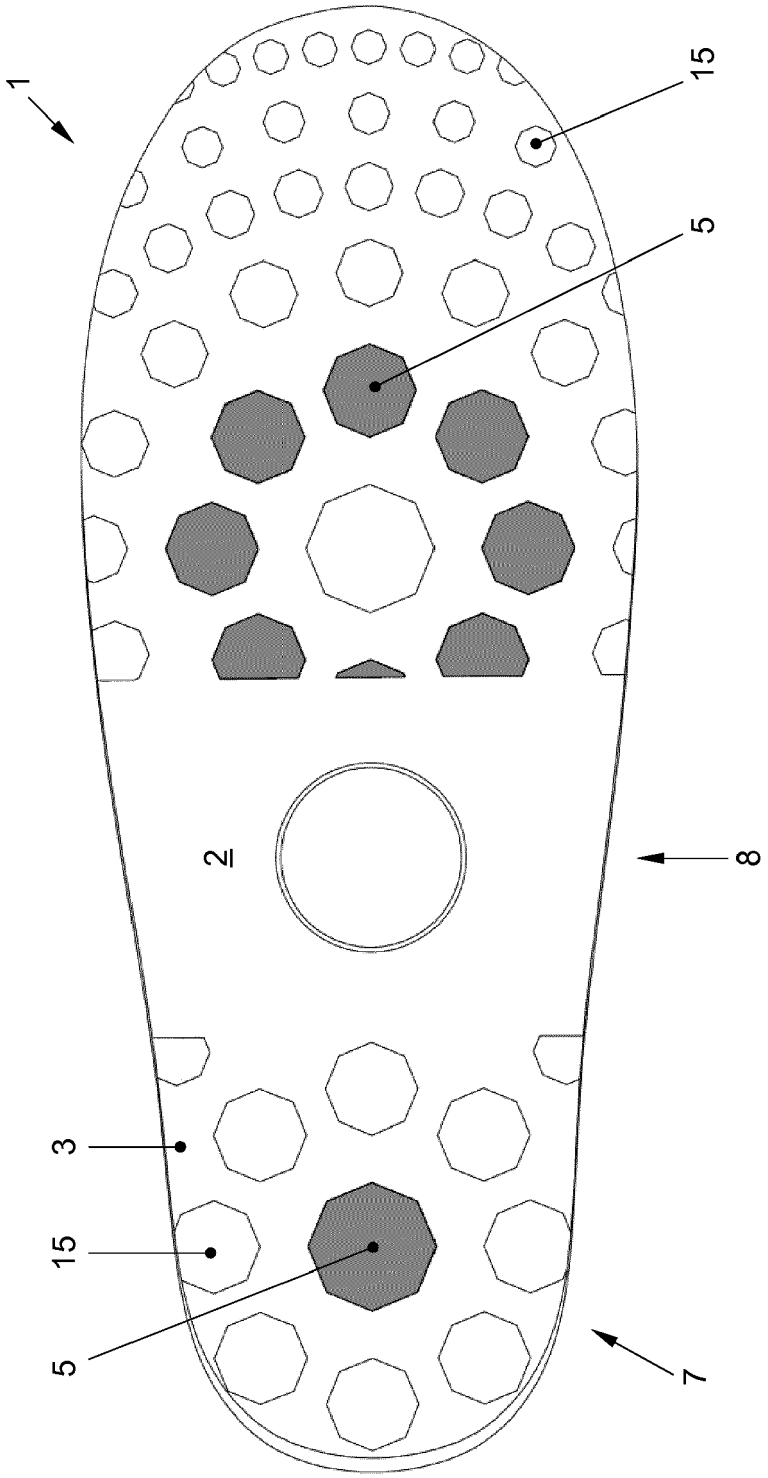


Fig. 1

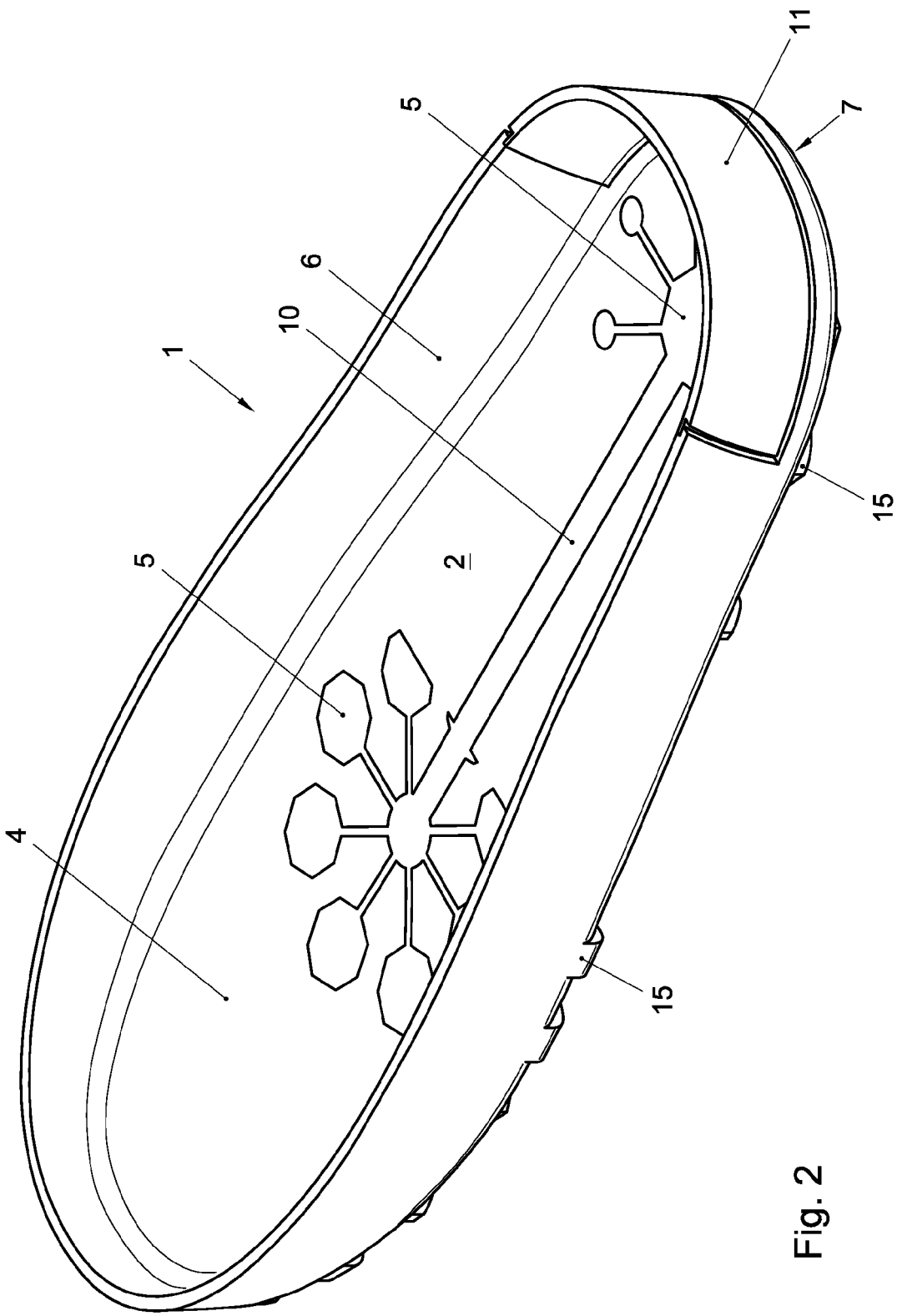


Fig. 2

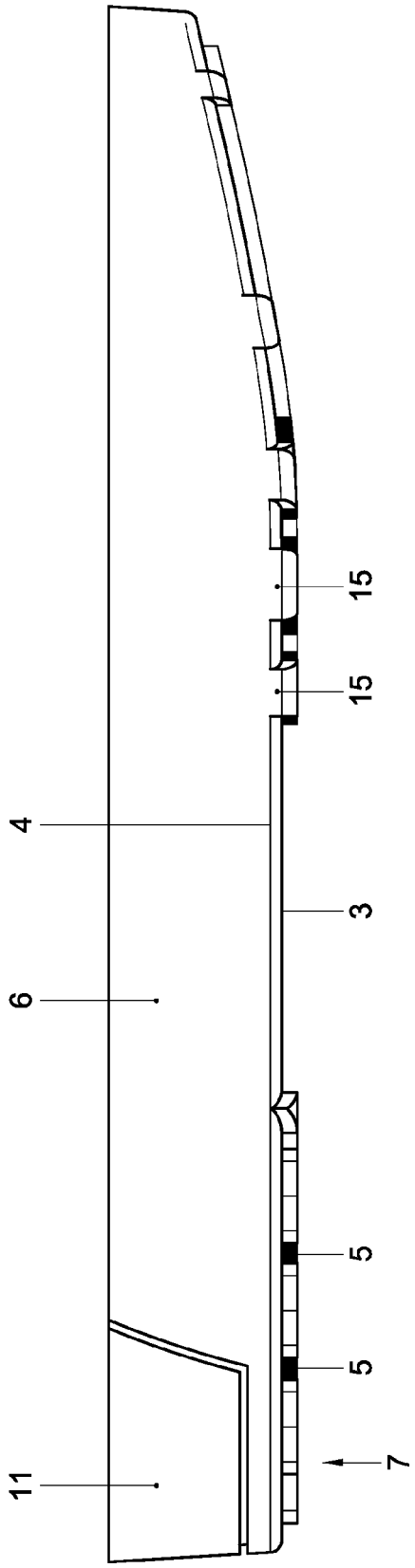


Fig. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 13 19 3362

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	14 March 2014	Oelschläger, Holger

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