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(54) **A COMPOSITION FOR THE IMPREGNATION OF TEXTILE MATERIALS, COMPOSITE TEXTILE MATERIALS COMPRISING SUCH A COMPOSITION, AND A PROCESS FOR OBTAINING THEM**

(57) The present invention generally relates to the field of composite textile materials and impregnating compositions used for the production thereof.

In particular, the present invention relates to an im-

pregnating composition comprising plant- and/or animal-derived reinforcing fillers, a composite textile material impregnated with such a composition, and the process for the production thereof.

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Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention generally relates to the field of composite textile materials and impregnating compositions used for the production thereof.

[0002] In particular, the present invention relates to an impregnating composition comprising plant- and/or animal-derived reinforcing fillers, a composite textile material impregnated with such a composition, and the process for the production thereof.

PRIOR ART

[0003] In recent years, the need has been increasingly perceived to lower the environmental impact of industrial production processes, and thus of the products resulting therefrom.

15 **[0004]** One of the solutions used to meet such a need is to reduce the use of polluting and/or toxic chemicals, replacing them with more environmentally friendly substances.

[0005] Another solution is to use recycled raw materials, preferably resulting from the recovery of waste materials from other production processes.

[0006] However, both of these solutions often have disadvantages.

20 **[0007]** Firstly, the replacement of chemicals that have become standard in the reference industry over the years implies expensive research by companies, since it is necessary for the substances chosen to replace the polluting ones to be compatible with the production process, i.e., with the processing conditions and with the other ingredients used.

[0008] Secondly, the products obtained with more environmentally friendly raw materials and processes should ensure performance levels at least comparable to those of the materials already marketed, in terms of both aesthetic aspect and functional properties for their use.

25 **[0009]** Composite textile materials are used in a wide range of applications, e.g., in footwear, vehicle interiors, leather goods, furnishing items, etc.

[0010] These materials are typically obtained from a textile substrate, which can be a woven or non-woven fabric, which is treated with substances to impart specific mechanical properties, such as resilience, rigidity, elasticity, etc..

30 **[0011]** The composite textile materials are typically impregnated with elastomeric compositions, also referred to as "primers", comprising mineral reinforcing fillers. These compositions typically comprise a high percentage of synthetic chemicals and/or resulting from non-renewable sources.

SUMMARY OF THE INVENTION

35 **[0012]** The Applicant thus aims to obtain composite textile materials comprising a high percentage of plant- and/or animal-derived ingredients, preferably recycled and/or resulting from production waste, while maintaining the mechanical characteristics of the traditional materials.

[0013] The Applicant also aims to obtain such materials through a process with low environmental impact, thus significantly reducing the use of toxic, polluting substances and/or resulting from non-renewable sources.

40 **[0014]** After extensive experimentation, the Applicant found that it is possible to obtain such materials using plant- and/or animal-derived reinforcing fillers, thus from renewable sources, preferably resulting from production waste from the agri-food industry. Surprisingly, the composite materials thus obtained have performance levels, both in terms of finishes and mechanical properties, which are not only comparable, but even better than those of the composite textile materials known in the art. Surprisingly, such performance levels are obtained against a decrease in the overall density of the composite textile materials according to the present invention, compared to those known in the art for which the use of greater amounts of raw materials is necessary for the preparation of the finished products.

[0015] Hence, the composite materials according to the present invention allow not only the recycling of materials that would otherwise be considered waste, but also a reduction in the use of raw materials.

50 **[0016]** Therefore, in a first aspect the present invention relates to an aqueous elastomeric composition, for the impregnation of textile materials, comprising at least one latex, at least one dispersant, at least one plant- and/or animal-derived reinforcing filler, and water.

[0017] In a second aspect, the present invention relates to an aqueous elastomeric composition also comprising at least one emulsifier.

55 **[0018]** In a third aspect, the present invention relates to a process for the production of a composite textile material, comprising the following steps:

- a) Preparing an aqueous elastomeric composition comprising at least one latex, at least one dispersant, at least

- one plant- and/or animal-derived reinforcing filler, and water;
- b) Soaking a textile substrate in the composition obtained in step a);
- c) Pressing the impregnated textile substrate;
- d) Drying the textile substrate obtained in step c); and
- e) Calendering the dry textile substrate.

[0019] In a further embodiment, said aqueous elastomeric composition also comprises at least one emulsifier.

[0020] Finally, the present invention relates to a composite textile material obtainable through the process according to the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The description is disclosed herein with reference to the accompanying drawing, provided solely by way of a non-limiting example of the invention.

[0022] Figure 1 shows a flow diagram describing the process for the production of a composite textile material according to embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0023] In the present text and in the appended claims, the term "latex(es)" refers to a stable dispersion of polymer microparticles in water.

[0024] In the present text and in the appended claims, the term "emulsifier(s)" means an additive that mixes two immiscible substances together. In a preferred embodiment, an emulsifier is a surfactant which stabilizes an aqueous component and an oily component in a mixture.

[0025] In the present text and in the appended claims, the term "dispersant(s)" means an additive which avoids the formation of precipitates and increases the stability of mixtures, minimizing clumping problems.

Detailed description

[0026] In a first aspect, the present invention relates to an aqueous elastomeric composition, for the impregnation of textile materials, comprising at least one latex, at least one dispersant, at least one plant- and/or animal-derived reinforcing filler, and water.

[0027] In embodiments, said latex is selected from a natural latex, such as natural rubber latex, a synthetic latex, such as latex made of styrene, butadiene, styrene butadiene copolymers, neoprene, and mixtures thereof.

[0028] In an embodiment, said latex comprises or consists of a mixture of styrene butadiene latex and neoprene latex.

[0029] In embodiments, said latex is present in an amount greater than or equal to 40% by weight with respect to the total weight of the composition, preferably of 40-80% by weight with respect to the total weight of the composition, even more preferably of 40-70% by weight with respect to the total weight of the composition, e.g., of 50-65% by weight with respect to the total weight of the composition.

[0030] In an embodiment, where said latex consists of a mixture of styrene butadiene latex and neoprene latex, said latexes are in the ratio of styrene-butadiene latex < neoprene latex, preferably in a ratio of about 1: 1.1.

[0031] Therefore, the percentages described above with reference to such a component of the composition according to the present invention are intended to refer to the weight of the aqueous latex dispersion, i.e., to the total weight of water and polymer component of the selected latex.

[0032] In embodiments, said dispersant is selected from the group comprising esters of polycarboxylic acids with linear or branched aliphatic alcohols, such as sodium polyacrylate.

[0033] In embodiments, said dispersant is present in an amount greater than or equal to 0.05% by weight with respect to the total weight of the composition, preferably of 0.05-0.6% by weight with respect to the total weight of the composition, even more preferably of 0.05-0.3% by weight with respect to the total weight of the composition, e.g., of 0.1-0.4% by weight with respect to the total weight of the composition. In embodiments, such percentages refer to the weight of an aqueous solution of the selected dispersant agent. In alternative embodiments, such percentages refer to the weight of the pure dispersant agent.

[0034] In embodiments, said plant- and/or animal-derived reinforcing filler is selected from the group comprising rice husk, rice chaff, peanut pod, hemp, bamboo fibers, hay, almond shell, hazelnut shell, walnut shell, eggshell, miscanthus, cherry stone, olive pit, straw, hide and leather scraps, regenerated leather scraps, corn cob, grapes, and mixtures thereof.

[0035] Such natural reinforcing fillers result from waste from the agri-food and tanning industries. These materials are

generally ground so as to be reduced to powder or granules of a predefined particle size.

[0036] In embodiments, said plant- and/or animal-derived reinforcing filler essentially consists of eggshell.

[0037] Therefore, in embodiments, said natural reinforcing filler is in the form of powder or granules with an average size less than or equal to 500 microns, preferably from 1 to 500 microns, even more preferably from 1 to 200 microns, e.g., 10-200 microns, 50-200 microns, 100-200 microns.

[0038] In embodiments, said natural reinforcing filler is present in an amount greater than or equal to 0.5% by weight with respect to the total weight of the composition, preferably greater than or equal to 1% by weight with respect to the total weight of the composition, e.g., greater than or equal to 5% by weight with respect to the total weight of the composition.

[0039] In embodiments, when said natural reinforcing filler essentially consists of eggshell, it is present in an amount from 0.5% to 50% by weight with respect to the total weight of the composition, preferably from 10% to 45% by weight with respect to the total weight of the composition, even more preferably from 20% to 40% by weight with respect to the total weight of the composition, or even more from 25% to 40% by weight with respect to the total weight of the composition.

[0040] In the embodiment where said reinforcing filler essentially consists of eggshell, said composition could not comprise any emulsifiers.

[0041] In the embodiment where said reinforcing filler essentially consists of eggshell, said composition does not comprise any emulsifiers.

[0042] In embodiments, said aqueous elastomeric composition can further comprise one or more inorganic reinforcing fillers selected from the group comprising natural or synthetic metal carbonates, such as calcium carbonate; natural or synthetic metal oxides, such as zinc oxide; clays, such as kaolin; silicates; talc; and mixtures thereof.

[0043] In the embodiment where said reinforcing filler essentially consists of eggshell, said composition could not comprise any inorganic reinforcing fillers.

[0044] In the embodiment where said reinforcing filler essentially consists of eggshell, said composition does not comprise any inorganic reinforcing fillers.

[0045] In such embodiments, said one or more inorganic reinforcing fillers are thus present in an amount of 0.5-40% by weight with respect to the total weight of the composition, preferably of 0.5-30% by weight with respect to the total weight of the composition, even more preferably of 0.5-20% by weight with respect to the total weight of the composition, or even more of 0.5-15% by weight with respect to the total weight of the composition.

[0046] In embodiments, said aqueous elastomeric composition can further comprise additional additives such as: thickeners, such as methyl hydroxyethyl cellulose; dyes, such as on titanium dioxide-based dyes; antifoam agents, such as silicones; and mixtures thereof.

[0047] In embodiments, said aqueous elastomeric composition comprises an amount of water greater than or equal to 20% by weight with respect to the total weight of the composition, preferably of 25-50% by weight with respect to the total weight of the composition, even more preferably of 25-45% by weight with respect to the total weight of the composition. The percentages of water are to be understood as inclusive of the amount of water resulting from the selected aqueous latex dispersion.

[0048] In embodiments, the water used is at least partially demineralized water, e.g., distilled water.

[0049] In a particular embodiment, the aqueous elastomeric composition, for the impregnation of textile materials, according to the present invention, comprises:

- from 40% to 80% by weight of one or more latexes;
- from 0.05% to 0.6% by weight of one or more dispersant agents;
- from 0.5% to 50% by weight, preferably from 10% to 40% by weight, of one or more plant- and/or animal-derived reinforcing fillers; and
- water up to 100%.

[0050] In a preferred embodiment, said reinforcing filler is essentially eggshell and is present from 25 to 40% by weight.

[0051] In embodiments, said elastomeric composition does not comprise any emulsifiers.

[0052] In embodiments, said elastomeric composition does not comprise any inorganic reinforcing fillers.

[0053] In a preferred embodiment, said reinforcing filler essentially consists of eggshell and is present from 25 to 40% by weight, and said elastomeric composition does not comprise any emulsifiers and no inorganic reinforcing fillers.

[0054] In a second aspect, the present invention relates to an aqueous elastomeric composition, for the impregnation of textile materials, comprising at least one latex, at least one dispersant, at least one emulsifier, at least one plant- and/or animal-derived reinforcing filler, and water.

[0055] In embodiments, said latex is selected from a natural latex, such as natural rubber latex, a synthetic latex, such as latex made of styrene, butadiene, styrene butadiene copolymers, neoprene, and mixtures thereof.

[0056] In embodiments, said latex is present in an amount greater than or equal to 40% by weight with respect to the total weight of the composition, preferably of 40-80% by weight with respect to the total weight of the composition, even

more preferably of 40-70% by weight with respect to the total weight of the composition, e.g., of 50-65% by weight with respect to the total weight of the composition.

[0057] In the present text and in the appended claims, the term "latex(es)" refers to a stable dispersion of polymer microparticles in water. Therefore, the percentages described above with reference to such a component of the composition according to the present invention are intended to refer to the weight of the aqueous latex dispersion, i.e., to the total weight of water and polymer component of the selected latex.

[0058] In embodiments, said dispersant is selected from the group comprising esters of polycarboxylic acids with linear or branched aliphatic alcohols, such as sodium polyacrylate.

[0059] In embodiments, said dispersant is present in an amount greater than or equal to 0.05% by weight with respect to the total weight of the composition, preferably of 0.05-0.6% by weight with respect to the total weight of the composition, even more preferably of 0.05-0.3% by weight with respect to the total weight of the composition, e.g., of 0.1-0.4% by weight with respect to the total weight of the composition. In embodiments, such percentages refer to the weight of an aqueous solution of the selected dispersant agent. In alternative embodiments, such percentages refer to the weight of the pure dispersant agent.

[0060] In embodiments, said emulsifier is selected from a natural emulsifier, a synthetic emulsifier, and mixtures thereof.

[0061] In embodiments, said emulsifier is present in an amount greater than or equal to 0.1% by weight with respect to the total weight of the composition, preferably of 0.1-4% by weight with respect to the total weight of the composition, even more preferably of 0.1-2.5% by weight with respect to the total weight of the composition. In embodiments, such percentages refer to the weight of an aqueous solution of the selected emulsifier. In alternative embodiments, such percentages refer to the weight of the pure emulsifier.

[0062] In embodiments, said natural emulsifier is selected from the group comprising phospholipids, glycerophospholipids and mixtures thereof, such as phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, phosphatidylserine, phosphatidic acid, for example, and mixtures thereof. Preferably, said natural emulsifier is a lecithin, i.e., a mixture of glycerophospholipids and phospholipids, such as soy lecithin, egg yolk lecithin, milk lecithin, canola lecithin, cottonseed lecithin, or sunflower oil lecithin.

[0063] The natural emulsifier is particularly suitable for dispersing and making the plant- and/or animal-derived reinforcing fillers compatible with the elastomeric matrix of the composition. Moreover, the use of a natural emulsifier increases the eco- friendliness of the composition and the process according to the present invention since they are non-toxic and environmentally friendly substances.

[0064] In embodiments, said synthetic emulsifier is selected from the group comprising anionic surfactants, such as, for example, sodium salts of C10-C18 linear or branched alkyl sulfonates, ethoxylated saturated C16-C18 alkyl alcohols, ethoxylated unsaturated C18 alkyl alcohols, styrenated phenols, and mixtures thereof.

[0065] In embodiments, said at least one emulsifier is a mixture of said at least one natural emulsifier and said at least one synthetic emulsifier.

[0066] In embodiments, said natural emulsifier is present in an amount greater than or equal to 0.1 % by weight with respect to the total weight of the composition, preferably of 0.1-0.5% by weight with respect to the total weight of the composition. In embodiments, said synthetic emulsifier is present in an amount greater than or equal to 0.8% by weight with respect to the total weight of the composition, preferably of 0.8-3% by weight with respect to the total weight of the composition.

[0067] In embodiments, said plant- and/or animal-derived reinforcing filler is selected from the group comprising rice husk, rice chaff, peanut pod, hemp, bamboo fibers, hay, almond shell, hazelnut shell, walnut shell, eggshell, miscanthus, cherry stone, olive pit, straw, hide and leather scraps, regenerated leather scraps, corn cob, grapes, and mixtures thereof.

[0068] In preferred embodiments, said plant- and/or animal-derived reinforcing filler is selected from the group comprising rice chaff, corncob, hemp, olive pit, hide and leather scraps, regenerated leather scraps, almond shell, hazelnut shell and mixtures thereof.

[0069] Rice chaff is a multi-layered, brownish or yellowish coating that coats the freshly harvested grain of rice. Rice husk is the layer that covers the grain, situated below the chaff.

[0070] Miscanthus is a perennial herb derived from a hybrid between *Miscanthus Sinensis* and *Miscanthus sacchariflorus*, typically used for the production of biomasses.

[0071] Corncob is the part of the corn ear where the kernels are fixed.

[0072] Regenerated leather is a material made by recovering natural leather fibers, shavings and defibrated scraps, re-tanned with specific natural binding agents and additives.

[0073] Such plant- or animal-derived reinforcing fillers result from waste from the agri-food and tanning industries. These materials are generally ground so as to be reduced to powder or granules of a predefined particle size.

[0074] Therefore, in embodiments, said plant- and/or animal-derived reinforcing filler is in the form of powder or granules with an average size less than or equal to 500 microns, preferably from 1 to 500 microns, even more preferably from 1 to 200 microns, e.g., 10 -200 microns, 50-200 microns, 100-200 microns.

[0075] In embodiments, said plant- and/or animal-derived reinforcing filler is present in an amount greater than or

equal to 0.5% by weight with respect to the total weight of the composition, greater than or equal to 1 % by weight with respect to the total weight of the composition, e.g., greater than or equal to 5% by weight with respect to the total weight of the composition.

[0076] In embodiments, said plant- and/or animal-derived reinforcing filler is present in an amount from 0.5% to 30% by weight with respect to the total weight of the composition, preferably from 1% to 20% by weight with respect to the total weight of the composition, even more preferably from 5% to 15% by weight with respect to the total weight of the composition, or even more from 5% to 10% by weight with respect to the total weight of the composition.

[0077] In embodiments, said aqueous elastomeric composition can further comprise one or more inorganic reinforcing fillers selected from the group comprising natural or synthetic metal carbonates, such as calcium carbonate; natural or synthetic metal oxides, such as zinc oxide; clays, such as kaolin; silicates; talc; and mixtures thereof.

[0078] In such embodiments, said one or more inorganic reinforcing fillers are thus present in an amount of 0.5-40% by weight with respect to the total weight of the composition, preferably of 0.5-30% by weight with respect to the total weight of the composition, even more preferably of 0.5-20% by weight with respect to the total weight of the composition, or even more of 0.5-15% by weight with respect to the total weight of the composition.

[0079] In embodiments, said aqueous elastomeric composition can further comprise additional additives such as: thickeners, such as methyl hydroxyethyl cellulose; dyes, such as on titanium dioxide-based dyes; antifoam agents, such as silicones; and mixtures thereof.

[0080] In embodiments, said aqueous elastomeric composition comprises an amount of water greater than or equal to 20% by weight with respect to the total weight of the composition, preferably of 25-50% by weight with respect to the total weight of the composition, even more preferably of 25-45% by weight with respect to the total weight of the composition. The percentages of water are to be understood as inclusive of the amount of water resulting from the selected aqueous latex dispersion.

[0081] Typically, the water used is at least partially demineralized water, e.g., distilled water.

[0082] In a particular embodiment, the aqueous elastomeric composition, for the impregnation of textile materials, according to the present invention, comprises:

- from 40% to 80% by weight of one or more latexes;
- from 0.05% to 0.6% by weight of one or more dispersant agents;
- from 0.1% to 4% by weight of one or more natural and/or synthetic emulsifiers;
- from 0.5% to 30% by weight, preferably from 5% to 30% by weight, of one or more plant- and/or animal-derived reinforcing fillers; and
- water up to 100%.

[0083] In a third aspect, the present invention relates to a process for the production of a composite textile material, comprising the following steps:

- a) Preparing an aqueous elastomeric composition comprising at least one latex, at least one dispersant, at least one plant- and/or animal-derived reinforcing filler, and water;
- b) Soaking a textile substrate in the composition obtained in step a);
- c) Pressing the impregnated textile substrate;
- d) Drying the textile substrate obtained in step c); and
- e) Calendering the dry textile substrate.

[0084] Said aqueous elastomeric composition is as defined above in the first or second aspect of the present invention.

[0085] Step a) of the process according to the present invention can be carried out with methods known in the prior art, e.g., in a dissolving device (identified by numeral 10 in Fig. 1) provided with propellers or cowles, under continuous stirring of the mixture.

[0086] Typically, at least one dispersant is added to an aqueous mixture of the at least one latex. Optionally, when at least one emulsifier is also present, said at least one dispersant and said at least one emulsifier are sequentially added. Optionally, other additives can be added in this step, such as antifoaming agents, dyes and thickeners, for example (this mixture is identified by numeral 2 in Fig. 1).

[0087] The additions can be made by vacuum suction or direct introduction into the dissolver.

[0088] Optionally, in embodiments where the compositions comprise inorganic reinforcing fillers, a suspension comprising water, at least one dispersant and/or emulsifier, and one or more inorganic reinforcing fillers is prepared in a different mixing device (this suspension is identified by numeral 3 in Fig. 1). The suspension thus obtained is then added to the aqueous mixture.

[0089] Finally, said at least one plant- and/or animal-derived reinforcing filler (identified by numeral 1 in Fig. 1) is added, directly in solid form, to the mixture, by vacuum suction or direct introduction into the dissolver.

[0090] The aqueous elastomeric composition thus obtained is then left under stirring for about one hour.

[0091] The essential and optional ingredients mentioned above, as well as the amounts thereof, are selected from the lists described in the previous paragraphs with reference to the composition according to the first aspect of the present invention.

[0092] Step b) of the process according to the present invention is an impregnation step which can be carried out according to techniques known in the art. It typically occurs using a machine referred to as an impregnating machine (identified by numeral 11 in Fig. 1) or Rameuse (such as Brückner), in which the textile substrate (identified by numeral 20 in Fig. 1) is soaked in the impregnation bath, i.e., a tank containing the aqueous elastomeric composition obtained from step a).

[0093] In embodiments, the textile substrate is a woven fabric or a non-woven fabric.

[0094] Advantageously, said fabric is a brushed fiber, preferably with a percentage of recycled yarns between 60 and 80%, preferably of about 68%.

[0095] Preferably, said textile substrate comprises fibers selected from the group comprising cotton, polyester, viscose, polyamide, wool, hemp, silk, elastane and mixtures thereof.

[0096] In embodiments, the process according to the present invention occurs continuously, e.g., by means of a transport system.

[0097] The pressing step c) according to the present invention is a step that allows determining the weight of the finished product, by adjusting the amount of elastomeric composition remaining impregnated on the textile substrate. For the purposes of the present invention, the term "pressing" means a process step in which a textile substrate is subjected to compression by devices suitable for the purpose.

[0098] In embodiments, the pressing in step c) of the process according to the present invention is carried out by calendaring: the textile substrate is passed into a system of calenders, typically at room temperature, the opening of which is used to determine the weight of the finished product.

[0099] In embodiments, the drying step d) occurs by passing the textile substrate through a heated and ventilated area, e.g., an oven, so as to allow it to dry and remove the water.

[0100] In embodiments, said step d) is carried out at a temperature of 140-180°C, preferably of 150-170°C, for a time of 5-15 minutes.

[0101] Finally, in step e), the impregnated textile substrate passes through a system of calenders, which allows adjusting the thickness of the product. Advantageously, step e) can be carried out at room temperature (about 25°C), or at low temperatures, preferably at 10-20°C, or at high temperatures, preferably at 50-70°C.

[0102] The composite textile material thus obtained is in the form of reels (identified by numeral 21 in Fig. 1).

[0103] Optionally, the process according to the present invention further comprises a step f), after step e), in which the composite textile material obtained is finished by removing the side selvages by cutting.

[0104] In embodiments, the process according to the present invention further comprises a step g), after step e) and optionally step f), in which the composite textile material obtained is further coated with an adhesive, so as to obtain at least one adhesive-coated side. Such an adhesive can be a polymer adhesive, e.g., based on polyurethane, ethylene vinyl acetate, polycaprolactone, or mixtures thereof.

[0105] In embodiments, the adhesive coating is applied to both sides of the composite textile material, i.e., at the end of step g), the coating is applied to the second side of the composite textile material with a step g') (identified by numeral 15 in Fig. 1) substantially equivalent to step g) (identified by numeral 14 in Fig. 1).

[0106] Step g), and optionally step g'), is carried out by techniques known in the prior art, e.g., by powder coating or by a hot-melt process.

[0107] The powder used for coating is prepared from powders of individual raw polymer materials (identified by numeral 4 in Fig. 1) mixed using a mixer (identified by numeral 12 in Fig. 1).

[0108] It is possible to use a powder coater (identified by numeral 13 in Fig. 1) which releases a defined amount of powder onto the composite textile material, which is conveyed into an oven kept at a temperature between 130 and 170°C, causing the fusion of the polymers. At the oven outlet, the fabric passes through a water-cooled calender, and is then wound in reels again.

[0109] The adhesive-coated composite textile material (identified by numeral 22 in Fig. 1) thus obtained is in the form of reels.

[0110] Finally, in a further aspect, the present invention relates to a composite textile material soaked in a composition comprising at least one latex, at least one dispersant, at least one plant- and/or animal-derived reinforcing filler. In an embodiment, said reinforcing filler essentially consists of eggshell and said composition does not comprise any emulsifiers.

[0111] In an embodiment, said composition also comprises at least one emulsifier.

[0112] In particular, in a further aspect, the present invention relates to a composite textile material directly obtainable by the process according to the present invention.

[0113] In embodiments, said textile material comprises a woven fabric or a non-woven fabric. Preferably, said textile

material comprises fibers selected from cotton, polyester, viscose, polyamide, wool, hemp, silk, elastane fibers and mixtures thereof.

[0114] The composite textile materials according to the present invention can be used in many fields, e.g., for producing buttresses for shoes, or for reinforcements in the leather goods and furnishing industries.

EXPERIMENTAL SECTION

[0115] The present description will be better disclosed in the following examples having only an exemplifying and non-limiting purpose.

Example 1 - preparation of aqueous elastomeric compositions

[0116] Various aqueous elastomeric compositions and a comparison composition, i.e., not comprising any plant- or animal-derived reinforcing filler, were prepared according to the present invention.

[0117] Fig. 1 shows a flow diagram describing the entire process for the production of the composite materials according to an embodiment of the present invention, starting from the preparation of the aqueous elastomeric composition. In brief, the following were sequentially poured into a dissolver: synthetic latexes in aqueous dispersion, an aqueous solution of a wetting agent for textile substrates (sodium alkane sulphonate, CAS 97489-15-1), and an aqueous dispersion of inorganic reinforcing fillers (calcium carbonate and zinc oxide) and a dispersant (sodium polyacrylate) obtained separately. All the additions were made by vacuum suction or direct introduction into the dissolver.

[0118] For the samples according to the present invention (samples A-I), the selected plant- or animal-derived filler in the form of powder was added to the mixture thus obtained. For these samples, in the first preparation step a natural emulsifier (soy lecithin) was further added, specifically selected for making the plant- or animal-derived reinforcing fillers more compatible with the elastomeric composition.

[0119] The mixtures thus obtained were kept under stirring for another hour in order to promote the mixing of all the components.

[0120] Table 1 below shows the qualitative and quantitative composition of the samples according to the present invention, samples A-L, and the comparative one, sample 1.

Table 1

	SAMPLE (percentage by weight of the components)										
	1 [^]	A	B	C	D	E	F	G	H	I	L
Styrene-butadiene aqueous dispersion (low butadiene %)	23,4	21	21	21	21	21	21	21	21	21	21
Styrene-butadiene aqueous dispersion	16	14	14	14	14	14	14	14	14	14	14
Neoprene aqueous dispersion	32.3	29	29	29	29	29	29	29	29	29	29
Water	7.5	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
Calcium carbonate	17.6	16	16	16	16	16	16	16	16	16	16
Zinc oxide	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sodium polyacrylate (40% by weight aqueous solution)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Sodium alkane sulphonate (20-30% by weight aqueous solution)	2	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Soy lecithin	0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Plant or animal-derived reinforcing filler	0	10	10	10	10	10	10	10	10	10	10
[^] comparison sample											

[0121] The plant- or animal-derived reinforcing fillers used in the samples according to the present invention are as follows:

- A. Rice chaff;
 B. Corncob;
 C. Hemp;
 D. Olive pit;
 E. Hide and leather scraps;
 F. Almond and hazelnut shell;
 G. Miscanthus;
 H. Rice husk;
 I. Grape scraps;
 L. Eggshell

[0122] An antifoam agent (an aqueous emulsion of 10% by weight silicones) and a titanium dioxide-based dye were also added to the compositions.

[0123] As shown in Table 1, the compositions according to the present invention (samples A-L) contain about 8% less synthetic latexes than the comparison composition (sample 1) and about 2% less inorganic reinforcing fillers.

[0124] Moreover, the compositions according to the present invention contain 10% recycled materials, i.e., plant- or animal-derived reinforcing fillers.

Example 2 - preparation of the composite textile materials

[0125] The aqueous elastomeric compositions obtained in example 1 were used as the impregnating compositions in a process for the production of composite textile materials.

[0126] Fig. 1 shows the steps described below, after the preparation of the aqueous elastomeric composition, of impregnation and adhesive-coating of the textile substrate. In brief, a mixed fiber (cotton and polyester) fabric was soaked in a tank containing one of the aqueous elastomeric compositions obtained in Example 1, then passed through a first system of calendars at room temperature to adjust the weight thereof.

[0127] The fabric was then passed into an oven at 150-170°C for about 10 minutes so as to allow drying it and removing water.

[0128] Finally, the impregnated fabric was passed through a second calender at room temperature, to allow adjusting the thickness of the product, and finished by cutting the side selvages.

[0129] The fabric was then subjected to a powder coating process with thermoplastic adhesives so as to obtain a composite fabric adhesive-coated on both sides.

Example 3 - characterization of the mechanical properties of the fabrics

[0130] The composite fabrics obtained in example 2 were tested according to the certified method TM83 SATRA - (*Measurement of the area shape retention and collapsing load of formed box toe (toe puff) and counter (stiffener) materials*). This method is mainly applicable to round toe footwear and reinforcing materials, but can be used to evaluate any deformable material.

[0131] This method aims at determining the shape retention properties and the compressive strength of a preformed dome-shaped specimen. The following can be measured through the method:

- **AREA SHAPE RETENTION**, i.e., an assessment of the material thermoformability, understood as a shape amount imposed on a fabric and maintained by the latter over time;
- **COLLAPSING LOAD**, assessment of the behavior of the materials forming the toe caps/buttresses of shoes, simulating the situation of use with a cyclical action of repeated compression and recording the response of the materials in terms of force over the cycle;
- **RESILIENCE** (as a percentage), i.e., the ability of the material to withstand mechanical stresses; and
- **RIGIDITY**, i.e., the ability of the material to oppose an elastic deformation.

[0132] For each of the fabrics obtained in example 2, three specimens, known as "cups", were formed according to the SATRA TM83 standard with the appropriate circular punch with a diameter of 57 ± 1 mm. The specimens were then subjected to a shaping process, to give them a dome shape, in appropriate forming devices (STD 153D).

[0133] Since the fabrics are adhesive-coated on both sides, in order to avoid the fabrics from sticking to the forming devices, polyethylene specimens were also cut for each cup with appropriate punches (a ring-shaped one, external diameter 57 ± 1 mm and internal diameter 38 ± 1 mm, and a circular one with a diameter of 57 ± 1 mm).

[0134] The forming process occurs in a ventilated oven previously heated to a temperature of 95 ± 5 °C for a time of 8.5 ± 0.5 minutes, followed by a step in a suitable press (STD 153P).

[0135] The samples thus obtained were allowed to cool inside the forming device for about 1 hour and 30 minutes in a controlled environment at 23 ± 2 °C/ 50 ± 5 % rh.

[0136] Once removed from the forming device, the cups were kept for at least 24 hours in a controlled standard environment of 23 ± 2 °C/ 50 ± 5 % rh before testing.

[0137] The instrumentation used for testing is as follows:

- Test specimen holding jig - STD 153H
- Compression cage - STD 153A
- Dynamometer
- Repeated collapsing device - STD 153C
- Metal sheet.

[0138] For testing, the flat plate associated with the STD 153H device was positioned under the jig, with the clamping ring facing downwards. A metal sheet was fixed so that the hole on the flat plate was completely covered by the sheet. The jig was then lowered until contact of the tip with the surface of the sheet. It was thus possible to measure the initial value for the calculation of the AREA SHAPE RETENTION, which value was identified as [X].

[0139] The flat plate was then removed and the sample cup was inserted between the plate and the clamping ring with the dome facing downwards. The flat plate was then repositioned under the jig, which was lowered until the tip was in contact with the sample surface. The value identified as [Y] was thus measured.

[0140] The compression cage STD 153A was then mounted on the dynamometer using the appropriate adapters so that the punch is on the top of the device. A method-specific program was used, which, after the first compression of the sample by the dynamometer, requires the operator to perform 8 manual compressions of the cup, with the instrument STD 153C. An additional compression was then performed with the dynamometer. It is thus possible to obtain the load recorded at the first compression (INITIAL COLLAPSING LOAD - RIGIDITY) and the load recorded after the tenth cycle of compressions. These two values are also used for calculating the RESILIENCE of the sample.

[0141] After the dynamometer test was finished, a further measurement was carried out using the device STD 153H.

[0142] The data obtained are summarized in Table 2 below.

Table 2

Sample	Final weight (g/m ²)	Thickness (mm)	Area Shape Retention (%)	Rigidity (N)	Resilience (%)
1 [^]	1099	1.40	83%	30.3	39%
A	1132	1.35	86%	35.9	43%
B	1086	1.35	83%	34.5	45%
C	1090	1.45	79%	40.8	46%
D	1110	1.40	83%	38.4	46%
E	1077	1.45	84%	34.2	43%
F	1122	1.40	85%	36.4	45%
G	1093	1.40	80%	37.1	43%
H	1127	1.35	83%	34.8	43%
I	1130	1.35	85%	36.2	44%
L	1115	1.35	86%	43.2	46%
[^] comparison sample					

[0143] The experimental data show that the use of plant- or animal-derived reinforcing fillers results, at comparable values of AREA SHAPE RETENTION, in an increase in rigidity of about 15%, particularly marked when said reinforcing filler essentially consists of eggshell, and an increase in resilience of the item equal to about 10%, which values are indicative of an improvement in performance.

[0144] Moreover, the increase in the values relating to rigidity and resilience allow comparing the performance levels of the composite textile materials according to the present invention (samples A-L) with those of the comparison material (sample 1[^]), and more generally, with those of the composite textile materials known in the art but which typically have a higher density, thus for which a use of greater amounts of raw materials is required to prepare the finished products.

Example 4 - preparation of aqueous elastomeric compositions with reinforcing filler essentially consisting of eggshell

[0145] Various aqueous elastomeric compositions were prepared according to the present invention and a comparison composition, i.e., not comprising any plant- and/or animal-derived reinforcing filler.

[0146] The production process is the process already described in Example 1.

[0147] Table 3 below shows the qualitative and quantitative composition of the samples according to the present invention, samples 1, 3 5 and the comparative ones, samples STD, 2 and 4.

Table 3

	SAMPLE (percentage by weight of the components)					
	STD^	1	2^	3	4^	5
Styrene-butadiene aqueous dispersion (low butadiene %)	23,4	21	14	14	10	10
Styrene-butadiene aqueous dispersion	16	14	10	10	10	10
Neoprene aqueous dispersion	32.1	28.8	18.3	18.3	23.3	23.3
Water	7.5	6.8	20	20	20	20
Calcium carbonate	17.6	16	34	0	33	0
Zinc oxide	0.9	0.8	0	0	0	0
Sodium polycarboxylate (40% by weight aqueous solution)	0.3	0.3	0.5	0.5	0.5	0.5
Sodium alkane sulphonate (20-30% by weight aqueous solution)	2	1.9	2	2	2	2
Soy lecithin	0	0.2	0	0	0	0
Silicone aqueous solution	0.2	0.2	0.2	0.2	0.2	0.2
Fatty acids of coconut and potassium salt	0	0	1	1	1	1
Eggshell	0	10	0	34	0	33
^ comparison sample						

[0148] Said fatty acids of coconut and potassium salt which are, for example, coconut potassium soap, are added as coconut potassium soap.

[0149] As shown in Table 3, the compositions according to the present invention (samples 1, 3, 5) contain 10% recycled materials, in a preferred form, over 30% recycled material i.e., eggshell.

[0150] Samples 3 and 5 do not comprise the emulsifier lecithin.

Example 5 - preparation of composite textile materials, where the aqueous composition includes eggshell.

[0151] The aqueous elastomeric compositions obtained in example 4 were used as impregnating compositions in a process for the production of composite textile materials.

[0152] In brief, a mixed fiber (cotton and polyester) fabric was soaked in a tank containing one of the aqueous elastomeric compositions obtained in Example 4, then passed through a first system of calenders at room temperature to adjust the weight thereof.

[0153] The fabric was then passed into an oven at 150-170°C for about 10 minutes so as to allow drying it and removing water.

[0154] Finally, the impregnated fabric was passed through a second calender at room temperature, to allow adjusting the thickness of the product, and finished by cutting the side selvages.

[0155] The fabric was then subjected to a powder coating process with thermoplastic adhesives so as to obtain a composite fabric adhesive-coated on both sides.

Example 6 - characterization of the mechanical properties of the fabrics obtained in Example 5

[0156] The composite fabrics obtained in example 5 were tested according to the certified method TM83 SATRA,

described in Example 3 above.

[0157] The samples used had a final weight of 1100 g/m², with a $\pm$ 5% tolerance. The data obtained are summarized in Table 4 below.

Table 4

Sample	% mineral filler	% natural filler	Area Shape Retention (%)	Rigidity (N)	Resilience (%)
STD [^]	17.6	0	83%	30.3	39%
1	16	10	86%	43.2	46%
2 [^]	34	0	74%	38.1	40%
3	0	34	82%	34.7	49%
4 [^]	33	0	77%	38.6	42%
5	0	33	88%	40.5	52%
[^] comparison sample					

[0158] The experimental data shows how the use of eggshell as a filler to replace the mineral filler (CaCO₃) (samples 3, 5) not only brings about improvements in relation to environmental impact, but surprisingly improves the performance levels of the item in hand. Formulation 5, which differs from formulation 3 because it comprises a higher % of neoprene latex (from 18.3% to 23.3%) to the detriment of SBR, was the best performing overall: the AREA SHAPE RETENTION value, an indication of good thermoformability, was higher than in the other samples, including those tested in Example 3. The RESILIENCE of the fabric, a feature connected to the resistance to mechanical stress, was the highest observed, confirming the advantages of the formulation.

Claims

1. An aqueous elastomeric composition, for the impregnation of textile materials, comprising at least one latex, at least one dispersant, at least one plant- and/or animal-derived reinforcing filler, and water.
2. The aqueous elastomeric composition according to claim 1, wherein said plant- and/or animal-derived reinforcing filler is selected from the group comprising rice husk, rice chaff, peanut pod, hemp, bamboo fibers, hay, almond shell, hazelnut shell, walnut shell, eggshell, miscanthus, cherry stone, olive pit, straw, hide and leather scraps, regenerated leather scraps, corn cob, grapes, and mixtures thereof.
3. The aqueous elastomeric composition according to any one of claims 1-2, wherein said plant- and/or animal-derived reinforcing filler is present in an amount from 0.5% to 30% by weight with respect to the total weight of the composition.
4. The aqueous elastomeric composition according to claim 1, wherein said reinforcing filler essentially consists of eggshell and said composition does not comprise an emulsifier.
5. The aqueous elastomeric composition according to claim 4, wherein said eggshell is present in an amount from 10 to 45% by weight, or from 20 to 40% by weight, or from 30 to 40% by weight with respect to the total weight of the composition.
6. The aqueous elastomeric composition according to any one of claims 1-5, wherein said latex is selected from a synthetic latex, a natural latex, and mixtures thereof.
7. The aqueous elastomeric composition according to any one of claims 1-3, which also comprises at least one emulsifier in an amount of 0.1-4% by weight with respect to the total weight of the composition.
8. The aqueous elastomeric composition according to claim 7, wherein said emulsifier is selected from a natural emulsifier, a synthetic emulsifier, and mixtures thereof.
9. The aqueous elastomeric composition according to claim 8, wherein said natural emulsifier is a lecithin.

10. The aqueous elastomeric composition according to claim 8, wherein said synthetic emulsifier is selected from the group comprising anionic surfactants, sodium salts of C10-C18 linear or branched alkyl sulfonates, ethoxylated saturated C16-C18 alkyl alcohols, ethoxylated unsaturated C18 alkyl alcohols, styrenated phenols, and mixtures thereof.

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11. A process for the production of a composite textile material comprising the following steps:

- a) Preparing an aqueous elastomeric composition as defined in any one of claims 1-10;
- b) Soaking a textile substrate in the composition obtained in step a);
- c) Pressing the impregnated textile substrate;
- d) Drying the textile substrate obtained in step c); and
- e) Calendering the dry textile substrate.

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12. The process according to claim 11, wherein said textile substrate comprises fibers selected from the group comprising cotton, polyester, viscose, polyamide, wool, hemp, silk, elastane and mixtures thereof.

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13. The process according to any one of claims 11-12, wherein said step c) is performed by calendering.

14. A composite textile material directly obtainable by the process according to any one of claims 11-13.

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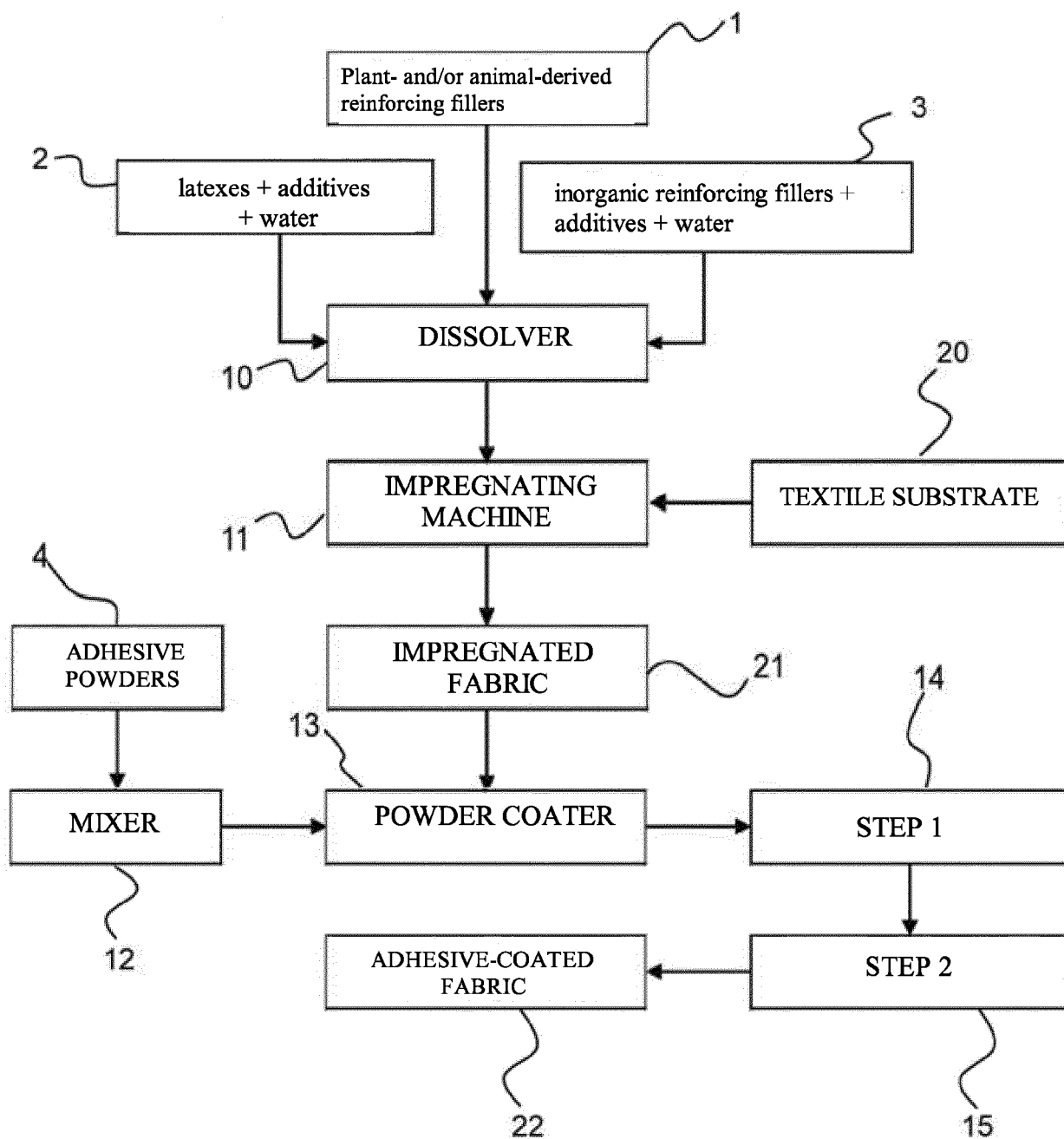


Fig. 1



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