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(54) **Titre : MATERIAUX COMPOSITES MULTICOUCHES COMPORTANT UNE STRUCTURE TEXTILE, PROCEDES DE FABRICATION ET UTILISATION DE CES MATERIAUX**

(54) **Title: MULTI-LAYER COMPOSITE MATERIALS COMPRISING A TEXTILE SHEET MATERIAL, PRODUCTION AND CORRESPONDING METHOD OF USE THEREOF**

(57) **Abrégé/Abstract:**
The invention relates to multi-layer composite materials which comprise the following components: (A) a textile sheet material, (B) optionally at least one connecting layer and (C) a polyurethane layer having capillaries that extend through the entire thickness of the polyurethane layer, the textile sheet material (A) and the polyurethane layer (C) being interconnected di-rectly or via the connecting layer (B).

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(54) Title: MULTI-LAYER COMPOSITE MATERIALS COMPRISING A TEXTILE SHEET MATERIAL, CORRESPONDING METHOD OF PRODUCTION AND USE THEREOF

(54) Bezeichnung: MEHRSCHICHTIGE VERBUNDMATERIALIEN, DIE EIN TEXTILES FLÄCHENGEBILDE UMFASSEN, VERFAHREN ZU IHRER HERSTELLUNG UND IHRE VERWENDUNG

(57) Abstract: The invention relates to multi-layer composite materials which comprise the following components: (A) a textile sheet material, (B) optionally at least one connecting layer and (C) a polyurethane layer having capillaries that extend through the entire thickness of the polyurethane layer, the textile sheet material (A) and the polyurethane layer (C) being interconnected directly or via the connecting layer (B).

(57) Zusammenfassung: Mehrschichtige Verbundmaterialien, umfassend als Komponenten: (A) ein textiles Flächengebilde, (B) gegebenenfalls mindestens eine Verbindungsschicht und (C) eine Polyurethanschicht, die Kapillaren aufweist, die über die gesamte Dicke der Polyurethanschicht gehen, wobei textiles Flächengebilde (A) und Polyurethanschicht (C) miteinander direkt oder über Verbindungsschicht (B) verbunden sind.

Multi-layer composite materials comprising a textile sheet material, production and corresponding method of use thereof

The present invention relates to multilayered composite materials comprising as components:

(A) a textile sheet material,

(B) optionally at least one bonding layer, and

(C) a polyurethane layer with capillaries passing through the entire thickness of the polyurethane layer,

wherein textile sheet material (A) and polyurethane layer (C) are bonded to each other directly or via bonding layer (B).

More specifically, it relates to a multilayered composite material comprising as components:

(A) a textile sheet material,

(B) optionally at least one bonding layer, and

(C) a polyurethane layer with capillaries passing through the entire thickness of the polyurethane layer, and patterning which corresponds to a velvet surface with small hairs having an average length in the range from 20 to 500 µm,

wherein textile sheet material (A) and polyurethane layer (C) are bonded to each other directly or via bonding layer (B), wherein the small hairs of polyurethane layer (C) have an average spacing of 50 to 350 µm from one hair to the next, wherein said bonding layer (B) comprises a layer of a cured organic adhesive and wherein said textile sheet material (A) comprises wovens, drawn-loop knits and non-wovens and comprises at least one polymer deposited by coagulation.

The present invention further relates to a process for producing the multilayered composite materials of the present invention and to their use.

Textiles are not only used for apparel but also at numerous places which serve partly or predominantly decorative purposes. Examples are drapes, textiles on seats such as for example automotive seats or sitting furniture, interior trim of vehicles such as for example automobiles, textile wall coverings and so on and on. An appealing appearance is therefore essential.

It is also hugely important that such textiles shall be easy to clean, for example of dust and grease. Textiles are very prone to soiling/staining. Washing a textile curtain is possible, but the textile first has to be removed and is not at its rightful place for a time at least. In addition, large-area textiles in particular can be very inconvenient to remove and wash, theater curtains for example.

Velvetlike textiles in particular are very difficult to wash in some cases.

True, textiles can be coated with plastic film to make them wipeable, but in such a case the haptic properties leave a great deal to be desired, and an undesirable plasticky hand or feel is observed in many cases.

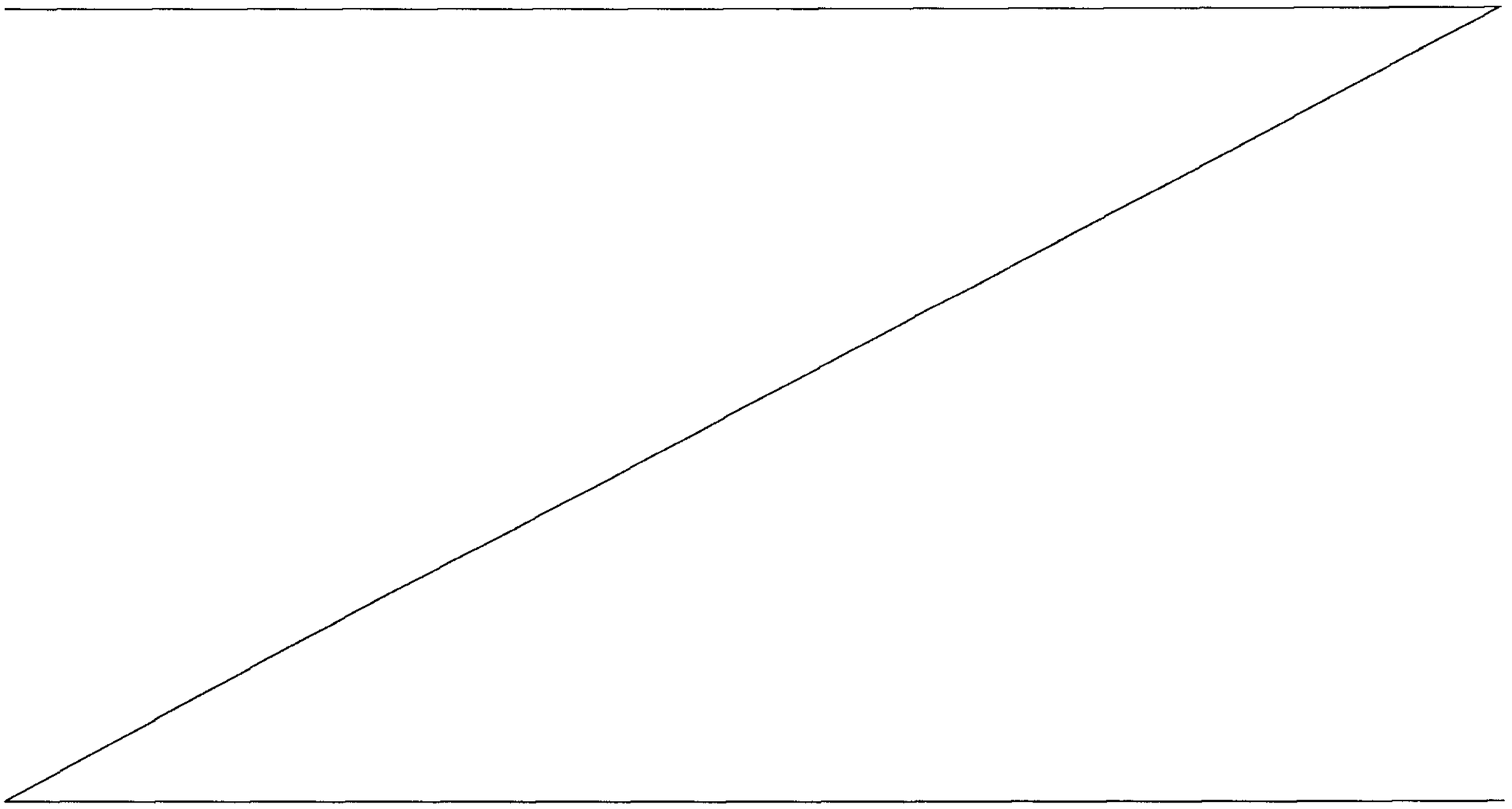
It is an object of the present invention to process textile sheet materials such that they have an attractive visual exterior and pleasant haptics and are impervious to fingerprints, sweat stains and moisture.

We have found that this object is achieved by the multilayered composite materials defined at the beginning. They comprise as components:

(A) a textile sheet material,

(B) optionally at least one bonding layer, and

(C) a polyurethane layer with capillaries passing through the entire thickness of the



polyurethane layer,

wherein textile sheet material (A) and polyurethane layer (C) are bonded to each other directly or via bonding layer (B).

Textile sheet materials (A), herein also referred to as textile (A) or textiles (A), may have various manifestations. Suitable are for example wovens, felt, drawn-loop knits (knitwear), formed-loop knits, waddings, laid scrims and microfiber fabrics.

Textile (A) preferably comprises wovens, formed-loop knits or drawn-loop knits.

Textile sheet materials (A) may be obtained from lines, cords, ropes, yarns or threads. Textiles (A) may be of natural origin, for example cotton, wool or flax, or synthetic, for example polyamide, polyester, modified polyesters, polyester blend fabrics, polyamide blend fabrics, polyacrylonitrile, triacetate, acetate, polycarbonate, polyolefins such as for example polyethylene and polypropylene, polyvinyl chloride, also polyester microfibers and glass fiber fabrics. Very particular preference is given to polyester, cotton and polyolefins such as for example polyethylene and polypropylene and also selected blend fabrics selected from cotton-polyester blend fabric, polyolefin-polyester blend fabric and polyolefin-cotton blend fabric.

Textile sheet materials (A) may be untreated or treated, for example bleached or dyed. Preferably, textile sheet materials are coated on one side only or uncoated.

In an advantageous embodiment of the present invention, textile sheet material (A) comprises wovens, drawn-loop knits or preferably non-wovens wherein at least one polymer, for example polyamide or more particularly polyurethane, was deposited by coagulation, but preferably such that the textile sheet material concerned retains its breathability or air permeability. Polymers can be for example deposited by coagulation by initially providing a solution of a polymer in a so-called good solvent, examples of what is suitable for polyurethanes being N,N-dimethylformamide (DMF), tetrahydrofuran (THF) and N,N-dimethylacetamide (DMA). From this solution, a porous film of the polymer in question is initially deposited, for example by exposing the solution to the vapors of a so-called poor solvent which is not capable of either dissolving or swelling the polymer in question. Water or methanol are suitable poor solvents for many polymers, and water is preferred. When water is to be used as poor solvent, the solution can be exposed to a moist atmosphere for example. The porous film thus obtainable is peeled off and transferred to the textile sheet material in question. Before or after this transfer, the residue of good solvent is separated off, for example by washing off with a poor solvent.

In a very advantageous embodiment of the present invention, the material comprises a poromer wherein porosities are generated in polymer deposited as described above,

for example by washing off salts or by other methods as described for example in chapters 6 et seq. of the book New Materials Permeable to Water Vapor, Harro Träubel, Springer Verlag 1999.

Textile sheet materials (A) may be finished; they have an easy care and/or flame-retardant finish in particular.

Textile sheet materials (A) may have an areal weight in the range from 10 to 500 g/m^2, preference being given to the range from 50 to 300 g/cm^2.

Multilayered composite material of the present invention further comprises at least one polyurethane layer (C) with capillaries passing through the entire thickness of the polyurethane layer. Polyurethane layer (C) with capillaries passing through the entire thickness of the polyurethane layer is herein also referred to in brief as polyurethane layer (C).

In one embodiment of the present invention, polyurethane layer (C) has an average thickness in the range from 15 to 300 µm, preferably in the range from 20 to 150 µm and more preferably in the range from 25 to 80 µm.

In one preferred embodiment of the present invention, polyurethane layer (C) has capillaries which pass through the entire thickness (cross section) of the polyurethane layer (C).

In one embodiment of the present invention, polyurethane layer (C) has on average at least 100 and preferably at least 250 capillaries per 100 cm^2.

In one embodiment of the present invention, the capillaries have on average diameter in the range from 0.005 to 0.05 mm and preferably in the range from 0.009 to 0.03 mm.

In one embodiment of the present invention, the capillaries are uniformly distributed over polyurethane layer (C). In one preferred embodiment of the present invention, however, the capillaries are nonuniformly distributed over the polyurethane layer (C).

In one embodiment of the present invention, the capillaries are essentially arcuate. In another embodiment of the present invention, the capillaries have an essentially straight-line course.

The capillaries endow the polyurethane layer (C) with an air and water vapor permeability without any need for perforation. In an embodiment of the present invention, the water vapor permeability of the polyurethane layer (C) can be above 1.5 mg/cm^2·h, measured according to German standard specification DIN 53333. It is

thus possible for moisture such as sweat for example to migrate through the polyurethane layer (C).

In one embodiment of the present invention, polyurethane layer (C) as well as capillaries has pores which do not pass through the entire thickness of the polyurethane layer (C).

In one embodiment, polyurethane layer (C) exhibits patterning. The patterning is freely choosable and can reproduce for example the patterning of a leather or of a wood surface. In an embodiment of the present invention, the patterning may reproduce a nubuck leather.

In one embodiment of the present invention, polyurethane layer (C) has a velvetlike appearance.

In one embodiment of the present invention, the patterning can correspond to a velvet surface, for example with small hairs having an average length in the range from 20 to 500 µm, preferably in the range from 30 to 200 µm and more preferably in the range from 60 to 100 µm. The small hairs can have for example a circle-shaped diameter. In a particular embodiment of the present invention, the small hairs have a cone-shaped form.

In one embodiment of the present invention, polyurethane layer (C) has small hairs with an average spacing of 50 to 350, preferably 100 to 250 µm from one hair to the next.

When the polyurethane layer (C) has small hairs, the statements about the average thickness apply to the polyurethane layer (C) without the small hairs.

Polyurethane layer (C) is preferably bonded to textile (A) via at least one bonding layer (B).

Bonding layer (B) may comprise an interrupted, i.e., discontinuous, layer, preferably of a cured organic adhesive.

In another embodiment, (B) is a continuous layer of a cured organic adhesive, which may be in a completely filmed state.

In one embodiment of the present invention, bonding layer (B) comprises a layer applied in point form, stripe form or lattice form, for example in the form of diamonds, rectangles, squares or a honeycomb structure. In that case, polyurethane layer (C) comes into contact with textile (A) in the gaps of the bonding layer (B).

In one embodiment of the present invention, bonding layer (B) comprises a layer of a cured organic adhesive, for example based on polyvinyl acetate, polyacrylate or in particular polyurethane, preferably based on polyurethanes having a glass transition temperature below 0°C.

The organic adhesive may for example be cured thermally, through actinic radiation or by aging.

In another embodiment of the present invention, bonding layer (B) comprises an adhesive gauze.

In one embodiment of the present invention, bonding layer (B) has a maximum thickness of 100 µm, preferably 50 µm, more preferably 30 µm, most preferably 15 µm.

In one embodiment of the present invention, bonding layer (B) may comprise microballoons. Microballoons herein are spherical particles having an average diameter in the range from 5 to 20 µm and composed of polymeric material, in particular of halogenated polymer such as for example polyvinyl chloride or polyvinylidene chloride or copolymer of vinyl chloride with vinylidene chloride. Microballoons may be empty or preferably filled with a substance whose boiling point is slightly lower than room temperature, for example with n-butane and in particular with isobutane.

In one embodiment of the present invention, polyurethane layer (C) may be bonded to textile (A) via at least two bonding layers (B) which have an identical or different composition. One bonding layer (B) may comprise a pigment with the other bonding layer (B) being pigmentfree.

In one variant, one bonding layer (B) may comprise microballoons with the other bonding layer (B) not comprising microballoons.

In one embodiment of the present invention, multilayered composite material of the present invention may comprise at least one interlayer (D) disposed between textile (A) and bonding layer (B), between bonding layer (B) and polyurethane layer (C) or between two bonding layers (B), which can be the same or different. Interlayer (D) is selected from paper, metal foils and plastics foils, foam and in particular open-cell foam.

Molds are not embodiments of interlayers (D) for the purposes of the present invention.

In a preferred embodiment of the present invention, multilayered composite material of the present invention can include no further layers.

In those embodiments in which multilayered composite material of the present invention includes at least one interlayer (D), polyurethane layer (C) comes into direct contact with interlayer (D) and not with textile (A).

In one embodiment of the present invention, interlayer (D) may have an average diameter (thickness) in the range from 0.05 mm to 5 cm, preferably in the range from 0.1 mm to 0.5 cm and more preferably in the range from 0.2 mm to 2 mm.

Preferably, interlayer (D) has a water vapor permeability in the range of greater than 1.5 mg/cm^2.h, measured according to German standard specification DIN 53333.

Multilayered composite materials of the present invention have a high mechanical strength and fastnesses. They further have a high water vapor permeability. Drops of spilt liquid are easy to remove, for example with a rag. In addition, multilayered composite materials of the present invention have an appealing appearance and a very pleasant soft hand or feel.

Multilayered composite materials of the present invention are useful for decoration, for example as decoration material. In addition, multilayered composite materials of the present invention can be back-foamed or back-molded and structural components thus produced can be used in various ways, for example in the automotive sector.

Furthermore, multilayered composite materials of the present invention are useful as or in the manufacture of home textiles such as for example drapes or wall coverings. Such drapes or wall coverings are easy to clean without their having to be removed, and they have a very pleasant hand or feel.

The present invention further provides a process for producing multilayered composite materials of the present invention, herein also referred to as inventive production process. One embodiment of the inventive production process proceeds by forming a polyurethane layer (C) with the aid of a mold, applying at least one organic adhesive uniformly or partially onto textile (A) and/or onto polyurethane layer (C) and then bonding polyurethane layer (C) pointwise, stripwise or areawise to said textile (A).

In one embodiment of the present invention, multilayered composite material of the present invention is produced by a coating process by first providing a polyurethane film (C), providing, for example spraying or coating, at least a textile (A) or the polyurethane film (C) or both with organic adhesive on one face in each case, partially, for example in the form of a pattern, and then bringing the two faces into contact with each other. Thereafter, the system thus obtainable can additionally be pressed together or thermally treated or pressed together while being heated.

The polyurethane film (C) forms the later polyurethane layer (C) of the multilayered composite material of the present invention. The polyurethane film (C) can be produced as follows:

An aqueous polyurethane dispersion is applied to a mold, which is preheated, the water is allowed to evaporate and then the resulting polyurethane film (C) is transferred to textile (A).

Aqueous polyurethane dispersion can be applied to the mold by conventional methods, in particular by spraying, for example with a spray gun.

The mold may exhibit patterning, also referred to as structuring, for example produced by laser engraving or by molding with a negative mold.

An embodiment of the present invention comprises providing a mold having an elastomeric layer or a layer composite, comprising an elastomeric layer on a support, the elastomeric layer comprising a binder and also if appropriate further, additive and auxiliary materials. Providing a mold can then comprise the following steps:

1) applying a liquid binder, comprising additive and/or auxiliary materials if appropriate, to a patterned surface, for example another mold or an original pattern,

2) curing the binder, for example by thermal curing, radiative curing or by allowing to age,

3) separating the mold thus obtainable and if appropriate applying it to a support, for example a metal plate or a metal cylinder.

One embodiment of the present invention proceeds by a liquid silicone being applied to a pattern, the silicone being allowed to age and thus cure and then stripping. The silicone film is then adhered to an aluminum support.

A preferred embodiment of the present invention provides a mold comprising a laser-engravable layer or a layer composite comprising a laser-engravable layer on a support, the laser-engravable layer comprising a binder and also, if appropriate, further, additive and auxiliary materials. The laser-engravable layer is preferably also elastomeric.

In a preferred embodiment, the providing of a mold comprises the steps of:

1) providing a laser-engravable layer or a layer composite comprising a laser-

engravable layer on a support, the laser-engravable layer comprising a binder and also, preferably, additive and auxiliary materials,

2) thermochemical, photochemical or actinic amplification of the laser-engravable layer,

3) engraving into the laser-engravable layer, using a laser, a surface structure corresponding to the surface structure of the surface-structured coating.

The laser-engravable layer, which is preferably elastomeric, or the layer composite can be and preferably are present on a support. Examples of suitable supports comprise woven fabrics and self-supporting films/sheets of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polybutylene terephthalate (PBT), polyethylene, polypropylene, polyamide or polycarbonate, preferably PET or PEN self-supporting films/sheets.

Useful supports likewise include papers and knits, for example of cellulose. As supports there may also be used conical or cylindrical sleeves of the materials mentioned. Also suitable for sleeves are glass fiber fabrics or composite materials comprising glass fibers and polymeric materials of construction. Suitable support materials further include metallic supports such as for example solid or fabric-shaped, sheetlike or cylindrical supports of aluminum, steel, magnetizable spring steel or other iron alloys.

In one embodiment of the present invention, the support may be coated with an adhesion-promoting layer to provide better adhesion of the laser-engravable layer. Another embodiment of the present invention requires no adhesion-promoting layer.

The laser-engravable layer comprises at least one binder, which may be a prepolymer which reacts in the course of a thermochemical amplification to form a polymer. Suitable binders can be selected according to the properties desired for the laser-engravable layer or the mold, for example with regard to hardness, elasticity or flexibility. Suitable binders can essentially be divided into 3 groups, without there being any intention to limit the binders thereto.

The first group comprises those binders which have ethylenically unsaturated groups. Ethylenically unsaturated groups are crosslinkable photochemically, thermochemically, by means of electron beams or by means of any desired combination thereof. In addition, mechanical amplification is possible by means of fillers. Such binders are for example those comprising 1,3-diene monomers such as isoprene or 1,3-butadiene in polymerized form. The ethylenically unsaturated group may either function as a chain building block of the polymer (1,4-incorporation), or it may be bonded to the polymer

chain as a side group (1,2-incorporation). As examples there may be mentioned natural rubber, polybutadiene, polyisoprene, styrene-butadiene rubber, nitrile-butadiene rubber, acrylonitrile-butadiene-styrene (ABS) copolymer, butyl rubber, styrene-isoprene rubber, polychloroprene, polynorbornene rubber, ethylene-propylene-diene monomer (EPDM) rubber or polyurethane elastomers having ethylenically unsaturated groups.

Further examples comprise thermoplastic elastomeric block copolymers of alkenyl-aromatics and 1,3-dienes. The block copolymers may comprise either linear block copolymers or else radial block copolymers. Typically they are three-block copolymers of the A-B-A type, but they may also comprise two-block polymers of the A-B type, or those having a plurality of alternating elastomeric and thermoplastic blocks, for example A-B-A-B-A. Mixtures of two or more different block copolymers can also be used. Commercially available three-block copolymers frequently comprise certain proportions of two-block copolymers. Diene units may be 1,2- or 1,4-linked. Block copolymers of the styrene-butadiene type and also of the styrene-isoprene type can be used. They are commercially available under the name Kraton® for example. It is also possible to use thermoplastic elastomeric block copolymers having end blocks of styrene and a random styrene-butadiene middle block, which are available under the name Styroflex®.

Further examples of binders having ethylenically unsaturated groups comprise modified binders in which crosslinkable groups are introduced into the polymeric molecule through grafting reactions.

The second group comprises those binders which have functional groups. The functional groups are crosslinkable thermochemically, by means of electron beams, photochemically or by means of any desired combination thereof. In addition, mechanical amplification is possible by means of fillers. Examples of suitable functional groups comprise –Si(HR^1)O-, –Si(R^{1}R^2)O-, –OH, -NH$_2$, -NHR^1, -COOH, -COOR^1, -COHN$_2$, -O-C(O)NHR^1, -SO$_3$H or -CO-. Examples of binders comprise silicone elastomers, acrylate rubbers, ethylene-acrylate rubbers, ethylene-acrylic acid rubbers or ethylene-vinyl acetate rubbers and also their partially hydrolyzed derivatives, thermoplastic elastomeric polyurethanes, sulfonated polyethylenes or thermoplastic elastomeric polyesters. In the formulae, R^1 and - if present - R^2 are different or preferably the same and are each selected from organic groups and in particular C$_1$-C$_6$-alkyl.

One embodiment of the present invention comprises using binders having both ethylenically unsaturated groups and functional groups. Examples comprise addition-crosslinking silicone elastomers having functional groups and ethylenically unsaturated groups, copolymers of butadiene with (meth)acrylates, (meth)acrylic acid or acrylonitrile, and also copolymers or block copolymers of butadiene or isoprene with

styrene derivatives having functional groups, examples being block copolymers of butadiene and 4-hydroxystyrene.

The third group of binders comprises those which have neither ethylenically unsaturated groups nor functional groups. There may be mentioned for example polyolefins or ethylene-propylene elastomers or products obtained by hydrogenation of diene units, for example SEBS rubbers.

Polymer layers comprising binders without ethylenically unsaturated or functional groups generally have to be amplified mechanically, with the aid of high-energy radiation or a combination thereof in order to permit optimum crisp structurability via laser.

It is also possible to use mixtures of two or more binders, in which case the two or more binders in any one mixture may all just come from one of the groups described or may come from two or all three groups. The possible combinations are only limited insofar as the suitability of the polymer layer for the laser-structuring operation and the negative-molding operation must not be adversely affected. It may be advantageous to use for example a mixture of at least one elastomeric binder having no functional groups with at least one further binder having functional groups or ethylenically unsaturated groups.

In one embodiment of the present invention, the proportion of binder or binders in the elastomeric layer or the particular laser-engravable layer is in the range from 30% by weight to 99% by weight based on the sum total of all the constituents of the particular elastomeric layer or the particular laser-engravable layer, preferably in the range from 40% to 95% by weight and most preferably in the range from 50% to 90% by weight.

In one embodiment of the present invention, polyurethane layer (C) is formed with the aid of a silicone mold. Silicone molds herein are molds prepared using at least one binder having at least one and preferably at least three O-Si(R^1R^2)-O- groups per molecule, where the variables are each as defined above.

Optionally, the elastomeric layer or laser-engravable layer may comprise reactive low molecular weight or oligomeric compounds. Oligomeric compounds generally have a molecular weight of not more than 20 000 g/mol. Reactive low molecular weight and oligomeric compounds are hereinbelow simply referred to as monomers.

Monomers may be added to increase the rate of photochemical or thermochemical crosslinking or of crosslinking via high-energy radiation, if desired. When binders from the first and second groups are used, the addition of monomers for acceleration is generally not absolutely essential. In the case of binders from the third group, the

addition of monomers is generally advisable without being absolutely essential in every case.

Irrespective of the issue of crosslinking rate, monomers can also be used for controlling crosslink density. Depending on the identity and amount of low molecular weight compounds added, wider or narrower networks are obtained. Known ethylenically unsaturated monomers can be used first of all. The monomers should be substantially compatible with the binders and have at least one photochemically or thermochemically reactive group. They should not be volatile. Preferably, the boiling point of suitable monomers is at least 150°C. Of particular suitability are amides of acrylic acid or methacrylic acid with mono- or polyfunctional alcohols, amines, amino alcohols or hydroxy ethers and hydroxy esters, styrene or substituted styrenes, esters of fumaric or maleic acid, or allyl compounds. Examples comprise n-butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, 1,9-nonanediol diacrylate, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, dioctyl fumarate, N-dodecylmaleimide and triallyl isocyanurate.

Monomers suitable for thermochemical amplification in particular comprise reactive low molecular weight silicones such as for example cyclic siloxanes, Si-H-functional siloxanes, siloxanes having alkoxy or ester groups, sulfur-containing siloxanes and silanes, dialcohols such as for example 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol, diamines such as for example 1,6-hexanediamine, 1,8-octanediamine, amino alcohols such as for example ethanolamine, diethanolamine, butylethanolamine, dicarboxylic acids such as for example 1,6-hexanedicarboxylic acid, terephthalic acid, maleic acid or fumaric acid.

It is also possible to use monomers having both ethylenically unsaturated groups and functional groups. As examples there may be mentioned ω-hydroxyalkyl (meth)acrylates, such as for example ethylene glycol mono(meth)acrylate, 1,4-butanediol mono(meth)acrylate or 1,6-hexanediol mono(meth)acrylate.

It is of course also possible to use mixtures of different monomers, provided that the properties of the elastomeric layer are not adversely affected by the mixture. In general, the amount of added monomers is in the range from 0% to 40% by weight, based on the amount of all the constituents of the elastomeric layer or of the particular laser-engravable layer, preferably in the range from 1% to 20% by weight.

In one embodiment, one or more monomers may be used together with one or more catalysts. It is thus possible to accelerate silicone molds by addition of one or more acids or via organotin compounds to accelerate step 2) of the providing of the mold.

Suitable organotin compounds can be: di-n-butyltin dilaurate, di-n-butyltin dioctanoate, di-n-butyltin di-2-ethylhexanoate, di-n-octyltin di-2-ethylhexanoate and di-n-butylbis-(1-oxoneodecyloxy)stannane.

The elastomeric layer or the laser-engravable layer may further comprise additive and auxiliary materials such as for example IR absorbers, dyes, dispersants, antistats, plasticizers or abrasive particles. The amount of such additive and auxiliary materials should generally not exceed 30% by weight, based on the amount of all the components of the elastomeric layer or of the particular laser-engravable layer.

The elastomeric layer or the laser-engravable layer may be constructed from a plurality of individual layers. These individual layers may be of the same material composition, of substantially the same material composition or of differing material composition. The thickness of the laser-engravable layer or of all individual layers together is generally between 0.1 and 10 mm and preferably in the range from 0.5 to 3 mm. The thickness can be suitably chosen depending on use-related and machine-related processing parameters of the laser-engraving operation and of the negative-molding operation.

The elastomeric layer or the laser-engravable layer may optionally further comprise a top layer having a thickness of not more than 300 µm. The composition of such a top layer is chooseable with regard to optimum engravability and mechanical stability, while the composition of the layer underneath is chosen with regard to optimum hardness or elasticity.

In one embodiment of the present invention, the top layer itself is laser-engravable or removable in the course of the laser-engraving operation together with the layer underneath. The top layer comprises at least one binder. It may further comprise an absorber for laser radiation or else monomers or auxiliaries.

In one embodiment of the present invention, the silicone mold comprises a silicone mold structured with the aid of laser engraving.

It is very particularly advantageous for the process according to the present invention to utilize thermoplastic elastomeric binders or silicone elastomers. When thermoplastic elastomeric binders are used, production is preferably effected by extrusion between a support film/sheet and a cover film/sheet or a cover element followed by calendering, as disclosed in EP-A 0 084 851 for flexographic printing elements for example. Even comparatively thick layers can be produced in a single operation in this way. Multilayered elements can be produced by coextrusion.

To structure the mold with the aid of laser engraving, it is preferable to amplify the laser-engravable layer before the laser-engraving operation by heating

(thermochemically), by exposure to UV light (photochemically) or by exposure to high-energy radiation (actinically) or any desired combination thereof.

Thereafter, the laser-engravable layer or the layer composite is applied to a cylindrical (temporary) support, for example of plastic, glass fiber-reinforced plastic, metal or foam, for example by means of adhesive tape, reduced pressure, clamping devices or magnetic force, and engraved as described above. Alternatively, the planar layer or the layer composite can also be engraved as described above. Optionally, the laser-engravable layer is washed using a rotary cylindrical washer or a continuous washer with a cleaning agent for removing engraving residues during the laser-engraving operation.

The mold can be produced in the manner described as a negative mold or as a positive mold.

In a first variant, the mold has a negative structure, so that the coating which is bondable to textile (A) is obtainable directly by application of a liquid plastics material to the surface of the mold and subsequent solidification of the polyurethane.

In a second variant, the mold has a positive structure, so that initially a negative mold is produced from the laser-structured positive mold. The coating bondable to a sheetlike support can then be obtained from this negative mold by application of a liquid plastics material to the surface of the negative mold and subsequent solidification of the plastics material.

Preferably, structure elements having dimensions in the range from 10 to 500 µm are engraved into the mold. The structure elements may be in the form of elevations or depressions. Preferably, the structure elements have a simple geometric shape and are for example circles, ellipses, squares, rhombuses, triangles and stars. The structure elements may form a regular or irregular screen. Examples are a classic dot screen or a stochastic screen, for example a frequency-modulated screen.

In an embodiment of the present invention, the mold is structured using a laser to cut wells into the mold which have an average depth in the range from 50 to 250 µm and a center-to-center spacing in the range from 50 to 250 µm.

For example, the mold can be engraved such that it has wells having a diameter in the range from 10 to 500 µm at the surface of the mold. The diameter at the surface of the mold is preferably in the range from 20 to 250 µm and more preferably 30 - 150 µm. The spacing of the wells can be for example in the range from 10 to 500 µm, preferably in the range from 20 to 200 µm and more preferably up to 80 µm.

In one embodiment of the present invention, the mold preferably has a surface fine structure as well as a surface coarse structure. Both coarse structure and fine structure can be produced by laser engraving. The fine structure can be for example a microroughness having a roughness amplitude in the range from 1 to 30 µm and a roughness frequency in the range from 0.5 to 30 µm. The dimensions of the microroughness are preferably in the range from 1 to 20 µm, more preferably in the range from 2 to 15 µm and more preferably in the range from 3 to 10 µm.

IR lasers in particular are suitable for laser engraving. However, it is also possible to use lasers having shorter wavelengths, provided the laser is of sufficient intensity. For example, a frequency-doubled (532 nm) or frequency-tripled (355 nm) Nd-YAG laser can be used, or else an excimer laser (248 nm for example). The laser-engraving operation may utilize for example a CO_2 laser having a wavelength of 10 640 nm. It is particularly preferable to use lasers having a wavelength in the range from 600 to 2000 nm. Nd-YAG lasers (1064 nm), IR diode lasers or solid-state lasers can be used for example. Nd/YAG lasers are particularly preferred. The image information to be engraved is transferred directly from the lay-out computer system to the laser apparatus. The lasers can be operated either continuously or in a pulsed mode.

The mold obtained can generally be used directly as produced. If desired, the mold obtained can additionally be cleaned. Such a cleaning step removes loosened but possibly still not completely detached layer constituents from the surface. In general, simply treating with water, water/surfactant, alcohols or inert organic cleaning agents which are preferably low-swelling will be sufficient.

In a further step, an aqueous formulation of polyurethane is applied to the mold. The applying may preferably be effected by spraying. The mold should have been heated when the formulation of polyurethane is applied, for example to temperatures of at least 80°C, preferably at least 90°C. The water from the aqueous formulation of polyurethane evaporates and forms the capillaries in the solidifying polyurethane layer.

Aqueous in connection with the polyurethane dispersion is to be understood as meaning that the polyurethane dispersion comprises water, but less than 5% by weight, based on the dispersion, preferably less than 1% by weight of organic solvent. It is particularly preferable for there to be no detectable volatile organic solvent. Volatile organic solvents herein are such organic solvents as have a boiling point of up to 200°C at standard pressure.

The aqueous polyurethane dispersion can have a solids content in the range from 5% to 60% by weight, preferably in the range from 10% to 50% by weight and more preferably in the range from 25% to 45% by weight.

Polyurethanes (PUs) are common general knowledge, commercially available and consist in general of a soft phase of comparatively high molecular weight polyhydroxy compounds, for example of polycarbonate, polyester or polyether segments, and a urethane hard phase formed from low molecular weight chain extenders and di- or polyisocyanates.

Processes for preparing polyurethanes (PUs) are common general knowledge. In general, polyurethanes (PUs) are prepared by reaction of

(a) isocyanates, preferably diisocyanates, with

(b) isocyanate-reactive compounds, typically having a molecular weight (M_w) in the range from 500 to 10 000 g/mol, preferably in the range from 500 to 5000 g/mol and more preferably in the range from 800 to 3000 g/mol, and

(c) chain extenders having a molecular weight in the range from 50 to 499 g/mol

if appropriate in the presence of

(d) catalysts

(e) and/or customary additive materials.

In what follows, the starting components and processes for preparing the preferred polyurethanes (PUs) will be described by way of example. The components (a), (b), (c) and also if appropriate (d) and/or (e) customarily used in the preparation of polyurethanes (PUs) will now be described by way of example:

As isocyanates (a) there may be used commonly known aliphatic, cycloaliphatic, araliphatic and/or aromatic isocyanates, examples being tri-, tetra-, penta-, hexa-, hepta- and/or octamethylene diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 2-ethylbutylene 1,4-diisocyanate, pentamethylene 1,5-diisocyanate, butylene 1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), 1,4- and/or 1,3-bis(isocyanatomethyl)cyclohexane (HXDI), 1,4–cyclohexane diisocyanate, 1-methyl-2,4- and/or -2,6-cyclohexane diisocyanate and/or 4,4'-, 2,4'- and 2,2'-dicyclohexylmethane diisocyanate, 2,2'-, 2,4'- and/or 4,4'-diphenylmethane diisocyanate (MDI), 1,5-naphthylene diisocyanate (NDI), 2,4- and/or 2,6-tolylene diisocyanate (TDI), diphenylmethane diisocyanate, 3,3'-dimethylbiphenyl diisocyanate, 1,2-diphenylethane diisocyanate and/or phenylene diisocyanate. Preference is given to using 4,4'-MDI. Preference is also given to aliphatic diisocyanates, in particular hexamethylene diisocyanate (HDI), and particular preference is given to aromatic diisocyanates such as 2,2'-, 2,4'- and/or 4,4'-diphenyl-methane diisocyanate (MDI) and mixtures of the aforementioned isomers.

As isocyanate-reactive compounds (b) there may be used the commonly known isocyanate-reactive compounds, examples being polyesterols, polyetherols and/or polycarbonate diols, which are customarily also subsumed under the term "polyols", having molecular weights (M_w) in the range of 500 and 8000 g/mol, preferably in the

range from 600 to 6000 g/mol, in particular in the range from 800 to 3000 g/mol, and preferably an average functionality of 1.8 to 2.3, preferably 1.9 to 2.2, in particular 2, with regard to isocyanates. Preference is given to using polyether polyols, for example those based on commonly known starter substances and customary alkylene oxides, for example ethylene oxide, 1,2-propylene oxide and/or 1,2-butylene oxide, preferably polyetherols based on polyoxytetramethylene (poly-THF), 1,2-propylene oxide and ethylene oxide. Polyetherols have the advantage of having a higher hydrolysis stability than polyesterols, and are preferably used as component (b), in particular for preparing soft polyurethanes polyurethane (PU1).

As polycarbonate diols there may be mentioned in particular aliphatic polycarbonate diols, for example 1,4-butanediol polycarbonate and 1,6-hexanediol polycarbonate.

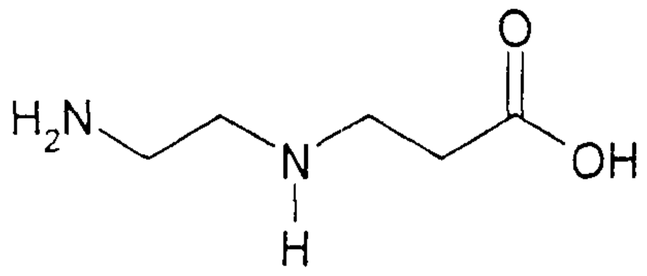
As polyester diols there are to be mentioned those obtainable by polycondensation of at least one primary diol, preferably at least one primary aliphatic diol, for example ethylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol or more preferably 1,4-dihydroxymethylcyclohexane (as isomer mixture) or mixtures of at least two of the aforementioned diols, and at least one, preferably at least two dicarboxylic acids or their anhydrides. Preferred dicarboxylic acids are aliphatic dicarboxylic acids such as adipic acid, glutaric acid, succinic acid and aromatic dicarboxylic acids such as for example phthalic acid and particularly isophthalic acid.

Polyetherols are preferably prepared by addition of alkylene oxides, in particular ethylene oxide, propylene oxide and mixtures thereof, onto diols such as for example ethylene glycol, 1,2-propylene glycol, 1,2-butylene glycol, 1,4-butanediol, 1,3-propanediol, or onto triols such as for example glycerol, in the presence of high-activity catalysts. Such high-activity catalysts are for example cesium hydroxide and dimetal cyanide catalysts, also known as DMC catalysts. Zinc hexacyanocobaltate is a frequently employed DMC catalyst. The DMC catalyst can be left in the polyetherol after the reaction, but preferably it is removed, for example by sedimentation or filtration.

Mixtures of various polyols can be used instead of just one polyol.

To improve dispersibility, isocyanate-reactive compounds (b) may also include a proportion of one or more diols or diamines having a carboxylic acid group or sulfonic acid group (b'), in particular alkali metal or ammonium salts of 1,1-dimethylolbutanoic acid, 1,1-dimethylolpropionic acid or

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Useful chain extenders (c) include commonly known aliphatic, araliphatic, aromatic and/or cycloaliphatic compounds having a molecular weight in the range from 50 to 499 g/mol and at least two functional groups, preferably compounds having exactly two functional groups per molecule, examples being diamines and/or alkanediols having 2 to 10 carbon atoms in the alkylene radical, in particular 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and/or di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and/or decaalkylene glycols having 3 to 8 carbon atoms per molecule, preferably corresponding oligo- and/or polypropylene glycols, and mixtures of chain extenders (c) can also be used.

It is particularly preferable for components (a) to (c) to comprise difunctional compounds, i.e., diisocyanates (a), difunctional polyols, preferably polyetherols (b) and difunctional chain extenders, preferably diols.

Useful catalysts (d) to speed in particular the reaction between the NCO groups of the diisocyanates (a) and the hydroxyl groups of the building block components (b) and (c) are customary tertiary amines, for example triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'–dimethylpiperazine, 2-(dimethylaminoethoxy)ethanol, diazabicyclo(2,2,2)octane (DABCO) and similar tertiary amines, and also in particular organic metal compounds such as titanic esters, iron compounds such as for example iron(III) acetylacetonate, tin compounds, for example tin diacetate, tin dioctoate, tin dilaurate or the tin dialkyl salts of aliphatic carboxylic acids such as dibutyltin diacetate, dibutyltin dilaurate or the like. The catalysts are typically used in amounts of 0.0001 to 0.1 part by weight per 100 parts by weight of component (b).

As well as catalyst (d), auxiliaries and/or additives (e) can also be added to the components (a) to (c). There may be mentioned for example blowing agents, antiblocking agents, surface-active substances, fillers, for example fillers based on nanoparticles, in particular fillers based on $CaCO_3$, nucleators, glidants, dyes and pigments, antioxidants, for example against hydrolysis, light, heat or discoloration, inorganic and/or organic fillers, reinforcing agents and plasticizers, metal deactivators. In a preferred embodiment, component (e) also includes hydrolysis stabilizers such as for example polymeric and low molecular weight carbodiimides. The soft polyurethane preferably comprises triazole and/or triazole derivative and antioxidants in an amount of 0.1% to 5% by weight based on the total weight of the soft polyurethane in question. Useful antioxidants are generally substances that inhibit or prevent unwanted oxidative processes in the plastics material to be protected. In general, antioxidants are

commercially available. Examples of antioxidants are sterically hindered phenols, aromatic amines, thiosynergists, organophosphorus compounds of trivalent phosphorus and hindered amine light stabilizers. Examples of sterically hindered phenols are to be found in Plastics Additive Handbook, 5th edition, H. Zweifel, ed., Hanser Publishers, Munich, 2001 ([1]), pages 98-107 and page 116 - page 121. Examples of aromatic amines are to be found in [1] pages 107-108. Examples of thiosynergists are given in [1], pages 104-105 and pages 112-113. Examples of phosphites are to be found in [1], pages 109-112. Examples of hindered amine light stabilizers are given in [1], pages 123-136. Phenolic antioxidants are preferred for use in the antioxidant mixture. In a preferred embodiment, the antioxidants, in particular the phenolic antioxidants, have a molar mass of greater than 350 g/mol, more preferably greater than 700 g/mol and a maximum molar mass (M_w) of not more than 10 000 g/mol, preferably up to not more than 3000 g/mol. They further preferably have a melting point of not more than 180°C. It is further preferable to use antioxidants that are amorphous or liquid. Mixtures of two or more antioxidants can likewise be used as component (e).

As well as the specified components (a), (b) and (c) and if appropriate (d) and (e), chain regulators (chain-terminating agents), customarily having a molecular weight of 31 to 3000 g/mol, can also be used. Such chain regulators are compounds which have only one isocyanate-reactive functional group, examples being monofunctional alcohols, monofunctional amines and/or monofunctional polyols. Such chain regulators make it possible to adjust flow behavior, in particular in the case of soft polyurethanes, to specific values. Chain regulators can generally be used in an amount of 0 to 5 parts and preferably 0.1 to 1 part by weight, based on 100 parts by weight of component (b), and by definition come within component (c).

As well as the specified components (a), (b) and (c) and if appropriate (d) and (e), it is also possible to use crosslinkers having two or more isocyanate-reactive groups toward the end of the polyurethane-forming reaction, for example hydrazine hydrate.

To adjust the hardness of polyurethane (PU), the components (b) and (c) can be chosen within relatively wide molar ratios. Useful are molar ratios of component (b) to total chain extenders (c) in the range from 10:1 to 1:10, and in particular in the range from 1:1 to 1:4, the hardness of the soft polyurethanes increasing with increasing (c) content. The reaction to produce polyurethane (PU) can be carried out at an index in the range from 0.8 to 1.4:1, preferably at an index in the range from 0.9 to 1.2:1 and more preferably at an index in the range from 1.05 to 1.2:1. The index is defined by the ratio of all the isocyanate groups of component (a) used in the reaction to the isocyanate-reactive groups, i.e., the active hydrogens, of components (b) and if appropriate (c) and if appropriate monofunctional isocyanate-reactive components as chain-terminating agents such as monoalcohols for example.

Polyurethane (PU) can be prepared by conventional processes in a continuous manner, for example by the one-shot or the prepolymer process, or batchwise by the conventional prepolymer operation. In these processes, the reactant components (a), (b), (c) and if appropriate (d) and/or (e) can be mixed in succession or simultaneously, and the reaction ensues immediately.

Polyurethane (PU) can be dispersed in water in a conventional manner, for example by dissolving polyurethane (PU) in acetone or preparing it as a solution in acetone, admixing the solution with water and then removing the acetone, for example distillatively. In one variant, polyurethane (PU) is prepared as a solution in N-methylpyrrolidone or N-ethylpyrrolidone, admixed with water and the N-methylpyrrolidone or N-ethylpyrrolidone is removed.

In one embodiment of the present invention, aqueous dispersions of the present invention comprise two different polyurethanes polyurethane (PU1) and polyurethane (PU2), of which polyurethane (PU1) is a so-called soft polyurethane which is constructed as described above for polyurethane (PU), and at least one hard polyurethane (PU2).

Hard polyurethane (PU2) can in principle be prepared similarly to soft polyurethane (PU1), but other isocyanate-reactive compounds (b) or other mixtures of isocyanate-reactive compounds (b), herein also referred to as isocyanate-reactive compounds (b2) or in short compound (b2), are used.

Examples of compounds (b2) are in particular 1,4-butanediol, 1,6-hexanediol and neopentyl glycol, either mixed with each other or mixed with polyethylene glycol.

In one version of the present invention, diisocyanate (a) and polyurethane (PU2) are each mixtures of diisocyanates, for example mixtures of HDI and IPDI, larger proportions of IPDI being chosen for the preparation of hard polyurethane (PU2) than for the preparation of soft polyurethane (PU1).

In one embodiment of the present invention, polyurethane (PU2) has a Shore A hardness in the range from above 60 to not more than 100, the Shore A hardness being determined in accordance with German standard specification DIN 53505 after 3 s.

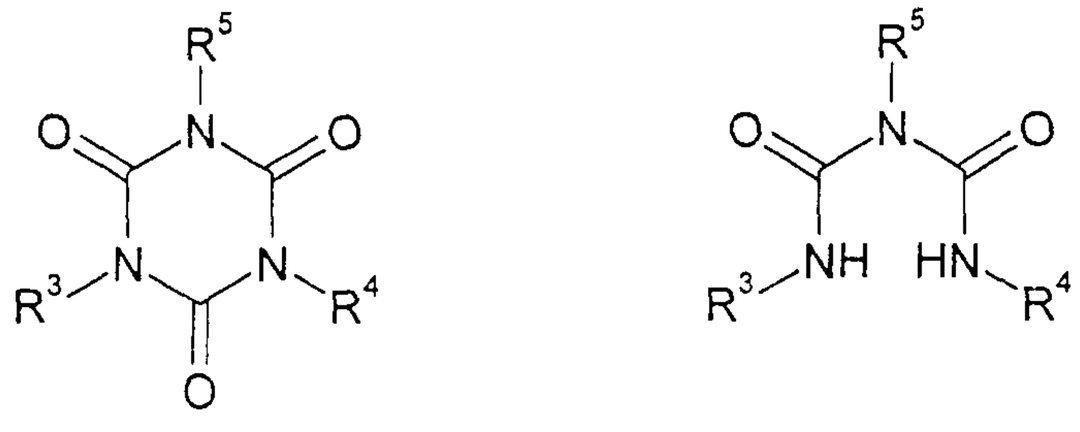
In one embodiment of the present invention, polyurethane (PU) has an average particle diameter in the range from 100 to 300 nm and preferably in the range from 120 to 150 nm, determined by laser light scattering.

In one embodiment of the present invention, soft polyurethane (PU1) has an average

particle diameter in the range from 100 to 300 nm and preferably in the range from 120 to 150 nm, determined by laser light scattering.

In one embodiment of the present invention, polyurethane (PU2) has an average particle diameter in the range from 100 to 300 nm and preferably in the range from 120 to 150 nm, determined by laser light scattering.

The aqueous polyurethane dispersion may further comprise at least one curative, which may also be referred to as a crosslinker. Compounds are useful as a curative which are capable of crosslinking a plurality of polyurethane molecules together, for example on thermal activation. Of particular suitability are crosslinkers based on trimeric diisocyanates, in particular based on aliphatic diisocyanates such as hexamethylene diisocyanate. Very particular preference is given to crosslinkers of formula I a or I b, herein also referred to in brief as compound (V)



I a I b

where R^3, R^4 and R^5 may be different or preferably the same and are each selected from A^1-NCO and A^1-NH-CO-X, where

A^1 is a spacer having 2 to 20 carbon atoms, selected from arylene, unsubstituted or substituted with one to four C_1-C_4-alkyl groups, alkylene and cycloalkylene, for example 1,4-cyclohexylene. Preferred spacers A^1 are phenylene, in particular para-phenylene, also tolylene, in particular para-tolylene, and C_2-C_{12}-alkylene such as for example ethylene (CH_2CH_2), also $-(CH_2)_3$-, $-(CH_2)_4$-, $-(CH_2)_5$-, $-(CH_2)_6$-, $-(CH_2)_8$-, $-(CH_2)_{10}$-, $-(CH_2)_{12}$-.

X is selected from $O(AO)_xR^6$, where

AO is C_2-C_4-alkylene oxide, for example butylene oxide, in particular ethylene oxide (CH_2CH_2O) and propylene oxide ($CH(CH_3)CH_2O$) or ($CH_2CH(CH_3)O$),

x is an integer from 1 to 50, preferably 5 to 25, and

R^6 is selected from hydrogen and C_1-C_{30}-alkyl, in particular C_1-C_{10}-alkyl such as methyl,

ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, more preferably C_1-C_4-alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl.

Particularly preferred compounds (V) are those wherein R^3, R^4 and R^5 are each the same $(CH_2)_4$-NCO, $(CH_2)_6$-NCO or $(CH_2)_{12}$-NCO.

Aqueous polyurethane dispersions may comprise further constituents, for example

(f) a silicone compound having reactive groups,
herein also referred to as silicone compound (f).

Examples of reactive groups in connection with silicone compounds (f) are for example carboxylic acid groups, carboxylic acid derivatives such as for example methyl carboxylate or carboxylic anhydrides, in particular succinic anhydride groups, and more preferably carboxylic acid groups.

Examples of reactive groups further include primary and secondary amino groups, for example NH(iso-C_3H_7) groups, NH(n-C_3H_7) groups, NH(cyclo-C_6H_{11}) groups and NH(n-C_4H_9) groups, in particular NH(C_2H_5) groups and NH(CH_3) groups, and most preferably NH_2 groups.

Preference is further given to aminoalkylamino groups such as for example -NH-CH_2-CH_2-NH_2 groups, -NH-CH_2-CH_2-CH_2-NH_2 groups, -NH-CH_2-CH_2-NH(C_2H_5) groups, -NH-CH_2-CH_2-CH_2-NH(C_2H_5) groups, -NH-CH_2-CH_2-NH(CH_3) groups, -NH-CH_2-CH_2-CH_2-NH(CH_3) groups.

The reactive group or groups are attached to silicone compound (f) either directly or preferably via a spacer A^2. A^2 is selected from arylene, unsubstituted or substituted with one to four C_1-C_4-alkyl groups, alkylene and cycloalkylene such as for example 1,4-cyclohexylene. Preferred spacers A^2 are phenylene, in particular para-phenylene, also tolylene, in particular para-tolylene, and C_2-C_{18}-alkylene such as for example ethylene (CH_2CH_2), also –$(CH_2)_3$-, –$(CH_2)_4$-, –$(CH_2)_5$-, –$(CH_2)_6$-, –$(CH_2)_8$-, –$(CH_2)_{10}$-, –$(CH_2)_{12}$-, –$(CH_2)_{14}$-, –$(CH_2)_{16}$- and –$(CH_2)_{18}$-.

In addition to the reactive groups, silicone compound (f) comprises non-reactive groups, in particular di-C_1-C_{10}-alkyl-SiO_2 groups or phenyl-C_1-C_{10}-alkyl-SiO_2 groups, in particular dimethyl-SiO_2 groups, and if appropriate one or more $Si(CH_3)_2$-OH groups or $Si(CH_3)_3$ groups.

In one embodiment of the present invention, silicone compound (f) has on average one to four reactive groups per molecule.

In an advantageous embodiment of the present invention, silicone compound (f) has on average one to four COOH groups per molecule.

In another advantageous embodiment of the present invention, silicone compound (f) has on average one to four amino groups or aminoalkylamino groups per molecule.

Silicone compound (f) comprises Si-O-Si units in a chain-shaped or branched arrangement.

In one embodiment of the present invention, silicone compound (f) has a molecular weight M_n in the range from 500 to 10 000 g/mol, preferably up to 5000 g/mol.

When silicone compound (f) has two or more reactive groups per molecule, these reactive groups can be attached - directly or via spacer A^2 - to the Si-O-Si chain via two or more silicon atoms or pairwise via the same silicon atom.

The reactive group or groups may be attached to one or more of the terminal silicon atoms of silicone compound (f) - directly or via spacer A^2. In another embodiment of the present invention, the reactive group or groups are attached to one or more of the non-terminal silicon atoms of silicone compound (f) - directly or via spacer A^2.

In one embodiment of the present invention, aqueous polyurethane dispersion further comprises
a polydi-C_1-C_4-alkylsiloxane (g) having neither amino groups nor COOH groups, preferably a polydimethylsiloxane, herein also referred to in brief as polydialkylsiloxane (g) or polydimethylsiloxane (g).

The C_1-C_4-alkyl in polydialkylsiloxane (g) may be different or preferably the same and selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl, of which unbranched C_1-C_4-alkyl is preferred and methyl is particularly preferred.

Polydialkylsiloxane (g) and preferably polydimethylsiloxane (g) preferably comprises unbranched polysiloxanes having Si-O-Si chains or such polysiloxanes as have up to 3 and preferably not more than one branching per molecule.

Polydialkylsiloxane (D) and in particular polydimethylsiloxane (g) may have one or more $Si(C_1$-C_4-alkyl$)_2$-OH groups.

In one embodiment of the present invention, aqueous polyurethane dispersion comprises
altogether from 20% to 30% by weight of polyurethane (PU), or altogether from 20% to 30% by weight of polyurethanes (PU1) and (PU2),

if appropriate from 1% to 10%, preferably 2% to 5% by weight of curative,
if appropriate from 1% to 10% by weight of silicone compound (f),
from zero to 10%, preferably 0.5% to 5% by weight of polydialkylsiloxane (g).

In one embodiment of the present invention, aqueous polyurethane dispersion comprises
from 10% to 30% by weight of soft polyurethane (PU1) and
from zero to 20% by weight of hard polyurethane (PU2).

In one embodiment of the present invention, aqueous polyurethane dispersion has a solids content of altogether 5% to 60% by weight, preferably 10% to 50% by weight and more preferably 25% to 45% by weight.

These weight %ages each apply to the active or solid ingredient and are based on the total aqueous polyurethane dispersion. The remainder ad 100% by weight is preferably continuous phase, for example water or a mixture of one or more organic solvents and water.

In an embodiment of the present invention, aqueous polyurethane dispersion comprises at least one additive (h) selected from pigments, antilusterants, light stabilizers, antistats, antisoil, anticreak, thickening agents, in particular thickening agents based on polyurethanes, and microballoons.

In one embodiment of the present invention, aqueous polyurethane dispersion comprises altogether up to 20% by weight of additives (h).

Aqueous polyurethane dispersion may also comprise one or more organic solvents. Suitable organic solvents are for example alcohols such as ethanol or isopropanol and in particular glycols, diglycols, triglycols or tetraglycols and doubly or preferably singly C_1-C_4-alkyl-etherified glycols, diglycols, triglycols or tetraglycols. Examples of suitable organic solvents are ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, 1,2-dimethoxyethane, methyltriethylene glycol ("methyltriglycol") and triethylene glycol n-butyl ether ("butyltriglycol").

Aqueous polyurethane dispersions can be produced by mixing polyurethane (PU), curative and silicone compound (f) with water and if appropriate one or more of the aforementioned organic solvents. If desired, polydialkylsiloxane (g) and additives (h) are also mixed in. The mixing can take the form of stirring for example. The order of addition of polyurethane (PU), curative, silicone compound (f) and water and if appropriate one or more of the aforementioned organic solvents and also - if desired - polydialkylsiloxane (g) and additives (h) is freely choosable.

It is preferable to proceed from a polyurethane (PU) dispersed in water or a mixture of water and organic solvent or from dispersed soft polyurethane (PU1) and hard polyurethane (PU2) and adding, preferably with stirring, curative and silicone compound (f) and also, if desired, polydialkylsiloxane (g) and if appropriate one or more organic solvents. Preferably, however, no organic solvent is added.

In an advantageous embodiment, thickening agent as an example of additive (h) is added last to thus adjust the viscosity of the aqueous polyurethane dispersion to the desired value.

After polyurethane layer (C) has cured, it is separated from the mold, for example by peeling off, to obtain a polyurethane film (C) which forms the polyurethane layer (C) in multilayered composite material of the present invention.

In a further operation of the inventive production process, preferably organic adhesive is applied to polyurethane film (C) or textile (A), non-uniformly, for example in the form of points, dots or stripes. In one version of the present invention, one preferably organic adhesive is applied to polyurethane film (C) and one preferably organic adhesive is applied to textile (A), the two adhesives differing, for example by virtue of one or more additives or because they comprise chemically different preferably organic adhesives. Thereafter, polyurethane film (C) and textile (A) are bonded together, such that the layer(s) of adhesive come to reside between polyurethane film (C) and textile (A). The adhesive or adhesives are cured, for example thermally, by means of actinic radiation or by aging, to obtain multilayered composite material of the present invention.

Preferably, there are no interlayers between textile (A) and polyurethane layer (C). As a result, textile sheet material (A) and polyurethane layer (C) are bonded together directly or via bonding layer (B).

The present invention further provides for the use of multilayered composite materials of the present invention as or in the manufacture of decoration materials. The present invention further provides decoration materials consisting of or obtained using multilayered composite materials of the present invention. Examples are garlands and laminations.

The present invention further provides for the use of multilayered composite materials of the present invention as or in the manufacture of home textiles. The present invention further provides home textiles consisting of or obtained using multilayered composite materials of the present invention. Examples of home textiles are drapes, curtains and wall hangings. Curtains for theaters, for example, are herein also subsumed under the term “home textiles”.

The present invention further provides for the use of multilayered composite materials of the present invention in the manufacture of seats, for example for vehicles, for example for boats, ships, airplanes, railroad cars and particularly automobiles, but also for sitting furniture or lying furniture. The present invention further provides seats, sitting furniture and lying furniture obtained using multilayered composite materials of the present invention.

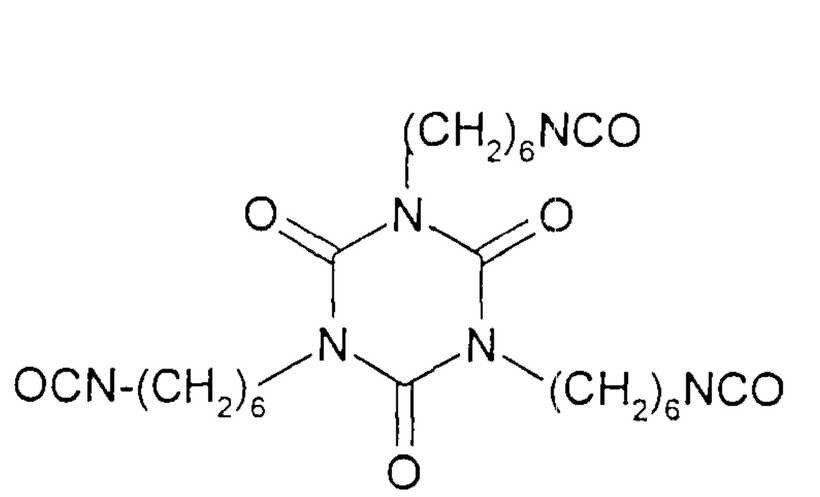
The present invention further provides parts in the automotive interior sector, for example door trim, center consoles and package trays, obtained using multilayered composite materials of the present invention.

Working examples further elucidate the present invention.

I. Production of starting materials

I.1 Production of an aqueous polyurethane dispersion Disp.1

The following were mixed in a stirred vessel:
7% by weight of an aqueous dispersion (particle diameter: 125 nm, solids content: 40%) of a soft polyurethane (PU1.1) prepared from hexamethylene diisocyanate (a1.1) and isophorone diisocyanate (a1.2) in a weight ratio of 13:10 as diisocyanates and as diols, a polyester diol (b1.1) having a molecular weight M_w of 800 g/mol, prepared by polycondensation of isophthalic acid, adipic acid and 1,4-dihydroxymethylcyclohexane (isomer mixture) in a molar ratio of 1:1:2, 5% by weight of 1,4-butanediol (b1.2) and also 3% by weight of monomethylated polyethylene glycol (c.1) and also 3% by weight of H2N-CH2CH2-NH-CH2CH2-COOH, % by weight all based on polyester diol (b1.1), softening point of soft polyurethane (PU1.1): 62°C, softening starts at 55°C, Shore A hardness 54,
65% by weight of an aqueous dispersion (particle diameter: 150 nm) of a hard polyurethane (PU2.2), obtainable by reaction of isophorone diisocyanate (a1.2), 1,4-butanediol, 1,1-dimethylolpropionic acid, hydrazine hydrate and polypropylene glycol having a molecular weight M_w of 4200 g/mol, softening point of 195°C, Shore A hardness 86,
3.5% by weight of a 70% by weight solution (in propylene carbonate) of compound (V.1),



(V.1)

6% by weight of a 65% by weight aqueous dispersion of the silicone compound

according to Example 2 of EP-A 0 738 747 (f.1)
2% by weight of carbon black,
0.5% by weight of a thickening agent based on polyurethane,
1% by weight of microballoons of polyvinylidene chloride, filled with isobutane, diameter 20 µm, commercially obtainable for example as Expancel® from Akzo Nobel.

This gave an aqueous dispersion Disp.1 having a solids content of 35% and a kinematic viscosity of 25 seconds at 23°C, determined in accordance with DIN EN ISO 2431, as of May 1996.

I.2 Production of an aqueous formulation Disp.2

The following were mixed in a stirred vessel:
7% by weight of an aqueous dispersion (particle diameter: 125 nm, solids content: 40%) of a soft polyurethane (PU1.1) prepared from hexamethylene diisocyanate (a1.1) and isophorone diisocyanate (a1.2) in a weight ratio of 13:10 as diisocyanates and as diols, a polyester diol (b1.1) having a molecular weight M_w of 800 g/mol, prepared by polycondensation of isophthalic acid, adipic acid and 1,4-dihydroxymethylcyclohexane (isomer mixture) in a molar ratio of 1:1:2, 5% by weight of 1,4-butanediol (b1.2), 3% by weight of monomethylated polyethylene glycol (c.1) and also 3% by weight of H2N-CH2CH2-NH-CH2CH2-COOH, % by weight all based on polyester diol (b1.1), softening point of 62°C, softening starts at 55°C, Shore A hardness 54,
65% by weight of an aqueous dispersion (particle diameter: 150 nm) of a hard polyurethane (α2.2), obtainable by reaction of isophorone diisocyanate (a1.2), 1,4-butanediol (PU1.2), 1,1-dimethylolpropionic acid, hydrazine hydrate and polypropylene glycol having a molecular weight M_w of 4200 g/mol (b1.3), polyurethane (PU2.2) had a softening point of 195°C, Shore A hardness 90,
3.5% by weight of a 70% by weight solution (in propylene carbonate) of compound (V.1),
NCO content 12%,
2% by weight of carbon black.

This gave a polyurethane dispersion Disp.2 having a solids content of 35% and a kinematic viscosity of 25 seconds at 23°C, determined in accordance with DIN EN ISO 2431, as of May 1996.

II. Production of a mold

A liquid silicone was poured onto a surface having the pattern of full grain calf leather. The silicone was cured by adding a solution of di-n-butylbis(1-oxoneodecyloxy)-stannane as 25% by weight solution in tetraethoxysilane as an acidic curative to obtain a silicone rubber layer 2 mm in thickness on average, which served as the mold. The

mold was adhered onto a 1.5 mm thick aluminum support.

III. Application of aqueous polyurethane dispersions onto mold from II.

The mold from II. was placed on a heatable surface and heated to 91°C. Disp.1 was then sprayed onto it through a spray nozzle, at 88 g/m^2 (wet). No air was admixed during application, which was done with a spray nozzle having a diameter of 0.46 mm, at a pressure of 65 bar. This was followed by solidification at 91°C until the surface was no longer tacky.

The spray nozzle was located 20 cm above the surface passing underneath it, and could be moved in the transport direction of the surface, and moved transversely to the transport direction of the surface. The surface took about 14 seconds to pass the spray nozzle and had a temperature of 59°C. After being exposed for about two minutes to a stream of dry hot air at 85°C, the polyurethane film (C.1) thus produced, which had a netlike appearance, was almost water-free.

In an analogous arrangement, Disp.2 was immediately thereafter applied to the mold thus coated, as bonding layer (B.1) at 50 g/m^2 wet, and subsequently allowed to dry.

This gave a mold coated with polyurethane film (C.1) and bonding layer (B.1).

A woven polyester fabric (A.1) having an areal weight of 180 g/m^2 was sprayed with Disp.2 at 30 g/m^2 (wet). The woven polyester fabric thus sprayed was subsequently allowed to dry for several minutes.

IV. Production of an inventive multilayered composite material

Woven polyester fabric (A.1) is then placed with the sprayed side onto the still warm bonding layer (B.1), which is present on the mold together with the polyurethane film (C.1), and the entire assembly is compressed in a press at 4 bar and 110°C for 15 seconds. The inventive multilayered composite material MSV.1 thus obtained is subsequently removed from the press and the mold is removed from it.

The inventive multilayered composite material MSV.1 thus obtained is notable for pleasant haptics, an appearance which is identical to the appearance of a leather surface, and also breathability. In addition, the inventive multilayered composite material MSV.1 is easy to clean of soiling such as dust for example.

CLAIMS

1. A multilayered composite material comprising as components:

(A) a textile sheet material,

(B) optionally at least one bonding layer, and

(C) a polyurethane layer with capillaries passing through the entire thickness of the polyurethane layer, and patterning which corresponds to a velvet surface with small hairs having an average length in the range from 20 to 500 µm,

wherein textile sheet material (A) and polyurethane layer (C) are bonded to each other directly or via bonding layer (B), wherein the small hairs of polyurethane layer (C) have an average spacing of 50 to 350 µm from one hair to the next, wherein said bonding layer (B) comprises a layer of a cured organic adhesive and wherein said textile sheet material (A) comprises wovens, drawn-loop knits and non-wovens and comprises at least one polymer deposited by coagulation.

2. The multilayered composite material according to claim 1, wherein said average spacing of the small hairs is 100 to 250 µm.

3. The multilayered composite material according to claim 1, wherein said bonding layer (B) comprises an interrupted layer of a cured organic adhesive.

4. The multilayered composite material according to claim 1, wherein said bonding layer (B) comprises a continuous layer of a cured organic adhesive.

5. The multilayered composite material according to any one of claims 1 to 4 without an interlayer (D) between said textile sheet material (A) and said polyurethane layer (C).

6. A process for producing a multilayered composite material according to any one of claims 1 to 5, which comprises forming a polyurethane layer (C) with the aid of a mold, applying at least one organic adhesive uniformly or partially onto textile sheet material (A) and/or onto polyurethane layer (C) and then bonding polyurethane layer (C) pointwise, stripwise or areawise to said textile sheet material (A), wherein polyurethane layer (C) is formed with the aid of a silicone mold, wherein said silicone mold comprises a silicone mold structured with the aid of laser engraving, wherein said mold is structured by using a laser to cut wells into the mold which have an average

depth in the range from 50 to 250 µm and a center-to-center spacing in the range from 50 to 250 µm.

7. The use of a multilayered composite material according to any one of claims 1 to 5 as or in the manufacture of a decoration material.

8. A decoration material consisting of or obtained using a multilayered composite material according to any one of claims 1 to 5.

9. The use of a multilayered composite material according to any one of claims 1 to 5 as or in the manufacture of a home textile.

10. A home textile consisting of or obtained using a multilayered composite material according to any one of claims 1 to 5.

11. A seat or an article of sitting or lying furniture, obtained using a multilayered composite material according to any one of claims 1 to 5.

12. An automotive interior part selected from door linings, center consoles and package trays, obtained using a multilayered composite material according to any one of claims 1 to 5.