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(54) Title: PROCESS COMPRISING THE APPLICATION OF AN ANTIPERSPIRANT MATERIAL CONTAINING AT LEAST TWO ZONES OF DIFFERENT POLYMERS

(57) Abstract: The present invention relates to a process for cosmetic treatment of human perspiration, and optionally underarm odours, in which an antiperspirant polymeric cosmetic material comprising at least two zones A and B is applied to the skin, zone A being formed from at least one hydrophilic polymer and zone B being formed from at least one non-pressure-sensitive-adhesive, hydrophobic polymer.



**Process comprising the application of an antiperspirant material
containing at least two zones of different polymers**

5 The present invention relates to a process for cosmetic treatment of human perspiration, and optionally of underarm odours, in which an antiperspirant polymeric cosmetic material as described hereinafter is applied to the skin. Similarly, the invention relates to the use of said material for the cosmetic treatment of human
10 perspiration and also to an antiperspirant polymeric cosmetic material.

 The armpits and also certain other parts of the body are generally the site of much discomfort that may arise directly or indirectly from perspiration. This perspiration often leads to unpleasant and disagreeable sensations that are mainly due to the
15 presence of sweat resulting from perspiration, which may, in certain cases, make the skin and clothing wet, in particular in the region of the armpits or on the back, thus leaving visible marks. Moreover, the presence of sweat most commonly gives rise to the production of body odours, which most of the time are unpleasant. Finally, during its
20 evaporation, sweat may also leave salts and/or proteins at the surface of the skin, thus creating whitish marks on clothing. Such discomfort is noted including in the case of moderate perspiration.

 In the cosmetics field, it is thus well known to use, by topical application, antiperspirant products containing substances that have
25 the effect of limiting or even eliminating the flow of sweat in order to remedy the problems mentioned above. These products are generally available in the form of roll-ons, sticks, aerosols or sprays.

 Antiperspirant substances generally consist of aluminium salts, such as aluminium chloride and aluminium hydroxyhalides, or of
30 complexes of aluminium and zirconium. These substances make it possible to reduce the flow of sweat by forming a plug in the sweat duct.

However, the use of these substances at high concentrations for the purposes of obtaining good antiperspirant effectiveness, most commonly has the drawback of leading to formulation difficulties.

5 Furthermore, it has been found that the antiperspirant effectiveness of these substances can prove to be limited, which implies that they need to be applied to the skin several times in order to obtain a satisfactory effective antiperspirant effect. However, in the case of certain users, repeated application of these substances has the drawback of leading to skin irritation.

10 Moreover, another drawback linked to the use of these aluminium salts lies in the fact that the antiperspirant effect conferred by such substances generally has a tendency to disappear, in particular in the case of successive washing or in the case of heavy perspiration.

15 Finally, these antiperspirant substances can also leave marks during their application to the skin, which results in the staining of clothing.

20 As a variant, it has been proposed to provide, in particular for consumers who have a problem in terms of tolerance to aluminium salts, deodorant wipes intended to be attached to the clothing in order to absorb perspiration.

However, such a method remains relatively impractical since it requires attaching wipes inside clothing and does not allow bare arms. Furthermore, such a method is also not aesthetic since the wipes remain visible owing to their thickness.

25 In order to remedy all the drawbacks mentioned above, it has been proposed to seek new approaches for easily and discreetly depositing on the skin effective antiperspirant products which are permeable to water vapour, impermeable to sweat and suitably tolerated by the skin.

30 Indeed, limiting the flow of sweat can be achieved by partially obstructing the sweat ducts by means of the formation of a plug in the sweat duct, but also by forming, at the surface of the skin, a film that is resistant to sweat. Thus, numerous approaches aimed at covering the

surface of the skin with a film or a patch have been developed in order to limit the flow of sweat.

By way of examples, patent application US 2007/0218092 describes a deodorant patch intended to be used under the arms, which comprises a top carrier sheet positioned on the top face of the patch and a bottom carrier sheet positioned on the bottom face of the patch. The patch comprises one or more deodorant and/or antiperspirant active agents that can in particular be chosen from complexes of aluminium and zirconium, cyclomethicone or stearyl alcohol. In particular, the deodorant patch dissolves on contact with the skin, which allows the deodorant substances and also the other ingredients of the formulation to be released and to act in order to treat perspiration.

Similarly, patent application WO 2004/024113 relates to a deodorant patch intended for administering deodorant substances, comprising at least two layers. The first layer contains at least one deodorant active agent that may be an aluminium salt and at least one film-forming compound and the second layer contains at least one compound capable of producing adhesion between the patch and the surface of the skin to which the patch is applied. The patch decomposes on contact with the skin without leaving residues, and in so doing enables better dosage of the amount of deodorant active agents to be applied.

However, these films do not make it possible to obtain entirely satisfactory antiperspirant effectiveness and still give rise to formulation problems. In particular, the antiperspirant effects conferred by such compositions still remain too limited over time.

In patent application WO 93/24105, the use, as antiperspirant active agents, of polymers forming an occlusive film on the skin has already been proposed. The occlusive nature of the polymers promotes bacterial proliferation, which can result in an unpleasant odour being given off.

In application WO 95/27473, the use, as antiperspirant active agents, of insoluble cationic polymers, the main chain of which is

hydrocarbon-based and which comprise pendant hydrophobic quaternary ammonium groups, has already been proposed.

Patent application WO 01/54658 describes anhydrous compositions containing a cyanoacrylate monomer which reacts with sweat so as to form, in situ by polymerization, a film on the skin which blocks the sweat ducts.

These polymers have the drawbacks of reacting directly on the skin in the presence of water, thereby causing an increase in temperature which is undesired in an underarm zone.

Patent US 6 387 356 B1 (Colgate) describes alcoholic compositions comprising a film of an ester of cellulose acetate butyrate (CAB 553-0.4, CAB 504-0.2) capable of forming a thin film on the skin, characterized by a certain hardness and water transport properties that reduce or eliminate the feeling of wetness associated with perspiration.

Document DE2947060 describes antiperspirant compositions containing an aqueous dispersion of acrylic resin without plasticizer.

These polymeric antiperspirant systems are not yet sufficiently effective or not always cosmetic in terms of effectiveness with respect to human perspiration.

Thus, there is therefore a real need to develop materials which do not have the drawbacks mentioned above, i.e. that confer a satisfactory antiperspirant effect, in particular in terms of effectiveness while at the same time being permeable to water vapour and impermeable to sweat, and which are suitably tolerated by the skin and sufficiently discreet.

The applicant has discovered, surprisingly, that by applying to the skin a polymeric cosmetic material containing at least one zone formed from at least one hydrophilic film-forming polymer and at least one zone formed from at least one non-pressure-sensitive-adhesive, hydrophobic film-forming polymer, it was possible to obtain the desired properties, i.e. such a material made it possible to effectively treat human perspiration while at the same time exhibiting a suitable toxicological profile for the skin and being easy to formulate.

Indeed, the applicant has noted that the use of such a polymeric material comprising at least two zones of hydrophilic and hydrophobic film-forming polymers made it possible to satisfactorily reduce or limit the flow of sweat.

5 In particular, the combined presence of the two zones of hydrophilic and hydrophobic film-forming polymers makes it possible to satisfactorily control the permeability of the polymeric material, by making it in particular permeable to water vapour and impermeable to sweat.

10 In other words, the presence of the two zones of hydrophilic and hydrophobic film-forming polymers contributes to conferring a satisfactory antiperspirant effect.

Indeed, the antiperspirant material exhibits an impermeability to liquid water that is capable of reducing liquid water flows by at
15 least 50%, and a high permeability to water vapour.

Moreover, the antiperspirant material deposited on the skin also exhibits a satisfactory resistance, in particular with respect to the pressure exerted by the droplets of water, by the movements of the body or by the sweat leaving the pores of the skin.

20 A subject of the present invention is therefore in particular a process for cosmetic treatment of human perspiration, and optionally of underarm odours, in which an antiperspirant polymeric cosmetic material comprising at least two zones A and B is applied to the skin, zone A being formed from at least one hydrophilic film-forming
25 polymer and zone B being formed from at least one non-pressure-sensitive-adhesive, hydrophobic film-forming polymer.

In other words, the polymeric cosmetic material comprises two or more zones of hydrophilic and hydrophobic film-forming polymers.

30 The polymeric cosmetic material according to the present invention therefore constitutes a hybrid or heterogeneous patch, i.e. the structure of this material has at least two different polymeric films.

The polymeric material thus forms an antiperspirant cosmetic film on the skin.

Moreover, the present invention also relates to the use of a polymeric material as described above, for the cosmetic treatment of human perspiration.

5 In other words, the polymeric cosmetic material is used as an agent for cosmetic treatment of human perspiration.

For the purpose of the present invention, the term “agent for treatment of perspiration” is intended to mean any substance which, by itself, has the effect of reducing or limiting the flow of sweat.

10 In particular, the use of a polymeric material as described above makes it possible to confer an antiperspirant effect.

Another subject of the present invention consists of an antiperspirant polymeric cosmetic material comprising at least two zones A and B, zone A being formed from at least one hydrophilic film-forming polymer and zone B being formed from at least one non-
15 pressure-sensitive-adhesive, hydrophobic film-forming polymer.

Other subjects, characteristics, aspects and advantages of the invention will emerge even more clearly on reading the description and the examples which follow.

20 For the purpose of the present invention, the term “antiperspirant material” is intended to mean a material capable, on its own, of reducing or limiting the flow of sweat.

For the purpose of the present invention, the term “polymeric material” is intended to mean a material prepared from one or more polymers.

25 The term “film-forming polymer” is intended to mean any polymer capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous and adherent film on a support, in particular on human keratin materials such as the skin, the hair, the eyelashes, the eyebrows or the nails.

30 According to one embodiment, the antiperspirant cosmetic material of the present invention corresponds to a layer comprising at least one zone A formed from at least one hydrophilic film-forming polymer and a zone B formed from at least one non-pressure-sensitive-

adhesive, hydrophobic film-forming polymer, zones A and B being arranged adjacently.

5 In other words, in accordance with this embodiment, the antiperspirant cosmetic material is a layer comprising at least two adjacent zones formed from different polymers, in particular two zones of different polymeric films.

10 In particular, the antiperspirant cosmetic material may be a hybrid or heterogeneous monolayer since it comprises two distinct adjacent zones formed from a hydrophilic film-forming polymer and from a non-pressure-sensitive-adhesive, hydrophobic film-forming polymer.

The cosmetic material may also be a layer comprising at least two zones of different polymeric films.

15 Thus, the antiperspirant cosmetic material is a multizone material, in particular a multizone layer.

20 According to another embodiment, the antiperspirant cosmetic material of the present invention is a material comprising at least two layers A and B superimposed on one another, layer A being formed from at least one hydrophilic film-forming polymer, and layer B being formed from at least one non-pressure-sensitive-adhesive, hydrophobic film-forming polymer.

In other words, zones A and B of the material may be distinct layers of polymers which are superimposed on one another.

25 Thus, the antiperspirant cosmetic material according to the invention may be a multilayer material.

The cosmetic material may be applied in a single step directly to the skin or in two steps so as to form the cosmetic material in situ on the skin.

30 Preferably, the cosmetic material comprises at least two layers A and B superimposed on one another as described above.

Preferably, the cosmetic material is applied in a single step directly to the skin.

As indicated previously, zone B of the antiperspirant polymeric material according to the present invention is formed from

one or more non-pressure-sensitive-adhesive, hydrophobic film-forming polymers.

For the purpose of the present invention, the term “pressure-sensitive adhesive” is intended to mean viscous and elastic substances which have satisfactory adhesion, cohesion, stretching capacity and elasticity properties. The performance levels of a pressure-sensitive adhesive (PSA) are generally evaluated by means of three properties: its immediate tack at ambient temperature, its stretching capacity and its shear stress. The properties such as the shear stress or the cohesion can be measured using the standard tests which are described in detail in the scientific literature (ref: A. Zosel, J. Adhesion, 1994, 44 pp 1-6). Pressure-sensitive adhesives usually consist of chemical fragments which are responsible for the elastomeric behaviour and immediate tack at ambient temperature. Thus, by controlling the amounts of these fragments, the various properties sought can be obtained.

The pressure-sensitive adhesives are preferably defined according to the Dahlquist criterion, i.e. according to their storage modulus G' (as described in the “Handbook of Pressure Sensitive Adhesive Technology, second edition, D. Satas, published by Van Nostrand Reinhold, New York, NY, 1989, pages 171-176” which is incorporated by way of reference).

For the purposes of the present invention, the storage modulus G' represents the rigidity and the elasticity of a material. In other words, this modulus expresses the capacity of a material to store up mechanical energy, when the latter is subjected to a stress, and its capacity to release this mechanical energy in the form of elastic deformation. This storage modulus G' is preferably measured using a dynamic mechanical analyser.

Thus, in the context of the Dahlquist criterion, pressure-sensitive adhesives preferentially have a storage modulus G' value of less than 3×10^5 Pascals, measured at a rate of 10 radians per second at a temperature ranging from 20°C to 22°C.

Pressure-sensitive adhesives are compounds which give the support that is coated there with an immediate tack at ambient

temperature, which allows its instantaneous adhesion to a substrate under the effect of a slight and brief pressure. Even more particularly, pressure-sensitive adhesives are compounds which exhibit an immediate tack at ambient temperature and which adhere to a surface by simple contact without needing more than the pressure of a finger or a hand. Moreover, given their chemical properties, pressure-sensitive adhesives exhibit particular properties such as a low glass transition temperature (T_g), a small energy surface (σ), a high flexibility and a high bonding capacity.

Pressure-sensitive adhesive compounds are compounds which comprise one or more adhesive organic polymers.

In other words, the hydrophobic polymer constituting zone B of the polymeric material according to the present invention is not a pressure-sensitive adhesive organic polymer.

Thus, zone B of the antiperspirant polymeric material is not a pressure-sensitive adhesive zone.

The term "hydrophobic film-forming polymer" is intended to mean any polymer (1°) which is capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous or discontinuous and adherent film on a support, in particular on human keratin materials such as the skin, the hair, the eyelashes, the eyebrows or the nails, and (2°) which the film formed is capable of adsorbing a water content less than or equal to 30% by weight, relative to the weight of the dry film of polymer (before immersion in water) when it is immersed in liquid water.

The content of water absorbed by the hydrophobic polymers according to the present invention can be measured under the following conditions:

In order to measure the content of water adsorbed, also called water uptake, 12 grams of an aqueous or aqueous-alcoholic solution comprising 7% by weight of polymers are poured into an aluminium dish having a diameter of 5.5 centimetres, in order to form a film. The internal surface of the aluminium dish is covered with a Teflon support disc in order to limit unwanted edge effects and to facilitate

removal of the film. Evaporation is allowed to take place for 24 hours with ventilation in order to allow optimum drying. A circular film measuring between 300 and 350 μm in thickness is obtained and is removed from the aluminium dish. The film is then cut into two rectangles of 1 $\times$ 2 cm.

One of the rectangular films obtained is weighed dry, which corresponds to the mass of the film before immersion in water or dry mass of the film. The same film is then immersed in a 30 ml flask filled with water for a period of 60 minutes.

After each immersion in water, the excess surface water is removed by pressing the film very lightly onto cotton rag paper and the film is weighed, which corresponds to the mass of the film after immersion in the water. The percentage of water absorbed or the water uptake of the polymer is calculated after 60 minutes according to the following equation:

$$\% \text{ water absorbed} = \frac{m_{\text{film after immersion}} - m_{\text{dry film}}}{m_{\text{dry film}}}$$

The operation is repeated three times for each of the polymers tested. The average of the three absorption percentages is calculated so as to deduce therefrom the percentage of water absorbed by the polymer.

HYDROPHOBIC FILM-FORMING POLYMERS

According to one particular form of the invention, the hydrophobic film-forming polymer(s) is (are) a synthetic polymer or synthetic polymers.

The term "synthetic polymer" is intended to mean any polymer obtained chemically or by a production in an organism of the elements required for this production.

The synthetic hydrophobic polymers used according to the invention may comprise:

- (i) polymers of interpenetrating polymer network type;
(ii) grafted silicone polymers;
(iii) nonneutralized (meth)acrylic acetate/N-tert-butylacrylamide copolymers,
5 (iv) nonneutralized crotonic acid/vinyl acetate copolymers;
(v) (meth)acrylic acid/(meth)acrylate/C₈-C₂₄ alkyl (meth)acrylate tetrapolymers; and
(vi) polymers which have been obtained following reaction between one or more compounds X and one or more compounds Y, at
10 least one of the compounds X and Y being a silicone compound, said compounds X and Y having reacted together via a hydrosilylation reaction or a condensation reaction or a crosslinking reaction in the presence of peroxide when they were brought into contact with one another;
15 (vii) blends thereof.

Interpenetrating polymer network

20 According to a first variant, the hydrophobic film-forming polymers are polymers of interpenetrating polymer network type.

For the purpose of the present invention, the term “interpenetrating polymer network” is intended to mean a blend of two interlaced polymers, obtained by simultaneous polymerization and/or crosslinking of two types of monomers, the blend obtained having a
25 single glass transition temperature range.

A particularly preferred IPN is in the form of an aqueous dispersion of particles having a number-average size ranging from 50 nm to 100 nm.

30 The IPN preferably has a glass transition temperature (T_g) range which goes from approximately -50°C to +130°C, and preferably from -45°C to +130°C.

The T_g is in particular measured by differential scanning calorimetry (or DSC) using the DSC 7 apparatus from the company Perkin Elmer, with the polymer sample being preconditioned in a

climatic chamber for 48 h at 25°C, 50% relative humidity, in an aluminium dish.

The measurement is carried out under nitrogen scanning, with a first heating ranging from -45°C to +140°C at a speed of 10°C/minute and a second heating ranging from -45°C to +230°C.

IPNs are described in the publication Solvent-free urethane-acrylic hybrid polymers for coating; E. Galgoci et al, JCT Coatings Tech, 2(13), 28-36 (February 2005), and also in patents US 4 644 030 and US 5 173 526.

Preferably, the polymers are polymers of interpenetrating polymer network type comprising a polyurethane polymer and an acrylic polymer.

Even more preferentially, the polymers are interpenetrating polymer networks (termed IPNs) of polyurethane and of acrylic polymer in the form of an aqueous dispersion of particles.

Advantageously, the polyurethane/acrylic interpenetrating polymer network can be prepared according to the process described in patent US 5 173 526.

This process comprises the following steps:

(a) forming a polyurethane prepolymer with an isocyanate ending comprising carboxylic groups which is water-dispersible;

(b) adding to the prepolymer a mixture of vinyl monomer containing an ethylenically unsaturated monomer;

(c) adding a tertiary amine to the prepolymer/vinyl monomer mixture;

(d) dispersing the prepolymer/vinyl monomer mixture in water;

(e) adding a radical initiator (soluble in oil) and a chain extender to the aqueous dispersion; and

(f) polymerizing the vinyl monomers and completing the prepolymer chain extension by heating the aqueous dispersion.

The polyurethane prepolymer with an isocyanate ending can be obtained by reaction of an organic monomer containing at least two active hydrogen atoms per molecule, in particular a diol, and

preferably a polyester polyol, with an excess of diisocyanate monomer.

5 Preferably, the polyurethane prepolymer comprises unreacted carboxylic acid groups which are neutralized in the form of a tertiary amine salt after the formation of the prepolymer and addition of the vinyl monomers, but before the formation of the aqueous dispersion.

10 The polyisocyanates used for the production of the prepolymer may be aliphatic, cycloaliphatic or aromatic. As an example of polyisocyanates, mention may be made of ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 1,5-naphthylene diisocyanate, and mixtures thereof.

15 The polymeric polyols having a molecular weight ranging from 500 to 6000, preferably ranging from 700 to 3000, which can be used for the preparation of the prepolymer may be chosen from diols and triols or mixtures thereof. The polyols can in particular be chosen from polyesters, polyesteramides, polyethers, polythioethers, polycarbonates and polyacetals.

20 The polyester polyols may be chosen from products with a hydroxyl ending from reaction of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, furan dimethanol, cyclohexane dimethanol, glycerol, trimethylolpropane, pentaerythritol, or mixtures thereof, with polycarboxylic acids, in particular dicarboxylic acids or their ester form, such as succinic acid, glutaric acid, adipic acid or their methyl ester, phthalic anhydride or dimethyl terephthalate. Use may also be made of polyesters obtained by polymerization of lactones, such as caprolactone, and of polyol. The polyesteramides may be obtained using amino alcohols such as ethanolamine in the polyesterification mixture.

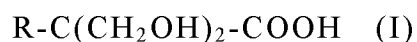
The polyether polyols which can be used comprise the products obtained by polymerization of a cyclic oxide, for example ethylene oxide, propylene oxide, or tetrahydrofuran, or by addition of these cyclic oxides to polyfunctional initiators such as water, ethylene glycol, propylene glycol, diethylene glycol, cyclohexane dimethanol, glycerol, trimethylolpropane, pentaerythritol or bisphenol A. The polyethers may also be chosen from polyoxypropylene diols and triols, poly(oxyethylene-oxypropylene) diols and triols obtained by simultaneous or sequential addition of propylene oxide and of ethylene oxide with the appropriate initiators, and polytetramethylene glycol ethers obtained by polymerization of tetrahydrofuran.

The polythioether polyols can be chosen from the products obtained by condensation of thiodiglycol, either alone, or with other glycols, dicarboxylic acids, formaldehyde, amino alcohols or aminocarboxylic acids.

The polycarbonate polyols can be chosen from the products from reaction of diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol or tetraethylene glycol with diaryl carbonates, such as diphenyl carbonate, or with phosgene.

The polyacetal polyols can be chosen from the products from reaction of glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde.

The compounds with a reactive isocyanate group containing acid groups which can be used in the preparation of the water-dispersible anionic prepolymers comprise diols and triols containing carboxylic acid groups, for example those of formula (I):



in which R is a hydrogen or a C₁-C₁₀ alkyl group. The diol with a carboxylic group is preferably 2,2-dimethylolpropionic acid. The diol or triol with a carboxylic group can be incorporated into a polyester by reaction with a dicarboxylic acid before being introduced into the prepolymer. Compounds with an acid group are, for example,

aminocarboxylic acids, for example lysine, cysteine or 3,5-diaminobenzoic acid.

5 The water-dispersible anionic polyurethane prepolymer with an isocyanate ending can be prepared conventionally by reaction of a stoichiometric excess of an organic polyisocyanate with a polymeric polyol and any other necessary compound that reacts with an isocyanate under anhydrous conditions at a temperature between 30 and 130°C until the reaction between the isocyanate groups and the hydroxyl groups is complete.

10 The polyisocyanate and the compounds containing an active hydrogen are advantageously used such that the ratio of the number of isocyanate groups to the number of hydroxyl groups ranges from 1.1/1 to 6/1, preferably from 1.5/1 to 3/1. It is possible to use a tin catalyst well known to assist the formation of the prepolymer.

15 A mixture of water-dispersible polyurethane prepolymer containing carboxylic groups and the vinyl monomer is obtained by simple addition of the composition of vinyl monomer to the prepolymer. The composition of vinyl monomer should contain at least one ethylenically unsaturated monomer.

20 The vinyl monomers which can be added to the prepolymer may be ethylenically unsaturated hydrocarbon-based monomers, ethylenically unsaturated esters, ethylenically unsaturated ethers, in particular (meth)acrylic acid esters, vinyl alcohol esters, or styrene.

25 Mention may in particular be made of butadiene, isoprene, styrene, alkyl (meth)acrylates having a C₁-C₆ alkyl group, alkyl maleates having a C₁-C₆ alkyl group, vinyl acetate, vinyl butyrate, acrylonitrile, vinyl methyl ether, vinyl propyl ether, vinyl butyl ether, vinyl chloride and vinylidene chloride. The unsaturated polyethylenic monomers can be chosen from butadiene, isoprene, allyl methacrylate, diesters of acrylic acid and of C₂-C₆ diols, such as butylene diacrylate and hexylene diacrylate, divinylbenzene, divinyl ether, divinyl sulphide and trimethylolpropane triacrylate.

30 Advantageously, the vinyl monomer is methyl methacrylate.

Before dispersing the prepolymer/vinyl monomer mixture in water, a tertiary amine is added to the mixture in a sufficient amount to make the prepolymer water-dispersible, i.e. in a sufficient amount to neutralize the carboxylic groups. For example, the amine can be added in an amount ranging from 65 to 100% of amine equivalent per carboxylic function equivalent.

The tertiary amines which can be used are relatively volatile such that they are evaporated off from the film after film formation.

Mention may be made, for example, of the amines of formula $R-N(R_1)(R_2)$ in which R, R_1 and R_2 independently represent a C_1 - C_4 alkyl or hydroxyalkyl group. Mention may, for example, be made of triethylamine, dimethylethanolamine, methyldiethanolamine and methyldiethylamine.

It is important for the tertiary amine to be added to the prepolymer/monomer mixture before this mixture is dispersed in water in order to ensure compatibility of the organic and aqueous phases in the dispersion obtained.

The prepolymer/vinyl monomer mixture can be dispersed in water using known technologies. Preferably, the mixture is added to water with stirring, or the water can be poured into the mixture.

The chain extender containing the active hydrogen which reacts with the prepolymer may be a polyol, an amino alcohol, aqueous ammonia, a primary or secondary amine, and more particularly a diamine.

Mention may, for example, be made of ethylenediamine, diethylenetriamine, triethylenetetramine, propylenediamine, butylenediamine, hexamethylenediamine, cyclohexylenediamine, piperazine, 2-methylpiperazine, phenylenediamine, toluenediamine, tris(2-aminoethyl)amine, 4,4'-methylenebis(2-chloroaniline), 3,3'-dichloro-4,4'-diphenyldiamine, 2,6-diaminopyridine, 4,4'-diaminodiphenylmethane and isophorone diamine.

The free-radical initiator may be an initiator of azo type, such as 2,2'-azobis(2,4-dimethylpentanenitrile) and 2,2'-azobis(2-methylpropanenitrile) [or AIBN].

The radical polymerization of the mixture of vinyl monomers and the prepolymer chain extender is advantageously carried out at high temperature, for example between 50°C and 90°C, and preferably between 60°C and 80°C.

5 The amount of chain extender used is advantageously equivalent to the free isocyanate groups in the prepolymer, the ratio of the number of active hydrogens in the chain extender to the number of isocyanate groups in the prepolymer preferably ranging from 0.7 to 1.3.

10 The polymerization of the vinyl monomers can be carried out according to two methods. According to a first method, the monomers are added and can swell the polyurethane prepolymer before the addition of the tertiary amine. The monomers are then polymerized using the free-radical initiator.

15 The proportion of the vinyl monomers can range from 25 to 75%, preferably from 40 to 60%, by weight of the total weight of solid matter of the aqueous dispersion.

 According to a second polymerization method, a part of the vinyl monomers is added to the prepolymer, and then neutralization is
20 carried out with the tertiary amine and the prepolymer/vinyl monomer mixture is dispersed in water, followed by the polymerization during which the remaining monomers are added. Alternatively, the second portion of monomers can be added to the prepolymer/vinyl monomer dispersion after addition of the amine and the mixture is stirred before
25 the beginning of the polymerization.

The polymer dispersion may contain from 20 to 60% by weight of solid matter.

 According to one preferred embodiment of the invention, the polyurethane present in the IPN is a copolymer of polyester
30 polyol/diol with a carboxylic acid/diisocyanate/diamine group, such as those previously described for example; the acrylic polymer present in the IPN is a poly(methyl methacrylate).

The polyurethane/acrylic polymer IPN sold by the company Air Products under the trade name Hybridur[®] 875 polymer dispersion

(INCI name: Polyurethane-2 (and) Polymethyl Methacrylate), or else under the trade names Hybridur[®] 870 or Hybridur[®] 880, is preferably used.

5 Grafted silicone polymers

For the purpose of the present invention, the term “grafted silicone polymer” is intended to mean a polymer comprising a main chain of silicone or polysiloxane (polymer of Si-O-) onto which is
10 grafted, within said chain and also, optionally, at at least one of its ends, one or more organic groups not comprising silicone.

Examples of polymers with a polysiloxane backbone grafted with non-silicone organic monomers that is suitable for implementation of the present invention, and also the particular
15 method for preparing same, are in particular described in patent applications EP-A-0582152, WO 93/23009 and WO 95/03776, the teachings of which are entirely included in the present description by way of nonlimiting references.

According to one particularly preferred embodiment of the
20 present invention, the silicone polymer with a polysiloxane backbone grafted with non-silicone organic monomers that is used comprises the result of radical polymerization between, on the one hand, one or more non-silicone anionic organic monomers having an ethylenic unsaturation and/or one or more non-silicone hydrophobic organic
25 monomers having an ethylenic unsaturation and, on the other hand, a silicone having in its chain one or more functional groups capable of reacting with said ethylenic unsaturations of said non-silicone monomers by forming a covalent bond, in particular thiofunctional groups.

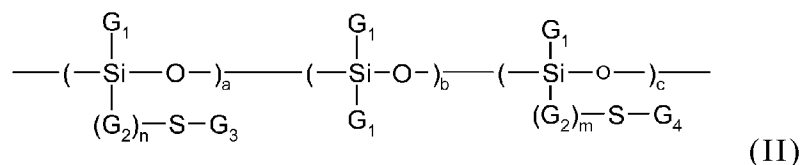
30 According to the present invention, said ethylenically unsaturated anionic monomers are preferably chosen, alone or as mixtures, from neutralized unsaturated, and linear or branched, carboxylic acids, it being possible for this or these unsaturated carboxylic acid(s) to be more particularly acrylic acid, methacrylic

acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid and crotonic acid. It will be noted that, likewise, in the final grafted silicone polymer, the organic group of anionic nature comprises the result of the radical (homo)polymerization of one or more anionic monomers of unsaturated carboxylic acid type.

For the purpose of the present invention, the term "hydrophobic monomer" is intended to mean a monomer which has a solubility in water of less than 10 g per 100 ml of water at a temperature of 20°C.

According to the present invention, the ethylenically unsaturated hydrophobic monomers are preferably chosen, alone or as mixtures, from esters of acrylic acid and of alkanols and/or esters of methacrylic acid and of alkanols. The alkanols are preferably C₁-C₁₈ and more particularly C₁-C₁₂. The preferential monomers are chosen from the group consisting of isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isopentyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, tert-butyl (meth)acrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate, or mixtures thereof.

A family of silicone polymers with a polysiloxane backbone grafted with non-silicone organic monomers that are particularly suitable for implementing the present invention consists of the silicone polymers comprising in their structure the following unit of formula (II):



in which the G₁ radicals, which may be identical or different, represent hydrogen or a C₁-C₁₀ alkyl radical or else a phenyl radical; the G₂ radicals, which may be identical or different, represent a C₁-C₁₀ alkylene group; G₃ represents a polymeric residue resulting from the (homo)polymerization of at least one ethylenically unsaturated anionic monomer; G₄ represents a polymeric residue resulting from

the (homo)polymerization of at least one ethylenically unsaturated hydrophobic monomer; m and n are, independently of one another, equal to 0 or 1; a is an integer ranging from 0 to 50; b is an integer that may be included between 10 and 350, c is an integer ranging from 0 to 50; with the proviso that one of the parameters a and c is other than 0.

Preferably, the unit of formula (II) above has at least one, and even more preferentially all, of the following characteristics:

the G_1 radicals denote a C_1 - C_{10} alkyl radical,

n is non-zero and the G_2 radicals represent a C_1 - C_3 divalent radical;

G_3 represents a polymeric radical resulting from the (homo)polymerization of at least one ethylenically unsaturated monomer of the carboxylic acid type, preferably acrylic acid and/or methacrylic acid;

G_4 represents a polymeric radical resulting from the (homo)polymerization of one or more monomers of the C_1 - C_{10} alkyl (meth)acrylate type.

Examples of grafted silicone polymers corresponding to formula (II) are thus in particular polydimethylsiloxanes (PDMSs) onto which are grafted, by means of a thiopropylene-type connecting link, mixed polymer units of the poly((meth)acrylic acid) type and/or the poly(alkyl, in particular C_1 - C_3 , or even C_1 , alkyl, (meth)acrylate) type. These polymers are referenced under the INCI name Polysilicone-8.

It may thus be a propylthio(poly(methyl acrylate/methyl methacrylate/methacrylic acid))-grafted polydimethylsiloxane or a propylthio(poly(methyl acrylate))-, propylthio(poly(methyl methacrylate))- and propylthio(poly(methacrylic acid))-grafted polydimethylsiloxane. As a variant, it may be a propylthio(poly)(isobutyl methacrylate))- and propylthio(poly(methacrylic acid))-grafted polydimethylsiloxane.

Such grafted silicone polymers are in particular sold by the company 3M under the trade names VS 80 and VS 70.

A propylthio(poly(methyl acrylate/methyl methacrylate/methacrylic acid))-grafted polydimethylsiloxane sold under the name VS80 by the company 3M is preferably used.

5 Among the hydrophobic film-forming polymers in accordance with the invention, use will more preferentially be made of the polymers which are interpenetrating polymer networks (IPNs) of polyurethane and of acrylic polymer in the form of an aqueous dispersion of particles, in particular the polyurethane/acrylic polymer IPN sold by the company Air Products under the trade name
10 Hybridur[®] 875 polymer dispersion (INCI name: Polyurethane-2 (and) Polymethyl Methacrylate), or else under the trade names Hybridur[®] 870 and Hybridur[®] 880.

Acrylic acid/N-tert-butylacrylamide copolymers

15

Among the acrylic acid/N-tert-butylacrylamide copolymers, use will preferably be made of the non-neutralized acrylic acid/ethyl acrylate/N-tert-butylacrylamide copolymers (in which the acrylic acid is in free form) such as the products Ultrahold Strong and Ultrahold 8
20 (INCI name: Acrylates/t-Butylacrylamide Copolymer) in non-neutralized form from the company BASF.

The term “non-neutralized (meth)acrylic acid/N-tert-butylacrylamide copolymer” is intended to mean any (meth)acrylic acid/N-tert-butylacrylamide copolymer of which the (meth)acrylic
25 acid function is free and is not neutralized with an organic or inorganic base.

Vinyl acetate/crotonic acid copolymers

30

The term “non-neutralized crotonic acid/vinyl acetate copolymer is intended to mean any crotonic acid/vinyl acetate copolymer of which the crotonic acid function is not neutralized with an organic or inorganic base.

Among the non-neutralized vinyl acetate/crotonic acid copolymers, use will preferably be made of those described in patent FR 2 439 798, and in particular the vinyl acetate/crotonic acid/vinyl tert-butyl-4-benzoate copolymer (65/10/25) (INCI name: Vinyl Acetate/Vinyl Butyl Benzoate/Crotonates Copolymer) in non-neutralized form, such as the commercial product Mexomere PW produced by the company Chimex.

(Meth)acrylic acid tetrapolymer

For the purpose of the present invention, the term “tetrapolymer” is intended to mean a polymer resulting from the copolymerization of four comonomers.

Among the tetrapolymers of (meth)acrylic acid, of (meth)acrylates and of C₈-C₂₄ alkyl (meth)acrylate, mention may be made of those described in application US2003021847, such as the copolymer sold under the name Soltex OPT-PG by the company Rohm & Haas having the INCI name: Acrylates/C₁₂-C₂₂ Alkyl Methacrylate Copolymer.

Polymers obtained following reaction between one or more compounds X and one or more compounds Y

According to another particular form of the invention, the hydrophobic polymer(s) may also be chosen from polymers which were obtained following reaction between one or more compounds X and one or more compounds Y, at least one of the compounds X and Y being a silicone compound, said compounds X and Y having reacted together via a hydrosilylation reaction or a condensation reaction or a crosslinking reaction in the presence of peroxide when they were brought into contact with one another.

The term “silicone compound” is intended to mean a compound comprising at least two organosiloxane units. According to one particular embodiment, the compounds X and the compounds Y are

silicone compounds. The compounds X and Y may be aminated or nonaminated. They may comprise polar groups that may be chosen from the following groups: -COOH, -COO⁻, -COO-, -OH, -NH₂, -NH-, -NR-, -SO₃H, -SO₃⁻, -OCH₂CH₂-, -O-CH₂CH₂CH₂-, -O-CH₂CH(CH₃)-,
 5 -NR₃⁺, -SH, -NO₂, I, Cl, Br, -CN, -PO₄³⁻, -CONH-, -CONR-, -CONH₂, -CSNH-, -SO₂-, -SO-, -SO₂NH-, -NHCO-, -NHSO₂-, -NHCOO-, -OCONH-, -NHCSO- and -OCSNH-, R representing an alkyl group.

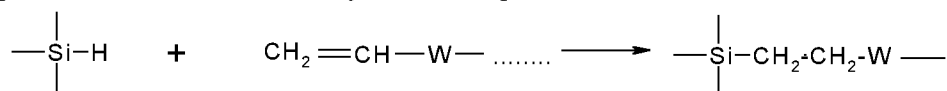
According to another embodiment, one or more of the compounds X and Y is a polymer of which the main chain is formed predominantly of organosiloxane units.
 10

Among the silicone compounds mentioned hereinafter, some may exhibit both film-forming and adhesive properties, depending, for example, on their proportion of silicone or depending on whether they are used as a mixture with a particular additive. It is consequently
 15 possible to modulate the film-forming properties or the adhesive properties of such compounds according to the use envisaged; this is in particular the case for reactive silicone elastomers known as “room temperature vulcanization” silicones.

The compounds X and Y may react together at a temperature ranging between ambient temperature and 180°C.
 20

Advantageously, the hydrophobic polymers are obtained following reaction of the compounds X and Y which are capable of reacting together at ambient temperature (20±5°C) and atmospheric pressure, advantageously in the presence of a catalyst, via a
 25 hydrosilylation reaction or a condensation reaction, or a crosslinking reaction in the presence of a peroxide.

According to one particular embodiment, the hydrophobic polymers are obtained following reaction of the compounds X and Y which have reacted together by hydrosilylation, this reaction possibly
 30 being represented schematically in a simplified manner as follows:

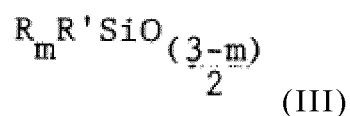


with W representing a carbon-based and/or silicone-based chain containing one or more unsaturated aliphatic groups.

In this case, the compound X may be chosen from silicone-based compounds comprising two or more unsaturated aliphatic groups. By way of example, the compound X may comprise a main silicone chain of which the unsaturated aliphatic groups are pendant to the main chain (side group) or located at the ends of the main chain of the compound (end group). These particular compounds will be referred to, in the remainder of the description, as polyorganosiloxanes with unsaturated aliphatic groups.

According to one embodiment, the compound X is chosen from polyorganosiloxanes comprising two or more unsaturated aliphatic groups, for example two or three vinyl or allyl groups, each bonded to a silicon atom.

According to one advantageous embodiment, the compound X is chosen from polyorganosiloxanes comprising siloxane units of formula (III):



in which:

- R represents a linear or cyclic, monovalent hydrocarbon-based group comprising from 1 to 30 carbon atoms, preferably from 1 to 20, and better still from 1 to 10 carbon atoms, such as, for example, a short-chain alkyl radical comprising, for example, from 1 to 10 carbon atoms, in particular a methyl radical or else a phenyl group, preferably a methyl radical;

- m is equal to 1 or 2; and

- R' represents:

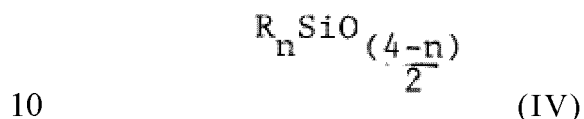
- an unsaturated aliphatic hydrocarbon-based group comprising from 2 to 10, preferably from 2 to 5 carbon atoms, such as, for example, a vinyl group or an -R''-CH=CHR''' group in which R'' is a divalent aliphatic hydrocarbon-based chain comprising from 1 to 8 carbon atoms, which is bonded to the silicon atom, and R''' is a

hydrogen atom or an alkyl radical comprising from 1 to 4 carbon atoms, preferably a hydrogen atom; mention may be made, as an R' group, of vinyl and allyl groups and mixtures thereof; or

- an unsaturated cyclic hydrocarbon-based group comprising from 5 to 8 carbon atoms, such as, for example, a cyclohexenyl group.

Preferably, R' is an unsaturated aliphatic hydrocarbon-based group, preferably a vinyl group.

According to one particular embodiment, the polyorganosiloxane also comprises units of formula (IV):



in which R is a group as defined above, and n is equal to 1, 2 or 3.

According to one variant, the compound X may be a silicone resin comprising two or more ethylenic unsaturations, said resin being capable of reacting with the compound B via hydrosilylation. Mention may be made, for example, of resins of MQ or MT type that themselves bear unsaturated $-\text{CH}=\text{CH}_2$ reactive ends.

These resins are crosslinked organosiloxane polymers.

The nomenclature of silicone resins is known under the name "MDTQ", the resin being described as a function of the various siloxane monomer units that it comprises, each of the letters "MDTQ" characterizing a type of unit.

The letter M represents the monofunctional unit of formula $(\text{CH}_3)_3\text{SiO}_{1/2}$, the silicon atom being bonded to a single oxygen atom in the polymer comprising this unit.

The letter D signifies a difunctional unit $(\text{CH}_3)_2\text{SiO}_{2/2}$ in which the silicon atom is bonded to two oxygen atoms.

The letter T represents a trifunctional unit of formula $(\text{CH}_3)\text{SiO}_{3/2}$.

In the units M, D and T defined previously, at least one of the methyl groups may be substituted with an R group different from the methyl group, such as a hydrocarbon-based (in particular alkyl) radical

containing from 2 to 10 carbon atoms or a phenyl group or else a hydroxyl group.

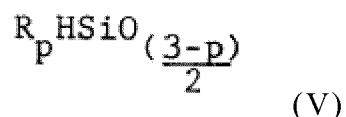
Finally, the letter Q signifies a tetrafunctional unit $\text{SiO}_{4/2}$ in which the silicon atom is bonded to four hydrogen atoms themselves bonded to the rest of the polymer. As examples of such resin, mention may be made of MT silicone resins such as poly(phenyl-vinylsilsesquioxane)s, for instance the product sold under the reference SST-3PV1 by the company Gelest.

Preferably, the compounds X comprise from 0.01 to 1% by weight of unsaturated aliphatic groups.

Advantageously, the compound X is chosen from polyorgano-polysiloxanes, in particular those comprising the siloxane units (III) and optionally (IV) described previously.

The compound Y preferably comprises at least two free Si-H groups (hydrogenosilane groups).

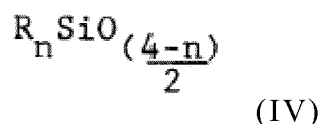
The compound Y may be advantageously chosen from organosiloxanes comprising one or more alkylhydrogenosiloxane units of formula below:



in which:

R represents a linear or cyclic monovalent hydrocarbon-based group comprising from 1 to 30 carbon atoms, such as, for example, an alkyl radical containing from 1 to 30 carbon atoms, preferably from 1 to 20 and better still from 1 to 10 carbon atoms, in particular a methyl radical, or else a phenyl group, and p is equal to 1 or 2. Preferably, R is a hydrocarbon-based group, preferably methyl.

These compounds Y that are organosiloxanes with alkylhydrogenosiloxane units may also comprise units of formula:



as defined above.

The compound Y may be a silicone resin comprising at least one unit chosen from the M, D, T and Q units as defined above and comprising at least one Si-H group, such as the poly(methylhydrido-silsesquioxane)s sold under the reference SST-3MH1.1 by the company Gelest.

Preferably, these organosiloxane compounds Y comprise from 0.5 to 2.5% by weight of Si-H groups.

Advantageously, the R radicals represent a methyl group in formulae (III), (IV) and (V) above.

Preferably, these organosiloxanes Y comprise end groups of formula $(\text{CH}_3)_3\text{SiO}_{1/2}$.

Advantageously, the organosiloxanes Y comprise two or more alkylhydrogenosiloxane units of formula $(\text{H}_3\text{C})(\text{H})\text{SiO}$ and optionally comprise $(\text{H}_3\text{C})_2\text{SiO}$ units.

Such compounds Y that are organosiloxanes with hydrogenosilane groups are described, for example, in document EP 0 465 744.

According to one variant, the compound X is chosen from organic oligomers or polymers (the term "organic" is intended to mean compounds of which the main chain is not silicone-based, preferably compounds not comprising silicon atoms) or from organic/silicone hybrid polymers or oligomers, said oligomers or polymers bearing at least two reactive unsaturated aliphatic groups, the compound Y being chosen from the hydrogenosiloxanes mentioned above.

The compound X, which is of organic nature, may then be chosen from vinyl or (meth)acrylic polymers or oligomers, polyesters, polyurethanes and/or polyureas, polyethers, perfluoropolyethers, polyolefins such as polybutene or polyisobutylene, dendrimers or organic hyperbranched polymers, or mixtures thereof.

In particular, the organic polymer or the organic part of the hybrid polymer may be chosen from the following polymers:

a) ethylenically unsaturated polyesters:

This is a group of polymers of polyester type containing two or more ethylenic double bonds, randomly distributed in the main chain of

the polymer. These unsaturated polyesters are obtained by polycondensation of a mixture:

5 - of linear or branched aliphatic or cycloaliphatic dicarboxylic acids containing in particular from 3 to 50 carbon atoms, preferably from 3 to 20 and better still from 3 to 10 carbon atoms, such as adipic acid or sebacic acid, of aromatic dicarboxylic acids containing in particular from 8 to 50 carbon atoms, preferably from 8 to 20 and better still from 8 to 14 carbon atoms, such as phthalic acids, in particular terephthalic acid, and/or of dicarboxylic acids derived from
10 ethylenically unsaturated fatty acid dimers such as the oleic or linoleic acid dimers described in application EP-A-959 066 (paragraph [0021]) sold under the names Pripol[®] by the company Uniqema or Empol[®] by the company Henkel, all these diacids needing to be free of polymerizable ethylenic double bonds,

15 - of linear or branched aliphatic or cycloaliphatic diols containing in particular from 2 to 50 carbon atoms, preferably from 2 to 20 and better still from 2 to 10 carbon atoms, such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol or cyclohexanedimethanol, of aromatic diols containing from 6 to 50
20 carbon atoms, preferably from 6 to 20 and better still from 6 to 15 carbon atoms, such as bisphenol A and bisphenol B, and/or of diol dimers resulting from the reduction of the fatty acid dimers as defined above, and

25 - of one or more dicarboxylic acids or anhydrides thereof comprising at least one polymerizable ethylenic double bond and containing from 3 to 50 carbon atoms, preferably from 3 to 20 and better still from 3 to 10 carbon atoms, such as maleic acid, fumaric acid or itaconic acid;

30 b) polyesters with (meth)acrylate side groups and/or end groups:

This is a group of polymers of polyester type that are obtained by polycondensation of a mixture:

- of linear or branched aliphatic or cycloaliphatic dicarboxylic acids containing in particular from 3 to 50 carbon atoms, preferably

from 3 to 20 and better still from 3 to 10 carbon atoms, such as adipic acid or sebacic acid, of aromatic dicarboxylic acids containing in particular from 8 to 50 carbon atoms, preferably from 8 to 20 and better still from 8 to 14 carbon atoms, such as phthalic acids, in particular terephthalic acid, and/or of dicarboxylic acids derived from ethylenically unsaturated fatty acid dimers such as the oleic or linoleic acid dimers described in application EP-A-959 066 (paragraph [0021]) sold under the names Pripol[®] by the company Uniqema or Empol[®] by the company Henkel, all these diacids needing to be free of polymerizable ethylenic double bonds,

- of linear or branched aliphatic or cycloaliphatic diols containing in particular from 2 to 50 carbon atoms, preferably from 2 to 20 and better still from 2 to 10 carbon atoms, such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol or cyclohexanedimethanol, of aromatic diols containing from 6 to 50 carbon atoms, preferably from 6 to 20 and better still from 6 to 15 carbon atoms, such as bisphenol A and bisphenol B, and

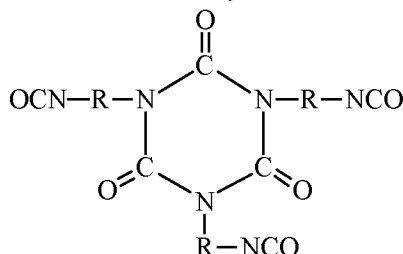
- of at least one ester of (meth)acrylic acid and of a diol or polyol containing from 2 to 20 carbon atoms, preferably from 2 to 6 carbon atoms, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and glyceryl methacrylate.

These polyesters differ from those described above in point a) by the fact that the ethylenic double bonds are not located in the main chain, but on side groups or at the end of the chains. These ethylenic double bonds are those of the (meth)acrylate groups present in the polymer.

Such polyesters are sold, for example, by the company UCB under the names Ebecryl[®] (Ebecryl[®] 450: molar mass 1600, on average 6 acrylate functions per molecule, Ebecryl[®] 652: molar mass 1500, on average 6 acrylate functions per molecule, Ebecryl[®] 800: molar mass 780, on average 4 acrylate functions per molecule, Ebecryl[®] 810: molar mass 1000, on average 4 acrylate functions per molecule, Ebecryl[®] 50 000: molar mass 1500, on average 6 acrylate functions per molecule);

c) polyurethanes and/or polyureas with (meth)acrylate groups, obtained by polycondensation:

- of aliphatic, cycloaliphatic and/or aromatic diisocyanates, triisocyanates and/or polyisocyanates containing in particular from 4 to 50, preferably from 4 to 30 carbon atoms, such as hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, diphenylmethane diisocyanate or the isocyanurates of formula:



resulting from the trimerization of 3 molecules of diisocyanates OCN-R-CNO, in which R is a linear, branched or cyclic hydrocarbon-based radical containing from 2 to 30 carbon atoms;

- of polyols, in particular of diols, free of polymerizable ethylenic unsaturations, such as 1,4-butanediol, ethylene glycol or trimethylolpropane, and/or of aliphatic, cycloaliphatic and/or aromatic polyamines, in particular diamines, containing in particular from 3 to 50 carbon atoms, such as ethylenediamine or hexamethylenediamine, and

- of at least one ester of (meth)acrylic acid and of a diol or polyol containing from 2 to 20 carbon atoms, preferably from 2 to 6 carbon atoms, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and glyceryl methacrylate.

Such polyurethanes/polyureas with acrylate groups are sold, for example, under the name SR 368 (tris(2-hydroxyethyl) isocyanurate-triacrylate) or Craynor[®] 435 by the company Cray Valley, or under the name Ebecryl[®] by the company UCB (Ebecryl[®] 210: molar mass 1500, 2 acrylate functions per molecule, Ebecryl[®] 230: molar mass 5000, 2 acrylate functions per molecule, Ebecryl[®] 270: molar mass 1500, 2 acrylate functions per molecule, Ebecryl[®] 8402: molar mass 1000, 2 acrylate functions per molecule, Ebecryl[®] 8804: molar mass 1300, 2

acrylate functions per molecule, Ebecryl[®] 220: molar mass 1000, 6
acrylate functions per molecule, Ebecryl[®] 2220: molar mass 1200, 6
acrylate functions per molecule, Ebecryl[®] 1290: molar mass 1000, 6
acrylate functions per molecule, Ebecryl[®] 800: molar mass 800, 6
5 acrylate functions per molecule).

Mention may also be made of the water-soluble aliphatic
diacrylate polyurethanes sold under the names Ebecryl[®] 2000, Ebecryl[®]
2001 and Ebecryl[®] 2002, and the diacrylate polyurethanes in aqueous
dispersion sold under the trade names IRR[®] 390, IRR[®] 400, IRR[®] 422
10 and IRR[®] 424 by the company UCB;

d) polyethers with (meth)acrylate groups obtained by
esterification, with (meth)acrylic acid, of the hydroxyl end groups of
C₁-C₄ alkylene glycol homopolymers or copolymers, such as
polyethylene glycol, polypropylene glycol, copolymers of ethylene
15 oxide and of propylene oxide preferably having a weight-average
molecular weight of less than 10 000, and polyethoxylated or
polypropoxylated trimethylolpropane.

Polyoxyethylene di(meth)acrylates of suitable molar mass are
sold, for example, under the names SR 259, SR 344, SR 610, SR 210,
20 SR 603 and SR 252 by the company Cray Valley or under the name
Ebecryl[®] 11 by UCB. Polyethoxylated trimethylolpropane triacrylates
are sold, for example, under the names SR 454, SR 498, SR 502, SR
9035 and SR 415 by the company Cray Valley or under the name
Ebecryl[®] 160 by the company UCB. Polypropoxylated
25 trimethylolpropane triacrylates are sold, for example, under the names
SR 492 and SR 501 by the company Cray Valley;

e) epoxyacrylates obtained by reaction between:
- at least one diepoxide chosen, for example, from:
(i) bisphenol A diglycidyl ether,
30 (ii) a diepoxy resin resulting from the reaction between
bisphenol A diglycidyl ether and epichlorohydrin,
(iii) an epoxy ester resin with α,β -diepoxy end groups resulting
from the condensation of a dicarboxylic acid containing from 3 to 50
carbon atoms with a stoichiometric excess of (i) and/or (ii),

(iv) an epoxy ether resin with α,β -diepoxy end groups resulting from the condensation of a diol containing from 3 to 50 carbon atoms with a stoichiometric excess of (i) and/or (ii),

5 (v) natural or synthetic oils bearing at least 2 epoxide groups, such as epoxidized soybean oil, epoxidized linseed oil or epoxidized vernonia oil,

(vi) a phenol-formaldehyde polycondensate (Novolac[®] resin), the end groups and/or side groups of which have been epoxidized, and

10 - one or more carboxylic acids or polycarboxylic acids comprising at least one ethylenic double bond in the α,β -position relative to the carboxylic group, for instance (meth)acrylic acid or crotonic acid or esters of (meth)acrylic acid and of a diol or polyol containing from 2 to 20 carbon atoms, preferably from 2 to 6 carbon atoms, such as 2-hydroxyethyl (meth)acrylate.

15 Such polymers are sold, for example, under the names SR 349, SR 601, CD 541, SR 602, SR 9036, SR 348, CD 540, SR 480 and CD 9038 by the company Cray Valley, under the names Ebecryl[®] 600 and Ebecryl[®] 609, Ebecryl[®] 150, Ebecryl[®] 860 and Ebecryl[®] 3702 by the company UCB and under the names Photomer[®] 3005 and Photomer[®] 3082 by the company Henkel;

25 f) poly(C₁-C₅₀ alkyl (meth)acrylate)s, said alkyl being linear, branched or cyclic, comprising at least two functions containing an ethylenic double bond borne by the hydrocarbon-based side chains and/or end chains.

Such copolymers are sold, for example, under the names IRR[®] 375, OTA[®] 480 and Ebecryl[®] 2047 by the company UCB;

g) polyolefins such as polybutene or polyisobutylene;

30 h) polyfluoropolyethers with acrylate groups obtained by esterification, for example with (meth)acrylic acid, of polyfluoropolyethers bearing hydroxyl side groups and/or end groups.

Such α,β -diol perfluoropolyethers are described in particular in EP-A-1 057 849 and are sold by the company Ausimont under the name Fomblin[®] Z Diol;

i) hyperbranched dendrimers and polymers bearing (meth)acrylate or (meth)acrylamide end groups obtained, respectively, by esterification or amidation of hyperbranched dendrimers and polymers containing hydroxyl or amino end functions, with
5 (meth)acrylic acid.

Dendrimers (from the Greek dendron = tree) are “arborescent”, i.e. highly branched, polymer molecules invented by D. A. Tomalia and the team thereof at the beginning of the 1990s (Donald A. Tomalia et al., *Angewandte Chemie, Int. Engl. Ed.*, vol. 29, n° 2, pages 138 - 175).
10 These are structures constructed about a central unit that is generally polyvalent. About this central unit are linked, in a fully determined structure, branched chain-extending units, thus giving rise to monodispersed symmetrical macromolecules having a well-defined chemical and stereochemical structure. Dendrimers of polyamidoamine
15 type are sold, for example, under the name Starbust® by the company Dendritech.

Hyperbranched polymers are polycondensates, generally of polyester, polyamide or polyethyleneamine type, obtained from multifunctional monomers, which have an arborescent structure similar
20 to that of dendrimers but are much less regular than dendrimers (see, for example, WO-A-93/17060 and WO 96/12754).

The company Perstorp sells hyperbranched polyesters under the name Boltorn®. Hyperbranched polyethyleneamines will be found under the name Combust® from the company Dendritech. Hyperbranched
25 poly(esteramides) with hydroxyl end groups are sold by the company DSM under the name Hybrane®.

These hyperbranched dendrimers and polymers esterified or amidated with acrylic acid and/or methacrylic acid are distinguished from the polymers described in points a) to h) above by the very large
30 number of ethylenic double bonds present. This high functionality, most commonly greater than 5, makes them particularly useful by allowing them to act as “crosslinking nodes”, i.e. sites of multiple crosslinking.

It is therefore possible to use these dendritic and hyperbranched polymers in combination with one or more of the polymers and/or oligomers a) to h) above.

5 The hydrosilylation reaction is advantageously carried out in the presence of a catalyst, preferably a platinum-based or tin-based catalyst.

10 Mention may be made, for example, of catalysts based on platinum deposited on a support of silica gel or charcoal powder (coal), platinum chloride, and salts of platinum and chloroplatinic acids.

Chloroplatinic acids in hexahydrate or anhydrous form, which are readily dispersible in organosilicone media, are preferably used.

15 Mention may also be made of platinum complexes such as those based on chloroplatinic acid hexahydrate and on divinyltetramethyldisiloxane.

20 Polymerization inhibitors or retardants, and more particularly catalyst inhibitors, may also be introduced in order to increase the stability of the composition over time or to retard the polymerization. In a nonlimiting manner, mention may be made of cyclic polymethylvinylsiloxanes, and in particular tetravinyltetramethylcyclotetrasiloxane, acetylenic alcohols, which are preferably volatile, such as methylisobutynol.

25 The presence of ionic salts, such as sodium acetate, in the composition may have an influence on the rate of polymerization of the compounds.

30 Advantageously, the compounds X and Y are chosen from silicone compounds capable of reacting by hydrosilylation; in particular, the compound X is chosen from polyorganosiloxanes comprising units of formula (III) described above and the compound Y is chosen from organosiloxanes comprising alkylhydrogenosiloxane units of formula (V) described above.

According to one particular embodiment, the compound X is a polydimethylsiloxane with vinyl end groups, and the compound Y is methylhydrogenosiloxane.

- By way of example of a combination of compounds X and Y that react via hydrosilylation, mention may be made of the following references provided by the company Dow Corning: DC 7-9800 Soft Skin Adhesive Parts A & B, and also the following mixtures A and B prepared by Dow Corning:
- 5

MIXTURE A:

Ingredient (INCI name)	CAS No.	Contents (%)	Function
Dimethylsiloxane, Dimethylvinyl-siloxy-terminated	68083-19-2	55-95	Polymer
Silica silylate	68909-20-6	10-40	Filler
1,3-Diethenyl-1,1,3,3-tetramethyldi-siloxane complexes	68478-92-2	Trace	Catalyst
Tetramethyldivinyl-disiloxane	2627-95-4	0.1-1	Polymer

MIXTURE B:

Ingredient (INCI name)	CAS No.	Contents (%)	Function
Dimethylsiloxane, Dimethylvinylsiloxyl-terminated	68083-19-2	55-95	Polymer
Silica silylate	6890920-6	10-40	Filler
Dimethyl, Methylhydrogensiloxane, with a trimethylsiloxyl end group	68037-59-2	1-10	Polymer

5 According to one embodiment, the hydrophobic polymers are
 10 obtained following reaction of the compounds X and Y which have
 reacted together via condensation, even in the presence of water
 (hydrolysis) via reaction of 2 compounds bearing alkoxysilane groups,
 or via “direct” condensation by reaction of a compound bearing
 15 alkoxysilane group(s) and a compound bearing silanol group(s) or by
 reaction of 2 compounds bearing silanol group(s).

When the condensation is carried out in the presence of water,
 said water may in particular be ambient moisture, residual water from
 the keratin fibres, or water provided by an external source, for
 example by premoistening of keratin fibres (for example with a
 15 mister).

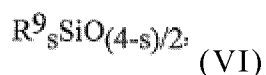
In this mode of reaction via condensation, the compounds X
 and Y, which may be identical or different, may thus be chosen from
 silicone compounds of which the main chain comprises two or more
 alkoxysilane groups and/or at least two silanol (Si-OH) groups, on the
 20 side and/or at the end of the chain.

According to one advantageous embodiment, the compounds X
 and/or Y are chosen from polyorganosiloxanes comprising two or
 more alkoxysilane groups. The term “alkoxysilane group” is intended

to mean a group comprising at least one -Si-OR portion, R being an alkyl group comprising from 1 to 6 carbon atoms.

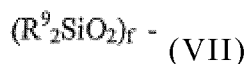
The compounds X and Y are in particular chosen from polyorganosiloxanes comprising alkoxysilane end groups, more specifically those which comprise two or more alkoxysilane end groups, preferably trialkoxysilane end groups.

These compounds X and/or Y preferably predominantly comprise units of formula:



in which R^9 independently represents a radical chosen from alkyl groups comprising from 1 to 6 carbon atoms, phenyl and fluoroalkyl groups, and s is equal to 0, 1, 2 or 3. Preferably, R^9 independently represents an alkyl group comprising from 1 to 6 carbon atoms. As alkyl group, mention may in particular be made of methyl, propyl, butyl, hexyl and mixtures thereof, preferably methyl or ethyl. As fluoroalkyl group, mention may be made of 3,3,3-trifluoropropyl.

According to one particular embodiment, the compounds X and Y, which are either identical or different, are polyorganosiloxanes comprising units of formula:

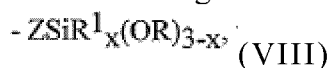


in which R^9 is as described above, preferably R^9 is a methyl radical, and

f is in particular such that the polymer has a viscosity at 25°C ranging from 0.5 to 3000 Pa.s, preferably ranging from 5 to 150 Pa.s, and/or

f is in particular a number ranging from 2 to 5000, preferably from 3 to 3000, even better still from 5 to 1000.

These polyorganosiloxane compounds X and Y comprise two or more trialkoxysilane end groups per polymer molecule, said groups having the following formula:



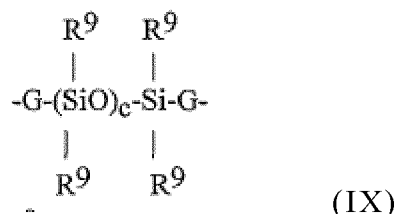
in which:

the R radicals independently represent a methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or isobutyl group, preferably a methyl or ethyl group,

5 R^1 is a methyl or ethyl group,

x is equal to 0 or 1, preferably x is equal to 0, and

Z is chosen from: divalent hydrocarbon-based groups not comprising any ethylenic unsaturation and comprising from 2 to 18 carbon atoms (alkylene groups), combinations of divalent hydrocarbon-based radicals and of siloxane segments of formula (IX) below:



R^9 being as described above, G is a divalent hydrocarbon-based radical not comprising any ethylenic unsaturation and comprising from 2 to 18 carbon atoms and c is an integer ranging from 1 to 6.

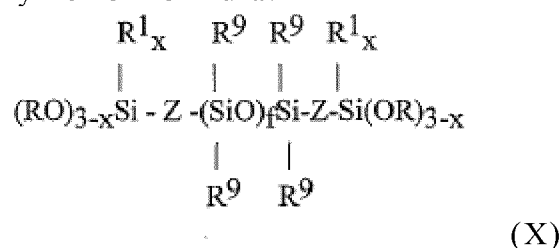
Z and G may be chosen in particular from alkylene groups such as ethylene, propylene, butylene, pentylene and hexylene, and arylene groups such as phenylene.

20 Preferably, Z is an alkylene group, and better still ethylene.

These polymers may have on average at least 1.2 trialkoxysilane end groups or end chains per molecule, and preferably on average at least 1.5 trialkoxysilane end groups per molecule. Since these polymers may have at least 1.2 trialkoxysilane end groups per molecule, some may comprise other types of end groups, such as end groups of formula $CH_2=CH-SiR^9_2-$ or of formula R^6_3-Si- , in which R^9 is as defined above and each R^6 group is independently chosen from R^9 groups or vinyl. As examples of such end groups mention may be made of trimethoxysilane, triethoxysilane, vinyl dimethoxysilane and vinylmethoxyphenylsilane groups.

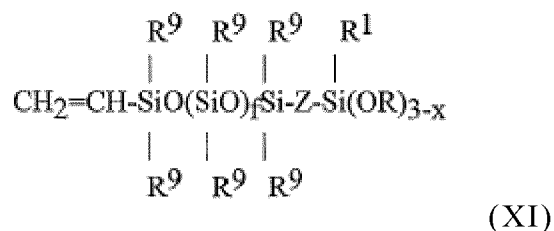
Such polymers are in particular described in US 3 175 993, US 4 772 675, US 4 871 827, US 4 888 380, US 4 898 910, US 4 906 719 and US 4 962 174, the content of which is incorporated into the present application by way of reference.

5 As compound X and/or Y, mention may in particular be made of the polymer of formula:



in which R, R¹, R⁹, Z, x and f are as described above.

10 The compounds X and/or Y may also comprise a blend of polymer of formula (X) above with polymers of formula (XI) below:



in which R, R¹, R⁹, Z, x and f are as described above.

15 When the polyorganosiloxane compound X and/or Y with alkoxyasilane group(s) comprises such a blend, the various polyorganosiloxanes are present in contents such that the organosilyl end chains represent less than 40%, preferably less than 25% by number of the end chains.

20 The polyorganosiloxane compounds X and/or Y that are particularly preferred are those of formula (X) described above. Such compounds X and/or Y are described, for example, in document WO 01/96450.

As indicated above, the compounds X and Y may be identical or different.

25 According to one variant, one of the 2 reactive compounds X or Y is silicone in nature and the other is organic in nature. For

example, the compound X is chosen from organic oligomers or polymers or organic/silicone hybrid oligomers or polymers, said polymers or oligomers comprising at least two alkoxysilane groups, and Y is chosen from silicone compounds such as the polyorgano-siloxanes described above. In particular, the organic oligomers or polymers are chosen from vinyl, (meth)acrylic, polyester, polyamide, polyurethane and/or polyurea, polyether, polyolefin or perfluoropolyether oligomers or polymers, and hyperbranched organic dendrimers and polymers, and mixtures thereof.

The organic polymers that are vinyl or (meth)acrylic in nature, bearing alkoxysilane side groups, may in particular be obtained by copolymerization of at least one vinyl or (meth)acrylic organic monomer with a (meth)acryloxypropyltrimethoxysilane, a vinyltrimethoxysilane, a vinyltriethoxysilane, an allyltrimethoxysilane, etc.

Mention may be made, for example, of the (meth)acrylic polymers described in the document by Kusabe, M, Pitture e Verniei – European Coating ; 12-B, pages 43-49, 2005, and in particular the polyacrylates with alkoxysilane groups referenced as MAX from Kaneka or those described in the publication by Probst, M, Adhesion-Kleben & Dichten, 2004, 481 (1-2), pages 12-14.

The organic polymers resulting from a polycondensation or a polyaddition, such as polyesters, polyamides, polyurethanes and/or polyureas, and polyethers, and bearing alkoxysilane side and/or end groups, may result, for example, from the reaction of an oligomeric prepolymer as described above with one of the following silane coreagents bearing at least one alkoxysilane group: aminopropyltrimethoxysilane, aminopropyltriethoxysilane, aminoethylaminopropyltrimethoxysilane, glycidoxypropyltriméthoxysilane, glycidoxypropyltriethoxysilane, epoxycyclohexylethyltrimethoxysilane, mercaptopropyltrimethoxysilane.

Examples of polyethers and polyisobutylenes with alkoxysilane groups are described in the publication by Kusabe, M., Pitture Verniei – European Coating; 12-B, pages 43-49, 2005. As examples of polyurethanes with alkoxysilane end groups, mention may

be made of those described in the document Probst, M., Adhesion-Kleben & Dichten, 2004, 481 (1-2), pages 12-14 or else those described in the document Landon, S., Pitture e Vernici vol. 73, No. 11, pages 18-24, 1997 or in the document Huang, Mow, Pitture e Vernici vol. 5, 2000, pages 61-67; mention may in particular be made of the polyurethanes with alkoxysilane groups from OSI-WITCO-GE.

By way of polyorganosiloxane compounds X and/or Y, mention may be made of resins of MQ or MT type themselves bearing alkoxysilane and/or silanol end groups, for instance the poly(isobutylsilsesquioxane) resins functionalized with silanol groups that are provided under the reference SST-S7C41 (3 Si-OH groups) by the company Gelest.

The condensation reaction can be carried out in the presence of a metal-based catalyst, a titanium-based catalyst.

Mention may in particular be made of the tetraalkoxytitanium-based catalysts of formula:



in which R^2 is chosen from tertiary alkyl radicals such as tert-butyl, tert-amyl and 2,4-dimethyl-3-pentyl; R^3 represents an alkyl radical comprising from 1 to 6 carbon atoms, preferably a methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or hexyl group, and Y is a number ranging from 3 to 4, better still from 3.4 to 4.

By way of example of a combination of compounds X and Y that bear alkoxysilane groups and react by condensation, mention may be made of the combination of the following mixtures A' and B' prepared by the company Dow Corning:

Mixture A':

Ingredient (INCI name)	CAS No.	<u>Contents</u> (%)	Function
bis-Trimethoxysiloxyethyl tetramethyldisiloxyethyl dimethicone (1)	PMN87176	25-45	Polymer

Silica silylate	68909-20-6	5-20	Filler
Disiloxane	107-46-0	30-70	Solvent

Mixutre B':

Ingredient (INCI name)	CAS No.	<u>Contents</u> (%)	Function
Disiloxane	107- 46-0	80-99	Solvent
Tetra-t-butyl titanate	-	1-20	Catalyst

5 It should, moreover, be noted that the identical compounds X and Y are combined in the mixture A'.

 According to one embodiment, the hydrophobic polymers are obtained following the reaction of the compounds X and Y that have reacted together by crosslinking in the presence of peroxide.

10 This reaction is preferably carried out by heating at a temperature greater than or equal to 50°C, preferably greater than or equal to 80°C, ranging up to 120°C.

 The compounds X and Y, which may be identical or different, comprise in this case two or more -CH₃ side groups and/or two or more side chains bearing a -CH₃ group.

15 The compounds X and Y are preferably silicone compounds and may be chosen, for example, from high-molecular-weight, non-volatile linear polydimethylsiloxanes, with a degree of polymerization of greater than 6, containing at least two -CH₃ side groups binded to the silicon atom and/or at least two side chains bearing a -CH₃ group. Mention may be made, for example, of the polymers described in the "Reactive Silicones" catalogue from the company Gelest Inc., edition 2004, page 6, and in particular the vinylmethylsiloxane-dimethylsiloxane copolymers (also referred to as gums) with molecular weights ranging from 500 000 to 900 000 and a viscosity of greater than 2 000 000 cSt.

20

25

By way of peroxides that can be used in the context of the invention, mention may be made of benzoyl peroxide and 2,4-dichlorobenzoyl peroxide, and mixtures thereof.

5 According to one embodiment, the hydrosilylation reaction or the condensation reaction or else the crosslinking reaction in the presence of a peroxide, between the compounds X and Y, is accelerated by supplying heat, for example by raising the temperature of the system to between 25°C and 180°C. The system will in particular react on keratin fibres.

10 Generally, irrespective of the type of reaction via which the compounds X and Y react together, the mole percentage of X relative to all of the compounds X and Y, i.e. the ratio $X/(X+Y) \times 100$, may range from 5% to 95%, preferably from 10% to 90%, even better still from 20% to 80%.

15 Similarly, the mole percentage of Y relative to all of the compounds X and Y, i.e. the ratio $Y/(X+Y) \times 100$, may range from 5% to 95%, preferably from 10% to 90%, even better still from 20% to 80%.

20 The compound X may have a weight-average molecular weight (Mw) ranging from 150 to 1 000 000, preferably from 200 to 800 000, more preferably from 200 to 250 000.

The compound Y may have a weight-average molecular weight (Mw) ranging from 200 to 1 000 000, preferably from 300 to 800 000, more preferably from 500 to 250 000.

25 The compound X may represent from 0.5% to 95% by weight relative to the total weight of the composition, preferably from 1% to 90% and better still from 5% to 80%.

30 The compound Y may represent from 0.05% to 95% by weight relative to the total weight of the composition, preferably from 0.1% to 90% and better still from 0.2% to 80%.

The ratio between the compounds X and Y may be varied so as to modify the rate of reaction and thus the rate of formation of the film, or alternatively so as to adapt the properties of the film formed

(for example its adhesive properties) according to the desired application.

In particular, the compounds X and Y may be present in an X/Y molar ratio ranging from 0.05 to 20 and better still from 0.1 to 10.

Preferably, the hydrophobic polymer(s) is (are) chosen from synthetic tensioning polymers of polyurethane and acrylic polymer interpenetrating polymer network (termed IPN) type in the form of an aqueous dispersion of particles.

In particular, the hydrophobic polymer(s) may be chosen from the non-neutralized acrylic acid/N-tert-butylacrylamide copolymers sold under the name Ultrahold Strong[®] by the company BASF, grafted silicone polymers such as propylthio(poly(methyl acrylate/methyl methacrylate/methacrylic acid))-grafted polydimethylsiloxane, and synthetic polymers of polyurethane and acrylic polymer interpenetrating polymer network (termed IPN) type in the form of an aqueous dispersion, in particular the polymer sold under the name Hybridur[®] 875 polymer dispersion by the company Air Products & Chemicals.

HYDROPHILIC FILM-FORMING POLYMERS

As indicated previously, zone A of the antiperspirant polymeric material is formed from one or more hydrophilic polymers.

5 The term “hydrophilic film-forming polymer” is intended to mean any polymer (1°) which is capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous or discontinuous and adherent film on a support, in particular on human keratin materials such as the skin, the hair, the eyelashes, the
10 eyebrows and the nails, and (2°) of which the film formed is capable of adsorbing a water content greater than 35%, preferably greater than or equal to 40% and more particularly greater than or equal to 60% by weight relative to the weight of the dry film of polymer (before immersion in water) when it is immersed in liquid water.

15 The content of water absorbed by the hydrophilic polymers according to the present invention can be measured under the same conditions as those described for the hydrophobic polymers.

 The hydrophilic polymer(s) used according to the invention is (are) film-forming polymers which are capable of forming, by
20 themselves or in the presence of an auxiliary film-forming agent, a continuous film capable of adhering to a support, in particular to the skin.

 The hydrophilic film-forming polymer(s) is (are) chosen from polyurethanes, vinyl polymers and natural polymers, and blends
25 thereof.

 The polyurethanes used according to the invention may be chosen from film-forming polyurethanes.

 The polyurethanes may be aliphatic, cycloaliphatic or aromatic polyurethane, polyurea-urethane or polyurea copolymers, comprising,
30 alone or as a mixture:

 - at least one block of aliphatic and/or cycloaliphatic and/or aromatic polyester origin, and/or

 - at least one branched or non-branched silicon block, for example polydimethylsiloxane or polymethylphenylsiloxane, and/or

- at least one block comprising fluoro groups.

The film-forming polyurethanes that can be used in the invention may also be obtained from branched or non-branched polyesters or from alkyls comprising labile hydrogens, which are modified by reaction with a diisocyanate and a difunctional organic compound (for example dihydroxy, diamino or hydroxyamino), also comprising either a carboxylic acid or carboxylate group, or a sulphonic acid or sulphonate group, or alternatively a neutralizable tertiary amine group or a quaternary ammonium group.

With a view to forming the polyurethane, monomers bearing an anionic group that can be used during the polycondensation include dimethylolpropionic acid, trimellitic acid or a derivative such as trimellitic anhydride, the sodium salt of 3-sulphopentanediol, and the sodium salt of 5-sulpho-1,3-benzenedicarboxylic acid.

Preferably, the monomer bearing an anionic group is dimethylolpropionic acid.

As film-forming polyurethanes that can be used according to the invention, mention may thus be made of the aqueous dispersions of polyurethane that are sold under the names Avalure UR-405[®], Avalure UR-410[®], Avalure UR-425[®] and Avalure UR-450[®] by the company Goodrich.

The film-forming polyurethanes may also be chosen from film-forming elastomeric polyurethanes capable of producing, by drying of said polyurethane(s), at ambient temperature and at a relative humidity of 55%, a material having a mechanical profile defined by at least:

- a) a degree of elongation at break (ϵ) greater than or equal to 150%,
- b) an instantaneous recovery (R_i) greater than or equal to 75% after an elongation of 150%,
- c) a recovery at 300 seconds (R_{300s}) greater than 80%, after an elongation of 150%.

The material obtained by drying said film-forming polyurethane(s) is therefore sufficiently extensible so as not to break

following the deformations caused by the movements of the skin and to regain a shape substantially identical to its initial shape.

For the purpose of the present invention, the instantaneous recovery (R_i) of a material defines the capacity of said material to
5 regain its initial shape or a shape substantially identical to its initial shape after having been deformed following an elongation during a tensile stress. The recovery of the material is also measured as a percentage.

For the purpose of the present invention, the degree of
10 elongation at break and the recovery are evaluated by means of the tensile tests described hereinafter.

To perform the tensile tests, a film intended for preparing test specimens is prepared by placing in a Teflon matrix the sufficient amount of mixture comprising the film-forming elastomeric
15 polymer(s) to obtain a film $500\text{ }\mu\text{m} \pm 50\text{ }\mu\text{m}$ thick. Drying is continued until the weight of the film no longer changes, which may typically take 12 days.

In particular, for the purpose of the present invention, the expression “film intended for preparing or producing test specimens”
20 is intended to mean a film obtained by drying said film-forming elastomeric polymer(s), at ambient temperature ($22^\circ\text{C} \pm 2^\circ\text{C}$) and at a relative humidity of $55\% \pm 5\%$, from a mixture containing at least 3% of active materials, i.e. 3% by weight of polyurethanes relative to the total weight of the mixture.

When the mixture used to prepare the film for the production of test specimens contains less than 3% by weight of active materials, a preliminary concentration operation is performed, for example by
25 evaporating off some of the solvent so that the mixture contains at least 3% of elastomeric polymers. This operation makes it possible to
30 avoid excessively long drying.

The film obtained is then cut up into rectangular test specimens 80 mm long and 15 mm wide.

The tests are carried out on an apparatus sold under the name Lloyd or sold under the name Zwick, under the same temperature and

humidity conditions as for the drying, i.e. at ambient temperature ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$) and at a relative humidity of $55\% \pm 5\%$.

The test specimens are drawn at a speed of 20 mm/min and the distance between the jaws is 50 ± 1 mm.

5 To determine the instantaneous recovery (R_i), the process is performed as follows:

- the test specimen is drawn by 150% ($\epsilon_{\max}$), i.e. 1.5 times its initial length (I_0),

10 - the stress is released by applying a return speed equal to the tensile speed, i.e. 20 mm/min, and the elongation of the test specimen is measured as a percentage, after returning to zero load (ϵ_i).

The percentage instantaneous recovery (R_i) is given by the formula below:

$$R_i = ((\epsilon_{\max} - \epsilon_i) / \epsilon_{\max}) \times 100$$

15 To determine the recovery at 300 seconds, the test specimen having undergone the preceding operations is maintained at zero stress for a further 300 seconds, and its degree of elongation is measured as a percentage (ϵ_{300s}). In other words, the recovery at 300 seconds corresponds to the residual degree of elongation of the test specimen
20 300 seconds after returning to zero load (ϵ_i).

Thus, the recovery at 300 seconds (R_{300s}) of a material defines the capacity of said material to regain its shape or a shape substantially identical to its initial shape a further 300 seconds after the return to zero load (ϵ_i) and after having been deformed following
25 an elongation during a tensile stress.

The percentage recovery at 300 seconds (R_{300s}) is therefore given by the formula below:

$$R_{300s} = ((\epsilon_{\max} - \epsilon_i) / \epsilon_{300s}) \times 100$$

30 Advantageously, the film-forming elastomeric polyurethane(s) according to the invention is (are) such that it (they) form(s), under the conditions of the tests described above, a material having a degree of elongation at break (ϵ) greater than 150%, preferably at least

greater than 250%, and even more preferentially ranging from 250% to 1000%, an instantaneous recovery (R_i) ranging from 75% to 100% and a recovery at 300 seconds (R_{300s}) ranging from 80% to 100%, preferably from 90% to 100%.

5 Preferably, the film-forming elastomeric polyurethanes are chosen from copolymers obtained by copolymerization of hexanediol, neopentyl glycol, adipic acid, hexamethylene diisocyanate, N-(2-aminoethyl)-3-aminoethanesulphonic acid and ethylenediamine.

10 Preferably, the polyurethanes may also be chosen from copolymers obtained by copolymerization of adipic acid, dicyclohexylmethane diisocyanate, ethylenediamine, hexanediol, neopentyl glycol and sodium N-(2-aminoethyl)-3-aminoethanesulphonate.

15 In particular, the polyurethanes are chosen from those sold under the name Baycusan C1001 or C1004, and more particularly the product sold under the name Baycusan C1001.

 The hydrophilic polymer(s) may be chosen from vinyl polymers.

20 Preferably, the vinyl polymer(s) is (are) chosen from polyvinyl alcohols, copolymers derived from C_4 - C_8 monounsaturated carboxylic acids or anhydrides, and methyl vinyl ether/butyl monomaleate copolymers.

 For the purpose of the present invention, the term "polyvinyl alcohol" is intended to mean a polymer comprising $-CH_2CH(OH)-$ units.

25 The polyvinyl alcohols are generally produced by hydrolysis of polyvinyl acetate. Most commonly, the reaction takes place in the presence of methanol (alcoholysis). The reaction is normally catalysed by acid catalysis or basic catalysis. The degree of hydrolysis of the commercial products is variable, often around 87%,
30 but products with a 100% degree of hydrolysis also exist. Copolymers with monomers other than vinyl acetate also exist, such as ethylene/vinyl alcohol copolymers.

 The polyvinyl alcohol polymers are preferably chosen from homopolymers or copolymers with vinyl acetate, the latter

corresponding in particular to a partial hydrolysis of polyvinyl acetate.

Use may, for example, be made of the products of the Celvol range provided by the company Celanese under the names Celvol 540, Celvol 350, Celvol 325, Celvol 165, Celvol 125, Celvol 540 S, Celvol 840 and Celvol 443.

Preferably, the polyvinyl alcohols are chosen from the products sold under the name Celvol 540 by the company Celanese.

The copolymer(s) derived from C₄-C₈ monounsaturated carboxylic acids or anhydrides may be chosen from copolymers comprising (i) one or more maleic, fumaric or itaconic acids or anhydrides and (ii) one or more monomers chosen from vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, and acrylic acid and its esters, the anhydride functions of these copolymers being optionally monoesterified or monoamidated.

Such polymers are described in particular in patents US 2 047 398, 2 723 248 and 2 102 113 and patent GB 839 805, and in particular those sold under the names Gantrez AN or ES and Advantage CP by the company ISP, having the INCI name: Butyl Ester of PVM/MA Copolymer.

Preferably, the copolymer(s) derived from C₄-C₈ monounsaturated carboxylic acids or anhydrides is (are) chosen from the monoesterified methyl vinyl ether/maleic anhydride copolymers sold, for example, under the name Gantrez ES 225 by the company ISP.

The hydrophilic polymer(s) may also be chosen from natural polymers, in particular polysaccharides which have monosaccharides or disaccharides as base units.

The natural polymers are preferably chosen from guar gums and modified guar gums, celluloses, and gellan gum and its derivatives.

The guar gums are galactomannans consisting of mannose and galactose.

For the purpose of the present invention, the term “modified guar gum” is intended to mean guar gums alkylated with at least one C₁-C₈ alkyl group, guar gums hydroxyalkylated with at least one C₁-C₈ hydroxyalkyl group and guar gums acylated with at least one C₁-C₈ acyl group.

Preferably, these are hydroxypropylated guar gums such as the product sold under the name Jaguar HP 105 by the company Rhodia.

The cellulose is a β 1-4-polyacetal of cellobiose, cellobiose being a disaccharide consisting of two glucose molecules.

The cellulose derivatives may be anionic, cationic, amphoteric or nonionic. Among these derivatives, cellulose ethers, cellulose esters and cellulose ester-ethers are distinguished.

Among the nonionic cellulose ethers, mention may be made of alkylcelluloses such as methylcelluloses and ethylcelluloses; hydroxyalkylcelluloses such as hydroxymethylcelluloses, hydroxyethylcelluloses and hydroxypropylcelluloses; and mixed hydroxyalkylalkylcelluloses such as hydroxypropylmethylcelluloses, hydroxyethylmethylcelluloses, hydroxyethylethylcelluloses and hydroxybutylmethylcelluloses.

Among the anionic cellulose ethers, mention may be made of carboxyalkylcelluloses and salts thereof. By way of example, mention may be made of carboxymethylcelluloses, carboxymethylmethylcelluloses and carboxymethylhydroxyethylcelluloses and sodium salts thereof. Among the cationic cellulose ethers, mention may be made of crosslinked or noncrosslinked, quaternized hydroxyethylcelluloses. The quaternizing agent may in particular be glycidyltrimethylammonium chloride or a fatty amine such as laurylamine or stearylamine. Another cationic cellulose ether that may be mentioned is hydroxyethylcellulosehydroxypropyltrimethylammonium. Among the cellulose esters are inorganic cellulose esters (cellulose nitrates, sulphates or phosphates, etc.), organic cellulose esters (cellulose monoacetates, triacetates, amidopropionates, acetate butyrates, acetate propionates or acetate trimellitates, etc.) and mixed organic/inorganic

cellulose esters such as cellulose acetate butyrate sulphates and acetate propionate sulphates.

Among the cellulose ester-ethers, mention may be made of hydroxypropylmethylcellulose phthalates and ethylcellulose sulphates.
5 The cellulose-based compounds of the invention may be chosen from unsubstituted celluloses and substituted celluloses.

The celluloses and derivatives are represented, for example, by the products sold under the names Avicel[®] (microcrystalline cellulose, MCC) by the company FMC Biopolymers, under the name Cekol
10 (carboxymethylcellulose) by the company Noviant (CP-Kelco), under the name Akucell AF (sodium carboxymethylcellulose) by the company Akzo Nobel, under the name Methocel[™] (cellulose ethers) and Ethocel[™] (ethylcellulose) by the company Dow, and under the names Aqualon[®] (carboxymethylcellulose and sodium carboxymethyl-
15 cellulose), Benecel[®] (methylcellulose), Blanose(TM) (carboxymethylcellulose), Culminai[®] (methylcellulose, hydroxypropylmethylcellulose), Klucel[®] (hydroxypropylcellulose), Polysurf[®] (cetylhydroxyethylcellulose) and Natrosol[®] CS (hydroxyethylcellulose) by the company Hercules Aqualon.

20 Gellan gum is a polysaccharide produced by aerobic fermentation of *Sphingomonas elodea*, more commonly known as *Pseudomonas elodea*. This linear polysaccharide is made up of the sequence of the following monosaccharides: D-glucose, D-glucuronic acid and L-rhamnose. In the natural state, gellan gum is highly
25 acylated.

The gellan gum preferably used in the film according to the present invention is a gellan gum that is at least partially deacylated. This at least partially deacylated gellan gum is obtained by high-temperature alkaline treatment. A solution of KOH or of NaOH will,
30 for example, be used.

The purified gellan gum sold under the trade name Kelcogel[®] by the company Kelco is suitable for preparing the compositions according to the invention.

The gellan gum derivatives are all products obtained by carrying out conventional chemical reactions, such as in particular esterifications, addition of a salt of an organic or inorganic acid.

Welan gum is used, for example, as a gellan gum derivative.
5 Welan gum is a gellan gum modified by fermentation by means of *Alcaligenes* strain ATCC 31 555. Welan gum has a recurring pentasaccharide structure formed from a main chain consisting of D-glucose, D-glucuronic acid and L-rhamnose units, onto which a pendant L-rhamnose or L-mannose unit is grafted.

10 The welan gum sold under the trade name Kelco Crete[®] by the company Kelco is suitable for preparing the compositions according to the invention.

As other saccharide polymers that can be used according to the invention, mention may be made of starches and derivatives thereof.

15 Preferably, the natural polymer(s) is (are) chosen from celluloses and derivatives thereof, in particular those sold under the name Avicel[®] (microcrystalline cellulose, MCC) by the company FMC Biopolymers.

20 The hydrophilic polymers may also be chosen from acrylate and methacrylate copolymers.

Preferably, the hydrophilic polymer(s) is (are) chosen from the polyurethanes sold under the name Baycusan C1004 and Baycusan C1001 by the company Bayer Material Science.

25 The antiperspirant polymeric material according to the present invention is a thin solid which can be grasped. The term "thin" is intended to mean a solid having a thickness of at most 100 μm . This material generally has a suitable size so that it can be easily handled by the user. It may have a square, rectangular or disc shape or any other shape.

30 Each layer of polymer has a thickness ranging from 1 to 100 μm , preferably ranging from 5 to 50 μm .

According to one embodiment, the antiperspirant polymeric material according to the present invention comprises at least one layer A superimposed on at least one layer B, the layer A being

formed from at least one hydrophilic film-forming polymer and the layer B being formed from at least one non-pressure-sensitive-adhesive, hydrophobic film-forming polymer,

5 (i) said non-pressure-sensitive-adhesive, hydrophobic film-forming polymer(s) being chosen from polymers of polyurethane and acrylic polymer interpenetrating polymer network (termed IPN) type in the form of an aqueous dispersion of particles, non-neutralized acrylic acid/N-tert-butylacrylamide copolymers, grafted silicone polymers, and polymers obtained following reaction between one or more
10 compounds X and one or more compounds Y, at least one of the compounds X and Y being a silicone compound, said compounds X and Y having reacted together via a hydrosilylation reaction, or a condensation reaction or a crosslinking reaction in the presence of peroxide when they are brought into contact with one another, and

15 (ii) said hydrophilic film-forming polymer(s) being chosen from polyurethanes, vinyl polymers, natural polymers, and alkyl acrylate and methacrylate copolymers.

The antiperspirant polymeric material may be deposited without distinction on the hydrophobic side in contact with the skin
20 and on the hydrophilic external face side, or conversely.

Preferably, the antiperspirant polymeric material according to the present invention comprises:

- a layer A formed from one or more hydrophilic film-forming polymers chosen from film-forming elastomeric polyurethanes, in
25 particular copolymers obtained by copolymerization of adipic acid, dicyclohexylmethane diisocyanate, ethylenediamine, hexanediol, neopentyl glycol and sodium N-(2-aminoethyl)-3-aminoethanesulphonate,

- a layer B formed from one or more hydrophobic film-forming
30 polymers chosen from non-neutralized acrylic acid/N-tert-butylacrylamide copolymers, and polymers of polyurethane and acrylic polymer interpenetrating polymer network (termed IPN) type in the form of an aqueous dispersion.

According to another particular embodiment, the antiperspirant polymeric material according to the present invention comprises:

5 - a layer A formed from one or more hydrophilic film-forming polymers chosen from film-forming elastomeric polyurethanes, in particular copolymers obtained by copolymerization of adipic acid, dicyclohexylmethane diisocyanate, ethylenediamine, hexanediol, neopentyl glycol and sodium N-(2-aminoethyl)-3-aminoethane-sulphonate, and

10 - a layer B formed from one or more hydrophobic film-forming polymers chosen from the non-neutralized acrylic acid/N-tert-butylacrylamide copolymers sold under the name Ultrahold Strong[®] by the company BASF.

15 The antiperspirant polymeric material according to the present invention may also comprise one or more additional adhesive zones.

In other words, the antiperspirant polymeric material may comprise at least two zones of polymers A and B and one adhesive zone.

20 Preferably, the adhesive zone(s) may be formed from pressure-sensitive adhesive compounds.

25 Preferably, the pressure-sensitive adhesive compounds according to the invention do not encompass oils, in particular hydrocarbon-based oils, vegetable oils or silicone oils. In other words, the pressure-sensitive adhesive compounds are not oils, and in particular hydrocarbon-based oils, vegetable oils or silicone oils.

The pressure-sensitive adhesive compounds may be chosen from adhesive organic polymers.

30 The adhesive nature of an organic polymer is generally linked to the glass transition temperature thereof. A necessary but not sufficient condition for a polymer to be adhesive is that of having a glass transition temperature (T_g) significantly below ambient temperature, i.e. below a temperature equal to 25°C.

The adhesive organic polymers used in the present invention preferably have a glass transition temperature (T_g) of less than or equal to 10°C , preferably of less than or equal to 0°C .

5 The glass transition temperature (T_g) of the adhesive organic polymers according to the present invention can be measured by differential scanning calorimetry (DSC) under the following conditions:

10 To measure the glass transition temperature, a film having a thickness of approximately 150 μm of the test polymer is prepared by depositing an aqueous solution or dispersion of the polymer in a circular Teflon mould 40 mm in diameter and by leaving the deposit to dry. The film is dried in an oven at a temperature of approximately 23°C with a relative humidity of 45%, until the weight no longer changes. Approximately 5 to 15 mg of the film are sampled and placed
15 in a crucible which is then placed in the analyser. The thermal analyser is a model DSC-2920 from the company TA Instruments. The initial and final temperatures of the temperature scanning are chosen so as to frame the desired glass transition temperature. The temperature scanning is carried out at a speed of $10^\circ\text{C}/\text{minute}$.

20 This analysis is performed according to standard ASTM D3418-97 except for the modifications above.

The adhesive organic polymers used in the present invention preferably have a self-adhesiveness such that the tensile force (F_{max} in newtons (N)) necessary to separate two surfaces coated with said
25 polymer is greater than 1N, preferably greater than 3N and in particular greater than 5N.

30 The tensile force F_{max} can be measured under the following conditions: two discs each having a surface area of 38 mm^2 , made of a rigid, inert and nonabsorbent solid material, preferably glass, are coated with a layer of the adhesive polymer to be tested. The polymer is deposited in an amount of $500\text{ }\mu\text{g}/\text{mm}^2$ from a solution in an appropriate solvent. After evaporating said solvent for 24 hours at 22°C under a relative humidity of 50%, the two coated surfaces of the discs are superimposed and the discs are pressed against one another

for 20 seconds at a pressure of 3 newtons using a Lloyd model LR5K extensometer.

The stuck discs are then pulled apart at a rate of 20 mm/minute and the tensile force is continuously recorded. The maximum tensile force, recorded at the moment of the separation of the two surfaces, referred to as $F_{\max}$, characterizes the self-adhesiveness of the polymer. The greater this force, the greater the self-adhesiveness of the polymer.

The adhesive polymers that can be used for the present invention can also be characterized by their adhesiveness on an inert material, such as glass. This adhesiveness can be expressed in the form of energy (E_s) supplied by the same extensometer (Lloyd model LR5K) to separate two surfaces with an area of 38 mm^2 each coated with said adhesive organic polymers, under the conditions above ($500 \mu\text{g}/\text{mm}^2$, dried for 24 hours at 22°C , 50% RH) of an adhesive polymer, from a surface made of polished glass, after compression of these two surfaces for 30 seconds with a force of 3 newtons. As above, the pull speed is 20 mm/min.

This energy E_s , corresponding to the sum of the work supplied up to separation, can be calculated according to the following formula:

$$\int_{X_{s1} + 0,05}^{X_{s2}} F(x) dx$$

in which:

$F(x)$ is the force necessary to produce a displacement (x),
 X_{s1} is the displacement (expressed in mm) produced by the maximum tensile force, and

X_{s2} is the displacement (expressed in mm) produced by the tensile force which makes possible complete separation of the two surfaces.

For the adhesive polymers used in the present invention, the separation energy E_s is preferably at most equal to 300 μJ , preferably at most equal to 250 μJ .

5 Thus, in order for the organic polymers according to the invention to be adhesive, the polymer deposit must therefore have the adhesiveness and/or self-adhesiveness characteristics as described above.

10 The adhesive polymer(s) may be chosen from silicone adhesive polymers, polyacrylic adhesive polymers such as adhesive polyesters having one or more sulphonic functions, or polyvinyls.

In particular, the adhesive polymers according to the invention may be chosen from adhesive polyesters having one or more sulphonic functions, in particular adhesive branched polyesters having one or more sulphonic functions.

15 More preferentially, the adhesive polymer according to the present invention corresponds to the branched sulphonic polyester sold by the company Eastman under the name AQ 1350. Such a branched sulphonic polyester is adhesive and is defined by a glass transition temperature (T_g) of 0°C and a maximum tensile force F_{max} equal to 23
20 newtons.

The adhesive layer has a thickness that can range from 1 to 100 μm , preferably ranging from 1 to 20 μm .

25 The adhesive zone may also comprise one or more additional active agents chosen from deodorant active agents such as cyclodextrins, fragrances, antibacterial active agents such as bacteriocins, zinc pidolate, odour absorbers such as zeolite, skincare agents, soothing agents, agents for reducing skin irritation, hair regrowth inhibitors, and mixtures thereof.

30 The additional active agent(s) may be present in the adhesive layer in contents ranging from 0.001 to 5% by weight, relative to the total weight of the adhesive zone.

According to one embodiment, the antiperspirant cosmetic material is a layer comprising at least two zones A and B as previously defined and at least one adhesive zone.

According to another embodiment, the antiperspirant cosmetic material comprises at least two layers A and B as previously defined, superimposed on one another, and an adhesive layer.

Preferably, the adhesive zone corresponds to an adhesive layer.

5 When the antiperspirant polymeric material also comprises an adhesive layer made up of one or more adhesive organic polymers having a glass transition temperature of less than 20°C, then the material is applied by bringing the skin into contact with the face of the adhesive layer.

10 When the antiperspirant polymeric material does not comprise an adhesive zone in its structure, pretreatment of the skin is carried out with an ethanol- or water-based solution in order to impart adhesion of the film on the skin via an effect of partial and limited solubilization of the layer brought into contact with the skin.

15 The antiperspirant polymeric material according to the present invention may also comprise one or more plasticizers in order to modulate the mechanical properties of the film.

20 Among the preferred plasticizers, mention may in particular be made of glycol ethers, benzyl alcohol, triethyl citrate, 1,3-butylene glycol, dipropylene glycol and propylene carbonate.

The antiperspirant polymeric material may also comprise fillers such as perlite or porous silica in order to modulate the permeability to water vapour or to modify the optical and mechanical properties.

25 The antiperspirant polymeric material may be provided between a peelable support, such as a polyethylene terephthalate film, the surface of which is film-coated, and a protective film in order to facilitate its storage and its positioning on the skin.

30 After having placed the material on the skin, various cosmetic compositions can be applied to the surface of the skin that is covered by the polymeric material of the present invention, in particular to the base layer of polyurethane elastomer.

The antiperspirant polymeric material can be cut up into varying geometrical shapes depending on the areas to which it is desired to apply the film.

5 In particular, the antiperspirant polymeric material may be applied to the area under the arms or at the level of the vertebral column in order to confer an antiperspirant effect.

The polymeric material may be cut up into rectangles or circles before being applied to the skin.

10 The present invention also relates to the use on the skin of an antiperspirant cosmetic polymeric material for the cosmetic treatment of human perspiration.

15 Another subject of the present invention consists of an antiperspirant polymeric cosmetic material comprising at least two zones A and B, zone A being formed from at least one hydrophilic film-forming polymer and zone B being formed from at least one non-pressure-sensitive-adhesive, hydrophobic film-forming polymer.

As previously indicated, the polymeric cosmetic material may be applied in a single step directly to the skin or in two steps so as to form the material on the skin.

20 According to another particular embodiment, the antiperspirant polymeric material according to the present invention comprises:

- a layer A formed from one or more film-forming hydrophilic polymers chosen from film-forming elastomeric polyurethanes, in particular copolymers obtained by copolymerization of adipic acid, dicyclohexylmethane diisocyanate, ethylenediamine, hexanediol, neopentyl glycol and sodium N-(2-aminoethyl)-3-aminoethanesulphonate, and

25

- a layer B formed from one or more film-forming hydrophobic polymers chosen from the non-neutralized acrylic acid/N-tert-butylacrylamide copolymers sold under the name Ultrahold Strong[®] by the company BASF.

30

The following examples serve to illustrate the present invention.

EXAMPLES

Example 1

a) An antiperspirant material is prepared in the following way:

5

An ethanol/water (50/50) aqueous-alcoholic solution containing 3% by weight of a branched sulphonic polyester sold by the company Eastman under the name AQ1350 is sprayed onto a siliconized sheet of paper constituting the detachable protective film coating, so as to form an adhesive layer.

10

On a polytetrafluoroethylene-based support, a first layer is formed from an aqueous solution containing 40% by weight of active material of polyurethane-35 sold under the name Baycusan C1004 by the company Bayer Material Science, and then, after drying this first layer, an aqueous solution containing 40% by weight of active materials of a non-neutralized acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymer, such as the product sold under the name Ultrahold Strong[®] by the company BASF, is deposited.

15

The antiperspirant material is prepared by laminating the adhesive layer and the stratified polymer layers.

20

The antiperspirant material and the protective film are removed from the support, the assembly is placed on the skin on the adhesive side, and then the protective film is removed.

25

Antiperspirant effectiveness is noted according to the effectiveness test defined below.

Firstly, the pre-cut polymeric material is applied to the underarm area and antiperspirant effectiveness is noted.

30

Secondly, 1 gram of the polymeric material is applied to the left arm over a surface area of approximately 10 cm². On the other arm, 1 gram of an aluminium salt-based composition (Narta Pole extreme) is applied over a surface area of approximately 10 cm².

After a period of 10 minutes spent in a sauna (48° without added humidity), the arms have perspired a great deal. The appearance

is much wetter on the side treated with the aluminium salt-based composition than on the side treated with the film.

After touching the skin, the area treated with the film gives a smooth and relatively dry feel. The area treated with the aluminium salt-based composition gives a very wet feel.

b) The antiperspirant polymeric material prepared in step a) makes it possible to provide good results which are measured using a Skinchip[®] apparatus.

The Skinchip[®] apparatus thus makes it possible to evaluate and compare the antiperspirant effectiveness of active agents by evaporimetry after one hour and to evaluate the persistence after 4 hours.

On a panel consisting of 22 volunteers having a broad flat back with skin ranging from normal to dry, measurement areas are delimited on the back ($3 \times 2.5 \text{ cm}^2$), in particular 16 areas treated with the polymeric material a) and 8 untreated control areas. Initially, the 22 volunteers are placed in a room for 30 minutes at a temperature of 22°C . The sebum is measured and the images are acquired before applying the product.

The polymeric material is applied to the 16 areas and then left to dry. The images of the treated and untreated areas are acquired.

A first round of sweating is carried out for one hour at 40°C . The cutaneous evaporation is measured and then the images of the treated and untreated areas are acquired. There is a pause of 2 hours in a room at 22°C . A second round of sweating is carried out for one hour at 40°C and then the images of the treated and untreated areas are acquired.

The amount applied to each area is 33 milligrams, which corresponds to an amount of 3.75 mg/cm^2 .

The Skinchip[®] apparatus is an apparatus which measures impedance and which retranscribes it into greyscale. It consists of a matrix of sensors measuring electrical permittivity. The latter depends on the moisturization of the skin and on the skin/sensor distance. Each

sensor of the matrix gives coded information which then constitutes a black and white image. The black pixels correspond to moisturized skin and/or to contact between the surface of the probe and the skin. The white pixels correspond to dry skin and/or to the probe being remote from the skin (wrinkle, groove).

After analysis of the ratio between black and white, it is possible to determine the state of moisturization of the skin but also its texture and its relief (wrinkles). For acquisition, the sensor is placed on the area studied (size of the area: $3 \times 2.5 \text{ cm}^2$). The surface of the skin can be visualized on the screen by means of the image acquisition software.

The images show that very good results are obtained for the polymeric material a).

After one hour at 40°C , the cutaneous evaporation is measured and then there is a pause for 2 hours in a room at 22°C .

CLAIMS

1. Process for cosmetic treatment of human perspiration, and optionally underarm odours, in which an antiperspirant polymeric cosmetic material comprising at least two zones A and B is applied to the skin, zone A being formed from at least one hydrophilic film-forming polymer and zone B being formed from at least one non-pressure-sensitive-adhesive, hydrophobic film-forming polymer.
2. Treatment process according to Claim 1, characterized in that the cosmetic material is a layer comprising at least two adjacent zones A and B.
3. Treatment process according to Claim 1, characterized in that the cosmetic material comprises at least two layers A and B superimposed on one another.
4. Treatment process according to any one of Claims 1 to 3, characterized in that the hydrophobic film-forming polymer(s) is (are) a synthetic hydrophobic polymer or synthetic hydrophobic polymers chosen from:
- (i) polymers of interpenetrating polymer network type;
 - (ii) grafted silicone polymers;
 - (iii) non-neutralized (meth)acrylic acid/N-tert-butylacrylamide copolymers;
 - (iv) non-neutralized crotonic acid/vinyl acetate copolymers;
 - (v) tetrapolymers of (meth)acrylic acid, of (meth)acrylates and of C₈-C₂₄ alkyl (meth)acrylate;
 - (vi) polymers which were obtained following reaction between one or more compounds X and one or more compounds Y, at least one of the compounds X and Y being a silicone compound, said compounds X and Y having reacted together via a hydrosilylation reaction or a condensation reaction or a crosslinking reaction in the presence of peroxide when they were brought into contact with one another;
 - (vii) blends thereof.

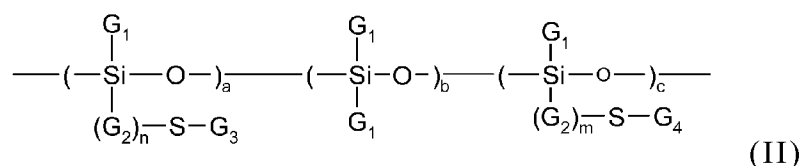
5. Treatment process according to Claim 4, characterized in that the polymers are polymers of interpenetrating polymer network type comprising a polyurethane polymer and an acrylic polymer.

6. Treatment process according to Claim 4, characterized in that:

- the non-neutralized (meth)acrylic acid/N-tert-butylacrylamide copolymers are chosen from non-neutralized acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymers, and

- the non-neutralized crotonic acid/vinyl acetate copolymer is the vinyl acetate/crotonic acid/vinyl tert-butyl-4-benzoate (65/10/25) terpolymer in non-neutralized form.

7. Treatment process according to Claim 4, characterized in that the grafted silicone polymers are silicone polymers with a polysiloxane backbone grafted with non-silicone organic monomers, said silicone polymers comprising in their structure the following unit of formula (II):



in which the G_1 radicals, which may be identical or different, represent hydrogen or a $\text{C}_1\text{-C}_{10}$ alkyl radical or else a phenyl radical; the G_2 radicals, which may be identical or different, represent a $\text{C}_1\text{-C}_{10}$ alkylene group; G_3 represents a polymeric residue resulting from the (homo)polymerization of at least one ethylenically unsaturated anionic monomer; G_4 represents a polymeric residue resulting from the (homo)polymerization of at least one ethylenically unsaturated hydrophobic monomer; m and n are, independently of one another, equal to 0 or 1; a is an integer ranging from 0 to 50; b is an integer that may be included between 10 and 350, c is an integer ranging from 0 to 50; with the proviso that one of the parameters a and c is other than 0.

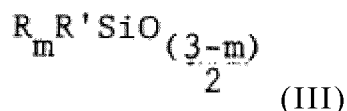
8. Treatment process according to Claim 7, characterized in that the grafted silicone polymers corresponding to formula (II) are

polydimethylsiloxanes (PDMSs) onto which are grafted, by means of a connecting link of thiopropylene type, polymer units of the poly((meth)acrylic acid) type and/or of the poly(alkyl, in particular C₁-C₃, or even C₁, alkyl, (meth)acrylate) type.

5 9. Treatment process according to Claim 4, characterized in that the film-forming hydrophobic polymer(s) is (are) capable of being obtained following reaction between one or more compounds X and one or more compounds Y, at least one of the compounds X and Y being a silicone compound, said compounds X and Y having reacted
10 together via a hydrosilylation reaction or a condensation reaction or a crosslinking reaction in the presence of peroxide when they are brought into contact with one another.

10. Treatment process according to Claim 9, characterized in that the compounds X and Y have reacted together via hydrosilylation.

15 11. Treatment process according to Claim 10, characterized in that the compound X is a polyorganosiloxane comprising a silicone main chain comprising two or more unsaturated aliphatic groups, each bonded to a silicon atom, in particular polyorganosiloxanes comprising siloxane units of formula:



20

in which:

- R represents a linear or cyclic, monovalent hydrocarbon-based group comprising from 1 to 30 carbon atoms, preferably from 1
25 to 20, and better still from 1 to 10 carbon atoms, such as, for example, a short-chain alkyl radical comprising, for example, from 1 to 10 carbon atoms, in particular a methyl radical or else a phenyl group, preferably a methyl radical;

-m is equal to 1 or 2; and

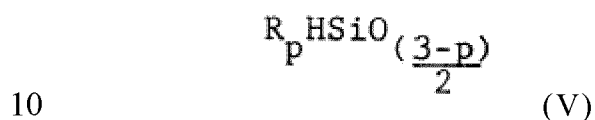
30 -R' represents:

- an unsaturated aliphatic hydrocarbon-based group comprising from 2 to 10, preferably from 2 to 5 carbon atoms, such as, for example, a vinyl group or an -R''-CH=CHR''' group in which

R'' is a divalent aliphatic hydrocarbon-based chain comprising from 1 to 8 carbon atoms, which is bonded to the silicon atom, and R''' is a hydrogen atom or an alkyl radical comprising from 1 to 4 carbon atoms,

- 5 • an unsaturated cyclic hydrocarbon-based group comprising from 5 to 8 carbon atoms, such as, for example, a cyclohexenyl group.

12. Treatment process according to Claim 10, characterized in that the compound Y is chosen from organosiloxanes comprising one or more alkylhydrogenosiloxane units of formula below:



in which:

R represents a linear or cyclic, monovalent hydrocarbon-based group comprising from 1 to 30 carbon atoms or a phenyl group, and p is equal to 1 or 2.

- 15 13. Treatment process according to Claim 9, characterized in that the compounds X and Y have reacted together via condensation, it being possible for the compounds X and Y to be chosen from silicon compounds of which the main chain comprises two or more alkoxysilane groups and/or at least two silanol (Si-OH) groups, on the
20 side and/or at the end of the chain.

14. Treatment process according to Claim 9, characterized in that the compounds X and Y have reacted together via crosslinking in the presence of peroxide.

- 25 15. Treatment process according to any one of the preceding claims, characterized in that the hydrophilic film-forming polymers are chosen from polyurethanes, vinyl polymers, natural polymers, and alkyl acrylate and methacrylate copolymers, and blends thereof.

- 30 16. Treatment process according to Claim 15, characterized in that the polyurethanes are chosen from film-forming polyurethanes in the form of aqueous dispersions, copolymers obtained by copolymerization of hexanediol, neopentyl glycol, adipic acid, hexamethylene diisocyanate, N-(2-aminoethyl)-3-aminoethane-

sulphonic acid and ethylenediamine, and copolymers obtained by copolymerization of adipic acid, dicyclohexylmethane diisocyanate, ethylenediamine, hexanediol, neopentyl glycol and sodium N-(2-aminoethyl)-3-aminoethanesulphonate.

5 17. Treatment process according to Claim 15, characterized in that the vinyl polymers are chosen from polyvinyl alcohols, copolymers derived from C₄-C₈ monounsaturated carboxylic acids or anhydrides, and methyl vinyl ether/butyl monomaleate copolymers.

10 18. Treatment process according to Claim 15, characterized in that the natural polymers are chosen from guar gums and modified guar gums, celluloses, and gellan gum and its derivatives, in particular celluloses.

15 19. Treatment process according to Claim 15, characterized in that the alkyl acrylate and methacrylate copolymers are chosen from C₁₂-C₂₂ alkyl acrylate and methacrylate copolymers.

20 20. Treatment process according to any one of the preceding claims, characterized in that the material also comprises one or more adhesive zones that can be formed from at least one adhesive organic polymer.

20 21. Use of an antiperspirant material as defined according to any one of Claims 1 to 20, for the cosmetic treatment of human perspiration.

22. Antiperspirant cosmetic polymeric material as defined according to any one of Claims 1 to 20.