(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 October 2012 (04.10.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/131070 A2

(51) International Patent Classification:
A61K 8/02 (2006.01) *A61Q 15/00* (2006.01)
A45D 34/04 (2006.01) *A61K 8/72* (2006.01)
A45D 40/26 (2006.01)

(21) International Application Number:
PCT/EP2012/055879

(22) International Filing Date:
30 March 2012 (30.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1152746 31 March 2011 (31.03.2011) FR
61/474,048 11 April 2011 (11.04.2011) US

(71) Applicant *(for all designated States except US)*: **L'OREAL** [FR/FR]; 14, rue Royale, F-75008 Paris (FR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **GAVILLON, Roxane** [FR/FR]; 51, rue Camelinat, F-91170 Viry-Chatillon (FR). **SIMONNET, Jean-Thierry** [FR/FR]; 53 bis avenue Carnot, F-94240 Cachan (FR).

(74) Agent: **DOSSMANN, Gérard**; Bureau D.A Casalonga & Josse, 8 Avenue Percier, F-75008 Paris (FR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

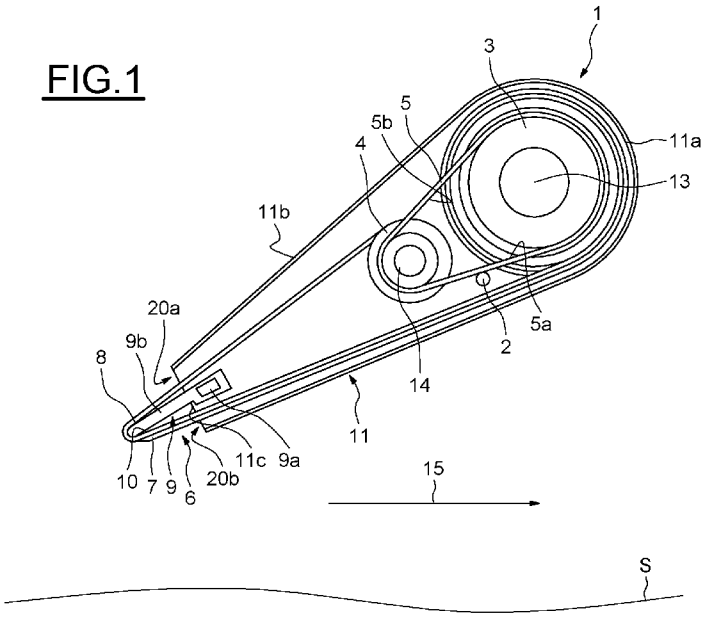
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) **Title**: USE OF A DEVICE FOR TRANSFERRING AN ANTIPERSPIRANT COSMETIC FILM APPLIED ONTO THE SKIN

FIG.1



(57) **Abstract**: The present invention relates to the use on the skin, for the application of an antiperspirant cosmetic film (7), of a transfer device (1) provided with a case (11) having an open end (11c) comprising: -a feed reel (3) on which is wound a transfer strip (6) comprising a base strip (8) coated with the antiperspirant cosmetic film (7) to be transferred, -an application head (9) intended to press the transfer strip (6) against a surface of skin in order to transfer the antiperspirant cosmetic film (7) onto the said surface, -a receiver reel (4) for receiving the used base strip (8), -a belt-type drive mechanism, the said drive mechanism comprising an endless belt (5) cooperatively connecting the feed reel (3) with the receiver reel (4).

WO 2012/131070 A2

Use of a device for transferring an antiperspirant cosmetic film applied onto the skin

The present invention relates to the use of a transfer device for applying to a user's skin a cosmetic film for treating human perspiration. Similarly, the present invention also relates to a cosmetic process for treating human perspiration, and possibly the body odour associated with human perspiration, especially underarm odour, involving the use of the said device for applying an antiperspirant cosmetic film to the surface of the skin.

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 presence of sweat resulting from perspiration, which may, in certain cases, make the skin and clothing wet, especially in the region of the armpits or on the back, thus leaving visible marks. Moreover, the presence of sweat usually gives rise to the production of body odour, which is generally unpleasant. Finally, during its evaporation, sweat may also leave salts and/or proteins on the surface of the skin, which may result in whitish marks on clothing. Such discomfort is noticed, including in the case of moderate perspiration.

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

Antiperspirant substances are generally formed from aluminium salts, such as aluminium chloride and aluminium hydroxyhalides, or complexes of aluminium and zirconium. These substances reduce the flow of sweat by forming a plug in the sweat duct.

However, the use of these substances at high concentrations for the purpose of obtaining good antiperspirant efficacy, usually has the drawback of leading to formulation difficulties.

Furthermore, it has been found that the antiperspirant efficacy of these substances may prove to be limited, which means that they need to be applied

regularly to the skin 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.

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

Finally, these antiperspirant substances may also leave marks during their application to the skin, which has the consequence of staining clothing.

As a variant, a method has been proposed, especially for consumers who have a problem of tolerance to aluminium salts, which consists in using deodorant textile supports intended to be attached to clothing in order to absorb perspiration.

By way of example, patent application WO 2005/058 082 describes a perspiration-absorbing pad intended mainly for absorbing perspiration from human armpits. In particular, the pad comprises a moisture-absorbing unit that is placed along the junction area of the sleeve and of the body of the clothing at an appropriate place to be able to attach the pad to the fabric.

Similarly, patent application DE 10139849 describes a device comprising an absorbent and cellulose, which is intended to be stuck to an item of clothing by means of an adhesive surface. The device comprises a support layer, a protective film for preventing untimely adhesion, an absorbent cushion, a backing layer with apertures and a fold that facilitates the positioning of the device.

However, such a method remains impractical since it requires wipes or textile supports to the attached on the inside of clothing and does not allow the arms to be left bare. Furthermore, such a method is not aesthetic either, since the wipes remain visible as a result of their thickness.

To overcome all the drawbacks mentioned above, it was proposed to seek new routes for easily and discreetly depositing on the skin efficient antiperspirant products that are permeable to water vapour, impermeable to sweat and suitably tolerated by the skin.

Specifically, limiting the flow of sweat may be achieved by partially obstructing the sweat ducts by means of forming a plug in the sweat duct, but also by forming at the surface of the skin a film that is resistant to sweat. Thus, many

approaches are directed towards covering the surface of the skin with a film or patch has been developed in order to limit the flow of sweat.

By way of example, patent application US 2007/0 218 092 describes a deodorant patch for use under the armpits, which comprises an upper support sheet positioned on the upper face of the patch and a lower support sheet positioned on the lower face of the patch. The patch comprises one or more deodorant and/or antiperspirant active agents that may be chosen especially from aluminium and zirconium complexes, cyclomethicone and stearyl alcohol. In particular, the deodorant patch dissolves on contact with the skin, enabling the deodorant substances and the other ingredients of the formulation to be released and to act for treating perspiration.

Patent application US 2007/0 053 959 describes an antiperspirant/deodorant strip intended to be applied to the skin, which may be oval or rectangular. A protective film is placed on the upper face of the antiperspirant/deodorant strip and an adhesive layer is placed on the lower face of the strip.

Similarly, patent application WO 2004/024 113 relates to a deodorant patch for administering deodorant substances, comprising at least two layers. The first layer contains at least one deodorant active agent, which may be an aluminium salt, and at least one film-forming compound, and the second layer contains at least one compound capable of achieving adhesion between the patch and the surface of skin onto which the patch is applied. The patch decomposes on contact with the skin without leaving any traces, which makes it possible to dose more accurately the amount of deodorant active agents to be applied.

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

Thus, there is still a real need to investigate novel pathways that do not have the drawbacks mentioned above, i.e. that involve the use, on the skin, in a sufficiently precise and discreet manner, of cosmetic compositions capable of imparting a satisfactory antiperspirant effect, especially in terms of efficacy, having satisfactory permeability to water vapour and impermeability to sweat, while at the same time being suitably tolerated by the skin.

The Applicant has discovered, surprisingly, that by using a particular transfer device, it is possible precisely and discreetly to deposit on a user's skin a cosmetic film that is capable of efficiently treating human perspiration.

In other words, the present invention involves a device that is simple to use, which is capable of efficiently delivering an antiperspirant cosmetic film on contact with the skin, in particular at suitable places on the surface of the skin, especially under the armpits.

In particular, the application head of the device has the advantage of being adapted to the deposition of the cosmetic film onto the armpits.

Moreover, the antiperspirant cosmetic film thus deposited has a suitable toxicological profile and makes it possible satisfactorily to reduce or limit the flow of sweat.

Furthermore, the present invention makes it possible to deposit an antiperspirant film that has satisfactory controlled permeability, in particular being permeable to water vapour and impermeable to sweat.

The antiperspirant film deposited on the skin also shows satisfactory strength, especially relative to the pressure exerted by water droplets, by the movements of the body or by sweat leaving the skin pores.

One subject of the present invention is thus especially the use, for the application to the skin of an antiperspirant cosmetic film, of a transfer device provided with a case having an open end comprising:

- a feed reel on which is wound a transfer strip comprising a base strip coated with the antiperspirant cosmetic film to be transferred,
- an application head mounted on the open end, intended to press the transfer strip against a surface of skin in order to transfer the antiperspirant cosmetic film onto the said surface,
- a receiver reel for receiving the used base strip,
- a belt-type drive mechanism, the said drive mechanism comprising an endless belt cooperatively connecting the feed reel with the receiver reel.

In other words, the present invention involves the use on the skin of a cosmetic film that is used as a cosmetic agent for treating human perspiration.

The term "agent for treating perspiration" means, for the purposes of the present invention, any substance which, by itself, has the effect of decreasing or limiting the flow of sweat.

In particular, the use of a film as described above makes it possible to impart an antiperspirant effect.

Thus, the present invention relates to the use of a device as described previously for applying to the skin a film intended for the cosmetic treatment of human perspiration.

A subject of the present invention is also a cosmetic process for treating human perspiration and possibly the body odour associated with human perspiration, especially underarm odour, comprising the use of a transfer device as described previously for applying to the skin an antiperspirant cosmetic film.

Another subject of the present invention consists of a transfer device as described previously, which serves for applying to the skin a particular antiperspirant cosmetic film.

Preferably, the antiperspirant cosmetic film comprises at least one adhesive layer in order to enable the adhesion of the film to the skin.

According to a first embodiment, the adhesive layer is formed from one or more pressure-sensitive adhesive compounds.

In accordance with this embodiment, the antiperspirant cosmetic film comprises at least one adhesive layer formed from one or more pressure-sensitive adhesive compounds.

Thus, the cosmetic film has the advantage both of adhering easily to the surface of the skin and of efficiently treating human perspiration.

The term pressure-sensitive adhesives (PSA) means viscous, elastic substances that have satisfactory adhesion, cohesion, stretchability and elasticity properties. The performance qualities of a pressure-sensitive adhesive are generally evaluated by means of three properties: its immediate bonding power at room temperature (often referred to as the "tack"), its stretchability and its shear stress. The properties such as the shear stress or the cohesion may be measured using standard tests that are detailed in the scientific literature (Ref.: A. Zosel, J. Adhesion, 1994, 44 pp. 1-6). Pressure-sensitive adhesives are usually formed from chemical fragments that are responsible for the elastomeric behaviour and the immediate tack at room temperature. Thus, by controlling the amounts of these fragments, the various desired properties may be obtained.

The pressure-sensitive adhesives used in accordance with the present invention are preferably defined according to the Dahlquist criterion, i.e. as a

function of their storage modulus G' (as described in the book "Handbook of Pressure Sensitive Adhesive Technology, Second Edition, D. Satas, ed., Van Nostrand Reinhold, New York, NY, 1989, pages 171-176", which is incorporated herein by reference).

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

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

The pressure-sensitive adhesives according to the invention are compounds that give the support coated therewith immediate tack power at room temperature, which allows its instantaneous adhesion to a substrate under the effect of a gentle and brief pressure. Even more particularly, the pressure-sensitive adhesives according to the invention are compounds that have immediate tack power at room temperature and that adhere to a surface by simple contact without the need for more than the pressure of a finger or a hand. Moreover, given their chemical properties, pressure-sensitive adhesives have particular properties such as a low glass transition temperature (Tg), a low surface energy (σ), high flexibility and substantial bonding capacity.

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

The pressure-sensitive adhesives used in the present invention are compounds that comprise one or more adhesive organic polymers. In other words, such compounds are made from one or more adhesive organic polymers.

In accordance with this first embodiment, the antiperspirant cosmetic film comprises at least one pressure-sensitive adhesive layer formed from one or more adhesive organic polymers.

The adhesive nature of an organic polymer is generally associated with its glass transition temperature. A necessary but insufficient condition for a polymer to be adhesive is that it must have a glass transition temperature (Tg) that is significantly below room 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 (Tg) of less than or equal to 10°C and preferably less than or equal to 0°C.

The glass transition temperature (Tg) of the adhesive organic polymers according to the present invention may be measured by differential calorimetric analysis (Differential Scanning Calorimetry, DSC) under the following conditions:

To measure the glass transition temperature, a film about 150 mm thick of test polymer is prepared by depositing an aqueous solution or dispersion of the polymer in a circular Teflon die 40 mm in diameter and leaving the deposit to dry. The film is dried in an oven at a temperature of about 23°C under a relative humidity of 45%, until the weight no longer changes. About 5 to 15 mg of the film are taken up and placed in a crucible, which is then introduced into the analyser. The thermal analyser is a DSC-2920 model from the company TA Instruments. The initial and final temperatures of the temperature sweep are chosen so as to surround the desired glass transition temperature. The temperature sweep is performed at a rate of 10°C/minute.

This analysis is performed according to ASTM standard D 3418-97 apart from the above changes.

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 the said polymer, is greater than 1 N, preferably greater than 3 N and in particular greater than 5 N.

The tensile force F_{max} may be measured under the following conditions: Two discs each with an area of 38 mm^2, made of a solid, rigid, inert and non-absorbent material, preferably glass, are coated with a layer of the adhesive polymer to be tested. The polymer is deposited in an amount of 500 $\mu g/mm^2$ from a solution in a suitable solvent. After evaporation of the said solvent for 24 hours at 22°C under a relative humidity of 50%, the two coated surfaces of the disks are superposed and the disks are pressed together for 20 seconds at a pressure of 3 newtons using an LR5K model Lloyd extensometer.

The bonded disks are then cooled so as to separate them from each other at a speed of 20 mm/minute, and the tensile force is recorded continuously. The maximum tensile force, recorded at the time of separation of the two surfaces, known as the 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 may be used for the present invention may also be characterized by their adhesiveness on an inert material, such as glass. This adhesiveness may be expressed in the form of the energy (Es) supplied by the same extensometer (Lloyd LR5K model) to separate two surfaces of 38 mm^2 each coated with the said adhesive organic polymers, under the above conditions (500 $\mu g/mm^2$, drying for 24 hours at 22°C, 50% RH) of an adhesive polymer, of a polished glass surface, after compression of these two surfaces for 30 seconds with a force of 3 newtons. As previously, the tensile speed is 20 mm/minute.

This energy Es, corresponding to the sum of work supplied up to the point of detachment, may be calculated according to the following formula:

$$\int_{Xs1+0.05}^{Xs2} F(x)dx$$

in which:

F(x) is the force necessary to produce a displacement (x),

Xs1 is the displacement (expressed in mm) produced by the maximum tensile force, and

Xs2 is the displacement (expressed in mm) produced by the tensile force that enables total separation of the two surfaces.

For the adhesive polymers used in the present invention, the separation energy Es is preferably not more than 300 µJ and preferably not more than 250 µJ.

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

The adhesive organic polymers may be crosslinked or non-crosslinked. To find concrete examples of adhesive polymers, reference may be made to the following patent applications describing adhesive polymers: WO98/38969, FR 2 833 960 (Self-adhesive cationic or amphoteric polyurethanes) and FR 2 833 959 (Self-adhesive cationic or amphoteric radical polymers).

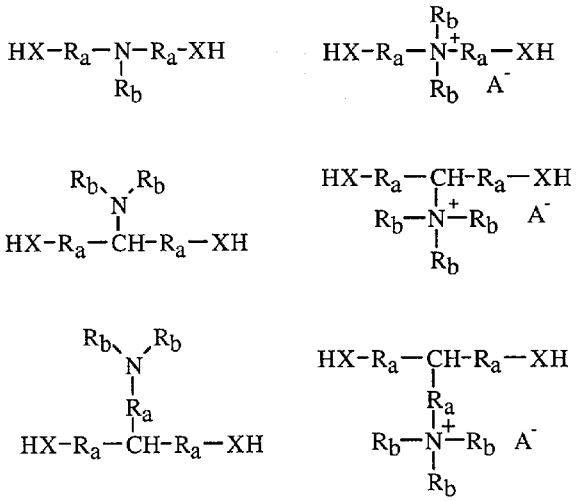
In particular, the adhesive organic polymers according to the invention may be chosen from adhesive polyesters containing one or more sulfonic functions, cationic or amphoteric polyurethanes comprising one or more self-adhesive tertiary or quaternary amine functions and self-adhesive cationic or amphoteric radical polymers.

Preferably, the adhesive organic polymers according to the invention may be chosen from adhesive polyesters containing one or more sulfonic functions, in particular from adhesive branched polyesters containing one or more sulfonic functions.

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

The adhesive organic polymers according to the invention may also be cationic polyurethanes that comprise (a) units derived from one or more tertiary or quaternary amines comprising two functions that are reactive with labile hydrogen, (b) units derived from one or more nonionic polymers comprising two functions that are reactive with labile hydrogen, and (c) units derived from one or more diisocyanates.

The tertiary or quaternary amines forming the cationic units (a) are preferably chosen from compounds corresponding to one of the following formulae:



in which:

each Ra independently represents a linear or branched C_{1-6} alkylene, C_{3-6} cycloalkylene or arylene group, all possibly being substituted with one or more halogen atoms and comprising one or more heteroatoms chosen from O, N, P and S,

each Rb independently represents a linear or branched C_1-C_6 alkyl, C_{3-6} cycloalkyl or aryl group, all possibly being substituted with one or more halogen atoms and comprising one or more heteroatoms chosen from O, N, P and S,

each X independently represents an oxygen or sulfur atom or a group NH or NRc in which Rc represents a C_1-C_6 alkyl group, and A^- represents a physiologically acceptable counterion.

As examples of tertiary amines that are particularly preferred for obtaining the self-adhesive cationic or amphoteric polyurethanes of the present invention, mention may be made of N-methyldiethanolamine and N-tert-butyldiethanolamine. These amines are preferably neutralized with mineral or organic acids such as hydrochloric acid or citric acid.

The self-adhesive polyurethanes of the present invention may also comprise anionic units (d) derived, for example, from carboxylic or sulfonic acids comprising two functions bearing labile hydrogen, such as dimethylolpropionic acid.

The self-adhesive polyurethanes of the present invention may also comprise nonionic monomer units (e) derived from nonionic monomer compounds comprising two functions bearing labile hydrogen, such as butanediol or neopentyl glycol.

In one embodiment of the present invention, the self-adhesive polyurethanes of the present invention are cationic self-adhesive polyurethanes not containing any units (d) and (e) and which are formed essentially from (a) units derived from one or more tertiary or quaternary amines comprising two reactive functions bearing labile hydrogen, (b) units derived from one or more nonionic polymers comprising two reactive functions bearing labile hydrogen, and (c) units derived from one or more diisocyanates.

The cationic polyurethanes have particularly advantageous self-adhesiveness properties when the polymer(s) forming the units (b) of the self-adhesive polyurethanes of the present invention have a glass transition temperature (Tg), determined by differential colorimetric analysis, of less than 0°C, preferably less than -5°C and better still less than -10°C.

Examples of nonionic polymers capable of forming the units (b) that may be indicated include polyethers, polyesters, polysiloxanes, copolymers of ethylene and

butylene, polycarbonates and fluoro polymers with a glass transition temperature of less than 0°C.

Polyethers are most particularly preferred, and among these poly(tetramethylene oxide).

These polymers preferably have a weight-average molar mass of between 400 and 10 000 and more particularly between 500 and 5000.

The number of cationic charges borne by the self-adhesive polyurethanes of the present invention depends directly on the mole ratio or weight ratio of the units (a) to the units (b). Needless to say, the units (c) are used in a virtually equimolar amount relative to the sum of the units (a) and (b).

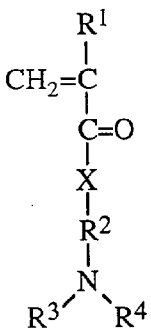
The mole ratio of the units (a) to the units (b) of the polyurethanes of the present invention is preferably between 0.01 and 50, more particularly between 0.1 and 6, better still between 0.2 and 5 and ideally between 0.3 and 5.

The diisocyanates forming the units (c) include aliphatic, alicyclic or aromatic diisocyanates.

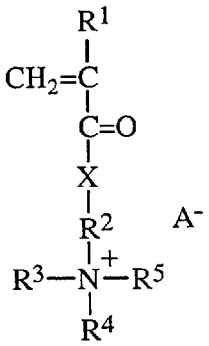
Preferred diisocyanates are chosen from tetramethylxylylene diisocyanate, methylenediphenyl diisocyanate, methylenecyclohexane diisocyanate, isophorone diisocyanate, toluene diisocyanate, naphthalene diisocyanate, butane diisocyanate and hexyl diisocyanate. Needless to say, these diisocyanates may be used alone or in the form of a mixture of two or more diisocyanates.

The adhesive organic polymers according to the invention may be self-adhesive cationic or amphoteric radical polymers. In particular, the self-adhesive cationic or amphoteric radical polymers comprise one or more derivatives of monomers chosen from those of formulae (Ia), (Ib), (Ic), (Id) and (Ie):

(Ia)



(Ib)



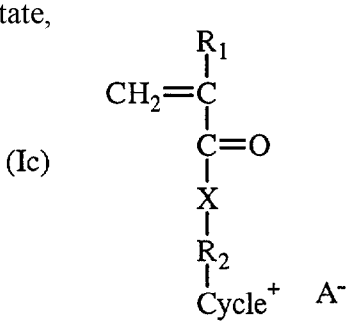
in which:

R_1 represents a hydrogen atom or a methyl group;

R_2 represents a linear, branched, cycloaliphatic or aromatic divalent C_1-C_{30} hydrocarbon-based group, which may contain one or more heteroatoms chosen from O, N and P,

R_3, R_4 and R_5 each independently represent a linear, branched, cycloaliphatic or aromatic C_1-C_{30} hydrocarbon-based group, which may contain one or more heteroatoms chosen from O, N and P,

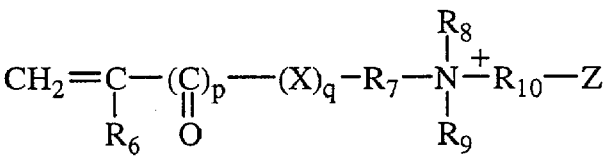
X represents an oxygen atom or an NH group, A^- represents the counterion of the quaternary amine, preferably chosen from halide, sulfate, phosphate and carboxylate ions such as acetate,

(Ic) 

in which:

X, R_1 and R_2 have the meaning indicated with regard to formulae (Ia) and (Ib), and

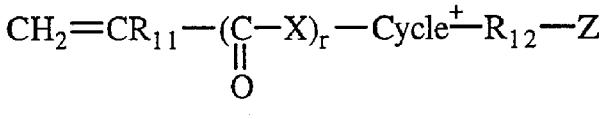
Cycle+ represents a cycloaliphatic or aromatic fused monocyclic or bicyclic system, comprising a tertiary or quaternary amine function, and which may contain one or more additional heteroatoms chosen from O, N and P;

(Id) 

in which R_6 represents a hydrogen atom or a linear or branched C_{1-4} alkyl group, R_8 and R_9 each independently represent a hydrogen atom or a linear or branched C_{1-4} alkyl group, optionally bearing a group COO-, SO_3- or PO_3H-, R_7 and R_{10} each independently represent a divalent hydrocarbon-based group, in particular a group -(CH_2)n with n being between 1 and 4 inclusive, and optionally interrupted with an oxygen atom,

X is an oxygen atom or an NH group, p and q are equal to 0 or 1, Z represents a group COO-, SO_3- or PO_3H-, in which R_7 may form with R_8, R_9 or X,

when the latter represents an NH group, an aromatic or non-aromatic 5-, 6- or 7-membered heterocycle;

(Ie) 

in which:

R_{11} represents a hydrogen atom or a methyl group;

R_{12} represents a divalent C_{1-4} hydrocarbon-based group,

X represents an oxygen atom or an NH group;

r is 0 or 1,

Cycle+ represents a cycloaliphatic or aromatic fused monocyclic or bicyclic system, comprising a tertiary or quaternary amine function, and which may contain one or more additional heteroatoms chosen from O, N and P, and Z represents a group COO-, SO_3- or PO_3H-.

As examples of cationic ethylenic monomers defined by the formulae (Ia) to (Ie) above, mention may be made of dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, dimethylaminoethyl(meth)acrylamide, dimethylaminopropyl(meth)acrylamide, N-morpholinoethyl (meth)acrylate, trimethylammonioethyl (meth)acrylate chloride, trimethylammoniopropyl (meth)acrylate chloride, trimethylammonioethyl(meth)acrylamide chloride, trimethylammoniopropyl(meth)acrylamide chloride and dimethylbenzylammonioethyl (meth)acrylate chloride.

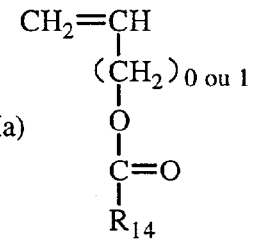
As examples of amphoteric monomers of formula (Id) or (Ie) that are particularly preferred, mention may be made of 1-vinyl-2-(3-sulfopropyl)imidazolium hydroxide, 1-vinyl-3-(3-sulfopropyl)imidazolium hydroxide, 1-vinyl-3-(4-sulfobutyl)imidazolium hydroxide, 1-vinyl-2-methyl-3-(4-sulfobutyl)imidazolium hydroxide, 2-vinyl-l-(3sulfopropyl)pyridinium hydroxide, 2-methyl-5-vinyl-l-(3-sulfopropyl)pyridinium hydroxide, 4-vinyl-l-(3-sulfopropyl)pyridinium hydroxide, dimethyl-(2-methacryloxyethyl)-3-sulfopropyl)ammonium hydroxide, diethyl-(2-methacryloxyethoxy)-2-ethyl-(3-sulfopropyl)ammonium hydroxide, 4-vinyl-4-(sulfobutyl)pyridinium, N-(3-sulfopropyl)-N-methacrylamidopropyl-N,N-dimethylammonium hydroxide, N,N-dimethyl-N-(3-(methacrylamido)propyl)-3-(sulfopropyl)ammonium hydroxide, N,N-

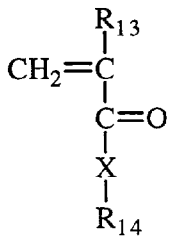
dimethyl-N-(3-methacrylamidopropyl)-N-(3-carboxypropyl) ammonium hydroxide and N,N-dimethyl-N-(2-methacryloxyethyl-N-(3-carboxypropyl)ammonium hydroxide.

The self-adhesive cationic or amphoteric polymers of the present invention preferably comprise, besides the units derived from cationic and/or amphoteric monomers, units derived from nonionic ethylenic monomers.

The self-adhesive cationic or amphoteric polymers of the present invention are particularly advantageous when they comprise nonionic monomers chosen from those that form, when they are homopolymerized, polymers with a glass transition temperature of less than 0°C.

These nonionic comonomers are known in the art and may be described by formula (IIa) or (IIb):

(IIa) 

(IIb) 

in which R_{13} represents a hydrogen atom or a methyl group, X represents an oxygen atom or an NH group, and R_{14} represents a linear, branched, cycloaliphatic or aromatic C_{2-30} hydrocarbon-based group, which may contain one or more atoms chosen from O, S and P.

Among the nonionic comonomers giving homopolymers with a Tg of less than 0°C, the ones that are particularly preferred are ethyl, n-butyl, n-hexyl, 2-ethylhexyl, n-nonyl, lauryl, n-octadecyl, isooctyl, isodecyl, hydroxyethyl, hydroxypropyl or methoxyethyl acrylate, and n-hexyl, 2-ethylhexyl, isodecyl or methoxyethyl methacrylate, C_{1-30} alkoxy-PEG (with 5 to 30 ethylene oxide units), vinyl propionate, and vinyl neoalkanoates such as vinyl neononanoate and vinyl neododecanoate.

The self-adhesive radical polymers of the present invention may also contain a small amount of highly hydrophobic nonionic monomers such as vinyl monomers bearing a silicone side chain, chlorotrifluoroethylene, tetrafluoroethylene, and vinyl, allylic or (meth)acrylic monomers with a perhalogenated and in particular perfluoro

hydrocarbon-based side chain, such as perfluorohexyl (meth)acrylate or perfluorooctyl (meth)acrylate.

The self-adhesive cationic or amphoteric polymers of the present invention are formed both from cationic or amphoteric monomers and from nonionic monomers giving homopolymers with a glass transition temperature Tg of less than 0°C, the units derived from cationic or amphoteric ethylenic monomers represent from 1% to 50% by weight of the polymer and preferably from 1% to 20% by weight of the polymer, and the units derived from nonionic ethylenic monomers giving homopolymers with a glass transition temperature Tg of less than 0°C represent from 50% to 99% by weight of the polymer and preferably from 80% to 99% by weight of the polymer.

The self-adhesive polymers of the present invention may comprise - in addition to the units derived from cationic or amphoteric monomers and the units derived from nonionic monomers giving homopolymers with a glass transition temperature Tg of less than 0°C - a certain proportion of anionic ethylenic comonomers.

These comonomers are ethylenic monomers bearing at least one carboxylic acid, sulfonic acid or phosphonic acid function.

They are chosen, for example, from acrylic acid, methacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid, vinylbenzoic acid, vinylbenzenesulfonic acid, acrylamidopropanesulfonic acid and vinylphosphonic acid or from the mineral or organic base-addition salts of these acids.

The introduction of these anionic comonomers makes it possible to adjust the equilibrium of the charges, to modify the hydrophilic nature and thus the solubility of the polymers obtained, or to modulate the compatibility of the polymers with certain cosmetic supports or substrates.

In accordance with this first embodiment, the antiperspirant cosmetic film comprises a pressure-sensitive adhesive layer formed from one or more adhesive organic polymers corresponding to the branched sulfonic polyester sold by the company Eastman under the name AQ 1350.

More preferentially, the cosmetic film is formed from a pressure-sensitive adhesive layer formed from an adhesive organic polymer, preferably a branched sulfonic polyester such as the product sold by the company Eastman under the name AQ 1350.

According to a second embodiment, the antiperspirant cosmetic film comprises at least one adhesive layer, optionally formed from one or more pressure-sensitive adhesive compounds, and at least one layer formed from a hydrophilic or hydrophobic film-forming antiperspirant polymer.

In accordance with this second embodiment, the cosmetic film is in contact with the skin by means of the adhesive layer so as to be able to adhere to the skin, and the layer formed from a hydrophilic or hydrophobic film-forming antiperspirant polymer enables efficient treatment of human perspiration.

For the purposes of the present invention, the expression "antiperspirant polymer" means a polymer which is capable, by itself, of reducing or limiting the flow of sweat.

The term "hydrophobic film-forming polymer" means any polymer (1°) that is capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous or discontinuous film that adheres to a support, especially to human keratin materials such as the skin, the hair, the eyelashes, the eyebrows or the nails, and (2°) for which the formed film is capable of absorbing an amount of water of less than or equal to 30% by weight relative to the weight of the dry polymer film (before immersion in water) when it is dipped into liquid water.

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

To measure the amount of water absorbed, also known as the water uptake, 12 g of an aqueous or aqueous-alcoholic solution comprising 7% by weight of polymer are poured into an aluminium crucible 5.5 cm in diameter, to form a film. The inner surface of the aluminium crucible is covered with a Teflon support disc so as to limit the undesirable edge effects and to facilitate the shrinkage of the film. The system is left to evaporate for 24 hours with ventilation, so as to enable optimum drying. A circular film measuring between 300 and 350 μm in thickness is obtained, which is removed from the aluminium crucible. The film is then cut into two rectangles of 1×2 cm.

One of the rectangular films obtained is weighed when dry, which gives the mass of the film before immersion in the water, also known as the mass of the dry film. The same film is then dipped in a 30 mL flask filled with water, for a duration of 60 minutes.

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

$$\%_{\text{absorbed water}} = \frac{m_{\text{Film after immersion}} - m_{\text{Dry film}}}{m_{\text{Dry film}}}$$

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

According to one particular form of the invention, the hydrophobic film-forming polymers are synthetic polymers.

The term "synthetic polymer" means any polymer obtained chemically or via production in an organism of the elements necessary for this production.

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

(i) polymers of interpenetrating polymer network type;

(ii) grafted silicone polymers;

(iii) non-neutralized copolymers of (meth)acrylic acid and of N-tert-butylacrylamide;

(iv) non-neutralized copolymers of crotonic acid and of vinyl acetate;

(v) tetrapolymers of (meth)acrylic acid, of (meth)acrylates and of C_8-C_{24} alkyl (meth)acrylates, and

(vi) polymers that have been obtained after 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, the said compounds X and Y having reacted together via a hydrosilylation, condensation or crosslinking reaction in the presence of peroxide when they are placed in contact with each other;

(vii) mixtures thereof.

Interpenetrating polymer network

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

For the purposes of the present invention, the expression "interpenetrating polymer network" means a blend of two interlaced polymers, obtained by simultaneous polymerization and/or crosslinking of two types of monomer, the blend obtained having a single glass transition temperature range.

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

The IPN preferably has a glass transition temperature, Tg, ranging from about -50°C to +130°C and preferably from -45°C to +130°C.

The glass transition temperature is especially measured by differential scanning colorimetry (or DSC) using the DSC 7 machine from the company Perkin-Elmer, the polymer sample being preconditioned in a climatic chamber for 48 hours at 25°C and 50% relative humidity, in an aluminium crucible.

The measurement is taken under a nitrogen flush, with a first heating ranging from -45°C to +140°C at a rate 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 of interpenetrating polymer network type (IPN) of polyurethane and of acrylic polymer in the form of an aqueous particle dispersion.

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

This process comprises the following steps:

(a) forming a water-dispersible isocyanate-terminated polyurethane prepolymer comprising carboxylate groups;

(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 chain extension of the prepolymer by heating the aqueous dispersion.

The isocyanate-terminated polyurethane prepolymer may be obtained by reaction of organic monomer containing at least two active hydrogen atoms per molecule, especially a diol and preferably a polyester polyol, with an excess of diisocyanate monomer.

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

The polyisocyanates used in the manufacture of the prepolymer may be aliphatic, cycloaliphatic or aromatic. Examples of polyisocyanates that may be mentioned include ethylene diisocyanate, hexamethylene 1,6-diisocyanate, isophorone diisocyanate, cyclohexane 1,4-diisocyanate, dicyclohexylmethane 4,4'-diisocyanate, phenylene 1,4-diisocyanate, toluene 2,4-diisocyanate, toluene 2,6-diisocyanate, diphenylmethane 4,4'-diisocyanate, diphenylmethane 2,4'-diisocyanate and naphthylene 1,5-diisocyanate, and mixtures thereof.

The polymeric polyols with a molecular weight ranging from 500 to 6000 and preferably ranging from 700 to 3000, which may be used for the preparation of the prepolymer, may be chosen from diols and triols, or mixtures thereof. The polyols may be chosen especially from polyesters, polyester amides, polyethers, polythioethers, polycarbonates and polyacetals.

The polyester polyols may be chosen from the hydroxyl oil-terminated reaction products of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, furandimethanol, cyclohexanedimethanol, glycerol, trimethylolpropane or pentaerythritol, or mixtures thereof, with polycarboxylic acids, in particular dicarboxylic acids or the ester form thereof, such as succinic acid, glutaric acid, adipic acid or the methyl ester thereof, phthalic anhydride or dimethyl terephthalate. Polyesters obtained by polymerization of lactones, for instance caprolactone, and of polyol may also be used. The polyesteramides may be obtained by using amino alcohols such as ethanolamine in the polyesterification mixture.

The polyether polyols that may be used include the products obtained by polymerization of cyclic oxide, for example ethylene oxide, propylene oxide,

tetrahydrofuran, or by addition of these cyclic oxides to polyfunctional initiators such as water, ethylene glycol, propylene glycol, diethylene glycol, cyclohexanedimethanol, 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 suitable initiators, and polytetramethylene glycol ethers obtained by polymerization of tetrahydrofuran.

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

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

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

The compounds bearing a reactive isocyanate group containing acid groups, which may 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):

$$R\text{-}C(CH_2OH)_2\text{-}COOH$$

(I)

in which R is a hydrogen or a C_1-C_{10} alkyl group. The diol containing a carboxylic group is preferably 2,2-dimethylolpropionic acid. The diol or triol containing a carboxylic group may be incorporated into a polyester by reaction with a dicarboxylic acid before being introduced into the prepolymer. Compounds bearing an acid group are, for example, aminocarboxylic acids, for example lysine, cystine or 3,5-diaminobenzoic acid.

The water-dispersible anionic isocyanate-terminated polyurethane prepolymer may be prepared in a conventional manner by reacting 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 of between 30 and 130°C until the reaction between the isocyanate groups and a hydroxyl groups is complete.

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 and preferably from 1.5/1 to 3/1. It is possible to use a well-known tin catalyst to assist the formation of the prepolymer.

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

The vinyl monomers that may 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.

Mention may be made especially of butadiene, isoprene, styrene, alkyl (meth)acrylates containing a C_1-C_6 alkyl group, alkyl maleates containing a C_1-C_6 alkyl group, vinyl acetate, vinyl butyrate, acrylonitrile, methyl vinyl ether, propyl vinyl ether, butyl vinyl ether, vinyl chloride and vinylidene chloride. The polyethylenically unsaturated monomers may be chosen from butadiene, isoprene, allyl methacrylate, diesters of acrylic acid and of C_2-C_6 diols such as butylene diacrylate and hexylene diacrylate, divinylbenzene, divinyl ether, divinyl sulfide and trimethylolpropane triacrylate.

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 an amount sufficient to make the prepolymer water-dispersible, i.e. in an amount sufficient to neutralize the carboxylic groups. For example, the amine may be added in an amount ranging from 65% to 100% of amine equivalent per equivalent of carboxylic function.

The tertiary amines that may be used are relatively volatile, such that they are evaporated from the film after the film formation.

Examples that may be mentioned include 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.

Examples that may be mentioned include triethylamine, dimethylethanolamine, methyldiethanolamine and methyldiethylamine.

It is important for the tertiary amine to be added to the mixture of prepolymer/monomers 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 may be dispersed in water using the known techniques. Preferably, the mixture is added to water with stirring, or water may be poured into the mixture.

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

Examples that may be mentioned include 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 isophoronediamine.

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 performed at high temperature, for example between 50°C and 90°C and preferably between 60°C and 80°C.

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.

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

The proportion of the vinyl monomers may range from 25% to 75% by weight and preferably from 40% to 60% by weight relative to the total weight of solids in the aqueous dispersion.

According to a second polymerization method, part of the vinyl monomers is added to the prepolymer, the mixture is then neutralized with the tertiary amine and the prepolymer/vinyl monomer mixture is dispersed in water, followed by polymerization, during which the rest of the monomers is added. Alternatively, the second portion of monomers may be added to the prepolymer/vinyl monomer dispersion after addition of the amine, and the mixture stirred before the start of the polymerization.

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

According to one preferred mode of the invention, the polyurethane present in the IPN is a copolymer of polyester polyol/diol containing a carboxylic acid group/diisocyanate/diamine, such as those described previously, for example; the acrylic polymer present in the IPN is a polymethyl methacrylate.

Use is preferably made of 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 alternatively under the trade names Hybridur® 870 and Hybridur® 880.

The IPN Hybridur® 875 Polymer Dispersion has, by itself, a tensioning effect, measured according to the protocol described previously, equal to +70%.

Grafted silicone polymers

For the purposes of the present invention, the term "grafted silicone polymer" means a polymer comprising a silicone or polysiloxane main chain (Si-O-polymer) onto which is grafted, within the said chain and also optionally on 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 are suitable for carrying out the present invention, and also their specific mode of preparation, are described in particular in patent applications EP-A-0 582 152, WO 93/23009 and WO 95/03776, the teachings of which are included in their entirety in the present description by way of non-limiting references.

According to a particularly preferred embodiment of the present invention, the silicone polymer with a polysiloxane backbone grafted with non-silicone organic monomers which is used comprises the result of the free-radical copolymerization

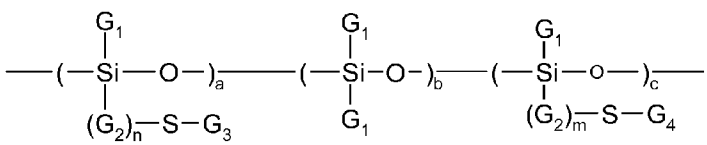
between, on the one hand, at least one non-silicone anionic organic monomer containing ethylenic unsaturation and/or a non-silicone hydrophobic organic monomer containing ethylenic unsaturation, and, on the other hand, a silicone containing in its chain at least one functional group capable of reacting with the said ethylenic unsaturations of the said non-silicone monomers, forming a covalent bond, in particular thio-functional groups.

According to the present invention, the said ethylenically unsaturated anionic monomers are preferably chosen, alone or as mixtures, from neutralized, linear or branched, unsaturated carboxylic acids, it being possible for these unsaturated carboxylic acids to be, more particularly, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid and crotonic acid. It will be noted that, similarly, 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 purposes of the present invention, the term "hydrophobic monomer" means a monomer that 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 acrylic acid esters of alkanols and/or methacrylic acid esters of alkanols. The alkanols are preferably C_1-C_{18} and more particularly C_1-C_{12}. The preferred 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 and stearyl (meth)acrylate, or mixtures thereof.

One family of silicone polymers containing a polysiloxane backbone grafted with non-silicone organic monomers that is particularly suitable for carrying out the present invention consists of silicone polymers comprising in their structure the unit of formula (II) below:



(II)

in which the radicals G, which may be identical or different, represent hydrogen, a C_1-C_{10} alkyl radical or a phenyl radical; the radicals G_2, which may be identical or different, represent a C_1-C_{10} alkylene group; G_3 represents a polymer residue resulting from the (homo)polymerization of at least one anionic monomer containing ethylenic unsaturation; G_4 represents a polymer residue resulting from the (homo)polymerization of at least one hydrophobic monomer containing ethylenic unsaturation; m and n are equal to 0 or 1; a is an integer ranging from 0 to 50; b is an integer which may be 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 radicals G_1 denote a C_1-C_{10} alkyl radical;

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

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

G_4 represents a polymer 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, via a thiopropylene-type connecting chain, mixed polymer units of the poly(meth)acrylic acid type and/or of the polyalkyl (meth)acrylate type, especially of a C_1-C_3, or even C_1, alkyl. These polymers are referenced under the INCI name Polysilicone-8.

It may thus be a polydimethylsiloxane grafted with propylthio(polymethyl acrylate/methyl methacrylate/methacrylic acid) or a polydimethylsiloxane 10 grafted with propylthio(polymethyl acrylate), propylthio(polymethyl methacrylate) and propylthio(polymethacrylic acid). As a variant, it may be a polydimethylsiloxane grafted with propylthio(polyisobutyl methacrylate) and propylthio(polymethacrylic acid).

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

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

Among the hydrophobic film-forming polymers in accordance with the invention, use will more preferentially be made of polymers of interpenetrating polymer network type (IPN) of polyurethane and of acrylic polymer in the form of an aqueous particle dispersion, in particular the IPN of polyurethane/acrylic polymer sold by the company Air Products under the trade name Hybridur® 875 Polymer Dispersion (INCI name: Polyurethane-2 (and) Polymethyl Methacrylate), or alternatively under the trade names Hybridur® 870 and Hybridur® 880.

Copolymers of acrylic acid and of N-tert-butyl acrylamide

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

The term "non-neutralized copolymer of (meth)acrylic acid and of N-tert-butylacrylamide" means any copolymer of (meth)acrylic acid and of N-tert-butylacrylamide in which the (meth)acrylic acid function is free and is not neutralized with an organic or mineral base.

Non-neutralized copolymers of vinyl acetate and of crotonic acid

The term "non-neutralized copolymer of crotonic acid and of vinyl acetate" means any copolymer of crotonic acid and of vinyl acetate in which the crotonic acid function is free and is not neutralized with an organic or mineral base.

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

(Meth)acrylic acid tetrapolymers

For the purposes of the present invention, the term "tetrapolymer" means a polymer derived from the copolymerization of four monomers.

Among the tetrapolymers of (meth)acrylic acid, (meth)acrylates and C_8-C_{24} alkyl (meth)acrylate, mention may be made of those described in patent application US 2003/021 847, for instance the copolymer sold under the name Soltex OPT-PG by the company Röhm & Haas, having the INCI name: Acrylates/C_{12}-C_{22} Alkyl Methacrylate Copolymer.

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

The hydrophobic film-forming polymer(s) may also be chosen from polymers that have been obtained after 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, the said compounds X and Y having reacted together via a hydrosilylation, condensation or crosslinking reaction in the presence of peroxide when they are placed in contact with each other.

The term “silicone compound” means a compound comprising at least two organosiloxane units. According to one particular embodiment, compounds X and compounds Y are silicone compounds. Compounds X and Y may be aminated or non-aminated. They may comprise polar groups that may be chosen from the following groups: -COOH, -COO^--, -COO-, -OH, -NH_2, -NH-,-NR-, -SO_3H, -SO_3-, -OCH_2CH_2-, -O-$CH_2CH_2CH_2$-, -O-$CH_2CH(CH_3)$-, -NR_3^+, -SH, -NO_2, I, Cl, Br, -CN, -PO_4^{3-}, -CONH-, -CONR-, -$CONH_2$, -CSNH-, -SO_2-, -SO-, -SO_2NH-, -NHCO-, -$NHSO_2$-, -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 whose main chain is mainly formed from organosiloxane units.

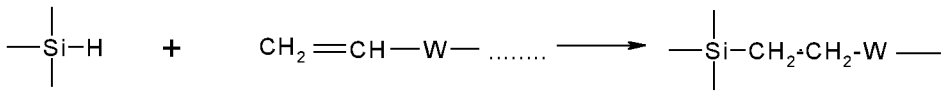
Among the silicone compounds mentioned below, some may have both film-forming and adhesive properties, depending, for example, on their proportion of silicone or depending on whether they are used as a mixture with a particular additive. It is consequently possible to modify the film-forming properties or the

adhesive properties of such compositions according to the intended use, and this is in particular the case for "room-temperature-vulcanizable" reactive elastomeric silicones.

Compounds X and Y may react together at a temperature ranging between room temperature and 180°C.

Advantageously, the hydrophobic film-forming polymers are obtained after the reaction of compounds X and Y that can react together at room temperature (20±5°C) and atmospheric pressure, advantageously in the presence of the catalyst, via a hydrosilylation reaction, a condensation reaction or a crosslinking reaction in the presence of a peroxide.

According to one particular embodiment, the hydrophobic film-forming polymers are obtained after the reaction of compounds X and Y that have reacted together via hydrosilylation, this reaction being represented schematically in simplified form as follows:



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

In this case, compound X may be chosen from silicone compounds comprising two or more unsaturated aliphatic groups. For example, compound X may comprise a silicone main chain whose unsaturated aliphatic groups are pendent on the main chain (side group) or located at the ends of the main chain of the compound (end group). In the rest of the description, these particular compounds will be referred to as polyorganosiloxanes containing unsaturated aliphatic groups.

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

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

$$R_m R'SiO_{\frac{(3-m)}{2}} \quad \text{(III)}$$

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, for instance a short-chain alkyl radical comprising, for example, from 1 to 10 carbon atoms, in particular a methyl radical, or alternatively a phenyl group, preferably a methyl radical;

- m is equal to 1 or 2; and
- R' represents:

• an unsaturated aliphatic hydrocarbon-based group containing from 2 to 10 and preferably from 2 to 5 carbon atoms, for instance a vinyl group or a group -R"-CH=CHR''' in which R" is a divalent aliphatic hydrocarbon-based chain containing from 1 to 8 carbon atoms, bonded to the silicon atom and R''' is a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms, preferably a hydrogen atom; groups R' that may be mentioned include vinyl and allylic groups and mixtures thereof; or

• an unsaturated cyclic hydrocarbon-based group containing from 5 to 8 carbon atoms, for instance 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):

$$R_nSiO_{\frac{(4-n)}{2}} \quad \text{(IV)}$$

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

According to one variant, compound X may be a silicone resin comprising two or more ethylenic unsaturations, the said resin being capable of reacting with compound B via hydrosilylation. Examples that may be mentioned include resins of MQ or MT type, themselves bearing -CH=CH_2 unsaturated 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 it comprises, each of the letters M, D, T and Q characterizing a type of unit.

The letter M represents the monofunctional unit of formula $(CH_3)_3SiO_{1/2}$, the silicon atom being bonded to only one oxygen atom in the polymer comprising this unit.

The letter D means a difunctional unit $(CH_3)_3SiO_{2/2}$ in which the silicon atom is bonded to two oxygen atoms.

The letter T represents a trifunctional unit of formula $(CH_3)SiO_{3/2}$.

In the units M, D and T defined above, at least one of the methyl groups may be substituted with a group R other than a methyl group, such as a hydrocarbon-based radical (especially alkyl) containing from 2 to 10 carbon atoms or a phenyl group, or alternatively a hydroxyl group.

Finally, the letter Q means a tetrafunctional unit $SiO_{4/2}$ in which the silicon atom is bonded to four hydrogen atoms, which are themselves bonded to the rest of the polymer. Examples of such resins that may be mentioned include MT silicone resins such as poly(phenylvinylsilsesquioxane), 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, compound X is chosen from polyorganopolysiloxanes, especially those comprising the siloxane units (III) and optionally (IV) described above.

Compound Y preferably comprises at least two free Si-H groups (hydrosilane groups).

Compound Y may be chosen advantageously from organosiloxanes comprising one or more alkylhydrogenosiloxane units having the following formula:

$$R_pHSiO_{\left(\frac{3-p}{2}\right)} \qquad (V)$$

in which:

R represents a linear or cyclic monovalent hydrocarbon-based group containing from 1 to 30 carbon atoms, for instance 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 alternatively a phenyl group, and p is equal to 1 or 2. Preferably, R is a hydrocarbon-based group, preferably methyl.

These organosiloxane compounds Y containing alkylhydrogenosiloxane units may also comprise units of formula:

$$R_nSiO_{\left(\frac{4-n}{2}\right)} \quad \text{(IV)}$$

as defined above.

Compound Y may be a silicone resin comprising at least one unit chosen from the units M, D, T and Q as defined above and comprising at least one Si-H group, such as the poly(methylhydridosilsesquioxanes) 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 radicals R represent a methyl group in formulae (III), (IV) and (V) above.

Preferably, these organosiloxanes Y comprise end groups of formula $(CH_3)_3SiO_{1/2}$.

Advantageously, the organosiloxanes Y comprise two or more alkylhydrosiloxane units of formula $(H_3C)(H)SiO$ and optionally comprise $(H_3C)_2SiO$ units.

Such organosiloxane compounds Y containing hydrosilane groups are described, for example, in document EP 0 465 744.

According to one variant, compound X is chosen from organic oligomers or polymers (the term “organic” means compounds whose main chain is not silicone-based, preferably compounds comprising no silicon atoms) or from organic/silicone hybrid polymers or oligomers, the said oligomers or polymers bearing at least two reactive unsaturated aliphatic groups, compound Y being chosen from the hydrogenosiloxane groups mentioned above.

Compound X, 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 and 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 polymer chain. These unsaturated polyesters are obtained by polycondensation of a mixture:

- of linear or branched aliphatic or cycloaliphatic dicarboxylic acids especially containing from 3 to 50 carbon atoms, preferably from 3 to 20 and better from 3 to 10 carbon atoms, such as adipic acid or sebacic acid, of aromatic dicarboxylic acids especially containing from 8 to 50 carbon atoms, preferably from 8 to 20 and better still from 8 to 14 carbon atoms, such as phthalic acids, especially terephthalic acid, and/or of dicarboxylic acids derived from ethylenically unsaturated fatty acid dimers such as the oleic or linoleic acid dimers described in patent 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 especially containing from 2 to 50 carbon atoms, preferably from 2 to 20 and better 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 from 6 to 15 carbon atoms, such as bisphenol A and bisphenol B, and/or of diol dimers obtained from the reduction of fatty acid dimers as defined above, and

- 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.

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

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

- of linear or branched aliphatic or cycloaliphatic dicarboxylic acids especially containing from 3 to 50 carbon atoms, preferably from 3 to 20 and better from 3 to 10 carbon atoms, such as adipic acid or sebacic acid, of aromatic dicarboxylic acids especially containing from 8 to 50 carbon atoms, preferably from 8 to 20 and better still from 8 to 14 carbon atoms, such as phthalic acids, especially terephthalic acid, and/or of dicarboxylic acids derived from ethylenically unsaturated fatty acid dimers such as the oleic or linoleic acid dimers described in patent

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 especially containing 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

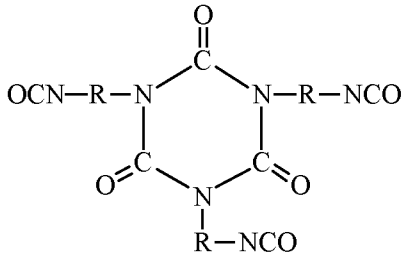
- of at least one ester of (meth)acrylic acid and of a diol or polyol containing from 2 to 20 carbon atoms and preferably from 2 to 6 carbon atoms, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate or glycerol methacrylate.

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 name 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® 50000: molar mass 1500, on average 6 acrylate functions per molecule).

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

- of aliphatic, cycloaliphatic and/or aromatic diisocyanates, triisocyanates and/or polyisocyanates especially containing from 4 to 50 and preferably from 4 to 30 carbon atoms, such as hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, diphenylmethane diisocyanate or 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 comprising from 2 to 30 carbon atoms;

- of polyols, especially 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, especially diamines, especially containing 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 and preferably from 2 to 6 carbon atoms, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate or glycerol methacrylate.

Such polyurethanes/polyureas containing acrylate groups 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 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 and IRR® 424 by the company UCB.

d) polyethers containing (meth)acrylate groups obtained by esterification, with (meth)acrylic acid, of the hydroxyl end groups of C_1-C_4 alkylene glycol

homopolymers or copolymers, such as polyethylene glycol, polypropylene glycol, copolymers of ethylene oxide and of propylene oxide preferably having a weight-average molecular mass 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, 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 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,

(ii) a diepoxy resin resulting from the reaction between bisphenol A diglycidyl ether and epichlorohydrin,

(iii) an epoxy ester resin containing αβ-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), and

(iv) an epoxy ether resin containing αβ-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), and

(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

- one or more carboxylic acids or polycarboxylic acids comprising at least one ethylenic double bond in the αβ-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 and preferably from 2 to 6 carbon atoms, such as 2-hydroxyethyl (meth)acrylate.

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, 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.

f) poly(C_{1-50} alkyl (meth)acrylates), the 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,

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

Such αβ-diol perfluoropolyethers are described especially 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 (meth)acrylic acid.

Dendrimers (from the Greek dendron = tree) are “arborescent”, i.e. highly branched, polymer molecules invented by D. A. Tomalia and his team at the start of the 1990s (Donald A. Tomalia et al., Angewandte Chemie, Int. Engl. Ed., Vol. 29, No. 2, pages 138-175). 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 type are sold, for example, under the name Starburst® 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 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 Comburst® from the company Dendritech. Hyperbranched poly(esteramides) containing 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 number of ethylenic double bonds present. This high functionality, usually greater than 5, makes them particularly useful by allowing them to act as "crosslinking nodes", i.e. sites of multiple crosslinking.

These dendritic and hyperbranched polymers may thus be used in combination with one or more of the polymers and/or oligomers a) to h) above.

The hydrosilylation reaction advantageously takes place in the presence of a catalyst, preferably based on platinum or tin.

Examples that may be mentioned include platinum-based catalysts deposited on a support of silica gel or charcoal powder (coal), platinum chloride, platinum salts and chloroplatinic acids.

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

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

Polymerization inhibitors or retarders, 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. Mention may be made, in a non-limiting manner, of cyclic polymethylvinylsiloxanes, and in particular tetravinyltetramethylcyclotetrasiloxane, and acetylenic alcohols, which are preferably volatile, such as methylisobutynol.

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

Advantageously, compounds X and Y are chosen from silicone compounds capable of reacting via hydrosilylation; in particular, compound X is chosen from polyorganosiloxanes comprising units of formula (III) described above and compound Y is chosen from organosiloxanes comprising alkylhydrosiloxane units of formula (IV) described above.

According to one particular embodiment, compound X is a polydimethylsiloxane containing vinyl end groups and compound Y is a methylhydrosiloxane.

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

MIXTURE A:

Ingredient (INCI Name)	CAS No.	Contents (%)	Function
Dimethyl Siloxane, Dimethylvinylsiloxy-terminated	68083-19-2	55-95	Polymer
Silica silylate	68909-20-6	10-40	Filler
1,3-Diethenyl-1,1,3,3-Tetramethyldisiloxane complexes	68478-92-2	Trace	Catalyst
Tetramethyldivinyldisiloxane	2627-95-4	0.1-1	Polymer

MIXTURE B:

Ingredient (INCI Name)	CAS No.	Contents (%)	Function
Dimethyl Siloxane, Dimethylvinylsiloxy-terminated	68083-19-2	55-95	Polymer
Silica Silylate	68909-20-6	10-40	Filler
Dimethyl, Methylhydrogen Siloxane, terminated with a trimethylsiloxy group	68037-59-2	1-10	Polymer

According to one embodiment, the hydrophobic polymers are obtained after reaction of the compounds X and Y that are capable of reacting via condensation, either in the presence of water (hydrolysis) by reaction of 2 compounds bearing

alkoxysilane groups, or via "direct" condensation by reaction of a compound bearing alkoxysilane group(s) and a compound bearing silanol group(s) or by reaction of 2 compounds bearing silanol group(s).

When the condensation is performed in the presence of water, this water may in particular be ambient moisture, residual water of the eyelashes, or the water provided by an external source, for example premoistening of the eyelashes (for example with a mister, or natural or artificial tears).

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

In one advantageous embodiment, compounds X and/or Y are chosen from polyorganosiloxanes comprising two or more alkoxysilane groups. The term "alkoxysilane group" means a group comprising at least one -Si-OR portion, R being an alkyl group containing from 1 to 6 carbon atoms.

Compounds X and Y are especially chosen from polyorganosiloxanes comprising alkoxysilane end groups, more specifically those comprising two or more alkoxysilane end groups and preferably trialkoxysilane end groups.

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

$$R^9_sSiO_{(4-s)/2} \quad \text{(VI)}$$

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. Alkyl groups that may especially be mentioned include methyl, propyl, butyl, and hexyl, and mixtures thereof, preferably methyl or ethyl. A fluoroalkyl group that may be mentioned is 3,3,3-trifluoropropyl.

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

$$(R^9_2SiO_2)_f \quad \text{(VII)}$$

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

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

f is especially a number ranging from 2 to 5000, preferably from 3 to 3000 and better still from 5 to 1000.

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

$$-ZSiR^1_x(OR)_{3-x}, \quad \text{(VIII)}$$

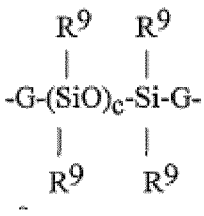
in which:

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

R^1 is a methyl or ethyl group,

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

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



(IX)

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

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

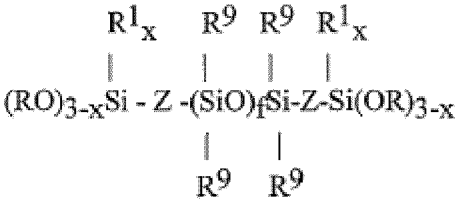
Preferably, Z is an alkylene group, and better still ethylene.

These polymers may contain 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 contain 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 or vinyl groups. Examples of such end groups that may be mentioned include

trimethoxysilane, triethoxysilane, vinyldimethoxysilane and vinylmethyloxyphenylsilane groups.

Such polymers are especially described in documents 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 patent application by reference.

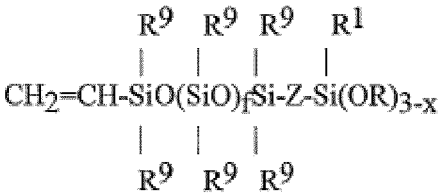
As compound X and/or Y, mention may be made in particular of the polymer of formula:



(X)

in which R, R^1, R^9, Z, x and f are as described above.

Compounds X and/or Y may also comprise a mixture of polymers of formula (X) above with polymers of formula (XI) below:



(XI)

in which R, R^1, R^9, Z, x and f are as described above.

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

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, compounds X and Y may be identical or different.

According to one variant, one of the two reactive compounds X or Y is of silicone nature and the other is of organic nature. For example, 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 polyorganosiloxanes 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 of vinyl or (meth)acrylic nature bearing alkoxysilane side groups may in particular be obtained via copolymerization of at least one organic vinyl or (meth)acrylic monomer with a (meth)acryloxypropyltrimethoxysilane, a vinyltrimethoxysilane, a vinyltriethoxysilane, an allyltrimethoxysilane, etc.

Examples that may be mentioned include the (meth)acrylic polymers described in the document by Kusabe, M., Pitture e Verniei - European Coating; 12-B, pages 43-49, 2005, and especially the polyacrylates containing alkoxysilane groups referenced as MAX from Kaneka or those described in the publication by Probster, 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, glycidoxypropyltrimethoxysilane, glycidoxypropyltriethoxysilane, epoxycyclohexylethyltrimethoxysilane, mercaptopropyltrimethoxysilane.

Examples of polyethers and polyisobutylenes containing alkoxysilane groups are described in the publication by Kusabe, M., Pitture e Verniei - European Coating; 12-B, pages 43-49, 2005. As examples of polyurethanes containing alkoxysilane end groups, mention may be made of those described in the document by Probster, M., Adhesion-Kleben & Dichten, 2004, 481 (1-2) pages 12-14 or else those described in the document by Landon, S., Pitture e Verniei vol. 73, No. 11, pages 18-24, 1997 or in the document by Huang, Mowo, Pitture e Verniei vol. 5, 2000, pages 61-67; mention may be made especially of the polyurethanes containing alkoxysilane groups from OSI-WITCO-GE.

Polyorganosiloxane compounds X and/or Y that may be mentioned include resins of MQ or MT type themselves bearing alkoxysilane and/or silanol ends, for instance the poly(isobutylsilsesquioxane) resins functionalized with silanol groups sold under the reference SST-S7C41 (3 Si-OH groups) by the company Gelest.

The condensation reaction may take place in the presence of a metal-based catalyst, a titanium-based catalyst.

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

$$Ti(OR^2)_y(OR^3)_{4-y},$$

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 containing 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 and better still from 3.4 to 4.

As examples of a combination of compounds X and Y bearing alkoxysilane groups and reacting via condensation, mention may be made of the combination of mixtures A' and B' below prepared by the company Dow Corning:

Mixture A':

Ingredient (INCI Name)	CAS No.	Contents (%)	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

Mixture B':

Ingredient (INCI Name)	CAS No.	Contents (%)	Function
Disiloxane	107-46-0	80-99	Solvent
Tetra-t-Butyl Titanate	-	1-20	Catalyst

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

According to one embodiment, the hydrophobic film-forming polymers are obtained after the reaction of compounds X and Y that have reacted together via crosslinking in the presence of peroxide.

This reaction is preferably performed by heating to a temperature of greater than or equal to 50°C, preferably greater than or equal to 80°C, which may be up to 120°C.

The identical or different compounds X and Y comprise in this case two or more $-CH_3$ side groups and/or two or more side chains bearing a $-CH_3$ group.

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 $-CH_3$ side groups bonded to the silicon atom and/or at least two side chains bearing a $-CH_3$ group. Mention may be made, for example, of polymers described in the "Reactive Silicones" catalogue from the company Gelest Inc., Edition 2004, page 6, and especially 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.

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

According to one embodiment, the hydrosilylation reaction or the condensation reaction, or alternatively the crosslinking reaction in the presence of a peroxide, between 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 especially react on keratin fibres.

In general, irrespective of the type of reaction via which 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% and better still from 20% to 80%.

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% and better still from 20% to 80%.

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

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

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

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

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, compounds X and Y may be present in a X/Y mole ratio ranging from 0.05 to 20 and better still from 0.1 to 10.

Preferably, the hydrophobic film-forming polymer(s) may be chosen from the non-neutralized copolymers of acrylic acid and of N-tert-butylacrylamide sold under the name Ultrahold Strong® by the company BASF, and tetrapolymers of (meth)acrylic acid, (meth)acrylates and C_8-C_{24} alkyl (meth)acrylate, such as those sold under the name Soltex OPT-PG by the company Röhm & Haas, having the INCI name: Acrylates/C_{12}-C_{22} Alkyl Methacrylate Copolymer, non-neutralized copolymers of vinyl acetate and of crotonic acid, in particular the copolymer of vinyl acetate/crotonic acid/vinyl tert-butyl-4-benzoate (65/10/25) (INCI name: Vinyl Acetate /Vinyl Butyl Benzoate/Crotonates Copolymer) in non-neutralized form, such as the commercial product Mexomer PW manufactured by the company Chimex; grafted silicone polymers such as polydimethylsiloxane grafted with propylthio(polymethyl acrylate/methyl methacrylate/methacrylic acid) and polymers of interpenetrating polymer network type (IPN) of polyurethane and of acrylic polymer in aqueous dispersion form, in particular the polymer sold under the name Hybridur® 875 Polymer Dispersion by the company Air Products & Chemicals.

The term "hydrophilic film-forming polymer" means any polymer (1°) that is capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous or discontinuous film that adheres to a support, especially to human keratin materials such as the skin, the hair, the eyelashes, the eyebrows or the nails, and (2°) for which the formed film is capable of absorbing an amount of water of 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 polymer film (before immersion in water) when it is dipped into liquid water.

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

The hydrophilic polymer(s) are chosen from:

(i) polyurethanes,

(ii) vinyl polymers,

(iii) natural polymers,

(iv) and mixtures 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, 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 unbranched silicone block, for example polydimethylsiloxane or polymethylphenylsiloxane, and/or

- at least one block comprising fluoro groups.

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

In order to form the polyurethane, as monomers bearing an anionic group that may be used in the polycondensation, mention may be made of dimethylolpropionic acid, trimellitic acid or a derivative such as trimellitic anhydride, the sodium salt of 3-sulfopentadiol acid or the sodium salt of 5-sulfo-1,3-benzenedicarboxylic acid.

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

As film-forming polyurethanes that may be used according to the invention, mention may thus be made of the aqueous polyurethane dispersions 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, which are capable of leading, by drying of the said polyurethane(s), at room temperature and at a relative humidity of 55%, to a material with 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) of greater than or equal to 75% after an elongation of 150%,

c) a recovery at 300 seconds (R_{300s}) of greater than 80%, after an elongation of 150%.

The material obtained by drying the said film-forming polyurethane(s) is thus sufficiently extensible so as not to break following deformations caused by the movements of the skin and to regain a shape substantially identical to its initial shape.

For the purposes of the present invention, the instantaneous recovery (R_i) of a material defines its capacity to 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 purposes of the present invention, the degree of elongation at break and the recovery are evaluated by means of the tensile tests described below.

To perform the tensile tests, a film intended for producing specimens is made by placing in a Teflon mould a sufficient amount of mixture comprising the film-forming elastomeric polymer(s) to obtain a film 500 μm ± 50 μm thick. Drying is continued until the weight of the film no longer changes, which may typically take 12 days.

In particular, for the purposes of the present invention, the term "film intended for producing or making specimens" means a film obtained by drying the said film-forming elastomeric polyurethane(s), at room temperature (22°C ± 2°C) and at a relative humidity of 55% ± 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 produce the film for the manufacture of specimens contains less than 3% by weight of active materials, a preliminary concentration operation is performed, for example by evaporating off some of the solvent so that the mixture contains at least 3% of elastomeric polymers. This operation makes it possible to avoid excessively long drying.

The film obtained is then chopped into rectangular specimens 80 mm long and 15 mm wide.

The tests are performed on a machine 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 room temperature (22°C ± 2°C) and at a relative humidity of 55% ± 5%.

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

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

- the specimen is drawn by 150% (ε_{max}), i.e. 1.5 times its initial length (I_0),
- the stress is removed by imposing a return speed equal to the tensile speed, i.e. 20 mm/minute, and the elongation of the specimen is measured as a percentage, after returning to zero load (ε_i).

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

$$R_i=((\varepsilon_{max}-\varepsilon_i)/\varepsilon_{max})\times 100$$

To determine the recovery at 300 seconds, the specimen is maintained at zero stress for a further 300 seconds, after having undergone the preceding operations, 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 specimen 300 seconds after returning to zero load (ε_i).

Thus, the recovery at 300 seconds (R_{300s}) of a material defines its capacity 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 an elongation during a tensile stress.

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

$$R_{300s}=((\varepsilon_{max}-\varepsilon_i)/\ \varepsilon_{300s})\times 100$$

Advantageously, the film-forming elastomeric polyurethane(s) according to the invention are such that they form, under the conditions of the tests described above, a material with 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% and preferably from 90% to 100%.

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-aminoethyl sulfonic acid and ethylenediamine.

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-aminoethane sulfonate.

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.

Preferably, vinyl polymer(s) 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 purposes of the present invention, the term "polyvinyl alcohol" means a polymer comprising $-CH_2CH(OH)-$ units.

The polyvinyl alcohols are generally produced by hydrolysis of polyvinyl acetate. Usually, the reaction takes place in the presence of methanol (alcoholysis). The reaction is usually acid-catalysed or base-catalysed. The degree of hydrolysis of commercial products is variable, often around 87% but there are also products with a degree of hydrolysis of 100%. 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 be made, for example, of the products from the Celvol range sold by the company Celanese under the names Celvol 540, Celvol 350, Celvol 325, Celvol 165, Celvol 125 Celvol 540 S, Celvol 840, Celvol 443.

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

The copolymer(s) of C_4-C_8 monounsaturated carboxylic acids or anhydrides may be selected from copolymers comprising (i) one or more maleic, fumaric or itaconic acids or anhydrides and (ii) one or more monomers selected from vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, the anhydride functions of these copolymers optionally being monoesterified or monoamidated.

Such polymers are described in particular in US patents 2 047 398, 2 723 248 and 2 102 113 and GB patent 839 805, and especially those sold under the names Gantrez® AN or ES and Avantage CP by the company ISP.

Preferably, the copolymers derived from C_4-C_8 monounsaturated carboxylic acids or anhydrides are chosen from acrylic acid and esters thereof, such as the methyl vinyl ether/monoesterified maleic anhydride copolymers sold, for example, under the name Gantrez ES 225 by the company ISP.

Among the methyl vinyl ether/butyl monomaleate copolymers, mention may be made especially of the copolymer sold by the company ISP.

The hydrophilic polymers may also be chosen from natural polymers, in particular polysaccharides bearing as base units monosaccharides or disaccharides.

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

Guar gums are galactomannans composed of mannose and of galactose.

For the purposes of the present patent application, the term "modified guar gum" means guar gums alkylated with at least one C_{1-8} alkyl group, guar gums hydroxyalkylated by at least one C_{1-8} hydroxyalkyl group or guar gums acylated by at least one C_{1-8} acyl group.

Preferably, they will be hydroxypropyl guar gums, such as the product sold under the name Jaguar HP 105 by the company Rhodia.

Cellulose is a β-1,4-polyacetal of cellobiose, cellobiose being a disaccharide composed 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; hydroxyalkyl-alkylcellulose mixed celluloses such as hydroxypropyl-methylcelluloses, hydroxyethyl-methylcelluloses, hydroxyethyl-ethylcelluloses and hydroxybutyl-methylcelluloses.

Among the anionic cellulose ethers, mention may be made of carboxyalkylcelluloses and salts thereof. Examples that may be mentioned include carboxymethylcelluloses, carboxymethylmethylcelluloses and carboxymethylhydroxyethylcelluloses, and the sodium salts thereof. Among the cationic cellulose ethers, mention may be made of crosslinked or non-crosslinked quaternized hydroxyethylcelluloses. The quaternizing agent may especially 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 esters of cellulose (cellulose nitrates, sulfates, phosphates, etc.), organic cellulose esters (cellulose monoacetates, triacetates, amidopropionates, acetatebutyrates, acetatepropionates and acetatetrimellitates, etc.), and mixed organic/inorganic esters of cellulose, such as cellulose acetatebutyrate sulfates and cellulose acetatepropionate sulfates.

Among the cellulose ester ethers, mention may be made of hydroxypropylmethylcellulose phthalates and ethylcellulose sulfates. The cellulose 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 name Avicel® (microcrystalline cellulose, MCC) by the company FMC Biopolymers, under the name Cekol (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, under the names Aqualon® (carboxymethylcellulose and sodium carboxymethylcellulose), Benecel® (methylcellulose), Blanose™ (carboxymethylcellulose), Culminai® (methylcellulose, hydroxypropyl methylcellulose), Klucel® (hydroxypropylcellulose), Polysurf® (cetyl hydroxyethylcellulose) and Natrosol® CS (hydroxyethylcellulose) by the company Hercules Aqualon.

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

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

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

The gellan gum derivatives are all products obtained by performing standard chemical reactions such as, especially, esterifications or addition of a salt of an organic or mineral acid.

Use is made, as derivative of gellan gum, for example, of welan gum. Welan gum is a gellan gum modified by fermentation using Alcaligenes strain ATCC 31 555. Welan gum has a repeating pentasaccharide structure formed from a main chain constituted by D-glucose, D-glucuronic acid and L-rhamnose units onto which is grafted an L-rhamnose or L-mannose side unit.

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

Mention may be made, as other saccharide polymers that may be used according to the invention, of starches and derivatives thereof.

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

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

According to a third embodiment, antiperspirant cosmetic film comprises at least one adhesive layer, at least one layer formed from one or more hydrophilic film-forming polymers and at least one layer formed from one or more hydrophobic film-forming polymers, the adhesive layer, the layer of hydrophilic film-forming polymer and the layer of hydrophobic film-forming polymer being superposed on each other.

The cosmetic film is thus placed in contact with the skin by means of the adhesive layer so as to make the film adhere.

The combined presence of the two layers of hydrophilic and hydrophobic polymers makes it possible to improve the permeability of the film.

According to this embodiment, the adhesive layer may also be formed from one or more pressure-sensitive adhesive compounds.

In accordance with this third embodiment, the hydrophobic polymers and the hydrophilic polymers are as described previously in the second embodiment.

Preferably, the antiperspirant cosmetic film comprises:

(a) at least one adhesive layer, which may be formed from one or more pressure-sensitive adhesive compounds,

(b) at least one layer 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 sulfonate,

(c) at least one layer formed from one or more hydrophobic film-forming polymers chosen from non-neutralized hydrophobic copolymers of (meth)acrylic or crotonic acid, such as non-neutralized acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymers, for instance the Ultrahold Strong products,

polymers of interpenetrating polymer network type (IPN) of polyurethane and of acrylic polymer in the form of an aqueous dispersion, or tetrapolymers of (meth)acrylic acid, (meth)acrylates and C_8-C_{24} alkyl (meth)acrylate, for instance the copolymer sold under the name Soltex OPT-PG.

More preferentially, the antiperspirant cosmetic film comprises:

(a) at least one adhesive layer, which may be formed from one or more pressure-sensitive adhesive compounds,

(b) at least one layer 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 sulfonate,

(c) at least one layer formed from one or more hydrophobic film-forming polymers chosen from non-neutralized hydrophobic copolymers of (meth)acrylic or crotonic acid, such as non-neutralized acrylic acid/ethyl acrylate/N-tert-butylacrylamide polymers, for instance the Ultrahold Strong products.

According to a fourth embodiment, the antiperspirant cosmetic film may comprise at least one pressure-sensitive adhesive layer positioned on one face of a monolayer comprising at least two zones A and B, zone A being formed from at least one hydrophilic film-forming a polymer and zone B being formed from at least one hydrophobic film-forming polymer, zones A and B being adjacent.

According to a fifth embodiment, the antiperspirant cosmetic film may comprise at least one pressure-sensitive adhesive layer positioned on one face of a polyurethane elastomer base layer, in which:

(a) the base layer is a layer of polyurethane elastomer with a glass transition temperature of less than or equal to 0°C,

(b) the pressure-sensitive adhesive layer is an acrylic layer comprising one or more copolymers containing at least 70% by weight, relative to the total weight of the said copolymer(s) of one or more units derived from monomers chosen from alkyl acrylates containing an alkyl group ranging from 8 to 12 carbon atoms and alkyl methacrylates containing an alkyl group ranging from 8 to 12 carbon atoms.

The cosmetic film thus adheres to the surface of the skin by means of the adhesive layer.

The base layer used in the antiperspirant film of the present invention corresponds to a layer of polyurethane elastomer with a glass transition temperature of less than or equal to 0°C.

The polyurethane elastomer serving to form the basal layer may be chosen from the film-forming elastomeric polyurethanes described previously.

The pressure-sensitive adhesive layer is an acrylic layer comprising one or more copolymers containing at least 70% by weight, relative to the total weight of the said copolymer(s) of one or more units derived from monomers chosen from alkyl acrylates comprising an alkyl group ranging from 8 to 12 carbon atoms and alkyl methacrylates comprising an alkyl group ranging from 8 to 12 carbon atoms.

Among the units derived from a monomer, alkyl acrylates containing an alkyl group ranging from 8 to 12 carbon atoms are particularly preferred.

Preferably, the alkyl acrylates containing an alkyl group ranging from 8 to 12 carbon atoms are chosen from 2-ethylhexyl acrylate, isooctyl acrylate, n-octyl acrylate and isononyl acrylate.

Thus, the copolymer(s) used in the pressure-sensitive adhesive acrylic layer may comprise one or more units derived from a monomer, in particular two or more units derived from a monomer, chosen from 2-ethylhexyl acrylate, isooctyl acrylate, n-octyl acrylate and isononyl acrylate.

Preferably, the copolymer(s) comprise one or more units derived from monomers chosen from alkyl acrylates and alkyl methacrylates in a content of at least 70% by weight and more preferentially in a content of at least 80% by weight relative to the total weight of the said copolymer(s).

In particular, the copolymer(s) comprise from 70% to 95% by weight and preferentially from 80% to 95% by weight of units derived from monomers chosen from alkyl acrylates containing an alkyl group ranging from 8 to 12 carbon atoms and alkyl methacrylates containing an alkyl group ranging from 8 to 12 carbon atoms.

The copolymer(s) may also comprise one or more other comonomers.

As examples of comonomers that may be envisaged, mention may be made especially of monomers containing a functional group, for instance monomers containing a carboxyl group, such as acrylic acid and methacrylic acid, and monomers containing a hydroxyl group, such as hydroxyethyl acrylate or hydroxypropyl acrylate.

As other comonomers that may be envisaged, mention may also be made of vinyl acetate, styrene, vinylpyrrolidone and acrylamide.

An alkyl acrylate or an alkyl methacrylate not containing an alkyl group ranging from 8 to 12 carbon atoms may also be used as comonomer, such as ethyl acrylate or butyl acrylate.

The copolymer(s) may be chosen from the copolymers obtained by copolymerization:

(1) of 70% to 95% by weight, relative to the total weight of the said copolymers, of one or more monomers chosen from alkyl acrylates containing an alkyl group ranging from 8 to 12 carbon atoms and/or alkyl methacrylates containing an alkyl group ranging from 8 to 12 carbon atoms,

(2) of 1% to 10% by weight, relative to the total weight of the said copolymer(s), of one or more comonomers chosen from monomers bearing a functional group other than the monomers (1), and

(3) of 0 to 25% by weight, relative to the total weight of the said copolymer(s), of one or more comonomers other than the monomers (1) and (2).

The pressure-sensitive adhesive copolymer(s) may be prepared by subjecting the monomers described above to a solution polymerization in an organic solvent such as toluene, hexane or ethyl acetate under a nitrogen atmosphere using a peroxide such as benzoyl peroxide or a nitrogenous compound such as AIBN (azobisisobutyronitrile) as initiators.

The antiperspirant cosmetic film according to the present invention may also comprise one or more antiperspirant active agents.

The antiperspirant active agent(s) that may be used according to the invention may be chosen from aluminium salts and/or zirconium salts, complexes of zirconium hydroxychloride and of aluminium hydroxychloride with an amino acid and/or mixtures thereof.

Among the aluminium salts, mention may especially be made of aluminium chlorohydrate in activated or unactivated form, aluminium chlorohydrex, the aluminium chlorohydrex-polyethylene glycol complex, the aluminium chlorohydrex-propylene glycol complex, aluminium dichlorohydrate, the aluminium dichlorohydrex-polyethylene glycol complex, the aluminium dichlorohydrex-propylene glycol complex, aluminium sesquichlorohydrate, the aluminium sesquichlorohydrex-polyethylene glycol complex, the aluminium

sesquichlorohydrex-propylene glycol complex, aluminium sulfate buffered with sodium aluminium lactate.

Among the aluminium-zirconium salts, mention may be made in particular of aluminium zirconium octachlorohydrate, aluminium zirconium pentachlorohydrate, aluminium zirconium tetrachlorohydrate and aluminium zirconium trichlorohydrate.

The complexes of zirconium hydroxychloride and of aluminium hydroxychloride with an amino acid are generally known under the name ZAG (when the amino acid is glycine). Among these products, mention may be made of the aluminium zirconium octachlorohydrex-glycine complexes, the aluminium zirconium pentachlorohydrex-glycine complexes, the aluminium zirconium tetrachlorohydrex-glycine complexes and the aluminium zirconium trichlorohydrex-glycine complexes.

Thus, the antiperspirant active agent(s) may be chosen from aluminium chlorohydrates and the complexes containing them used in the pressure-sensitive adhesive layer, mention may be made of the following substances used and approved by the FDA (Food & Drug Administration): aluminium chlorohydrate, aluminium chlorohydrex-PEG, aluminium chlorohydrex-PG, aluminium dichlorohydrate, aluminium dichlorohydrex-PEG, aluminium dichlorohydrex-PG, aluminium sesquichlorohydrate, aluminium sesquichlorohydrex-PEG, aluminium sesquichlorohydrex-PG, aluminium zirconium octachlorohydrate, aluminium zirconium octachlorohydrex-GLY, aluminium zirconium pentachlorohydrate, aluminium zirconium pentachlorohydrex-GLY, aluminium zirconium tetrachlorohydrate, aluminium zirconium trichlorohydrate, aluminium zirconium tetrachlorohydrex-GLY, and aluminium zirconium trichlorohydrex-GLY, given that the abbreviations PEG, PG and GLY denote, respectively, polyethylene glycol, propylene glycol and glycine. Commercial products of this type are sold, for example, by the company Clariant under the name Locron S (aluminium chlorohydrate), by the company Reheis under the name Reach 301 or by the company Guilini Chemie under the name Aloxicoll PF 40 (aluminium chlorohydrex), by the company Reheis under the name Rezal 67 Solution (aluminium zirconium pentachlorohydrate sold as an aqueous solution containing 40% active material).

Preferably, the antiperspirant active agent is chosen from aluminium salts and more specifically aluminium chlorohydrate salts.

The width of the cosmetic film transferred onto the skin by the transfer head of the device of the present invention may range from 3 to 10 cm, and the length of the film may range from 5 to 20 cm.

The thickness of the cosmetic film may range from 1 to 100 μm and preferably from 1 to 30 μm.

For the purposes of the present invention, the term "film" means a thin and grippable solid. The term "thin" means a solid with a maximum thickness of 100 μm. This film is generally appropriately dimensioned so as to be easy for the user to handle. It may have a square, rectangular or disc shape, or any other shape.

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

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

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

In order to protect the antiperspirant cosmetic film against any external contamination when it is outside the transfer device, a protective layer may be positioned over the antiperspirant film.

Similarly, in order to improve the handling of the cosmetic film when it is outside the transfer device, a support layer may also be positioned over the protective layer.

The support layer enables the user to manipulate the cosmetic film when he desires especially to place it in the transfer device of the present invention.

The support layer may be formed using a film that is composed of any thermoplastic resin, for example polyurethane, polyethylene, polypropylene, ionomers, polyamides, polyvinyl chloride, ethylene-vinyl acetate copolymers, thermoplastic polymers and polytetrafluoroethylene. The support may or may not also be composed of any biodegradable plastic material, for example polyhydroxybutyrates, polyhydroxyalkanoates, maltotriose, polylactic acid, polylactic acid resins, polyethylene succinate resins, polybutylene succinate resins, polycaprolactone resins, poly(butylene-adipate-co-terephthalate), poly(tetramethylene adipate-co-terephthalate), poly(ethylene terephthalate) resins,

polyvinyl alcohol, polyglycolic acid, fatty acid esters of starch, starch-based polyesters, cellulose acetate and chitosan. The various types of film may be laminated on paper.

According to one embodiment, the transfer device comprises a guide member intended to guide the belt that is arranged between the feed reel and the receiver reel.

Advantageously, the guide member prevents the part of the belt that is between the feed reel and the receiver reel from collapsing.

Preferably, the guide member is a roll, in particular an hourglass-shaped roll.

According to one embodiment, the application head overhangs relative to the case and has a rounded general shape at its end.

The application head thus enables the user to exert a pressure from the transfer strip onto the surface of the skin so as to deposit the antiperspirant cosmetic film. Moreover, the application head makes it possible to guide the unrolling of the transfer strip during the use of the transfer device. Specifically, the transfer strip is brought outside the case via the open end (or outlet orifice) of the case, and then returns inside the case by means of this same end, while at the same time forming a loop around the application head.

A subject of the present invention is also a cosmetic process for treating human perspiration and possibly the body odour associated with human perspiration, especially underarm odour, comprising the use of a transfer device as described previously for applying to the skin an antiperspirant cosmetic film.

In particular, the treatment process according to the present invention comprises at least one step that consists in applying to the skin the antiperspirant cosmetic film delivered by the transfer device as described previously.

More particularly, the application head of the transfer device is applied to the skin to deposit the antiperspirant cosmetic film.

Similarly, the present invention relates to a transfer device as described previously, comprising an antiperspirant cosmetic film comprising at least one adhesive layer, at least one layer formed from at least one hydrophobic film-forming polymer and at least one layer formed from at least one hydrophilic film-forming polymer, the said layers being superposed on each other.

Other characteristics and advantages of the invention will emerge on detailed examination of an embodiment, taken as a non-limiting example, of the application to the skin of an antiperspirant cosmetic film applied via a transfer device according to the invention and illustrated by the attached drawings, in which:

- figure 1 is a front view in cross section of a cosmetic film transfer device according to the invention,

- figure 2 schematically shows a transfer device comprising a precut antiperspirant cosmetic film having a rectangular geometrical shape and arranged on a base strip.

Figure 1 shows a transfer device, designated by the general reference numeral 1. The device is intended to be used for the transfer or application onto a surface of skin of an antiperspirant cosmetic film 7 arranged on a transfer strip 6.

The device 1 comprises a case 11 that has a substantially rectangular profile in cross section. The case 11 comprises at one end a rounded portion 11a, a cylindrical central portion 11b whose walls converge towards an open end or an outlet orifice 11c. The rounded portion 11a and the central portion 11b may be made as a single piece. However, it is also possible to envisage making the rounded-end portion 11a and the central portion 11b in the form of two separate pieces attached together, for example by click-fastening or by any other appropriate means. The rounded portion 11a enables the user to hold the case 11 against the palm of his hand.

The case 11 comprises a feed reel 3 on which is wound a transfer strip 6, a receiver reel 4 and an application head 9 which is mounted fixed onto the open end 11c of the case.

Thus, the feed reel 3 is surrounded by the transfer strip 6 which comprises a base strip 8 coated with an antiperspirant cosmetic film 7. In particular, the transfer strip 6 may be directly in contact with the feed reel 3. The feed reel 3 is mounted so as to rotate freely on a support axle 13. Initially, the majority of the transfer strip 6 is wound around the feed reel 3.

The receiver reel 4 is itself surrounded by the transfer strip 6 once the strip is depleted of cosmetic film 7. In other words, the receiver reel 4 is surrounded by the base strip 8. The receiver reel 4 is also mounted so as to rotate freely on a support axle 14.

The application head 9 overhangs relative to the case 11 and is held by means of a fixing member 9a. The application head 9 may, for example, have a

cylindrical shape or have the shape of a tongue. Preferably, the application head 9 has a rounded general shape at its end.

In particular, the application head 9 comprises a portion 9b and a pressing end 10 that may have a rounded shape. The application head 9 projects into the outlet orifice 11c and delimits two passages 20a and 20b.

Thus, the outlet orifice 11c has two passages 20a and 20b, noted as the upper passage 20a and lower passage 20b relative to the surface of the skin noted S, which are located on either side of the application head 9, which makes it possible to bring, outside the case 11, the transfer strip 6 bearing cosmetic film 7 via the passage 20b and to recover, inside the case 11, the transfer strip 6 depleted of the cosmetic film 7, i.e. the base strip 8 used, via the passage 20a. The passages 20a and 20b have sufficient dimensions so as not to impede the conveyance of the transfer strip 6 out of or into the case 11 and also the variation of thickness of the transfer strip 6.

In other words, the application head 9 is mounted projecting into the aperture of the case 11 so as to delimit two passages 20a and 20b whose dimensions are sufficient to allow for circulation of the transfer strip 6 and the variation in thickness of the transfer strip 6. Preferably, the passages 20a and 20b are of identical width.

As a variant, the application head 9 may correspond to a shoe-shaped end piece. The application head 9 may thus be removably mounted on the open end 11c, for example by click-fastening so as to facilitate its replacement with an end piece of a different shape that is adapted to the part of the body to be treated.

As shown in figure 1, an endless belt 5 that may be made of rubber extends between the feed reel 3 and the receiver reel 4 in order to connect them together and to make them function co-operatively, in particular such that the rotation of the feed reel 3 drives the rotation of the receiver reel 4. The endless belt 5 has an outer side 5a and an inner side 5b.

A guide member 2 serving to guide the belt 5 may be arranged between the feed reel 3 and the receiver reel 4 on the outer side 5a of the belt 5. In particular, the guide member 2 is in contact with the outer side 5a of the belt 5. The guide member 2 prevents the part of the belt 5 that is between the feed reel 3 and the receiver reel 4 from collapsing. The guide member 2 preferably has a circular cross section and is preferably a roll. The guide member 2 may be in the form of a circular jack, but is preferably an hourglass-shaped roll. The position of the guide member 2 is chosen so

as to prevent slackening of the belt 5 and to prevent the guide member from exerting a high resistance against the belt during its functioning.

When the user presses the application head 9 onto a surface of skin noted S and slides the transfer device 1 in the direction 15, the feed reel 3 moves by rotating about the support axle 13, which also entrains the clockwise unrolling of the transfer strip 6. Thus, the transfer strip 6 is brought outside the case 11 through the open end 11c via the passage 20b and then returns inside the case 11 via the passage 20a, forming a loop around the application head 9.

More particularly, when the user positions and slides the application head 9 on the surface of skin S, the transfer strip 6 becomes pressed against the surface of skin via the portion 9b, making it possible to apply the antiperspirant cosmetic film 7 to the said surface. The portion 9b has an area that is sufficient to apply a significant part of the transfer strip 6 onto the surface of skin S. This part of the transfer strip deposited onto the skin has a given area as a function of the width of the transfer strip 6 and of the area of the portion 9b of the application head 9. For example, the portion 9b may have an area ranging from 3 cm to 10 cm wide and 5 cm to 20 cm long. The application head 9 thus enables the user to exert a pressure from the transfer strip 6 onto the surface of skin S. Furthermore, the application head 9 guides the unrolling of the transfer strip 6.

Consequently, once the antiperspirant cosmetic film 7 is applied to the surface of skin S, the transfer strip 6 depleted of the cosmetic film 7 is conveyed to the receiver reel 4 which moves in rotation about the support axle 13.

Specifically, the rotation of the feed reel 3 about the support axle 13 results in tightening of the belt 5, which brings about rotation of the receiver reel 4 about the support axle 14.

The case 11 of the transfer device 1 may be formed from a transparent or semi-transparent resin to enable visual observation of the transfer strip 6. The case 11 may also be formed from any suitable material, such as an opaque resin. The guide member 2 and the case 11 may be formed as a single piece or may be formed separately. The guide member 2 may overhang relative to the case and may be produced from a metal or a resin.

As indicated previously, the antiperspirant cosmetic film 7 may have several geometrical shapes. In particular, the cosmetic film 7 may be oval, rectangular, circular or star-shaped.

As shown in figure 2, the antiperspirant cosmetic film 7 may be precut, in particular in a rectangular form, and may be positioned on the base strip 8.

The antiperspirant cosmetic film 7 may also become cut by removing the application head 9 from the surface of the skin.

The cosmetic film 7 deposited on the skin gives a satisfactory antiperspirant effect.

Advantageously, the case 11 of the transfer device 1 may be made in two parts that click together to enable the insertion of a refill of the transfer strip 6. In particular, the refill comprises a feed reel 3 on which the transfer strip 6 provided with antiperspirant cosmetic film 7 is wound and which is connected via an endless belt to a receiver reel 4.

CLAIMS

1. Use, for the application to the skin of an antiperspirant cosmetic film (7), of a transfer device (1) provided with a case (11) having an open end (11c) comprising:

- a feed reel (3) on which is wound a transfer strip (6) comprising a base strip (8) coated with the antiperspirant cosmetic film (7) to be transferred,

- an application head (9) mounted on the open end (11c), intended to press the transfer strip (6) against a surface of skin in order to transfer the antiperspirant cosmetic film (7) onto the said surface,

- a receiver reel (4) for receiving the used base strip (8),

- a belt-type drive mechanism, the said drive mechanism comprising an endless belt (5) cooperatively connecting the feed reel (3) with the receiver reel (4).

2. Use according to Claim 1, characterized in that the antiperspirant cosmetic film (7) comprises at least one adhesive layer.

3. Use according to Claim 2, characterized in that the antiperspirant cosmetic film (7) comprises at least one adhesive layer formed from one or more pressure-sensitive adhesive compounds.

4. Use according to Claim 3, characterized in that the pressure-sensitive adhesive compound(s) are chosen from adhesive organic polymers.

5. Use according to Claim 4, characterized in that the adhesive organic polymers are chosen from adhesive polyesters containing one or more sulfonic functions, cationic or amphoteric polyurethanes comprising one or more self-adhesive tertiary or quaternary amine functions and self-adhesive cationic or amphoteric radical polymers.

6. Use according to Claim 2, characterized in that the antiperspirant cosmetic film (7) also comprises at least one layer formed from one or more hydrophilic or hydrophobic film-sensitive antiperspirant polymers.

7. Use according to Claim 6, characterized in that the hydrophobic film-forming polymers are synthetic polymers chosen from:

(i) polymers of interpenetrating polymer network type (IPN) of polyurethane and of acrylic polymer in the form of an aqueous particle dispersion,

(ii) grafted silicone polymers,

(iii) non-neutralized copolymers of (meth)acrylic acid and of N-tert-butylacrylamide,

(iv) non-neutralized copolymers of crotonic acid and of vinyl acetate;

(v) tetrapolymers of (meth)acrylic acid, of (meth)acrylates and of C_8-C_{24} alkyl (meth)acrylate, and

(vi) polymers that have been obtained after 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, the said compounds X and Y having reacted together via a hydrosilylation, condensation or crosslinking reaction in the presence of peroxide when they are placed in contact with each other;

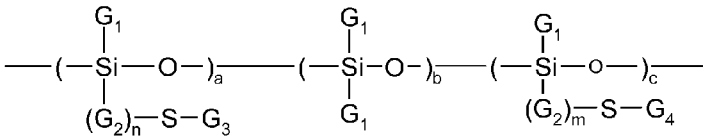
(vii) mixtures thereof.

8. Use according to Claim 7, characterized in that the hydrophobic film-forming polymers are chosen from:

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

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

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



(II)

in which the radicals G, which may be identical or different, represent hydrogen, a C_1-C_{10} alkyl radical or a phenyl radical; the radicals G_2, which may be identical or different, represent a C_1-C_{10} alkylene group; G_3 represents a polymer residue resulting from the (homo)polymerization of at least one ethylenically unsaturated anionic monomer; G_4 represents a polymer residue resulting from the (homo)polymerization of at least one ethylenically unsaturated hydrophobic monomer; m and n are, independently of each other, equal to 0 or 1; a is an integer ranging from 0 to 50; b is an integer which may be 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.

10. Use according to Claim 7, characterized in that the hydrophobic film-forming polymer(s) may be obtained after 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, the said compounds X and Y having reacted together via a hydrosilylation, condensation or crosslinking reaction in the presence of peroxide when they are placed in contact with each other.

11. Use according to Claim 6, characterized in that the hydrophilic film-forming polymers are chosen from:

(i) polyurethanes,

(ii) vinyl polymers,

(iii) natural polymers,

(iv) and mixtures thereof.

12. Use according to Claim 11, 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 sulfonic acid and ethylenediamine, and copolymers obtained by copolymerization of adipic acid, dicyclohexylmethane diisocyanate, ethylenediamine, hexanediol, neopentyl glycol and sodium N-(2-aminoethyl)-3-aminoethane sulfonate.

13. Use according to Claim 11, characterized in that the vinyl polymers are chosen from polyvinyl alcohols, copolymers derived from C_4-C_8 monounsaturated carboxylic acids or anhydrides, and methyl vinyl ether/butyl monomaleate copolymers.

14. Use according to Claim 11, characterized in that the natural polymers are chosen from guar gums and modified guar gums, celluloses, gellan gum and derivatives thereof, in particular celluloses.

15. Use according to Claim 2, characterized in that the antiperspirant cosmetic film (7) also comprises at least one layer formed from one or more hydrophilic film-forming polymers and at least one layer formed from one or more hydrophobic film-forming polymers, the adhesive layer, the layer of hydrophilic

film-forming polymer and the layer of hydrophobic film-forming polymer being superposed on each other.

16. Use according to Claim 2, characterized in that the antiperspirant cosmetic film (7) also comprises a monolayer 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 hydrophobic film-forming polymer, zones A and B being adjacent.

17. Cosmetic process for treating human perspiration, and optionally the body odour associated with human perspiration, especially underarm odour, which consists in applying to the skin the transfer device (1) as defined according to any one of Claims 1 to 16.

18. Transfer device (1) according to Claim 1, comprising an antiperspirant cosmetic film (7) comprising at least one adhesive layer, at least one layer formed from at least one hydrophobic film-forming polymer and at least one layer formed from at least one hydrophilic film-forming polymer, the said layers being superposed on each other.

FIG.1

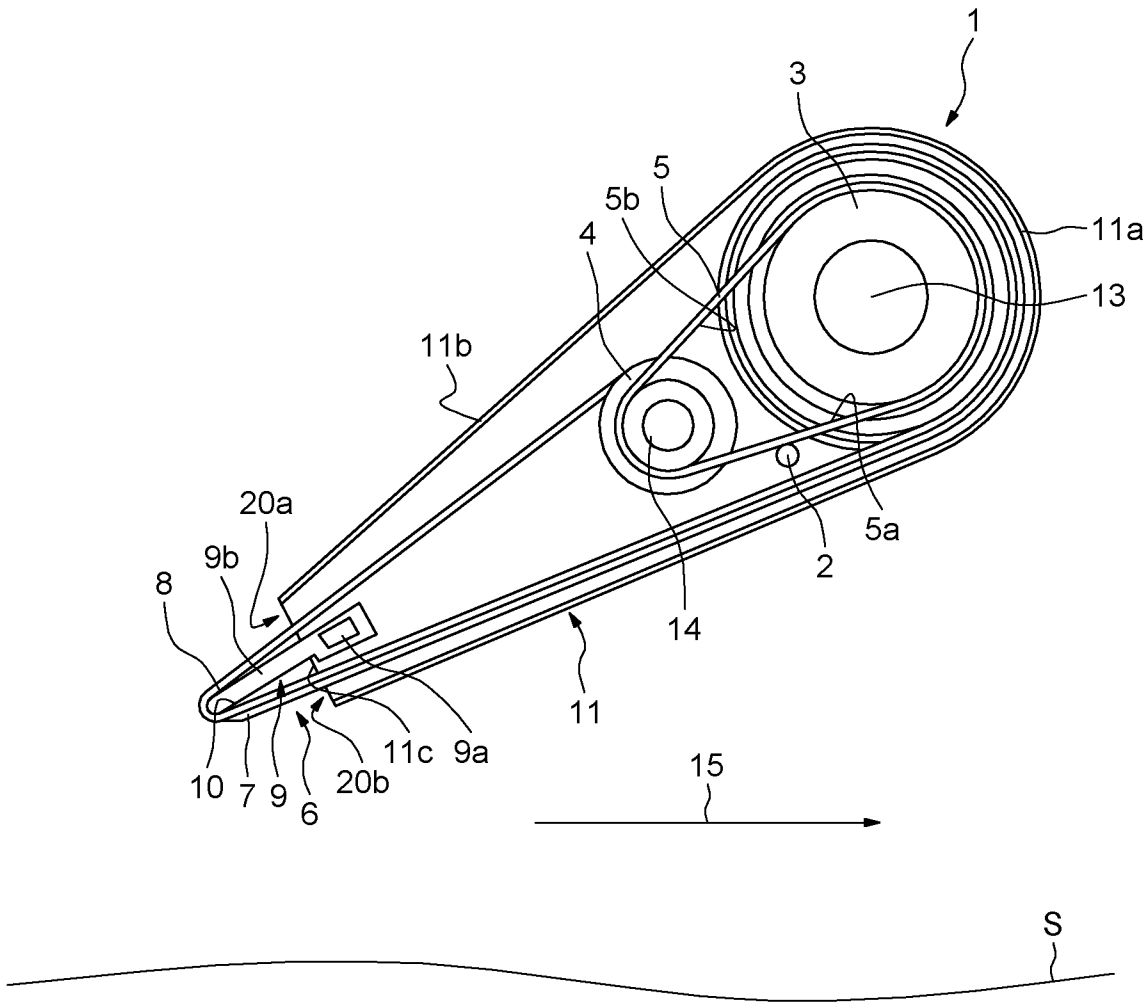


FIG.2