The present invention relates to an emulsion-type cosmetic composition for coating keratin fibres, comprising: - an aqueous phase, - at least one wax, - at least one anionic surfactant comprising a cationic counterion, and - at least one alkali metal or alkaline-earth metal halide in a total content of greater than or equal to 0.05% by weight relative to the total weight of the composition. The present invention also relates to a process for coating keratin fibres, and in particular for making up the eyelashes, comprising a step of applying the said cosmetic composition for coating keratin fibres.
Cosmetic composition for coating keratin fibres

The present invention relates to a cosmetic composition for coating keratin fibres, and in particular the eyelashes or the eyebrows. In particular, the said cosmetic composition is a composition for making up and optionally caring for the eyelashes. The present invention also relates to a process for coating keratin fibres, in particular a process for making up and optionally caring for the eyelashes.

The composition used may especially be in the form of an eyelash product such as a mascara, or an eyebrow product. More preferentially, the invention relates to a mascara. The term "mascara" means a composition intended to be applied to the eyelashes: it may be an eyelash makeup composition, an eyelash makeup base (also known as a base coat), a composition to be applied over a mascara, also known as a top coat, or a cosmetic composition for treating the eyelashes. The mascara is more particularly intended for human eyelashes, but also false eyelashes.

Mascaras are especially prepared according to two types of formulation: water-based mascaras known as cream mascaras, in the form of a dispersion of waxes in water; anhydrous mascaras or mascaras with a low water content, known as waterproof mascaras, in the form of dispersions of waxes in organic solvents. The present patent application more specifically relates to water-based mascaras.

Keratin fibre coating compositions of such a mascara type generally consist of at least one fatty phase generally formed from one or more waxes dispersed in an aqueous liquid phase by means of an emulsifying system or conveyed in an organic solvent.

The application of mascara is in particular directed towards increasing the volume of the eyelashes and consequently increasing the intensity of the gaze. Numerous thickening or volumizing mascaras exist to do this, the principle of which consists in depositing a maximum amount of material onto the eyelashes so as to obtain this volumizing (or charging) effect.

It is in particular by means of the amount of solid particles (especially the
waxes, which structure the composition) that the desired application specificities for compositions may be adjusted, for instance their fluidity or consistency, and also their thickening power (also known as the charging or makeup power).

These solid particles are dispersed in the cream mascara by means of an emulsifying system composed of one or more surfactant(s).

However, the makeup film obtained after applying these mascara compositions is generally not sufficiently resistant to water, for example during bathing or showering, to tears or to sweat, or even to sebum. The mascara then has a tendency to run - appearance of rings under the eyes - or to flake away over time: grains become deposited and unaesthetic marks appear around the eyes.

An aim of the present invention is thus to obtain a composition for coating keratin fibres, preferably a mascara, which gives rise to a volumizing effect on the eyelashes.

An aim of the present invention is to obtain a composition for coating keratin fibres, preferably a mascara, which has good staying power on the eyelashes.

An aim of the present invention is to obtain a composition for coating keratin fibres, preferably a mascara, which gives rise to a charging or covering deposit.

An aim of the present invention is to obtain a composition for coating keratin fibres, preferably a mascara, which has good application properties in terms of glidance and of playtime (redemption, retouching).

An aim of the present invention is to obtain a composition for coating keratin fibres, preferably a mascara, which has good lengthening properties for eyelashes coated with such a composition.

An aim of the present invention is to obtain a composition for coating keratin fibres, preferably a mascara, which has good curling properties for eyelashes coated with such a composition.
An aim of the present invention is to obtain a composition for coating keratin fibres, preferably a mascara, which has a good strength of black, from a point of view of colorimetry and chromaticity.

An aim of the present invention is to obtain a composition for coating keratin fibres, preferably a mascara, which shows good adherence to the eyelashes from a bonding point of view.

An aim of the present invention lies also in the development of a composition for coating keratin fibres and of a process for coating keratin fibres, which shows good staying power on the eyelashes or the eyebrows.

In particular, one aim of the present invention is to prepare a composition for coating keratin fibres which shows good staying power, and is resistant to rubbing and/or to water, and especially to ambient moisture, tears, sweat and/or sebum.

An aim of the present invention is also to propose a composition for coating keratin fibres that allows good separation of the eyelashes during its application, without formation of bunches of eyelashes, and while ensuring smooth and uniform deposition of material (without lumps of composition).

An aim of the present patent application is more particularly to propose a mascara in which not only the waxes but also the pigments are dispersed homogeneously, the said mascara having a sufficiently thick texture to obtain a charging deposit, of satisfactory consistency, which allows easy application to the eyelashes and a uniform deposition, i.e. smooth and homogeneous.

According to a first aspect, a subject of the present invention is thus an emulsion-type cosmetic composition for coating keratin fibres, comprising:

- an aqueous phase,
- at least one wax,
- at least one anionic surfactant comprising a cationic counterion, and
- at least one alkali metal or alkaline-earth metal halide present in a total content of
greater than or equal to 0.05% by weight relative to the total weight of the composition.

Surprisingly and unexpectedly, the inventors of the present patent application have solved this (these) problem(s) by means of such a composition.

This composition thus gives rise to a mascara of emulsion type which has good cosmetic properties and whose affinity for water is reduced.

According to a second aspect, a subject of the present invention is also an assembly or kit for coating keratin fibres, comprising:
- at least one cosmetic composition for coating keratin fibres as described previously, and
- at least one applicator for the composition, the said applicator comprising means, where appropriate in relief, configured to come into contact with the said keratin fibres, such as the eyelashes or the eyebrows, so as to smooth and/or separate the eyelashes or the eyebrows. Such reliefs may comprise teeth, bristles or the like. The said assembly, and in particular the said applicator, may optionally be equipped with means for vibrating and/or heating the said composition.

According to a third aspect, a subject of the present invention is also an assembly or kit for conditioning and applying a composition for coating keratin fibres, comprising:
- a device for conditioning the said cosmetic composition for coating keratin fibres as described previously,
- an applicator for the said composition.
The said applicator may be integrally attached to a handling member forming a cap for the said conditioning device. In other words, the said applicator may be mounted in a removable position on the said device between a closed position and an open position of a dispensing aperture of the device for conditioning the said composition.

According to a fourth aspect, a subject of the present invention is also a process for coating keratin fibres, and in particular for making up the eyelashes, comprising a step of applying a cosmetic composition for coating keratin fibres as described previously.
Throughout the description that follows, and unless otherwise mentioned:
- the term "alkyl" means a linear or branched saturated C₈-C₁₄, better still C₁₂-C₂₄ and more preferentially C₁₄-C₁₈ hydrocarbon-based chain.
- The term "acyl" means a linear or branched saturated C₈-C₂₄, better still C₁₂-C₂₄ and more preferentially C₁₄-C₁₈ hydrocarbon-based chain comprising a carboxylic function whose hydroxyl function (-OH) has been replaced.

According to particular preferred embodiments of the present invention:
- the said anionic surfactant(s) are chosen from:
  - alkyl phosphates;
  - alkyl sulfates, and in particular alkyl ether sulfates, alkylamido ether sulfates, alkylaryl polyether sulfates and monoglyceride sulfates;
  - alkylsulfonates, alkylamidesulfonates, alkylaryl sulfonates, α-olefin sulfonates and paraffin sulfonates;
  - alkylsulfosuccinates, alkyl ether sulfosuccinates and alkylamidesulfosuccinates;
  - alkyl sulfosuccinamates;
  - alkylsulfoacetates;
  - acylsarcosinates, acylglutamates, acylsethionates, N-acyltaurates and acyllactylates;
  - carboxylic alkylpolyglycoside esters such as alkylglucoside citrates, alkylpolyglycoside tartrates, alkylpolyglycoside sulfosuccinates and alkylpolyglycoside sulfosuccinamates; and
  - fatty acids, in particular oleic acid, ricinoleic acid, palmitic acid or stearic acid salts, coconut oil acid or hydrogenated coconut oil acid;
  - alkyl-D-galactosideuronic acids and salts thereof, polyoxyalkylenated (C₆-C₂₄)alkyl ether carboxylic acids, polyoxyalkylenated (C₃-C₂₄)alkylaryl ether carboxylic acids, polyoxyalkylenated (C₆-C₂₄)alkylamido ether carboxylic acids and salts thereof, in particular those comprising from 2 to 50 alkylene oxide and in particular ethylene oxide groups;
  - and mixtures thereof;
- the said ionic surfactant(s) are chosen from C_{12}-C_{22} and preferably C_{14}-C_{18} fatty acids, and preferably comprises stearic acid, and even more preferentially consists essentially of stearic acid, the stearic acid representing at least 75% by weight of the anionic surfactant(s) present in the composition;

- the said ionic surfactant(s) are present in a total content of greater than or equal to 1% by weight relative to the total weight of the composition, preferably ranging from 1.5% to 8% and better still from 2% to 5% by weight relative to the total weight of the composition;

- the said cationic counterion(s) are chosen from a cation of mineral origin, in particular chosen from alkali metal and alkaline-earth metal cations, or a cation of organic origin, preferably of organic origin;

- the said cationic counterion(s) are chosen from ammonium, and amine and amino alcohol derivatives thereof, or magnesium, preferably from ammonium, and amine and amino alcohol derivatives thereof;

- the said cationic counterion(s) comprise a primary (poly)hydroxyalkylamine, preferably aminomethylpropanediol;

  - the total content of cationic counterion(s) is greater than or equal to 0.01%, preferably inclusively between 0.1% and 4% by weight and better still between 0.5% and 2% by weight relative to the total weight of the composition;

- the said halide ion(s) are chosen from the chloride ion, the bromide ion and the iodide ion, preferably the chloride ion;

  - the said alkali metal of the halide ion(s) is chosen from sodium and potassium, preferably sodium;

  - the said alkaline-earth metal of the halide ion(s) is chosen from calcium and magnesium, preferably calcium;

  - the said alkali metal or alkaline-earth metal halide(s) are chosen from sodium chloride, calcium chloride and a mixture thereof, preferably sodium chloride;

  - the emulsion may be of the wax(es)-in-water type;

  - the said composition comprises a fatty phase dispersed in the aqueous phase;

  - the fatty phase may predominantly comprise waxes;

  - the said composition may comprise one or more wax(es), preferably several;

  - this or these wax(es) may be chosen from beeswax, lanolin wax, Chinese insect waxes, rice wax, carnauba wax, candelilla wax, ouricury wax, esparto grass wax,
cork fibre wax, sugarcane wax, Japan wax, sumach wax, montan wax, microcrystalline waxes, paraffin wax, ozokerite, polyethylene wax, the waxes obtained by Fisher-Tropsch synthesis, a C₂₀-C₄₀ alkyl (hydroxystearoxy)stearate, waxy copolymers, in particular the ethylene/vinyl acetate copolymer, and esters thereof, the waxes obtained by catalytic hydrogenation of animal or plant oils containing linear or branched C₈-C₃₂ fatty chains, the waxes obtained by hydrogenation of olive oil esterified with stearyl alcohol, the waxes obtained by hydrogenation of castor oil esterified with cetyl alcohol, silicone waxes, for instance alkyl or alkoxy dimethicones containing from 16 to 45 carbon atoms, and fluoro waxes, and mixtures thereof;

- the said composition may comprise at least one wax chosen from candelilla wax, carnauba wax, beeswax, paraffin wax, polyethylene wax and rice wax, and mixtures thereof;

- the wax(es) may be present in a content of greater than or equal to 5% by weight relative to the total weight of the composition, better still 7% by weight, or even 10% by weight relative to the total weight of the composition;

- the cosmetic composition comprises at least one hydrophilic or lipophilic film-forming polymer and/or at least one hydrophilic gelling agent;

- the cosmetic composition may comprise at least one volatile or non-volatile oil, for example a hydrocarbon-based oil;

- the said composition may comprise at least one volatile or non-volatile oil, for example a hydrocarbon-based oil;

- the cosmetic composition may comprise at least one pulverulent dyestuff chosen from pigments, and preferably chosen from metal oxides, in particular iron oxides and titanium oxides;

- the metal oxide(s) are preferably present in a content of greater than or equal to 2% by weight relative to the total weight of the composition, and advantageously inclusively between 3% and 15% by weight relative to the total weight of the composition;

- the composition may be a makeup composition, a makeup base, a "top coat" composition to be applied over a makeup, or a cosmetic composition for treating or caring for keratin fibres.

Other characteristics, properties and advantages of the present invention will emerge more clearly on reading the description and the examples that follow.
Aqueous phase
The composition according to the invention comprises an aqueous phase, which may form a continuous phase of the composition.

The aqueous phase comprises water. It may also comprise at least one water-soluble solvent.

In the present invention, the term "water-soluble solvent" denotes a compound that is liquid at room temperature and water-miscible.

The water-soluble solvents that may be used in the compositions according to the invention may also be volatile.

Among the water-soluble solvents that may be used in the compositions in accordance with the invention, mention may be made especially of lower monoalcohols containing from 1 to 5 carbon atoms such as ethanol and isopropanol, and glycols containing from 2 to 8 carbon atoms such as ethylene glycol, propylene glycol, 1,3-butylene glycol and dipropylene glycol.

The aqueous phase (water and optionally the water-miscible solvent) is generally present in the composition according to the present patent application in a content ranging from 20% to 90% by weight, preferably ranging from 25% to 80% by weight, preferentially ranging from 30% to 70% by weight and better still from 35% to 60% by weight relative to the total weight of the composition.

Fatty phase
A fatty phase in accordance with the invention comprises at least one waxy phase.

This waxy phase comprises one or more waxes.

This fatty phase may also comprise constituents chosen especially from at least one pasty fatty substance, at least one volatile oil and at least one non-volatile oil, and mixtures thereof.

The said fatty phase may predominantly comprise waxes.

Waxy phase or waxes
The wax(es) under consideration in the context of the present invention are generally a lipophilic compound that is solid at room temperature (25°C), with a solid/liquid reversible change of state, having a melting point of greater than or equal to 30°C, which may be up to 200°C and in particular up to 120°C.
In particular, the waxes that are suitable for the invention may have a melting point of greater than or equal to 45°C and in particular greater than or equal to 55°C.

For the purposes of the invention, the melting point corresponds to the temperature of the most endothermic peak observed on thermal analysis (DSC) as described in standard ISO 11357-3; 1999. The melting point of the wax may be measured using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name DSC Q2000 by the company TA Instruments.

Preferably, the waxes have a heat of fusion $AH_f$ of greater than or equal to 70 J/g.

Preferably, the waxes comprise at least one crystallizable part, which is visible by X-ray scattering observation.

The measuring protocol is as follows:

A sample of 5 mg of wax placed in a crucible is subjected to a first temperature rise ranging from -20°C to 120°C, at a heating rate of 10°C/minute, it is then cooled from 120°C to -20°C at a cooling rate of 10°C/minute and is finally subjected to a second temperature rise ranging from -20°C to 120°C at a heating rate of 5°C/minute. During the second temperature rise, the following parameters are measured:

- the melting point ($T_m$) of the wax, as mentioned previously corresponding to the temperature of the most endothermic peak of the melting curve observed, representing the variation of the difference in power absorbed as a function of the temperature,
- $AH_f$: the heat of fusion of the wax, corresponding to the integral entire melting curve obtained. This heat of fusion of the wax is the amount of energy required to make the compound change from the solid state to the liquid state. It is expressed in J/g.

The wax(es) may be hydrocarbon-based waxes, fluoro waxes and/or silicone waxes and may be of plant, mineral, animal and/or synthetic origin.

The wax(es) may be present in a content of greater than or equal to 5% by weight relative to the total weight of the composition, better still 7% by weight, or even 10% by weight relative to the total weight of the composition. Preferably, it is (they are) present in a content ranging from (or inclusively between) 10% and 40% by weight, better still from 12% to 35% by weight and even better still from 15% to 30% by weight relative to the total weight of the composition.

Hydrocarbon-based waxes, for instance beeswax, lanolin wax or Chinese insect wax; rice wax, carnauba wax, candelilla wax, ouricury wax, esparto grass wax, cork fibre wax, sugarcane wax, Japan wax and sumach wax; montan wax,
microcrystalline waxes, paraffin waxes and ozokerite; polyethylene waxes, the waxes obtained by Fisher-Tropsch synthesis and waxy copolymers, in particular ethylene/vinyl acetate copolymers, and also esters thereof, may preferably be used as wax(es).

Mention may also be made of waxes obtained by catalytic hydrogenation of animal or plant oils containing linear or branched C8-C32 fatty chains.

Among these waxes that may especially be mentioned are hydrogenated jojoba oil, isomerized jojoba oil such as the trans-isomerized partially hydrogenated jojoba oil manufactured or sold by the company Desert Whale under the commercial reference Iso-Jojoba-50®, hydrogenated sunflower oil, hydrogenated castor oil, hydrogenated coconut oil, hydrogenated lanolin oil and bis(1,1,1-trimethylolpropane) tetrastearate sold under the name Hest 2T-4S by the company Heterene, bis(1,1,1-trimethylolpropane) tetrabehenate sold under the name Hest 2T-4B by the company Heterene.

Mention may also be made of silicone waxes, for instance alkyl or alkoxy dimethicones containing from 16 to 45 carbon atoms, and fluoro waxes.

The wax obtained by hydrogenation of olive oil esterified with stearyl alcohol, sold under the name Phytowax Olive 18L57 or else the waxes obtained by hydrogenation of castor oil esterified with cetyl alcohol sold under the names Phytowax ricin 16L64 and 22L73 by the company Sophim may also be used. Such waxes are described in patent application FR-A-2 792 190.

The composition may comprise at least one apolar wax. Preferably, the wax(es) comprise(s) one or more apolar wax(es) chosen from polyethylene wax, paraffin wax and ozokerite, and mixtures thereof.

The composition may comprise at least one polar wax. The term "polar wax" means waxes comprising in their chemical structure, in addition to carbon and hydrogen atoms, at least one highly electronegative heteroatom, such as O, N or P.

Preferably, the wax(es) comprise(s) one or more polar wax(es) chosen from carnauba wax, candelilla wax, natural (or blanched) beeswax and synthetic beeswax, and mixtures thereof. A synthetic beeswax that may be mentioned is the wax sold under the name Cyclometh 326 A by Evonik Goldschmidt (INCI name: Synthetic Beeswax).

Preferably, the composition comprises a mixture of polar wax(es) and of apolar wax(es).

The composition may comprise at least one wax having a hardness ranging from 0.05 MPa to 15 MPa and preferably ranging from 6 MPa to 15 MPa. The hardness is
determined by measuring the compressive force, measured at 20°C using the texture
analyser sold under the name TA-TX2i by the company Rheo, equipped with a stainless-
steel cylinder with a diameter of 2 mm, travelling at a measuring speed of 0.1
mm/second, and penetrating the wax to a penetration depth of 0.3 mm.

According to one particular embodiment, the compositions according to the
invention may comprise at least one wax referred to as a tacky wax, i.e. a wax with a tack
of greater than or equal to 0.7 N.s and a hardness of less than or equal to 3.5 MPa.

Using such a tacky wax may especially make it possible to obtain a cosmetic
composition that applies easily to the eyelashes, attaches well to the eyelashes and leads
to the formation of a smooth, uniform and thickening makeup result.

The tacky wax used may especially have a tack ranging from 0.7 N.s to 30
N.s, in particular greater than or equal to 1 N.s, especially ranging from 1 N.s to 20 N.s, in
particular greater than or equal to 2 N.s, especially ranging from 2 N.s to 10 N.s and in
particular ranging from 2 N.s to 5 N.s.

The tack of the wax is determined by measuring the change in force
(compression force or stretching force) as a function of time, at 20°C, using the texture
analyser sold under the name TA-TX2i® by Rheo, equipped with a conical acrylic
polymer spindle forming an angle of 45°.

The measuring protocol is as follows:

The wax is melted at a temperature equal to the melting point of the wax +
10°C. The molten wax is poured into a container 25 mm in diameter and 20 mm deep.
The wax is recrystallized at room temperature (25°C) for 24 hours such that the surface
of the wax is flat and smooth, and the wax is then stored for at least 1 hour at 20°C
before measuring the tack.

The texture analyser spindle is displaced at a speed of 0.5 mm/s, then
penetrates the wax to a penetration depth of 2 mm. When the spindle has penetrated the
wax to a depth of 2 mm, the spindle is held still for 1 second (corresponding to the
relaxation time) and is then withdrawn at a speed of 0.5 mm/s.

During the relaxation time, the force (compression force) decreases greatly
until it becomes zero, and then, during the withdrawal of the spindle, the force (stretching
force) becomes negative and then rises again to the value 0. The tack corresponds to the
integral of the curve of the force as a function of time for the part of the curve
corresponding to negative values of the force (stretching force). The tack value is
expressed in N.s.
The tacky wax that may be used generally has a hardness of less than or equal to 3.5 MPa, in particular ranging from 0.01 MPa to 3.5 MPa, especially ranging from 0.05 MPa to 3 MPa or even ranging from 0.1 MPa to 2.5 MPa.

The hardness is measured according to the protocol described previously.

Tacky waxes that may be used include a C_{25-20} alkyl (hydroxystearyloxy)stearate (the alkyl group comprising from 20 to 40 carbon atoms), alone or as a mixture, in particular a C_{20-40} alkyl 12-(12'-hydroxystearyloxy)stearate, of formula (II):

\[
\text{HgC} \left( \text{CH}_2 \right)_{5-10} \text{CH} \left( \text{Cl}^{3/4} \right)_{10-0} \text{C} \left( \text{O} \right)_{m} \text{CH}_2 \text{CH}_3 \\
\text{O} \left( \text{Cl}^{3/4} \right)_{10-0} \text{CH} \left( \text{CH}_2 \right)_{5-10} \text{Cl}^{3/4} \text{OH}
\]

in which \( m \) is an integer ranging from 18 to 38, or a mixture of compounds of formula (II).

Such a wax is especially sold under the names Kester Wax K 82 P® and Kester Wax K 80 P® by the company Koster Keunen.

The waxes mentioned above generally have a starting melting point of less than 45°C.

Use may also be made of the microcrystalline wax sold under the reference SP 18 by Strahl and Pitsch, which has a hardness of around 0.46 MPa and a tack value of around 1 N.s.

The wax(es) may be present in the form of an aqueous wax microdispersion.

The term “aqueous wax microdispersion” means an aqueous dispersion of wax particles, in which the size of the said wax particles is less than or equal to about 1 \( \mu \text{m} \).

Wax microdispersions are stable dispersions of colloidal wax particles, and are described especially in Microemulsions Theory and Practice, L.M. Prince Ed., Academic Press (1977) pages 21-32.

In particular, these wax microdispersions may be obtained by melting the wax in the presence of a surfactant, and optionally some of the water, followed by gradual addition of hot water with stirring. Intermediate formation of an emulsion of the water-in-oil type is observed, followed by a phase inversion with final production of a microemulsion.
of the oil-in-water type. On cooling, a stable microdispersion of solid colloidal wax particles is obtained.

The wax microdispersions may also be obtained by stirring the mixture of wax, surfactant and water using an agitation means such as ultrasonic waves, a high-pressure homogenizer or turbomixers.

The particles of the wax microdispersion preferably have mean sizes of less than 1 µη (especially ranging from 0.02 µη to 0.99 µη), preferably less than 0.5 µη (especially ranging from 0.06 µη to 0.5 µη).

Pasty fatty substances

A composition according to the invention may comprise at least one pasty fatty substance.

For the purposes of the present invention, the term "pasty fatty substance" means a lipophilic fatty compound with a reversible solid/liquid change of state, which comprises at a temperature of 23°C a liquid fraction and a solid fraction.

In other words, the starting melting point of the pasty compound can be less than 23°C. The liquid fraction of the pasty compound measured at 23°C can represent 9% to 97% by weight of the compound. This fraction that is liquid at 23°C preferably represents between 15% and 85% and more preferably between 40% and 85% by weight.

Preferably, the pasty fatty substances have an end melting point of less than 60°C.

Preferably, the pasty fatty substances have a hardness of less than or equal to 6 MPa.

Preferably, the pasty fatty substances have, in the solid state, a crystal organization, which is visible by X-ray scattering observation.

For the purpose of the invention, the melting point corresponds to the temperature of the most endothermic peak observed on thermal analysis (DSC) as described in Standard ISO 11357-3; 1999. The melting point of a pasty substance or of a wax may be measured using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name DSC Q2000 by the company TA Instruments.
As regards the measurement of the melting point and the determination of the end melting point, the sample preparation and measurement protocols are as follows:

A sample of 5 mg of pasty fatty substance, preheated to 80°C and withdrawn with magnetic stirring using a spatula that is also heated, is placed in a hermetic aluminium capsule, or a crucible. Two tests are performed to ensure the reproducibility of the results.

The measurements are performed on the abovementioned calorimeter. The oven is flushed with nitrogen. Cooling is provided by an RCS 90 heat exchanger. The sample is then subjected to the following protocol: it is first of all placed at a temperature of 20°C, and then subjected to a first temperature rise passing from 20°C to 80°C, at a heating rate of 5°C/minute, then is cooled from 80°C to -80°C at a cooling rate of 5°C/minute and finally subjected to a second temperature rise passing from -80°C to 80°C at a heating rate of 5°C/minute. During the second temperature rise, the variation in the difference between the power absorbed by the empty crucible and the crucible containing the sample of paste or wax as a function of the temperature is measured. The melting point of the compound is the value of the temperature corresponding to the top of the peak of the curve representing the variation in the difference in power absorbed as a function of the temperature.

The end melting point corresponds to the temperature at which 95% of the sample has melted.

The liquid fraction by weight of the pasty compound at 23°C is equal to the ratio of the heat of fusion consumed at 23°C to the heat of fusion of the pasty compound.

The heat of fusion of the pasty compound is the heat consumed by the compound in order to pass from the solid state to the liquid state. The pasty compound is said to be in the solid state when all of its mass is in crystalline solid form. The pasty compound is said to be in the liquid state when all of its mass is in liquid form.

The heat of fusion of the pasty compound is equal to the integral of the entire melting curve obtained using the abovementioned colorimeter, with a temperature rise of 5 or 10°C/minute, according to standard ISO 11357-3:1999. The heat of fusion of the pasty compound is the amount of energy required to make the compound change from the solid state to the liquid state. It is expressed in J/g.

The heat of fusion consumed at 23°C is the amount of energy absorbed by the sample to change from the solid state to the state that it has at 23°C, constituted of a
liquid fraction and a solid fraction.

The liquid fraction of the pasty compound measured at 32°C preferably represents from 30% to 100% by weight of the compound, preferably from 50% to 100%, more preferably from 60% to 100% by weight of the compound. When the liquid fraction of the pasty compound measured at 32°C is equal to 100%, the temperature of the end of the melting range of the pasty compound is less than or equal to 32°C.

The liquid fraction of the pasty compound measured at 32°C is equal to the ratio of the heat of fusion consumed at 32°C to the heat of fusion of the pasty compound. The heat of fusion consumed at 32°C is calculated in the same way as the heat of fusion consumed at 23°C.

As regards the measurement of the hardness, the sample preparation and measurement protocols are as follows:

The pasty fatty substance is placed in a mould 75 mm in diameter, which is filled to about 75% of its height. In order to overcome the thermal history and to control the crystallization, the mould is placed in a Votsch VC 0018 programmable oven, where it is first placed at a temperature of 80°C for 60 minutes, then cooled from 80°C to 0°C at a cooling rate of 5°C/minute, and then left at the stabilized temperature of 0°C for 60 minutes, and then subjected to a temperature rise ranging from 0°C to 20°C, at a heating rate of 5°C/minute, and then left at the stabilized temperature of 20°C for 180 minutes.

The compression force measurement is taken using a TA/TX2i texturometer from Swantech. The spindle used is chosen according to the texture:

- cylindrical steel spindle 2 mm in diameter for very rigid starting materials;
- cylindrical steel spindle 12 mm in diameter for sparingly rigid starting materials.

The measurement comprises three steps: a first step after automatic detection of the surface of the sample, where the spindle moves at a measuring speed of 0.1 mm/s, and penetrates into the fatty substance to a penetration depth of 0.3 mm, the software notes the maximum force value reached; a second "relaxation" step where the spindle remains at this position for one second and the force is noted after 1 second of relaxation; finally, a third "withdrawal" step in which the spindle returns to its initial position at a speed of 1 mm/s, and the probe withdrawal energy (negative force) is noted.

The hardness value measured during the first step corresponds to the
maximum compression force measured in newtons divided by the area of the
texturometer cylinder expressed in mm² in contact with the pasty fatty substance. The
hardness value obtained is expressed in megapascals or MPa.

The pasty fatty substance is preferably chosen from synthetic compounds and
compounds of plant origin. A pasty compound may be obtained by the synthesis from
starting materials of plant origin.

The pasty compound is advantageously chosen from:
- lanolin and derivatives thereof,

- petroleum jelly, in particular the product whose INCI name is petrolatum and which is
  sold under the name Ultima White PET USP by the company Penreco,

- polyol ethers chosen from polyalkylene glycol pentaerythrityl ethers, fatty alcohol
  ethers of sugars, and mixtures thereof, polyethylene glycol pentaerythrityl ether
  comprising five oxyethylene (5 OE) units (CTFA name: PEG-5 Pentaerythrityl Ether),

- polypropylene glycol pentaerythrityl ether comprising five oxypropylene (5 OP) units
  (CTFA name: PEG-5 Pentaerythrityl Ether) and mixtures thereof, and more especially
  the mixture PEG-5 Pentaerythrityl Ether, PPG-5 Pentaerythrityl Ether and soybean oil,
  sold under the name Lanolide by the company Vevy, which is a mixture in which the
  constituents are in a 46/46/8 weight ratio: 46% PEG-5 Pentaerythrityl Ether, 46%
  PPG-5 Pentaerythrityl Ether and 8% soybean oil;

- polymeric or non-polymeric silicone compounds

- polymeric or non-polymeric fluoro compounds

- vinyl polymers, especially:
  - olefin homopolymers and copolymers,

- hydrogenated diene homopolymers and copolymers,

- linear or branched oligomers, homopolymers or copolymers of alkyl
  (meth)acrylates preferably containing a C₈-C₉₀ alkyl group,

- oligomers, homopolymers and copolymers of vinyl esters
  containing C₈-C₉₀ alkyl groups,

- oligomers which are homopolymers and copolymers of vinyl ethers
  containing C₈-C₉₀ alkyl groups,

- liposoluble polyethers resulting from the polyetherification between one or more C₂-
  C₁₀ and preferably C₁₂-C₂₀ diols,
- esters,
- and/or mixtures thereof.

The pasty compound is preferably a polymer, especially a hydrocarbon-based polymer.

Among the liposoluble polyethers that are particularly preferred are copolymers of ethylene oxide and/or of propylene oxide with \( \text{C}_6-\text{C}_{30} \) long-chain alkylene oxides, more preferably such that the weight ratio of the ethylene oxide and/or of the propylene oxide to the alkylene oxides in the copolymer is from 5:95 to 70:30. In this family, mention will be made especially of copolymers such that the long-chain alkylene oxides are arranged in blocks having an average molecular weight from 1000 to 10 000, for example a polyoxyethylene/polydodecyl glycol block copolymer such as the ethers of dodecanediol (22 mol) and of polyethylene glycol (45 OE) sold under the brand name Elfacos ST9 by Akzo Nobel.

Among the esters, the following are especially preferred:
- esters of a glycerol oligomer, especially diglycerol esters, in particular condensates of adipic acid and of glycerol, for which some of the hydroxyl groups of the glycerols have reacted with a mixture of fatty acids such as stearic acid, capric acid, stearic acid and isostearic acid, and 12-hydroxystearic acid, preferably such as bis-diglyceryl polyacyladipate-2 sold under the brand name Softisan 649 by the company Sasol,
- the arachidyl propionate sold under the brand name Waxenol 801 by Alzo,
- phytosterol esters,
- fatty acid triglycerides and derivatives thereof, for instance triglycerides of fatty acids, which are especially \( \text{C}_{16}-\text{C}_{18} \), and partially or totally hydrogenated such as those sold under the reference Softisan 100 by the company Sasol,
- pentaerythritol esters,
and mixtures thereof.

- esters of a diol dimer and of a diacid dimer, where appropriate esterified on their free alcohol or acid function(s) with acid or alcohol radicals, especially dimer dilinoleate esters; such esters may be chosen especially from the esters having the following INCI nomenclature: bis-behenyl/isostearyl/phytosteryl dimer dilinoleyl dimer
dilinoleate (Plandool G), phytosteryl/isostearyl/cetyl/stearyl/behenyl dimer dilinoleate (Plandool H or Plandool S), and mixtures thereof,
- mango butter, such as the product sold under the reference Lipex 203 by the company AarhusKarlshamn,
- shea butter, in particular the product for which the INCI name is Butyrospermum Parkii Butter, such as the product sold under the reference Sheasoft® by the company AarhusKarlshamn,
- and mixtures thereof.

Among the pasty compounds, bis-behenyl/iso-stearyl/phytosteryl dimer dilinoleyl, bis(diglyceryl) poly(2-acyladipate), hydrogenated castor oil dimer dilinoleate, for example Risocast DA-L sold by Kokyu Alcohol Kogyo, and hydrogenated castor oil isostearate, for example Salacos HCIS (V-L) sold by Nisshin Oil, mango butter, shea butter, and vinylpyrrolidone/eicosene copolymers, or a mixture thereof, will preferably be chosen.

A composition according to the invention is preferably free of pasty fatty substance. However, a composition according to the invention may comprise one or more pasty fatty substances in a total content of greater than or equal to 0.01% by weight relative to the total weight of the said composition, for example between 0.1% and 2% by weight relative to the total weight of the composition.

Oil or organic solvent

The compositions according to the present patent application may also contain one or more oil(s) or organic solvent(s). The term "oil" means a fatty substance that is liquid at room temperature and at atmospheric pressure. The composition according to the invention may comprise at least one volatile oil and/or at least one non-volatile oil, and mixtures thereof.

Volatile oil

The composition according to the invention may comprise at least one volatile oil.

The term "volatile oil" means an oil (or non-aqueous medium) that can evaporate on contact with the skin in less than one hour, at room temperature and atmospheric pressure. The volatile oil is a cosmetic volatile oil, which is liquid at room temperature. More specifically, a volatile oil has an evaporation rate of between 0.01 and
200 mg/cm²/min, limits included.

To measure this evaporation rate, 15 g of oil or of oil mixture to be tested are placed in a crystallizing dish 7 cm in diameter, which is placed on a balance in a large chamber of about 0.3 m³ that is temperature-regulated, at a temperature of 25°C, and hygrometry-regulated, at a relative humidity of 50%. The liquid is allowed to evaporate freely, without stirring it, while providing ventilation by means of a fan (Papst-Motoren, reference 8550 N, rotating at 2700 rpm) placed in a vertical position above the crystallizing dish containing the said oil or the said mixture, the blades being directed towards the crystallizing dish, 20 cm away from the bottom of the crystallizing dish. The mass of oil remaining in the crystallizing dish is measured at regular intervals. The evaporation rates are expressed in mg of oil evaporated per unit of area (cm²) and per unit of time (minutes).

This volatile oil may be hydrocarbon-based.

The volatile hydrocarbon-based oil may be chosen from hydrocarbon-based oils containing from 7 to 16 carbon atoms.

The composition according to the invention may contain one or more volatile branched alkane(s). The expression "one or more volatile branched alkane(s)" means, without preference, "one or more volatile branched alkane oil(s)".

As volatile hydrocarbon-based oils containing from 7 to 16 carbon atoms, mention may be made especially of C₈₋C₁₆ branched alkanes, for instance C₅₋C₁₆ isoalkanes (also known as isoparaffins), isododecane, isodecane, isohexadecane and for example the oils sold under the trade names Isopar or Permethyl, C₅₋C₁₆ branched esters such as isohexyl neopentanoate, and mixtures thereof. Preferably, the volatile hydrocarbon-based oil containing from 8 to 16 carbon atoms is chosen from isododecane, isodecane and isohexadecane, and mixtures thereof, and is especially isododecane.

The composition according to the invention may contain one or more volatile linear alkane(s). The term "one or more volatile linear alkane(s)" means, without preference, "one or more volatile linear alkane oil(s)".

A volatile linear alkane that is suitable for the invention is liquid at room temperature (about 25°C) and at atmospheric pressure (760 mmHg).

A "volatile linear alkane" that is suitable for the invention means a cosmetic
linear alkane, which is capable of evaporating on contact with the skin in less than one hour, at room temperature (25°C) and atmospheric pressure (760 mmHg, i.e. 101 325 Pa), which is liquid at room temperature, especially having an evaporation rate ranging from 0.01 to 15 mg/cm²/min, at room temperature (25°C) and atmospheric pressure (760 mmHg).

The linear alkanes, preferably of plant origin, comprise from 7 to 15 carbon atoms, in particular from 9 to 14 carbon atoms and more particularly from 11 to 13 carbon atoms.

As examples of linear alkanes that are suitable for the invention, mention may be made of the alkanes described in patent applications WO 2007/068 371 or WO 2008/155 059 by the company Cognis (mixtures of distinct alkanes that differ by at least one carbon). These alkanes are obtained from fatty alcohols, which are themselves obtained from coconut oil or palm oil.

As examples of linear alkanes that are suitable for the invention, mention may be made of n-heptane (C7), n-octane (C8), n-nonane (C9), n-decane (C10), n-undecane (C11), n-dodecane (C12), n-tridecane (C13), n-tetradecane (C14) and n-pentadecane (C15), and mixtures thereof, and in particular the mixture of n-undecane (C11) and n-tridecane (C13) described in Example 1 of patent application WO 2008/155 059 by the company Cognis. Mention may also be made of n-dodecane (C12) and n-tetradecane (C14) sold by Sasol under the references, respectively, Parafol 12-97 and Parafol 14-97, and also mixtures thereof.

The linear alkane may be used alone or as a mixture of at least two distinct alkanes that differ from each other by a carbon number of at least 1, and especially a mixture of at least two linear alkanes comprising from 10 to 14 distinct carbon atoms that differ from each other by a carbon number of at least 2, and in particular a mixture of C12C14 volatile linear alkanes or a mixture of C12C13 linear alkanes, in particular an n-undecane/n-tridecane mixture (such a mixture may be obtained according to Example 1 or Example 2 of WO 2008/155 059).

As a variant or additionally, the composition prepared may comprise at least one volatile silicone oil or solvent that is compatible with cosmetic use.

The term "silicone oil" means an oil containing at least one silicon atom, and especially containing Si-O groups. According to one embodiment, the said composition comprises less than 10% by weight of non-volatile silicone oil(s), relative to the total
weight of the composition, better still less than 5% by weight, or even is free of silicone oil.

Volatile silicone oils that may be mentioned include cyclic polysiloxanes and linear polysiloxanes, and mixtures thereof. Volatile linear polysiloxanes that may be mentioned include hexamethyldisiloxane, octamethyltrisiloxane, decamethyloxasiloxane, tetradecamethylhexasiloxane and hexadecamethylheptasiloxane. Volatile cyclic polysiloxanes that may be mentioned include hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane.

As a variant or additionally, the composition prepared may comprise at least one volatile fluoro oil.

The term "fluoro oil" means an oil containing at least one fluorine atom. Volatile fluoro oils that may be mentioned include nonafluoromethoxybutane and perfluoromethylcyclopentane, and mixtures thereof.

A composition according to the invention is preferably free of volatile oil. However, at least one volatile oil may be present in a total content ranging from 0.05% to 20% by weight, preferably ranging from 0.1% to 15% by weight and preferentially ranging from 0.1% to 10% by weight, relative to the total weight of the composition. In particular, the volatile oil may be present in the composition in a content ranging from 0.5% to 5% relative to the total weight of the composition.

According to one preferred embodiment, a composition according to the invention comprises less than 5% by weight of volatile oil(s) relative to the total weight of the composition.

Non-volatile oil

The composition according to the invention may comprise at least one non-volatile oil.

The term "non-volatile oil" means an oil that remains on the skin or the keratin fibre at room temperature and pressure. More specifically, a non-volatile oil has an evaporation rate strictly less than 0.01 mg/cm²/min.
The said at least one non-volatile oil that is suitable for the present invention may be chosen from hydrocarbon-based oils and silicone oils.

The non-volatile hydrocarbon-based oils that are suitable for the present invention may be chosen in particular from:

- hydrocarbon-based oils of plant origin, such as triglycerides formed from fatty acid esters of glycerol, the fatty acids of which may have varied chain lengths from C₄ to C₂₈, these chains possibly being linear or branched, and saturated or unsaturated; these oils are especially wheatgerm oil, sunflower oil, grapeseed oil, sesame seed oil, corn oil, apricot oil, castor oil, shea oil, avocado oil, olive oil, soybean oil, sweet almond oil, palm oil, rapeseed oil, cottonseed oil, hazelnut oil, macadamia oil, jojoba oil, alfalfa oil, poppy oil, pumpkin oil, sesame seed oil, marrow oil, rapeseed oil, blackcurrant oil, evening primrose oil, millet oil, barley oil, quinoa oil, rye oil, safflower oil, candlenut oil, passion flower oil and musk rose oil; or alternatively caprylic/capric acid triglycerides such as those sold by the company Stearineries Dubois or those sold under the names Miglyol 810®, 812® and 818® by the company Sasol;
- synthetic ethers containing from 10 to 40 carbon atoms;
- linear or branched hydrocarbons of mineral or synthetic origin, such as petroleum jelly, polydecenes, hydrogenated poly(iso)butene such as Parleam, and squalane, and mixtures thereof;
- synthetic esters such as oils of formula R₁COOR₂ in which R₁ represents a linear or branched fatty acid residue containing from 1 to 40 carbon atoms and R₂ represents an in particular branched hydrocarbon-based chain containing from 1 to 40 carbon atoms, on condition that R₁ + R₂ ≥ 10, for instance purcellin oil (cetostearyl octanoate), isopropyl myristate, isopropyl palmitate, C₁₂₋₁₅ alkyl benzoate, hexyl laurate, diisopropyl adipate, isononyl isononanoate, 2-ethylhexyl palmitate, isostearyl isostearate, alkyl or polyalkyl octanoates, decanoates or ricinoleates such as propylene glycol dioctanoate; hydroxylated esters such as isostearyl lactate and diisostearyl malate; and pentaerythritol esters;
- fatty alcohols that are liquid at room temperature, with a branched and/or unsaturated carbon-based chain containing from 12 to 26 carbon atoms, for instance octyl/dodecanol, isostearyl alcohol, oleyl alcohol, 2-hexyldecanol, 2-butyloctanol and 2-undecyl/pentadecanol; and
- higher fatty acids such as oleic acid, linoleic acid or linolenic acid, and mixtures thereof.

The non-volatile silicone oils that are suitable for the present invention may be...
chosen in particular from:
- non-volatile polydimethylsiloxanes (PDMSs), polydimethylsiloxanes comprising alkyl or alkoxy groups, that are pendent and/or at the end of a silicone chain, the groups each containing from 2 to 24 carbon atoms, phenyl silicones, for instance phenyl trimethicones, phenyl dimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenyl dimethicones, diphenylmethylidiphenyltrisiloxanes and 2-phenylethyl trimethylsiloxysilicates.

A composition according to the invention is preferably free of non-volatile oil. However, the total content of non-volatile oil in a composition in accordance with the invention may range from 0.01% to 10% by weight, in particular from 0.1% to 8% by weight and better still from 0.25% to 5% by weight relative to the total weight of the composition.

According to one preferred embodiment, a composition according to the invention comprises less than 5% by weight of non-volatile oil(s) relative to the total weight of the composition.

**Emulsifying system**

The compositions according to the invention comprise an emulsifying system.

This emulsifying system comprises at least one anionic surfactant.

A composition according to the invention also comprises at least one cationic counterion.

A composition in accordance with the invention also comprises at least one alkali metal or alkaline-earth metal halide present in a particular weight content.

**Anionic surfactant**

The anionic surfactant(s) that may be used, alone or as mixtures, in the context of the present invention are especially (non-limiting list) one (or more) salt(s) in particular alkaline salts, especially sodium salts, ammonium salts, amine salts, amino alcohol salts or magnesium salts) of the following compounds:
- alkyl phosphates, and in particular C<sub>12</sub>-C<sub>4</sub> and preferably C<sub>14</sub>-Ci<sub>8</sub> alkyl phosphate(s) and mixtures thereof; they may be chosen in particular from DEA oleth-10 phosphate (Crodafos N 10N from the company Croda), cetyl phosphate (Amphisol K from...
Givaudan or Arlatone MAP 160K from the company Uniqema), stearyl phosphate and cetearyl phosphate;
- alkyl sulfates, alkyl ether sulfates (such as sodium lauryl ether sulfate), alkylamido ether sulfates, alkylaryl polyether sulfates and monoglyceride sulfates;
- alkylsulfonates, alkylamidesulfonates, alkylaryl sulfonates, a-olefin sulfonates and paraffin sulfonates;
- alkylsulfosuccinates, alkyl ether sulfosuccinates, alkylamido sulfosuccinates such as Disodium PEG-5 citrate lauryl sulfosuccinate and Disodium ricinoleamido MEA sulfosuccinate;
- alkylsulfosuccinamates;
- alkylsulfoacetates;
- acylsarcosinates, acylglutamates such as Disodium hydrogenated tallow glutamate (Amisoft HS-21 R® sold by the company Ajinomoto), acylisethionates, N-acyltaurates and acyllactylates;
- carboxylic alkyl(poly)glycoside esters such as alkylglucoside citrates, alkylpolyglycoside tartrates, alkylpolyglycoside sulfosuccinates and alkylpolyglycoside sulfosuccinamates;
- fatty acids, in particular fatty acid salts and especially amine salts or alkali metal salts, such as oleic acid, ricinoleic acid, palmitic acid or stearic acid salts, coconut oil acid or hydrogenated coconut oil acid;
- alkyl-D-galactosideuronic acids and salts thereof, polyoxyalkylenated alkyl ether carboxylic acids, polyoxyalkylenated alkylaryl ether carboxylic acids, polyoxyalkylenated alkylamido ether carboxylic acids and salts thereof, in particular those comprising from 2 to 50 alkylene oxide and in particular ethylene oxide groups;
- and mixtures thereof.

Each of these said anionic surfactants may be used alone or as a mixture with one or more other said anionic surfactants.

Among the anionic surfactants, use is preferably made of fatty acids, especially \( C_{12} - C_{22} \) and preferably \( C_{14} - C_{18} \) fatty acids, and in particular stearic acid.

In particular, this (these) anionic surfactant(s) in accordance with the invention may be present in a content of greater than or equal to 1% by weight relative to
the total weight of the composition, especially ranging from 1.5% to 8% and better still 2% to 6% by weight relative to the total weight of the composition. Such contents ensure a good emulsion of the fatty phase in the aqueous phase and in particular of the waxes in the aqueous phase, which is stable and of a suitable viscosity for obtaining a coating, uniform and separating deposit.

According to a preferred embodiment, a composition in accordance with the invention is free of additional surfactant other than the said surfactant in accordance with the invention.

According to a preferred embodiment, a composition in accordance with the invention is free of nonionic surfactant, of cationic surfactant or of amphoteric surfactant.

For the purposes of the invention, the term "free" refers to a composition containing less than 1% and preferably less than 0.5% by weight of additional surfactant(s) relative to the total weight of the composition. In any case, this (these) additional surfactant(s) are not introduced deliberately into the composition.

According to one preferred embodiment, the cosmetic composition according to the present patent application comprises less than 1% and preferably less than 0.5% by weight of triethanolamine, and better still is free of triethanolamine.

According to one preferred embodiment, the cosmetic composition according to the present patent application comprises less than 1% and preferably less than 0.5% by weight of triethanolamine stearate, and better still is free of triethanolamine stearate.

The cream emulsions according to the invention advantageously have a pH preferably ranging from 5 to 9 and more preferentially from 7 to 9. This pH may be obtained and/or adjusted in a conventional manner.

_Cationic counterion_

The anionic surfactant in accordance with the invention comprises a cationic counterion.

This cationic counterion may be of mineral origin, in particular chosen from
alkali metal and alkaline-earth metal cations, or of organic origin.

The alkali metal cation(s) may be chosen from sodium and potassium.

The alkaline-earth metal cation(s) may be chosen from calcium and magnesium.

The cation(s) of organic origin may be chosen from ammonium, and amine and amino alcohol derivatives thereof, or magnesium. Preferably, the cation(s) of organic origin are chosen from ammonium, and amine and amino alcohol derivatives thereof.

According to one preferred embodiment, the cation is a primary (poly)hydroxyalkylamine.

The term "primary (poly)hydroxyalkylamine" in particular means a primary dihydroxyalkylamine, it being understood that the term "primary" means a primary amine function, i.e. \(-\text{NH}_2\), and the alkyl group being a linear or branched \(\text{Cl-C}_8\) and preferably a branched \(\text{C}_4\) hydrocarbon-based chain, such as 1,3-dihydroxy-2-methylpropyl.

The primary (poly)hydroxyalkylamine is preferentially 1,3-dihydroxy-2-methyl-2-propylamine (also known as aminomethylpropanediol or AMPD).

The total content of cationic counterion(s), and in particular of primary (poly)hydroxyalkylamine and especially of AMPD, is preferably greater than or equal to 0.01%, especially inclusively between 0.1% and 4% by weight and better still between 0.5% and 2% by weight relative to the total weight of the composition.

**Alkali metal or alkaline-earth metal halide**

The halide ion is preferably chosen from the chloride ion, the bromide ion and the iodide ion, preferably the chloride ion.

The alkali metal(s) may be chosen from sodium and potassium, preferably sodium.

The alkaline-earth metal(s) may be chosen from calcium and magnesium, preferably calcium.

The alkali metal or alkaline-earth metal halide is preferably chosen from sodium chloride, calcium chloride and a mixture thereof, preferably sodium chloride.

According to the invention, the total content of alkali metal or alkaline-earth metal halide(s), and in particular of sodium chloride and/or of calcium chloride, is greater than or equal to 0.05%, preferably inclusively between 0.08% and 3% by weight and better still between 0.1% and 2% by weight, relative to the total weight of the composition.
**Film-forming polymer**

The compositions according to the present patent application may also contain at least one hydrophilic or lipophilic film-forming polymer.

In the present patent application, the term "film-forming polymer" means a polymer that is capable, by itself or in the presence of an auxiliary film-forming agent, of forming a macroscopically continuous deposit, preferably a cohesive deposit and better still a deposit whose cohesion and mechanical properties are such that the said deposit can be isolated and manipulated individually, for example when the said deposit is prepared by pouring onto a non-stick surface such as a Teflon-coated or silicone-coated surface.

In general, the content of "film-forming polymer" solids in the compositions according to the present patent application ranges from 0.1% to 30%, preferably from 0.5% to 20% and better still from 1% to 10% by weight relative to the total weight of the composition.

The hydrophilic film-forming polymer may be a water-soluble polymer or may be in dispersion in an aqueous medium.

Among the film-forming polymers that can be used in the composition of the present invention, mention may be made of synthetic polymers, of free-radical type or of polycondensate type, and polymers of natural origin, and mixtures thereof.

Examples of water-soluble film-forming polymers that may be mentioned include:

- proteins, for instance proteins of plant origin such as wheat or soybean proteins; proteins of animal origin such as keratins, for example keratin hydrolysates and sulfonic keratins;
- cellulose polymers such as hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, ethylhydroxyethylcellulose and carboxymethylcellulose, and also quaternized cellulose derivatives;
- acrylic polymers or copolymers, such as polyacrylates or polymethacrylates;
- vinyl polymers, for instance polyvinylpyrrolidones, copolymers of methyl vinyl ether and of malic anhydride, the copolymer of vinyl acetate and of crotonic acid, copolymers of vinylpyrrolidone and of vinyl acetate; copolymers of vinylpyrrolidone and of caprolactam; polyvinyl alcohol;
- anionic, cationic, amphoteric or nonionic chitin or chitosan polymers;
- gum arabic, guar gum, xanthan derivatives, karaya gum;
- alginates and carrageenans;
- glycoaminoglycans, hyaluronic acid and derivatives thereof;
- shellac resin, sandarac gum, dammar resins, elemi gums and copal resins;
- deoxyribonucleic acid;
- mucopolysaccharides such as chondroitin sulfates; and mixtures thereof.

The film-forming polymer may also be present in the composition in the form of particles dispersed in an aqueous phase, which is generally known as a latex or pseudolatex. The techniques for preparing these dispersions are well known to those skilled in the art.

Aqueous dispersions of film-forming polymer that may be used include the acrylic dispersions sold under the names Neocryl XK-90®, Neocryl A-1070®, Neocryl A-1090®, Neocryl BT-62®, Neocryl A-1079® and Neocryl A-523® by the company Avecia-Neoresins, Dow Latex 432® by the company Dow Chemical, Daitosol 5000 AD® or Daitosol 5000 SJ® by the company Daito Kasei Kogyo; Syntran 5760® by the company Interpolymer, Allianz Opt® by the company Rohm & Haas or the aqueous polyurethane dispersions sold under the names Neorez R-981® and Neorez R-974® by the company Avecia-Neoresins, Avalure UR-405®, Avalure UR-410®, Avalure UR-425®, Avalure UR-450®, Sancure 875®, Avalure UR-445® and Sancure 2060® by the company Noveon, Impranil 85® by the company Bayer, Aquamere H-151 1® by the company Hydromer; the sulfopolyesters sold under the brand name Eastman AQ® by the company Eastman Chemical Products, vinyl dispersions, for instance Mexomer PAM®, aqueous polyvinyl acetate dispersions, for instance Vinybran® from the company Nisshin Chemical or those sold by the company Union Carbide, aqueous dispersions of vinylpyrrolidone, dimethylaminopropylmethacrylamide and lauryldimethylpropylmethacrylamidoammonium chloride terpolymer, such as Styleze W from ISP, aqueous dispersions of polyurethane/polyacrylic hybrid polymers such as those sold under the references Hybridur® by the company Air Products or Durometer® from National Starch, core/shell type dispersions: for example those sold by the company Atofina under the reference Kynar (core: fluoro, shell: acrylic) or those described in document US 5 188 899 (core: silica, shell: silicone), and mixtures thereof.

A preferred example of a film-forming polymer that may be mentioned is an
aqueous polyurethane dispersion.

The polyurethane may be present in an amount of solids of greater than or equal to 5% by weight, better still 6.5% by weight or even 8% by weight or more, relative to the total weight of the composition. The polyurethane may be present, for example, in an amount of solids ranging from 5% to 30% by weight, better still ranging from 6% to 25% and better still from 7% to 15% by weight relative to the total weight of the said composition.

The compositions in accordance with the invention advantageously comprise aqueous dispersions of particular polyurethane particles. Such compositions may be used in cosmetic applications, for making up or caring for the eyelashes or the eyebrows.

Polyurethane is a product of reaction of:

A) a prepolymer according to the formula:

\[
\text{OCN}-R_2\left\lbrack\begin{array}{cccc} H & O & N & H \\ R_1 & O & R_2 & O \end{array}\right\rbrack^{\text{m}} NCO
\]

where

- \( R_1 \) represents a hydrocarbon-based radical derived from a polyesterpolyol and especially from a polyesterdiol,
- \( R_2 \) represents a hydrocarbon-based radical derived from an aliphatic or cycloaliphatic polyisocyanate,
- \( R_3 \) represents a hydrocarbon-based radical derived from a diol, optionally of low molecular weight, optionally substituted with ionic groups,
- \( n \) is from 0 to 5, and
- \( m > 1 \);

B) at least one chain extender according to the formula:

\[
\text{H}_2\text{N}–\text{R}_4–\text{NH}_2
\]

where

- \( n_4 \) represents an alkylene or alkylene oxide radical that is not substituted with ionic or potentially ionic groups; and

C) at least one chain extender according to the formula:

\[
\text{H}_2\text{N}–\text{R}_5–\text{NH}_2
\]

where
R represents an alkylene radical substituted with ionic or potentially ionic groups.

Prepolymer A)
The compositions in accordance with the invention comprise aqueous dispersions of particular polyurethanes. Such compositions may be used in cosmetic applications, for making up or caring for the eyelashes or the eyebrows.

Radical R1
Compounds that are suitable for providing the polyhydroxyl and preferably dihydroxyl radical R1 are polyesterpolys, preferably polyesterdiois, and mixtures thereof. These compounds are advantageously divalent, preferably two hydroxyl groups.

Such compounds may have number-average molecular weights from about 700 to about 16 000 and preferably from about 750 to about 5000.

The polyesterdiois(s) may generally be prepared from:

- aliphatic, cycloaliphatic or aromatic dicarboxylic or polycarboxylic acids or anhydrides thereof, and
- dihydric alcohols such as diols chosen from aliphatic, alicyclic and aromatic diols.

The aliphatic dicarboxylic or polycarboxylic acids may be chosen from: succinic acid, fumaric acid, glutamic acid, 2,2-dimethylglutaric acid, adipic acid, itaconic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, malonic acid, 2,2-dimethylmalonic acid, nonanedicarboxylic acid, decanedicarboxylic acid, dodecanedioic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 2,5-norbornanedicarboxylic acid, diglycolic acid, thiodipropionic acid, 2,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, phthalic acid, terephthalic acid, isophthalic acid, oxanic acid, o-phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, trimellitic acid.

The acid anhydrides may be chosen in particular from o-phthalic, trimellitic or succinic acid anhydride, or a mixture thereof.

Preferably, the preferred dicarboxylic acid is adipic acid.

The dihydric alcohols may be chosen from ethanediol, ethylene glycol, diethylene glycol, triethylene glycol, trimethylene glycol, tetraethylene glycol, 1,2-
propanediol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, 1,3-
propanediol, 1,4-butanediol, 1,3-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-
hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-dihydroxycyclohexene, 1,4-
dimethylolcyclohexane, cyclohexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-
dodecanediol and neopentyl glycol, or mixtures thereof. The cycloaliphatic and/or
aromatic dihydroxylic compounds are also obviously suitable for use as dihydric
alcohol(s) for the preparation of polyesterpolyol(s).

The polyesterdiols may also be chosen from lactone homopolymers or
copolymers, which are preferably obtained via addition reactions of lactones or of
mixtures of lactones, such as butyrolactone, ε-caprolactone and/or methyl-s-caprolactone
with suitable polyfunctional and preferably difunctional initiator molecules, for instance the
dihydric alcohols mentioned above. The corresponding ε-caprolactone polymers are
preferred.

The polyester polyol and preferably polyester diol radical $R_1$ may
advantageously be obtained by polycondensation of dicarboxylic acids, such as adipic
acid, with polyols, especially diols such as hexanediol or neopentyl glycol, and mixtures
thereof.

**Radical R2**

Polyisocyanates that are suitable for providing the hydrocarbon-based radical
$R_2$ comprise organic diisocyanates with a molecular weight from about 112 to 1000 and
preferably from about 140 to 400.

Preferred diisocyanates are those represented by the general formula
$R_2(NCO)_2$ indicated above, in which $R_2$ represents a divalent aliphatic hydrocarbon-based
group comprising 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon-based
group comprising 5 to 15 carbon atoms, a divalent arylaliphatic hydrocarbon-based group
comprising 7 to 15 carbon atoms or a divalent aromatic hydrocarbon-based group
comprising 6 to 15 carbon atoms. Examples of organic diisocyanates that are suitable for
use comprise tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate,
dodecamethylene diisocyanate, 1,3-cyclohexane diisocyanate and 1,4-cyclohexane
diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (isophorone
diisocyanate or IPDI), bis(4-isocyanatocyclohexyl)methane, 1,3-
bis(isocyanatomethyl)cyclohexane, 1,4-bis(isocyanatomethyl)cyclohexane and bis-(4-
isocyanato-3-methylcyclohexyl)methane. Mixtures of diisocyanates may, of course, be used. Preferred diisocyanates are aliphatic and cycloaliphatic diisocyanates. 1,6-Hexamethylene diisocyanate, isophorone diisocyanate and dicyclohexylmethane diisocyanate, and mixtures thereof, are particularly preferred.

Radical R3

The use of diols $R_3$, especially of low molecular weight, may enable stiffening of the polymer chain and is optional. The expression "low molecular weight diols" means diols with a molecular weight from about 62 to 700 and preferably from 62 to 200. They may contain aliphatic, alicyclic or aromatic groups. The preferred compounds contain only aliphatic groups. The diols used preferably contain up to 20 carbon atoms and may be chosen from ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,3-buthylene glycol, neopentyl glycol, butylethylpropanediol, cyclohexanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, bisphenol A (2,2-bis(4-hydroxyphenyl)propane), and hydrogenated bisphenol A (2,2-bis(4-hydroxyphenyl)propane), and mixtures thereof. Preferably, $R_3$ is derived from neopentyl glycol.

Optionally, the low molecular weight diols may contain ionic or potentially ionic groups. Suitable low molecular weight diols containing ionic or potentially ionic groups are those disclosed in patent US 3 412 054. Preferred compounds comprise dimethylolethanoic acid (DMBA), dimethyiolpropionic acid (DMPA) and caproactone-polyesterdiol containing carboxyl. If low molecular weight diols containing ionic or potentially anionic groups are used, they are preferably used in an amount such that < 0.30 meq. of COOH is present per gram of polyurethane in the polyurethane dispersion. Preferably, low molecular weight diols containing ionic or potentially ionic groups are not used.

The prepolymer chain is extended using two classes of chain extender, B) and C).

B) Chain extenders

Compounds B) of the first class of chain extenders have the formula:

\[ H_2N \equiv R_4 \equiv NH_2 \]

in which $R_4$ represents an alkylene or alkylene oxide radical that is not
substituted with ionic or potentially ionic groups.

Thus, the chain extender may be chosen from:
- alkylenediamines such as hydrazine, ethylenediamine, propylenediamine, 1,4-butylenediamine and piperazine;
- alkylene oxide diamines such as dipropylaminediethylene glycol (DPA-DEG available from Tomah Products, Milton, WI), 2-methyl-1,5-pentanediamine (Dytec A from DuPont), hexanediamine, isophoronediamine and 4,4-methylenebis(cyclohexylamine), and the series of DPA-etheramines available from Tomah Products, Milton, WI, comprising dipropylaminepropylene glycol, dipropylaminedipropylene glycol, dipropylaminetripropylene glycol, dipropylaminepoly(propylene glycol), dipropylaminemethylene glycol, dipropylaminepoly(ethylene glycol), dipropylamine-1,3-propanediol, dipropylamine-2-methyl-1,3-propanediol, dipropylamine-1,4-butanediol, dipropylamine-1,3-butanediol, dipropylamine-1,6-hexanediol and dipropylaminecyclohexane-1,4-dimethanol, and mixtures thereof.

Preferably, the chain extender B) is chosen from ethylenediamine and diethanolamine, and mixtures thereof.

C) Chain extenders

The second class of chain extenders is that of the compounds C) having the formula:

$$\text{H}_2\text{N}-\text{R}_5-\text{NH}_2$$

in which $\text{R}_5$ represents an alkylenic radical substituted with ionic or potentially ionic groups. These compounds have an ionic or potentially anionic group and two groups that are reactive with isocyanates groups. The ionic or potentially ionic group may be chosen from the group consisting of tertiary or quaternary ammonium groups, groups that can be converted into such a group, a carboxyl group, a carboxylate group, a sulfonic acid group and a sulfonate group. The said at least partial conversion of the groups that can be converted into salt groups of the type mentioned may take place before or during the mixing with water. Specific compounds comprise diaminosulfonates, for instance the sodium salt of N-(2-aminoethyl)-2-aminoethanesulfonic acid (AAS) or the sodium salt of N-(2-aminoethyl)-2-aminopropionic acid.

Preferably, $\text{R}_5$ represents an alkylenic radical substituted with sulfonic acid or sulfonate groups.

Preferably, this compound is the sodium salt of N-(2-aminoethyl)-2-
aminoethanesulfonic acid (AAS).

**Chain terminators**
The polyurethane according to the invention may also comprise compounds that are located in each case at the ends of the chains and that terminate the said chains. These chain terminators may be derived from compounds having the formula:

\[
R_6^\text{NH} \\
\begin{array}{c}
R_7
\end{array}
\]

in which \( R_6 \) represents a hydrogen atom or an alkylene radical optionally bearing a hydroxyl end group and \( R_7 \) represents an alkylene radical optionally bearing a hydroxyl end group. Suitable compounds comprise compounds such as monoamines, in particular secondary monoamines, or monoalcohols. Examples comprise: methylamine, ethylamine, propylamine, butylamine, octylamine, laurylamine, stearylamine, isononyloxypropylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, \( \text{N-} \)methylaminopropylamine, diethyl(methyl)aminopropylamine, morpholine, piperidine, diethanolamine and suitable substituted derivatives thereof, amide-amines of primary diamines and of monocarboxylic acids, monoketimes of primary diamines, primary/tertiary amines such as \( \text{N,} \text{N-} \)dimethylaminopropylamine and the like. The chain-terminator alcohols may be chosen from \( \text{C_{1-10}} \) alcohols such as methanol, butanol, hexanol, 2-ethylhexyl alcohol and isodecyl alcohol, and mixtures thereof. Amino alcohols such as aminomethylpropanol (AMP) are also suitable for use.

In one embodiment of the invention, diethylene glycol is used to obtain the polyurethane either as a low molecular weight diol or as part of the nonionic chain extender via the use of dipropylenediethylene glycol. When diethylene glycol is used as low molecular weight diol, then, preferably, DPA-DEG is not used as nonionic chain extender. Similarly, if DPA-DEG is used as nonionic chain extender, then, preferably, diethylene glycol is not used as low molecular weight diol.

**Preparation processes**
The compositions according to the invention comprise an aqueous polyurethane dispersion that is suitable for use in products for making up or caring for
keratin fibres such as the eyelashes or the eyebrows, and can be obtained via a preparation process comprising the following steps:

A) the preparation of an aqueous polyurethane dispersion by

1) the formation of a prepolymer with isocyanate functionality by reacting:

   1a) a polyesterpolyol, and especially a polyesterdiol,

   1b) an aliphatic or cycloaliphatic polyisocyanate, and

   1c) a low molecular weight diol, optionally substituted with ionic groups;

2) extension of the prepolymer chain by:

   2a) at least one chain extender according to the formula:

\[ \text{H}_2\text{N—R}_4—\text{NH}_2 \]

in which \( R_4 \) represents an alkylene or alkylene oxide radical that is not substituted with ionic or potentially ionic groups, and

2b) at least one chain extender according to the formula:

\[ \text{H}_2\text{N—R}_5—\text{NH}_2 \]

in which \( R_5 \) represents an alkylene radical substituted with ionic or potentially ionic groups,

in the presence of an organic solvent to form a polyurethane;

3) dispersion of the polyurethane in water; and

4) removal of the organic solvent, to obtain an aqueous polyurethane dispersion;

and

mixing of the polyurethane dispersion with water or ethanol.

More particularly, a process for producing a polyurethane dispersion suitable for use in makeup products may include the following steps: a) the reaction in a first step of at least one polyesterpolyol compound and of at least one low molecular weight diol optionally substituted with an ionic group (dihydroxyl compounds) with diisocyanate to form the prepolymer A), and then b) the dissolution in a second step of the prepolymer in an organic solvent and c) the reaction in a third step of the solution of prepolymer containing the isocyanate with the two classes of chain extender and, optionally, the chain terminator, d) the formation, in a fourth step, of the dispersion by addition of water, and e) the removal in a fifth step of the organic solvent.

The free sulfonic acid groups incorporated are neutralized between the third and the fourth step. Suitable neutralizers included are primary, secondary or tertiary
amines. Among these, trialkyl-substituted tertiary amines are preferred. Examples of these amines are trimethylamine, triethylamine, triisopropylamine, tributylamine, N,N-dimethylcyclohexylamine, N,N-dimethylstearylamine, N,N-dimethylaniline, N-methylmorpholine, N-ethylmorpholine, N-methylpiperazine, N-methylpyrrolidine, N-methylpiperidinone, N,N-dimethylethanolamine, N,N-dimethylpropanol, 2-methoxyethyl(dimethylamine, N-hydroxyethylpiperazine, 2-(2-dimethylaminoethoxy)ethanol and 5-diethylamino-2-pentanone. The preferred tertiary amines are those not containing any active hydrogen as determined by the Zerewitinoff test, given that hydrogen can react with the isocyanate groups of the prepolymer, which may lead to gelation, the formation of insoluble particles or chain termination.

The polyurethane dispersions may be produced via what is known as the acetone process. In the acetone process, the synthesis of the aqueous polyurethane preparations based on the dispersions according to the invention is performed in a multi-step process.

In a first step, a prepolymer containing isocyanate groups is synthesized from the polyester polyol compound, the diisocyanate and the low molecular weight diol. The amounts of individual components are calculated such that the isocyanate content of the prepolymer is between 1.4% and 5.0% by weight, preferably between 2.0% and 4.5% by weight and particularly preferably between 2.6% and 4.0% by weight. The low molecular weight diol is present in an amount from 0 to 80 eq.% and preferably from 0 to 10 eq.% on the basis of the amount of NCO equivalents.

The prepolymer obtained has the structure:

\[
\text{OCN-R}_1\left[N\text{-N-C-O-R}_2\text{-O-C-N-R}_3\right]_m\text{NCO}
\]

where

- \(R_1\) represents a polyesterpolyol, and especially a polyesterdiol,
- \(R_2\) represents a hydrocarbon-based radical or an aliphatic or cycloaliphatic polyisocyanate,
- \(R_3\) represents a low molecular weight diol radical, optionally substituted with ionic groups,
\( n < 5 \), and
\( m > 1 \).

Preferably, \( n \) is from 1 to 3 and \( m \) is from 1 to 5.

In a second step, the prepolymer produced in step 1 is dissolved in an organic solvent that is at least partially water-miscible, not containing any groups that are reactive with isocyanate. The preferred solvent is acetone. Other solvents, for instance 2-butanol, tetrahydrofuran or dioxane, or mixtures of these solvents, may, however, also be used. The amounts of solvent to be used must be calculated such that a solids content of from 25% to 60% by weight, preferably from 30% to 50% by weight and particularly preferably from 35% to 45% by weight is obtained.

In a third step, the solution of prepolymer containing isocyanate is reacted with mixtures of chain extenders with amino functionality and, optionally, chain terminators, to form the high molecular weight polyurethane. Sufficient amounts of chain extenders and of chain terminators are used such that the calculated number-average molecular weight \( (M_n) \) of the polyurethane obtained is between 10 000 and 100 000 daltons and preferably between 10 000 and 50 000 daltons. The nonionic chain extender is present in an amount of from 15 eq.% to 90 eq.% and preferably from 35.0 eq.% to 55 eq.%, on the basis of the residual amount of NCO equivalents present in the prepolymer. The ionic chain extender is present in an amount of from 10 eq.% to 50 eq.% and preferably from 25 eq.% to 35 eq.%, on the basis of the residual amount of NCO equivalents present in the prepolymer. The chain terminator is present in an amount of from 0 eq.% to 35 eq.% and preferably from 20 eq.% to 30 eq.%, on the basis of the residual amount of NCO equivalents present in the prepolymer.

In a fourth step, the high molecular weight polyurethane is dispersed in the form of a dispersion of fine particles by the addition of water to the solution or of the solution to water.

In a fifth step, the organic solvent is partially or totally removed by distillation, optionally under reduced pressure. The amount of water in the fourth step is calculated such that the aqueous polyurethane dispersions according to the invention have a solids content of from 20% to 60% by weight and preferably from 28% to 42% by weight.

Such polyurethane dispersions are, for example, Polyurethane 34 sold under the trade names Baycusan C1000 and C1001 by the company Bayer, and Polyurethane 35 sold under the trade name Baycusan C1004 by the company Bayer.
A composition according to the invention may also comprise, as a variant or additionally, a lipophilic polymer that may be in solution or in dispersion in a non-aqueous solvent phase.

5 Hydrophilic gelling agents

The compositions according to the present patent application may also contain at least one hydrophilic gelling agent, and may be chosen from:

- acrylic or methacrylic acid homopolymers or copolymers or the salts thereof and esters thereof and in particular the products sold under the names Versicol F® or Versicol K® by the company Allied Colloid, Ultrahold 8® by the company Ciba Geigy, and polyacrylic acids of Synthalen K type,

- copolymers of acrylic acid and of acrylamide sold in the form of the sodium salt thereof under the names Reten® by the company Hercules, and the sodium salts of polyhydroxycarboxylic acids sold under the name Hydagen® F by the company Henkel,

- polyacrylic acid/alkyl acrylate copolymers of Pemulen type,

- AMPS (polyacrylamidomethylpropanesulfonic acid partially neutralized with aqueous ammonia and highly crosslinked) sold by the company Clariant,

- AMPS/acrylamide copolymers of Sepigel® or Simulgel® type sold by the company SEPPIC, and

- AMPS/polyoxyethylated alkyl methacrylate copolymers (crosslinked or non-crosslinked), and mixtures thereof.

- associative polymers and in particular associative polyurethanes such as the C₁₅₋₁₇O₁₂₀C₁₆ polymer from the company Servo Delden (sold under the name SER AD FX1 100, this molecule bearing a urethane function and having a weight-average molecular weight of 1300), OE being an oxyethylene unit, Rheolate 205 bearing a urea function, sold by the company Rheox, or Rheolate 208 or 204 (these polymers being sold in pure form) or DW 1206B from Rohm & Haas bearing a C₂₀ alkyl chain and a urethane bond, sold at 20% solids in water. It is also possible to use solutions or dispersions of these associative polyurethanes, especially in water or in aqueous-alcoholic medium.

Examples of such polymers that may be mentioned include SER AD FX1010, SER AD FX1035 and SER AD FX1070 from the company Servo Delden, and Rheolate 255, Rheolate 278 and Rheolate 244 sold by the company Rheox. It is also possible to use the products DW 1206F and DW 1206J, and also Acrysol RM 184 or Acrysol 44 from the
company Rohm & Haas, or alternatively Borchigel LW 44 from the company Borchers, and mixtures thereof.

Some of the water-soluble film-forming polymers mentioned above may also act as water-soluble gelling agent.

The hydrophilic gelling agents may be present in the compositions according to the invention in a content ranging from 0.05% to 10% by weight, preferably ranging from 0.1% to 8% by weight and preferentially ranging from 0.5% to 5% by weight, relative to the total weight of the composition.

**Lipophilic gelling agents**

A composition according to the invention advantageously comprises at least one lipophilic gelling agent.

The gelling agent(s) that may be used may be organic or mineral, polymeric or molecular lipophilic gelling agents.

Mineral lipophilic gelling agents that may be mentioned include clays and fumed silica optionally subjected to a hydrophobic surface treatment, the particle size of which is less than 1 μm.

The polymeric organic lipophilic gelling agents are, for example, partially or totally crosslinked elastomeric organopolysiloxanes of three-dimensional structure, for instance those sold under the names KSG6®, KSG16® and KSG18® by the company Shin-Etsu, Trefil E-505C® or Trefil E-506C® by the company Dow Corning, Gransil SR-CYC®, SR DMF 10®, SR-DC556®, SR 5CYC gel®, SR DMF 10 gel® and SR DC 556 gel® by the company Grant Industries and SF 1204® and JK 113® by the company General Electric; ethylcellulose, for instance the product sold under the name Ethocel® by the company Dow Chemical; polycondensates of polyamide type resulting from condensation between (a) at least one acid chosen from dicarboxylic acids containing at least 32 carbon atoms, such as fatty acid dimers, and (β) an alkylenediamine and in particular ethylenediamine, in which the polyamide polymer comprises at least one carboxylic acid end group esterified or amidated with at least one saturated and linear monoalcohol or one saturated and linear monoamine comprising from 12 to 30 carbon atoms, and in particular ethylenediamine/stearyl dilinoleate copolymers such as the product sold under the name Uniclear 100 VG® by the company Arizona Chemical; silicone polyamides of the polyorganosiloxane type such as those described in documents US-A-5 874 069, US-
A-5 919 441, US-A-6 051 216 and US-A-5 981 680, for instance those sold under the references Dow Corning 2-8179 and Dow Corning 2-8178 Gellant by the company Dow Corning; galactomannans comprising from 1 to 6 and in particular from 2 to 4 hydroxyl groups per saccharide, substituted with a saturated or unsaturated alkyl chain, for instance guar alkylated with C₁ to C₆ and in particular C₁ to C₃ alkyl chains, and mixtures thereof. Block copolymers of "diblock", "triblock" or "radial" type, of the polystyrene/polyisoprene or polystyrene/polybutadiene type, such as the products sold under the name Luvitol HSB® by the company BASF, of the polystyrene/copoly(ethylene-propylene) type, such as the products sold under the name Kraton® by the company Shell Chemical Co., or of the polystyrene/copoly(ethylene-butylene) type, and mixtures of triblock and radial (star) copolymers in isododecane, such as those sold by the company Penreco under the name Versagel®, for instance the mixture of butylene/ethylene/styrene triblock copolymer and of ethylene/propylene/styrene star copolymer in isododecane (Versagel M 5960).

The compositions according to the invention may also comprise as lipophilic gelling agent a non-emulsifying silicone elastomer. Among the lipophilic gelling agents, mention may also be made of organo-gelling agents.

**Dyestuffs**

The compositions in accordance with the invention comprise at least one dyestuff.

This (or these) dyestuff(s) are preferably chosen from pulverulent dyes, liposoluble dyes and water-soluble dyes, and mixtures thereof.

Preferably, the compositions according to the invention comprise at least one pulverulent dyestuff. The pulverulent dyestuffs may be chosen from pigments and nacres, and preferably from pigments.

The pigments may be white or coloured, mineral and/or organic, and coated or uncoated. Among the mineral pigments, mention may be made of metal oxides, in particular titanium dioxide, optionally surface-treated, zirconium, zinc or cerium oxide, and also iron, titanium or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue. Among the organic pigments that may be mentioned are carbon black, pigments of D & C type and lakes based on cochineal carmine or on barium, strontium, calcium or aluminium.

The nacres may be chosen from white nacreous pigments such as mica
coated with titanium or with bismuth oxychloride, coloured nacreous pigments such as

titanium mica with iron oxides, titanium mica especially with ferric blue or chromium oxide,

titanium mica with an organic pigment of the abovementioned type, and also nacreous

pigments based on bismuth oxychloride.

The liposoluble dyes are, for example, Sudan Red, D&C Red 17, D&C Green

6, β-carotene, soybean oil, Sudan Brown, D&C Yellow 11, D&C Violet 2, D&C Orange 5,
quinoline yellow and annatto.

Preferably, the pigments contained in the compositions according to the

invention are chosen from metal oxides.

These dyestuffs may be present in a content ranging from 0.01% to 30% by

weight, and in particular from 3% to 15% by weight, relative to the total weight of the

composition.

Preferably, the dyestuff(s) are chosen from one or more metal oxides that are

present in a content of greater than or equal to 2% by weight relative to the total weight of

the composition, and advantageously inclusively between 3% and 15% by weight relative

to the total weight of the composition.

**Fillers**

The compositions in accordance with the invention may also comprise at least

one filler.

The fillers may be selected from those that are well known to those skilled in

the art and commonly used in cosmetic compositions. The fillers may be mineral or

organic, and lamellar or spherical. Mention may be made of talc, mica, silica, kaolin,
polyamide powders, for instance the Nylon® sold under the name Orgasol® by the

company Atochem, poly-p-alanine powders and polyethylene powders, powders of

tetra-fluoro-ethylene polymers, for instance Teflon®, lauroyllysine, starch, boron nitride,
extended polymeric hollow microspheres such as those of polyvinylidene
chloride/acrylonitrile, for instance the products sold under the name Expancel® by the

company Nobel Industrie, acrylic powders such as those sold under the name Polytrap®

by the company Dow Corning, polymethyl methacylate particles and silicone resin

microbeads (for example Tospearls® from Toshiba), precipitated calcium carbonate,
magnesium carbonate and magnesium hydrocarbonate, hydroxyapatite, hollow silica
microspheres (Silica Beads® from Maprecos), glass or ceramic microcapsules, metal
soaps derived from organic carboxylic acids having from 8 to 22 carbon atoms and in
particular from 12 to 18 carbon atoms, for example zinc, magnesium or lithium stearate, zinc laurate and magnesium myristate.

It is also possible to use a compound that is capable of swelling on heating, and especially heat-expandable particles such as non-expanded microspheres of vinylidene chloride/acrylonitrile/methyl methacrylate copolymer or of acrylonitrile homopolymer or copolymer, for instance those sold, respectively, under the references Expancel® 820 DU 40 and Expancel® 007WU by the company Akzo Nobel.

The fillers may represent from 0.1% to 10% by weight and in particular from 0.2% to 5% by weight relative to the total weight of the composition.

**Fibres**

The compositions in accordance with the invention may also comprise at least one fibre that can improve the lengthening effect.

The term "fibre" should be understood as meaning an object of length L and of diameter D such that L is very much greater than D, D being the diameter of the circle in which the cross section of the fibre is inscribed. In particular, the ratio L/D (or aspect ratio) is chosen in the range from 3.5 to 2500, in particular from 5 to 500 and more particularly from 5 to 150.

The fibres that may be used in the composition of the invention may be mineral or organic fibres, of synthetic or natural origin. They may be short or long, individual or organized, for example braided, and hollow or solid. They may have any shape and may especially have a circular or polygonal (square, hexagonal or octagonal) cross section depending on the specific application envisaged. In particular, their ends are blunted and/or polished to prevent injury.

In particular, the fibres have a length ranging from 1 μm to 10 mm, in particular from 0.1 mm to 5 mm and more particularly from 0.3 mm to 3.5 mm. Their cross section may be included in a circle with a diameter ranging from 2 nm to 500 μm, in particular ranging from 100 nm to 100 μm and more particularly from 1 μm to 50 μm. The weight or yarn count of fibres is often given in denier or decitex and represents the weight in grams per 9 km of yarn. In particular, the fibres according to the invention may have a yarn count chosen within the range from 0.15 to 30 denier and better still from 0.18 to 18 denier.

The fibres that may be used in the composition of the invention may be chosen from rigid or non-rigid fibres, and may be mineral or organic fibres, of synthetic or...
Moreover, the fibres may or may not be surface-treated, may be coated or uncoated, and may be coloured or uncoloured.

As fibres that may be used in the composition according to the invention, mention may be made of non-rigid fibres such as polyamide (Nylon®) fibres or rigid fibres such as polyimideamide fibres, for instance those sold under the names Kermel® and Kermel Tech® by the company Rhodia or poly(p-phenyleneterephthalamide) (or aramid) fibres sold especially under the name Kevlar® by the company DuPont de Nemours.

The fibres may be present in the composition according to the invention in a content ranging from 0.01% to 10% by weight, in particular from 0.1% to 5% by weight and more particularly from 0.3% to 3% by weight relative to the total weight of the composition.

**Cosmetic active agents**

The compositions in accordance with the invention may also comprise at least one cosmetic active agent.

As cosmetic active agents that may be used in the compositions in accordance with the invention, mention may be made especially of antioxidants, preserving agents, fragrances, neutralizers, emollients, thickeners, coalescers, plasticizers, moisturizers, vitamins and screening agents, in particular sunscreens, and mixtures thereof.

Needless to say, a person skilled in the art will take care to select the optional additional additives and/or the amount thereof such that the advantageous properties of the composition according to the invention are not, or are not substantially, adversely affected by the envisaged addition.

Preferably, the composition according to the invention is a leave-in composition. Advantageously, the composition is a makeup composition and in particular a mascara.

The examples that follow are given as illustrations of the present invention, and shall not limit the scope thereof.
ASSEMBLY

An assembly for coating keratin fibres according to the invention may comprise an applicator suitable for applying the said cosmetic composition for coating keratin fibres and, where appropriate, a conditioning device suitable for receiving the said composition.

Applicator

The applicator comprises means for smoothing and/or separating keratin fibres, such as the eyelashes or the eyebrows, especially in the form of teeth, bristles or other reliefs.

The applicator is arranged to apply the composition to the eyelashes or the eyebrows, and may comprise, for example, a brush or a comb.

The applicator may also be used for finishing of the makeup, over a region of the eyelashes or eyebrows that is made up or laden with composition.

The brush may comprise a twisted core and bristles held between the turns of the core, or may be made in yet another way.

The comb is, for example, produced from a single part by moulding of a plastic.

In certain embodiments, the application member is mounted at the end of a wand, which wand may be flexible, which may contribute to improving the comfort during application.

Packaging device

The packaging device comprises a container for housing the composition for coating keratin fibres. This composition may then be withdrawn from the container by immersing the applicator therein.

This applicator may be firmly attached to a member for closing the container. This closing member may form a member for gripping the applicator. This gripping member may form a cap to be removably mounted on the said container by any suitable means, such as screwing, click-fastening, coupling, etc. Such a container may thus reversibly house the said applicator.

This container can be optionally equipped with a wiper suitable for removing a surplus of product taken by the applicator.
A process for applying the composition according to the invention to the eyelashes or the eyebrows may also include the following steps:

- forming a deposit of the cosmetic composition on the eyelashes or the eyebrows,
- leaving the deposit on the eyelashes or the eyebrows, it being possible for the deposit to dry.

It should be noted that, according to another embodiment, the applicator may form a product container. In such a case, a container may, for example, be provided for in the gripping member and an internal channel can internally connect this gripping member to the application members in relief.

Finally, it should be noted that the packaging and application assembly may be in the form of a kit, it being possible for the applicator and the packaging device to be housed separately in the same packaging article.

**EXAMPLES**

1. Preparation of a mascara composition according to the invention compared with a mascara composition outside the invention.
These compositions were prepared as follows:

**Preparation of the fatty phase**

All the starting materials used are carefully weighed out using a balance (accuracy 0.01 g).

The various waxes are melted in a 500 mL jacketed heating pan with circulation of hot oil to control the temperature. The mixture is heated to about 85-90°C. Once the waxes have melted, they are homogenized by stirring using a Moritz blender, which is stirring of rotor-stator type: this machine consists of a fixed part in which a second mobile part rotates at variable speed, and is used for making emulsions since it can produce a very high shear.

When the waxes are molten and homogenized, the pigments are added, and the whole is then homogenized again in the Moritz blender. The temperature is then checked
(by means of a probe) and adjusted to 85-90°C if necessary.

//. Preparation of the aqueous phase
A high-sided 600 ml beaker is used, which is first weighed empty in order to adjust the mass of water before emulsification. The amount of water required, preheated by an electric kettle, is stirred slowly in this beaker using a Rayneri blender. A Rayneri blender is a laboratory stirrer equipped with a paddle or turbomixer for stirring at variable speed while constituents are being incorporated.

The polymers and then the surfactants are successively introduced, with continued slow stirring. Between each introduction, care is taken to ensure good dissolution of the compound and homogenization of the medium.

When all the compounds are dissolved, it is necessary to adjust the mass of water in order to compensate for the evaporation that has taken place. The preserving system is then added.

The aqueous phase is then placed on a water bath until a temperature of 85-90°C is reached.

//. Emulsification
When the two phases are at the desired temperature, the aqueous phase is added very slowly into the fatty phase while gradually increasing the stirring; the phase inversion is then visible as a change in viscosity. The stirring is set to the maximum for 10 minutes (about 3500 rpm), but, for certain formulations, there is a risk of overspilling if the stirring is too vigorous. In order for the emulsion to be homogeneous, it is occasionally necessary to use a flexible spatula to scrape the edges and bring the product to the centre in order for it all to be entrained by the paddle.

iv. Temperature reduction
After the emulsification, the heating pan is placed on a Rayneri blender equipped with a butterfly paddle, which allows blending and homogenization during the temperature reduction, at low shear. The stirring speed is low so as not to incorporate air bubbles.

By means of the oil bath, the temperature is reduced gradually: in 10°C steps, homogenizing thoroughly at each step, especially at about 70°C (critical temperature where the mascara begins substantially to set to a solid). It is occasionally necessary to mix using the flexible spatula in order to avoid the formation of a block around the paddle,
which would then not be blended and would be inhomogeneous. However, there is a risk of incorporation of air bubbles via this method, and so the formulator must find the correct compromise between homogeneity and air bubbles.

5  v. **End of formulation**

The mascara thus obtained is transferred into a closed jar to prevent it from drying out on contact with air; it is then necessary to wait 24 hours to check the homogeneity of the formulation and the correct dispersion of the pigments.

10  21 Protocols and results

The compositions prepared are then tested on a specimen of clean hair, by application of these compositions using a brush. These specimens are then subjected to a water-resistance test protocol which consists in:

- immersing a specimen of false eyelashes in warm water (25°C) for 1 minute;
- rubbing the specimen to-and-fro on blotting paper using a pendulum; and then
- visually evaluating, with the naked eye, the marks left on the blotting paper.

On application, the compositions tested have a good consistency, the deposit is constructed coat after coat, the compositions coat the eyelashes well, the makeup result is uniform and the eyelash fringe is well separated.

After performing the rubbing test, the composition of the comparative example outside the invention leaves grey marks on the blotting paper, unlike the illustrative composition of the invention, which leaves no marks.

25  We may thus conclude that the composition according to the invention shows better resistance to water than the comparative composition outside the invention.

It is understood that, in the context of the present invention, the weight percentages given for a compound or a family of compounds are always expressed as weight of solids of the compound in question.

Throughout the application, the wording "comprising one" or "including one" means "comprising at least one" or "including at least one", unless otherwise specified.
CLAIMS

1. Emulsion-type cosmetic composition for coating keratin fibres, comprising:
   - an aqueous phase,
   - at least one wax,
   - at least one anionic surfactant comprising a cationic counterion, the said cationic counterion(s) comprising a primary (poly)hydroxyalkylamine, and
   - at least one alkali metal or alkaline-earth metal halide present in a total content of greater than or equal to 0.05% by weight relative to the total weight of the composition.

2. Composition according to Claim 1, in which the said anionic surfactant(s) are chosen from:
   - alkyl phosphates;
   - alkyl sulfates, and in particular alkyl ether sulfates, alkylamido ether sulfates, alkylaryl polyether sulfates and monoglyceride sulfates;
   - alkylsulfonates, alkylamidesulfonates, alkylaryl sulfonates, a-olefin sulfonates and paraffin sulfonates;
   - alkylsulfosuccinates, alkyl ether sulfosuccinates and alkylamidesulfosuccinates;
   - alkyl sulfosuccinamates;
   - alkylsulfoacetates;
   - acylsarcosinates, acylglutamates, acylisethionates, N-acyltaurates and acyllactylates;
   - carboxylic alkylpolyglycoside esters such as alkylglucoside citrates, alkylpolyglycoside tartrates, alkylpolyglycoside sulfosuccinates and alkylpolyglycoside sulfosuccinamates;
   - fatty acids, in particular oleic acid, ricinoleic acid, palmitic acid or stearic acid salts, coconut oil acid or hydrogenated coconut oil acid;
   - alkyl-D-galactosideuronic acids and salts thereof, polyoxyalkylated \((C_6-C_{24})\)alkyl ether carboxylic acids, polyoxyalkylated \((C_6-C_{24})\)alkylaryl ether carboxylic acids, polyoxyalkylated \((C_6-C_{24})\)alkylamido ether carboxylic acids and salts thereof, in particular those comprising from 2 to 50 alkylene oxide and in particular ethylene oxide groups;
and mixtures thereof.

3. Composition according to Claim 1 or 2, in which the anionic surfactant(s) are chosen from \( C_{12-22} \) and preferably \( C_{14-18} \) fatty acids, and preferably comprises stearic acid.

4. Composition according to Claim 1, 2 or 3, in which the said anionic surfactant(s) are present in a total content of greater than or equal to 1% by weight relative to the total weight of the composition, preferably ranging from 1.5% to 8% and better still from 2% to 5% by weight relative to the total weight of the composition.

5. Composition according to any one of the preceding claims, in which the said cationic counterion(s) are chosen from a cation of mineral origin, in particular chosen from alkali metal and alkaline-earth metal cations, or a cation of organic origin, preferably of organic origin.

6. Composition according to any one of the preceding claims, in which the said cationic counterion(s) comprise aminomethylpropanediol.

7. Composition according to any one of the preceding claims, in which the total content of cationic counterion(s) is greater than or equal to 0.01% and preferably inclusively between 0.1% and 4% by weight and better still between 0.5% and 2% by weight relative to the weight of the composition.

8. Composition according to any one of the preceding claims, in which the said halide ion(s) are chosen from the chloride ion, the bromide ion and the iodide ion, preferably the chloride ion.

9. Composition according to any one of the preceding claims, in which the said halide ion(s) comprise an alkali metal chosen from sodium and potassium, preferably sodium.
10. Composition according to any one of Claims 1 to 8, in which the said halide ion(s) comprise an alkaline-earth metal chosen from calcium and magnesium, preferably calcium.

11. Composition according to any one of the preceding claims, in which the said alkali metal or alkaline-earth metal halide(s) are chosen from sodium chloride, calcium chloride and a mixture thereof, preferably sodium chloride.

12. Composition according to any one of the preceding claims, in which the said wax(es) are present in a total content of greater than or equal to 5% by weight relative to the total weight of the said composition, and preferably inclusively between 10% and 40% by weight relative to the total weight of the composition.

13. Composition according to any one of the preceding claims, in which the said composition comprises at least one wax chosen from candelilla wax, carnauba wax, beeswax, paraffin wax, polyethylene wax and rice wax, and mixtures thereof.

14. Composition according to any one of the preceding claims, comprising at least one film-forming polymer.

15. Process for coating keratin fibres, in particular for making up the eyelashes, comprising a step of applying a cosmetic composition for coating keratin fibres according to any one of Claims 1 to 14.