The invention relates to a clear, microemulsion-based cosmetic formulation with reduced stickiness, comprising at least one antiperspirant active ingredient and/or deodorant active ingredient and α-hydroxycarboxylic acid.
The invention relates to a clear, cosmetic and dermatological emulsion-based formulation with reduced stickiness and yield point.

For aesthetic reasons in particular, transparent and translucent products are preferred by many consumers. Thus, transparent formulations are often used, for example, as deodorant or antiperspirant (AP). These can nowadays be realized by the following technologies:

1. aqueous-alcoholic formulations
2. water-in-silicone emulsions
3. microemulsions

The aqueous-alcoholic deodorant and AP formulations are mostly based on water and alcohol as medium, deodorant and antiperspirant agents as active ingredients, and also perfume, solubilizers and thickeners (mostly based on carbohydrate) as additional agents. They are perceived by the consumer as being fresh and cooling, but are at the same time encumbered with a whole series of disadvantages. Thus, for example, application primarily to freshly shaved skin is associated with incompatibilities as a result of the alcohol content. Another major disadvantage is the fact that relatively large amounts of oil cannot be incorporated into such systems. As a result of the high content of antiperspirant salt required for highly effective performance, a white residue remains following application to the skin; this is perceived by the consumer as being extremely troublesome. However, due to the absence of a sufficiently large oil phase for technical reasons, this cannot be concealed. Moreover, the use of carbohydrate thickeners leads to high stickiness of the product after the alcohol has evaporated.

Water-in-silicone emulsions belong to the group of water-in-oil emulsions. The water phase comprising ethanol or polyhydric alcohols, such as, for example, propylene glycol and water-soluble active ingredients, such as AP agent and/or deodorant active ingredient, constitutes about 75-90% of the formulation. The oil phase consists of a volatile and a nonvolatile silicone oil and also a silicone emulsifier.

The transparency of water-in-silicone emulsions is based on matching the refractive indices of the two phases. It is a drawback that even a difference in the indices of 0.0004 caused, for example, by evaporation, leads to cloudiness. WO 98/32418 and WO 92/05767 describe such deodorant or AP formulations based on W/S emulsion.

One approach for solving the described disadvantages has been made possible through cosmetically pleasing alcohol-free and transparent products which are based on so-called microemulsions. These have the major advantage that even relatively large amounts of various oils—with all of the described positive effects for the consumer—can be stably incorporated. Formulations of this type are in principle available by means of phase inversion temperature technology (PIT) or high-pressure homogenization. The required stability of the emulsifier system to high concentrations of antiperspirant salts, however, places high demands on the formulation skill of the product developer.

WO 9628132 and WO 9815255 describe microemulsions of this type. The disclosure of these documents is thus explicitly part of the present invention. However, a sticky feel on the skin sometimes caused by the thickener, and the lack of a yield point of the microemulsion is also disadvantageous in the case of these formulations.

It is an object of the present invention to provide a cosmetic preparation which enriches the prior art and helps to avoid its disadvantages.

In particular, it is the object of the present invention to provide a cosmetic and/or dermatological formulation which is transparent and is characterized by minimized stickiness. In particular, the object was to provide an antiperspirant formulation which is transparent and has no cloudiness at all, which is characterized by a minimized stickiness and which has a defined yield point for optimized discharge and application.

The bundle of objects is achieved by a cosmetic formulation corresponding to claim 1. The subject-matter of the dependent claims are advantageous embodiments of the preparation according to the invention. Furthermore, the invention includes the use of such preparations.

It was surprising and unforeseeable by the person skilled in the art that by adding at least one antiperspirant active ingredient, at least one α-hydroxyacid or carboxylic acid, preferably mandelic acid, and a microemulsion, in particular of the oil in water type, the provision of a transparent formulation with a defined yield point is possible and thus permits the provision of a transparent and low-stick cosmetic antiperspirant and/or deodorant preparation.

Through the surprisingly simple combination of antiperspirant active ingredients and mandelic acid in O/W microemulsions it is possible to prepare transparent cosmetic formulations which have reduced or no objectively or subjectively perceived stickiness.

Hydroxyphenylacetic acid or else phenylglycolic acid with the formula $H_2C_6O-\text{CH(OH)}-\text{COOH}, C_6H_2O_3$, is known under the name mandelic acid. Mandelic acid is readily soluble in water, alcohol, ether and 2-propanol. Synthetically, (±)-mandelic acid is obtained from benzaldehyde and hydrocyanic acid via the α-hydroxynitrile (cyanoaldimin) and its acidic hydrolysis corresponding to FIG. 1:

\[
\begin{align*}
H_2C_6O & \xrightarrow{\text{HCN}} H_2C_6\text{CH-CN} \xrightarrow{\text{+H}_2\text{O}} H_2C_6\text{CH-COOH} \\
& \quad \text{OH} \quad \text{NH}_3 \\
& \quad \text{OH}
\end{align*}
\]

By means of an α-hydroxy acid, preferably mandelic acid, it is surprisingly possible to prepare an AP or deodorant preparation which permits the required properties, such as transparency and low stickiness and, moreover, also the establishment of a specific yield point of the preparation. Furthermore, the formulation according to the invention is absorbed very rapidly into the skin without leaving residues behind.
Advantageously, the preparation according to the invention is based on microemulsions, preference being given to O/W microemulsions, in particular microemulsion gels, as are claimed in WO 9815255 and WO 9628132, the relevant disclosures therein thus belong explicitly to the disclosure of the present invention.

The cosmetic formulation is accordingly preferably based on microemulsion gels which are based a) on microemulsions of the oil-in-water type which comprise a oil phase which is essentially composed of constituents of low volatility, and a water phase comprising:  

one or more polyethoxylated O/W emulsifiers and/or

one or more polypropoxylated O/W emulsifiers and/or

one or more polyethoxylated and polypropoxylated O/W emulsifiers,

optionally also comprising one or more W/O emulsifiers having an emulsifier content of less than 20% by weight, based on the total weight of the emulsion,

obtainable by bringing a mixture of the base components, comprising water phase, oil phase, one or more of the O/W emulsifiers according to the invention, optionally, one or more W/O emulsifiers, and if desired further auxiliaries, additives and/or active ingredients, to a temperature within or above the phase inversion temperature range, and subsequently cooling to room temperature,

in which the droplets of the discontinuous oil phase are joined together by one or more crosslinker substances whose molecules are characterized by at least one hydrophilic region which has a size suitable for bridging the distance between the microemulsion droplets, and by at least one hydrophobic region which is able to enter into hydrophobic interaction with the microemulsion droplets.

However, it is a problem of the microemulsions described in WO 9815255 and WO 9628132 that a defined yield point could not be established. This object has likewise been achieved by the present invention.

In simple emulsions, finely disperse droplets of one phase (water droplets in the case of W/O emulsions or lipid vesicles in O/W emulsions) surrounded by an emulsifier sheath are present in the second phase. The droplet diameters of customary emulsions are in the range from about 1 μm to about 50 μm. Such “macroemulsions” are, without further coloring additives, milky white in color and opaque. Finer “macroemulsions”, the droplet diameters of which are in the range from about 10⁻³ μm to about 1 μm, are, again without coloring additives, bluish white in color and opaque.

Only micellar and molecular solutions with particle diameters of less than about 10⁻³ μm appear clear and transparent.

The droplet diameter of transparent or translucent microemulsions on the other hand is in the range from about 10⁻⁵ to about 10⁻⁴ μm. Such microemulsions are mostly of low viscosity. The viscosity of many microemulsions of the O/W type is comparable with that of water. The viscosity of these microemulsions can be increased with the help of associative thickeners, meaning that viscous gels are then present.

The preparation according to the invention is also advantageously in the form of a gel and has a yield point as a result of which discharge and application is improved compared to preparations from the prior art.

Besides those known from the prior art, the emulsifiers used are, in particular, fatty alcohol ethoxylates, such as, for example, polyethylene glycol(16) stearoyl ether, fatty acid ethoxylates, such as, for example, polyethylene glycol(14) stearate, polyethylene glycol glyceryl fatty acid esters, such as, for example, polyethylene glycol(15) glyceryl laurate, and the W/O emulsifier used is, for example, glyceryl monostearate.

The oil phase preferably consists of esters of saturated and unsaturated, branched and unbranched alkenecarboxylic acids or alcohols with chain lengths of 12-25 C atoms, such as, for example, octyldodecanol.

The combination according to the invention of AP active ingredient, mandelic acid and microemulsion, preferably the microemulsions disclosed in WO 9815255 and WO 9628132, makes it possible to produce a transparent cosmetic preparation via the unique thickening mechanism. The user thus has for the first time a water-clear and nevertheless extremely effective preparation at his disposal. The preparation according to the invention is easy to apply in gel form and has a pleasant feel on the skin on account of the lack of stickiness.

The combination of a-hydroxycarboxylic acid, preferably of mandelic acid, an anti-perspirant active ingredient and/or deodorant active ingredient and an O/W microemulsion as in WO 9815255 or WO 9628132 permit the preparation of a transparent AP or deodorant preparation which also has low stickiness and a specific yield point.

As antiperspirant active ingredient it is advantageously possible to incorporate acidic aluminum salts in aqueous solution. Here, the concentration ranges described refer to the so-called active contents of the antiperspirant complexes: in the case of the aluminum compounds, to anhydrous complexes. Moreover, preference is also given to the use of so-called activated aluminum chlorohydrates. The list which follows of antiperspirant active ingredients which are to be used advantageously is in no way intended to be limiting:

- aluminum salts (of the empirical formula \[\text{Al}_n(\text{OH})_m\text{Cl}_p\], where \(m+n+p\):
  - \[\text{Al}_3(\text{OH})_6\text{Cl}_3\] Standard Al complexes: Locron L, Locron LSC, Locron LIF (Clariant), Chlorhydrin (Reheis), ACH-303 (Summit), Aloxicoll L (Giulini)
  - \[\text{Al}_2(\text{OH})_3\text{Cl}_2\text{H}_2\text{O}\] Activated Al complexes: Rech 501 (Reheis), Aloxicoll 51 L
- aluminum sesquichlorohydrate \[\text{Al}_3(\text{OH})_3\text{Cl}_3\text{H}_2\text{O}\] Standard Al complexes: Aloxicoll 311. (Giulini), Westchlor 186 (Westwood Chemicals)
activated Al complexes: Reach 301 (Reheis)  

aluminum dichlorohydrate \[\text{Al}_2(\text{OH})_2\text{Cl}_2\cdot\text{H}_2\text{O}\]  
The antiperspirant active ingredients are used in the formulations according to the invention in an amount of from 1 to 35% by weight, preferably from 1 to 20% by weight.

Deodorants can also advantageously be added to preparations according to the invention. Customary cosmetic deodorants are based on various activity principles.

By using antimicrobial substances in cosmetic deodorants it is possible to reduce the bacteria flora on the skin. Here, in the ideal case, only the odor-causing microorganisms should be effectively reduced. The flow of perspiration itself is not influenced as a result, in an ideal case only the microbial decomposition of the perspiration is stopped temporarily. The combination of astringents with antimicrobially effective substances in one and the same composition is also customary.

All active ingredients customary for deodorants can be used advantageously, for example odor concealers, such as cosmetic perfume constituents, odor absorbers, for example the sheet silicates described in DE 40 09 347, of these in particular montmorillonite, kaolinite, illite, beidellite, nontronite, saponite, hectorite, bentonite, smectite, also, for example, zinc salts of ricinoleic acid. Antimicrobial agents are likewise suitable for incorporation into the preparations according to the invention. Advantageous substances are, for example, 2,4,4’-trichloro-2’-hydroxydiphenyl ether (Irgasan), 1,6-di(4-chlorophenyl)hexane (chlorhexidine), 3,4,4’-trichloroarsanilide, quaternary ammonium compounds, oil of cloves, mint oil, thyme oil, triethyl citrate, farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), and the active ingredients described in DE 37 40 186, DE 39 38 140, DE 42 04 321, DE 42 29 707, DE 42 29 737, DE 42 37 081, DE 43 09 372, DE 43 24 219. Sodium hydrogen carbonate can also be used advantageously.

The amount of deodorants (one or more compounds) in the preparations is preferably 0.01 to 10% by weight, preferably 0.05 to 5% by weight, based on the total weight of the preparation.

A combination of mandelic acid and aluminum chloride where the ratio of aluminum chloride to mandelic acid is 15:1 to 1:1, preferably 12:1 to 2:1, in particular 10:1 to 2:5:1, has proven to be particularly advantageous.

In particular, it was an object of the present invention to improve the sensory properties of the known AP and/or deodorant preparations as are described, for example, in WO 9628132 and WO 9815255.

For this purpose, the following comparative experiments on the basis of a micro-emulsion were set up.

Table 1 shows the comparison of various transparent formulations in a sensory research panel consisting of eight trained testers. For this, the samples were applied to the skin in a defined amount and evaluated by reference to an evaluation scale (1=not sticky; 10=considerably sticky).

<table>
<thead>
<tr>
<th>Example according to the invention</th>
<th>Comparative examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microemulsion containing mandelic acid</td>
<td>Microemulsion without mandelic acid, with more thickener</td>
</tr>
<tr>
<td>Ability to soak in, in seconds</td>
<td>148</td>
</tr>
<tr>
<td>Stickiness scale from 1-10</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Rheology Test

The yield point is a term for the smallest shear stress above which a plastic material behaves in rheological terms like a liquid (DIN 1342-1: 1983-10). The yield point is determined by recording a flow curve (in accordance with DIN 53019; 1980-05; DIN 53214; 1982-02). The value obtained is heavily dependent on the timescale (stress rate) on which the measurement is based. This is irrespective of whether the measurement is carried out using a shear stress-controlled or speed-controlled viscometer. Short timescales (rapid stresses) generally produce higher values for the yield point. An excessively high yield point may be the cause of flow disturbances. On the other hand, with a suitably dimensioned yield point it is possible to suppress the tendency of the liquid formulation to run.

The yield point measurements were carried out on a SR-2000 rheometer from Rheometric Scientific with the following requirements:

The temperature is kept constant at 25°C. Using a Peltier element; before the test a recovery time of 5 minutes is waited. With a coaxial plate consisting of plastic/plate measurement system with a diameter of 25 mm and a plate distance of 1 mm, a shear stress time ramp with 40 Pa/min from 0 Pa to 800 Pa is chosen. To determine the yield point, the viscosity is plotted logarithmically over the linear shear stress and the viscosity maximum, i.e. the critical shear stress, is given together with the maximum viscosity which goes with it. Formulations without a yield point have no maximum.

On account of their structurally viscous property, formulations with yield points have a lower tendency to run and are therefore suitable for easier discharge and application. Using the shear stress time ramp (40 Pa/min; 25°C) it was possible to establish the following maxima for the flow curves of preparations according to the invention:

<table>
<thead>
<tr>
<th>Shear stress (Pa)</th>
<th>Viscosity (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microemulsion without mandelic acid</td>
<td>No maximum</td>
</tr>
<tr>
<td>Microemulsion (0.7% PEG-150 distearate) with 1.5% mandelic acid</td>
<td>50</td>
</tr>
<tr>
<td>Microemulsion (0.7% PEG-150 distearate) with 2.0% mandelic acid</td>
<td>111</td>
</tr>
<tr>
<td>Microemulsion (1% PEG-150 distearate) with 1.5% mandelic acid</td>
<td>47</td>
</tr>
</tbody>
</table>
The advantage of the microemulsion according to the invention with yield point is that, as a result of the yield point, running out of the applicator is prevented since the formulation is not flowable without shearing.

The cosmetic and dermatological preparations according to the invention can comprise cosmetic auxiliaries as are customarily used in such preparations, e.g. preservatives, bactericides, UV filters, antioxidants, water-soluble vitamins, mineral substances, suspended solid particles, perfumes, substances for preventing foaming, dyes, pigments which have a coloring effect, thickeners, moisturizing and/or humectant substances or other customary constituents of a cosmetic or dermatological formulation, such as alcohols, polyols, polymers, foam stabilizers or silicone derivatives.

The preparation according to the invention is prepared by heating water phase and oil phase separately from one another to 85°C. The phases are then combined with stirring (paddle stirrer 200 rpm). Mandelic acid is dissolved in water, added to the emulsion at 30°C, and stirred for 30 min.

To apply the preparation, conventional packagings for deodorants and/or antiperspirants can be used, e.g. stick dispensers, gel dispensers, tubes and roll-ons.

In the examples the data in percent by weight are based on the total mass of the preparation.

EXAMPLES

| Glyceryl isostearate | 2.6 | 2.5 | 2.5 |
| Isetheth-20 | 5 | 5 | 5 |
| PEG-150 distearate | 1 | 1.5 | 0.7 |
| Dicaprylyl ether | 5 | 5 | 5 |
| Mandelic acid | 1.5 | 1.5 | 2 |
| Aluminum chlorohydrate | 10 | 10 | 10 |
| Perfume | 1 | 1 | 1 |
| Butylene glycol | 3 | — | 3 |
| Methylparaben | 0.2 | 0.2 | — |
| Water | 70.7 | 73.3 | 70.8 |

1.-15. (canceled)

16. A cosmetic formulation which is based on a microemulsion and comprises (a) at least one of an antiperspirant active ingredient and a deodorant active ingredient and (b) at least one \(\alpha\)-hydroxy carboxylic acid.

17. The cosmetic formulation of claim 16, wherein (b) comprises mandelic acid.

18. The cosmetic formulation of claim 16, wherein the microemulsion comprises an O/W microemulsion.

19. The cosmetic formulation of claim 16, wherein the formulation comprises a microemulsion gel.

20. The cosmetic formulation of claim 19, wherein the formulation comprises an oil-in-water microemulsion which comprises an oil phase, a water phase and less than 20% by weight of one or more emulsifiers, based on a total weight of the microemulsion.

21. The cosmetic formulation of claim 20, wherein the oil phase is essentially composed of constituents of low volatility.

22. The cosmetic formulation of claim 20, wherein the one or more emulsifiers comprise one or more O/W emulsifiers selected from polyethoxylated, polypropoxylated and polyethoxylated and polypropoxylated O/W emulsifiers and one or more optional W/O emulsifiers.

23. The cosmetic formulation of claim 22, wherein the microemulsion is obtainable by bringing a mixture comprising the water phase, the oil phase, the one or more O/W emulsifiers and the one or more optional W/O emulsifiers to a temperature within or above a phase inversion temperature range and subsequently cooling the mixture to room temperature.

24. The cosmetic formulation of claim 23, wherein droplets of a discontinuous oil phase are joined together by one or more crosslinker substances whose molecules comprise at least one hydrophilic region which has a size suitable for bridging a distance between the droplets and at least one hydrophobic region which is able to enter into hydrophobic interaction with the droplets.

25. The cosmetic formulation of claim 16, wherein the formulation comprises one or more antiperspirant active ingredients.

26. The cosmetic formulation of claim 25, wherein the one or more antiperspirant active ingredients comprises one or more aluminum salts.

27. The cosmetic formulation of claim 26, wherein the one or more aluminum salts comprise at least one of aluminum chlorohydrate and activated aluminum chlorohydrate.

28. The cosmetic formulation of claim 25, wherein the ratio of the one or more antiperspirant active ingredients to the at least one \(\alpha\)-hydroxy carboxylic acid is from 15:1 to 1:1.

29. The cosmetic formulation of claim 28, wherein the ratio is from 12:1 to 2:1.

30. The cosmetic formulation of claim 29, wherein the ratio is from 10:1 to 2.5:1.

31. The cosmetic formulation of claim 25, wherein the formulation comprises from 1% to 35% by weight of the one or more antiperspirant active ingredients, based on a total weight of the formulation.

32. The cosmetic formulation of claim 31, wherein the formulation comprises up to 25% by weight of the one or more antiperspirant active ingredients.

33. The cosmetic formulation of claim 32, wherein the formulation comprises up to 20% by weight of the one or more antiperspirant active ingredients.

34. The cosmetic formulation of claim 16, wherein the formulation comprises from 0.1% to 10% by weight of (b), based on a total weight of the formulation.

35. The cosmetic formulation of claim 34, wherein the formulation comprises up to 8% by weight of (b).

36. The cosmetic formulation of claim 16, wherein the formulation has a defined yield point.
37. The cosmetic formulation of claim 36, wherein the formulation has a yield point of from 40 to 120 Pa, determined at 25°C by means of a shear stress time ramp of 40 Pa/min.

38. The cosmetic formulation of claim 16, wherein the formulation is suitable for application to human skin.

39. The cosmetic formulation of claim 16, wherein the formulation is transparent.

40. An antiperspirant or deodorant product which comprises the cosmetic formulation of claim 16.

41. The antiperspirant or deodorant product of claim 40 which is transparent.

42. A process for making a transparent antiperspirant or deodorant product, wherein the process comprises combining an O/W microemulsion, at least one α-hydroxycarboxylic acid, and at least one of an antiperspirant active ingredient and a deodorant active ingredient.

43. The process of claim 42, wherein the at least one α-hydroxycarboxylic acid comprises mandelic acid.

44. A process for making an O/W microemulsion with a defined yield point, wherein the process comprises combining an O/W microemulsion with at least one α-hydroxycarboxylic acid and at least one of an antiperspirant active ingredient and a deodorant active ingredient.

45. The process of claim 44, wherein the at least one α-hydroxycarboxylic acid comprises mandelic acid.

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