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(54) Title: PROCESS FOR TREATING HUMAN PERSPIRATION USING POLYPHENOLS AND AN ENZYMATIC AND/OR CHEMICAL CATALYTIC OXIDATION SYSTEM

(57) Abstract: The invention relates to a cosmetic process for treating human perspiration, characterized in that it comprises the application to the surface of the skin of at least one polymer resulting from the polymerization of an antiperspirant agent-precursor polyphenol in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a chemical catalytic oxidation system. The invention relates to the cosmetic use, as an agent for treating human perspiration, of at least one polymer resulting from the polymerization of an antiperspirant agent-precursor polyphenol in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a chemical catalytic oxidation system.



PROCESS FOR TREATING HUMAN PERSPIRATION USING POLYPHENOLS AND AN ENZYMATIC AND/OR CHEMICAL CATALYTIC OXIDATION SYSTEM

5 The invention relates to a cosmetic process for treating human perspiration, characterized in that it comprises the application to the surface of the skin of at least one polymer resulting from the polymerization of at least one antiperspirant agent-precursor polyphenol in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a chemical catalytic oxidation system.

10 The invention relates to the cosmetic use, as an agent for treating human perspiration, of at least one polymer resulting from the polymerization of at least one antiperspirant agent-precursor polyphenol in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a chemical catalytic oxidation system.

15 In the cosmetics field, it is well known to use in topical application, as antiperspirants, astringent salts generally consisting of aluminium and/or zirconium chlorohydrates, which have the effect of limiting or even preventing the flow of sweat. These products are generally available in the form of roll-ons, sticks,
20 aerosols or sprays.

Metal salts of this type are efficient as antiperspirant active agents, but some people find that the application of such products causes skin irritation. Moreover, aluminium salts partly block perspiration via the formation of a partial plug in the
25 sweat duct, giving the consumer the impression of unnatural control of perspiration. The mechanism of action is not very well understood at the present time. One of the hypotheses is the formation of a precipitate with the glycoproteins secreted by sweat (mucins). Over time, a "plug" is thought to form in the pores. Many compounds are capable of precipitating proteins, but without necessarily
30 having an antiperspirant effect. Aluminium is an astringent substance, like tannins, zinc sulfate and silver nitrate. This protein-precipitating property alone cannot explain the efficacy of aluminium salts. Products that are capable of flocculating proteins do not give significant results (examples: magnesium sulfate, calcium chloride). However, these substances can cause discomfort in some users in
35 connection with the acidic pH of the formulations. Furthermore, it has been found that the antiperspirant efficacy of these substances is limited when they are used alone. This means that these substances need to be applied regularly to the skin in order to obtain a satisfactory effective antiperspirant effect. However, in the case of certain users, repeated application of these substances may lead to skin
40 irritation.

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

45 There is thus a need to find novel antiperspirant active agents that can replace aluminium salts and aluminium/zirconium salts, and that are efficient, easy to formulate and well tolerated.

The Applicant has discovered, surprisingly, that it is possible to obtain
50 antiperspirant properties by exploiting polyphenols, in particular ortho-diphenols,

and in polymerizing when they are placed in contact with at least one suitable catalytic system and in constituting, after this polymerization, a polymeric antiperspirant agent. Furthermore, the products formed have calmativ properties on the skin and antiodour activities. Such compounds are referred to hereinbelow as "antiperspirant agent-precursors".

Thus, a polyphenol compound and in particular an ortho-diphenol, namely a compound comprising at least one aromatic ring bearing at least two hydroxyl groups borne by two consecutive carbon atoms of the aromatic ring as defined below, proves to be capable of polymerizing *in situ* when it is placed in contact with a suitable catalytic system, in the presence of oxygen, and of forming an efficient, advantageously biocompatible polymeric antiperspirant agent, which is capable of reducing the flow of sweat and of reducing or even eliminating the body odour associated with human perspiration.

Such systems are especially described in documents EP 1 229 892 and EP 1 229 890. The Applicant has discovered, unexpectedly, that it is possible to use these polymers as antiperspirant agents in a cosmetic treatment process for reducing the flow of sweat and for reducing the body odour associated with human perspiration.

The Applicant has also discovered, surprisingly, that the application to the surface of the skin, in particular to the armpits, of these polymers by polymerization of these polyphenols in the presence of oxygen and of a catalytic system makes it possible to correct irregularities, imperfections and dyschromia in these particular areas of skin, while at the same time respecting the natural flesh tone of the skin, by selecting the appropriate polyphenol as a function of the skin type to be treated: fair skin or dark skin.

Skin types may be classified on the basis of their reactivity to the effects of solar radiation according to the scale proposed by Fitzpatrick.

According to this scale, the various existing skin types may be distinguished according to the following types:

Type	Skin reactivity	Origin
I	Always burns, never tans	Celtic
II	Always burns, tans very little	Germanic
III	Burns moderately, tans gradually	European
IV	Burns lightly, tans very easily	Mediterranean
V	Rarely burns, tans deeply	Middle Eastern - South American
VI	Never burns, highly pigmented	African

- 5 The invention relates to a cosmetic process for treating human perspiration, characterized in that it comprises the application to the surface of the skin of at least one polymer resulting from the polymerization of at least one antiperspirant agent-precursor polyphenol in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a chemical catalytic oxidation system.

10

The invention relates to the cosmetic use, as an agent for treating human perspiration, of at least one polymer resulting from the polymerization of at least one antiperspirant agent-precursor polyphenol in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a chemical catalytic oxidation system.

15

The term "antiperspirant" means any substance which has the effect of reducing the flow of sweat and/or of reducing the sensation of moisture associated with human sweat, and/or of masking human sweat.

20

The term "polyphenol" means any molecule comprising one or more aromatic rings, in particular benzene rings or fused aromatic rings bearing one or more hydroxyl functions.

25

The term "precursor of an antiperspirant agent" means any substance or any chemical compound that is capable via an oxidation reaction of forming a material constituting an antiperspirant agent.

ANTIPERSPIRANT AGENT-PRECURSOR POLYPHENOLS

30

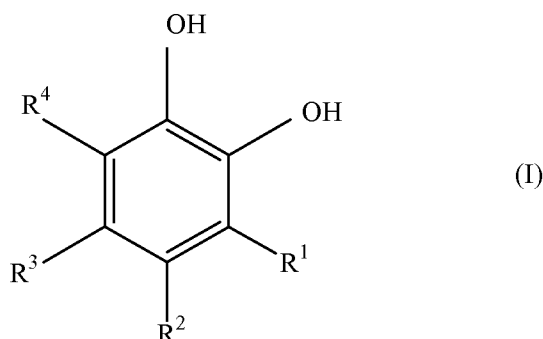
The antiperspirant agent-precursor polyphenols according to the invention are preferably compounds or compound mixtures comprising at least one aromatic ring, preferably a benzene ring or a fused aromatic ring, comprising at least two hydroxyl groups (OH) borne by two consecutive carbon atoms of the aromatic ring.

35

The aromatic ring may be a fused aromatic ring optionally containing one or more heteroatoms, such as naphthalene, tetrahydronaphthalene, indane, indene, anthracene, phenanthrene, indole, isoindole, indoline, isoindoline, benzofuran, dihydrobenzofuran, chroman, isochroman, chromene, isochromene, quinoline, tetrahydroquinoline and isoquinoline.

40

The antiperspirant agent-precursor polyphenols according to the invention may be represented by formula (I):



- 5 in which the substituents R_1 to R_4 , which may be identical or different, represent a hydrogen atom, a halogen, hydroxyl, carboxyl, alkyl carboxylate, optionally substituted amino, optionally substituted linear or branched alkyl, optionally substituted linear or branched alkenyl, optionally substituted cycloalkyl, alkoxy, alkoxyalkyl or alkoxyaryl radical, the aryl group possibly being substituted, an aryl
 10 or substituted aryl radical, an optionally substituted heterocyclic radical, or a radical containing one or more silicon atoms, in which two of the substituents R_1 to R_4 together form a saturated or unsaturated ring optionally containing one or more heteroatoms and optionally fused with one or more saturated or unsaturated rings optionally containing one or more heteroatoms.

- 15 The saturated or unsaturated, optionally fused rings may also be optionally substituted.

- 20 The alkyl radicals are generally C_1 - C_{10} alkyl radicals and preferably C_1 - C_6 alkyl radicals, such as methyl, ethyl, propyl, butyl, pentyl and hexyl.

The alkoxy radicals are generally C_1 - C_{20} alkoxy radicals, such as methoxy, ethoxy, propoxy and butoxy.

- 25 The alkoxyalkyl radicals are preferably (C_1-C_{20}) alkoxy (C_1-C_{20}) alkyl radicals, such as methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, etc.

- 30 The cycloalkyl radicals are generally C_4 - C_8 cycloalkyl radicals, preferably cyclopentyl and cyclohexyl radicals. The cycloalkyl radicals may be substituted cycloalkyl radicals, in particular substituted with alkyl, alkoxy, carboxylic acid, hydroxyl, amine and ketone groups.

The alkenyl radicals are preferably C_1 - C_{20} radicals, such as ethylene, propylene, butylene, pentylene, methyl-2-propylene and decylene.

- 35 The radicals containing one or more silicon atoms are preferably polydimethylsiloxane, polydiphenylsiloxane, polydimethylphenylsiloxane or stearoxydimethicone radicals.

The heterocyclic radicals are generally radicals comprising one or more heteroatoms chosen from O, N and S, preferably O or N, optionally substituted with one or more alkyl, alkoxy, carboxylic acid, hydroxyl, amine or ketone groups.

- 5 Among the preferred heterocyclic radicals, mention may be made of furyl, pyranlyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl and thienyl groups.

- More preferably, the heterocyclic groups are fused groups such as benzofuryl, chromenyl, xanthenyl, indolyl, isoindolyl, quinolyl, isoquinolyl, chromanyl,
10 isochromanyl, indolinyl, isoindolinyl, coumarinyl or isocoumarinyl groups, these groups possibly being substituted, in particular with one or more OH groups.

- The preferred antiperspirant agent-precursor polyphenols are in particular: flavanols, for instance catechin and epicatechin gallate,
15 flavonols, such as quercetin, anthocyanidins such as peonidin, anthocyanins, for example oenin, ortho-hydroxybenzoates, for example gallic acid salts, flavones, such as luteolin,
20 iridoids such as oleuropein, tannic acid, ellagic acid, luteolin, oleuropein and anthocyanins that may be osylated (for example glucosylated) and/or in the form of oligomers (procyanidins or proanthocyanidins),
25 hydroxystilbenes, for example tetrahydroxy-3,3', 4,5'-stilbene, optionally osylated (for example glucosylated), 3,4-dihydroxyphenylalanine and derivatives thereof, 2,3-dihydroxyphenylalanine and derivatives thereof, 4,5-dihydroxyphenylalanine and derivatives thereof,
30 4,5 dihydroxyindole and derivatives thereof, 5,6 dihydroxyindole and derivatives thereof, 6,7 dihydroxyindole and derivatives thereof, 2,3 dihydroxyindole and derivatives thereof, dihydroxycinnamates such as caffeic acid and chlorogenic acid,
35 hydroxycoumarins, hydroxyisocoumarins, hydroxycoumarones, hydroxyisocoumarones, hydroxychalcones,
40 hydroxychromones, anthocyanins, quinones, hydroxyxanthenes, 1,2-dihydroxybenzenes,
45 1,2,4-trihydroxybenzenes, 1,2,3-trihydroxybenzenes, 2,4,5-trihydroxytoluene, 5,6-dihydroxyindoline, and mixtures of the preceding compounds.

When these compounds have D and L forms, the two forms may be used in the compositions in accordance with the invention.

5 The antiperspirant agent-precursor polyphenols according to the invention may be extracted from plants, fruit, citrus plants, legumes, trees and shrubs, and mixtures of these extracts, which contain numerous polyphenols as defined previously.

Among the plant extracts, mention may be made of extracts of rose, sorghum and tea.

10 Among the fruit extracts, mention may be made of extracts of apple, of grape (in particular of grapeseed), or extracts of cocoa (beans and/or pods), of pomegranate and of banana.

15 Among the legume extracts, mention may be made of extract of potato and extract of artichoke.

Among the tree extracts, mention may be made of extracts of pine bark.

20 Mixtures of these extracts may also be used.

According to one preferred embodiment, an extract of pine is used.

25 It may especially be an extract of maritime pine (*Pinus pinaster*) bark, and in particular an extract of maritime pine bark containing at least 60% by weight and preferably at least 65% by weight of procyanidins.

30 According to a first variant, it may be an extract of maritime pine bark containing from 65% to 85% by weight of procyanidins, such as, for example, the maritime pine extract sold under the reference Pycnogenol® by the company Biolandes Arômes and/or Horphag Research.

35 According to another variant, it may be an extract of maritime pine bark containing at least 90% by weight and preferably from 90% to 98% by weight of procyanidins, such as, for example, the (Maritime) Pine Bark extracts from Layn Natural Ingredients and Pine Bark from Blue California.

40 For the purposes of the invention, the terms "procyanidin" and "proanthocyanidin" are equivalent and denote flavonoid oligomers comprising, for example, catechin units.

45 More particularly, the extract of maritime pine bark under consideration according to the invention may contain procyanidins consisting of catechin and epicatechin units linked together via C-C bonds so as to form dimers, trimers and other oligomers with a chain length of up to 6 or even 7 molecules.

50 The extract of maritime pine bark under consideration according to the invention may also contain other compounds, for example at least one compound chosen from catechins, epicatechins and organic acids, especially phenolic acids such as caffeic acid, ferulic acid, p-coumarinic acid and p-benzoic acid.

Among the abovementioned organic acids, some may be in free form or associated with glucose, and in this case form, for example, glucose esters or glucose ethers.

5

Use may be made especially of an extract of maritime pine bark obtained according to the processes described in patent applications US 4 698 360, US 6 372 266 and US 5 720 956.

10 As an example of such extracts, mention may be made especially of the compound referenced under the INCI name *Pinus pinaster* (bark extract) and under the CTFA name Pine (*Pinus pinaster*) bark extract.

15 It may especially be the maritime pine extract sold under the reference Pycnogenol® by the company Biolandes Arômes and/or Horphag Research.

Mention may also be made of the extracts (Maritime) Pine Bark from Layn Natural Ingredients, Pine Bark from Blue California and Oligopin® from D.R.T. (Les Dérivés Résiniques et Terpéniques).

20

The amount of antiperspirant agent-precursor polyphenol according to the invention must be sufficient to obtain after polymerization a satisfactory antiperspirant effect. This amount may vary over a wide range as a function of the nature of the precursor and of the desired intensity for the remanence of the efficacy.

25

According to one embodiment, the antiperspirant agent-precursor polyphenol may be present in a content ranging from 0.01% to 25% by weight, preferably from 0.05% to 5% by weight and especially from 0.1% to 2% by weight relative to the total weight of the combination of compositions before they are placed in contact.

30

CATALYTIC SYSTEM

a) Enzymatic catalytic oxidation system

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According to one particular mode of the invention, the cosmetic treatment process for treating human perspiration comprises the application to the said skin of at least one polymer resulting from the polymerization reaction of an antiperspirant agent-precursor polyphenol (i), in particular of a compound comprising at least one aromatic ring bearing at least two hydroxyl groups borne by two consecutive carbon atoms of the aromatic ring, the said compounds (i) and (ii) being included in one to three separate cosmetic compositions before the said placing in contact; the said polymerization reaction being performed by placing in contact, in the presence of oxygen, the said compound (i) with an effective amount of an enzymatic catalytic system (ii);

45

the said antiperspirant-agent precursor and the said catalytic system being placed in contact with each other in the presence of oxygen, such that the said polymerization reaction takes place at least partly on the skin; the said polymer being present in an amount that is effective to reduce the flow of sweat.

50

The enzymes catalysing the oxidation of the polyphenol antiperspirant-agent precursor may be chosen especially from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases, uricases, choline oxidases, 5 sarcosine oxidases, bilirubin oxidases, laccases, tyrosinases, peroxidases, **catalases and superoxide dismutases**, and mixtures thereof, or from plant extracts containing abovementioned enzymes, in the optional presence of a donor (or substrate) necessary for the functioning of the said enzymes, for instance L-tyrosine or L-dopa.

10

The enzymes used according to the invention may be of animal, microbiological (bacterial, fungal or viral) or synthetic (obtained via chemical or biotechnological synthesis) origin.

15 The enzyme(s) may be used in pure crystalline form or in a form diluted in an inert diluent for the said enzyme.

Examples of uricases that may especially be mentioned include uricases extracted from wild boar liver, uricase from *Arthrobacter globiformis* and uricase from 20 *Aspergillus flavus*.

Examples of sources of choline oxidase that may especially be mentioned include rat liver, bacteria such as *Arthrobacter globiformis*, *Achromobacter cholinophagum* or *Alcaligenes*, and fungi such as *Cylindrocarpon didymum*.

25

Examples of sources of sarcosine oxidase that may especially be mentioned include bacteria such as *Arthrobacter* and in particular *Arthrobacter ureafaciens* and *Arthrobacter globiformis*, *Streptomyces*, *Bacillus*, *Pseudomonas*, *Corynebacterium* or *Alcaligenes*, for instance *Alcaligenes denitrificans*, and fungi 30 such as *Cylindrocarpon didymum*.

Examples of sources of bilirubin oxidase that may especially be mentioned include rat liver and intestinal mucosae, and bacteria such as *Myrothecium verucania*, *Myrothecium cinctum* and *Myrothecium roridum*.

35 Among the laccases of plant origin that may be used according to the invention, mention may be made of laccases produced by plants that perform chlorophyll synthesis, such as those indicated in patent application FR-A-2 694 018.

Mention may be made especially of laccases extracted from *Anacardiaceae*, from 40 *Podocarpaceae*, from *Rosmarinus off.*, from *Solanum tuberosum*, from *Iris* sp., from *Coffea* sp., from *Daucus carota*, from *Vinca minor*, from *Persea americana*, from *Catharanthus roseus*, from *Musa* sp., from *Malus pumila*, from *Ginkgo biloba* and from *Monotropa hypopithys* (pinesap).

45 Among the laccases of microbial (especially fungal) origin, or obtained biotechnologically, which may be used according to the invention, mention may be made of laccases from *Polyporus versicolor*, from *Rhizoctonia praticola* and from *Rhus vernicifera* as described, for example, in patent applications FR- A-2 112 549 and EP-A-504 005; the laccases described in patent applications WO 95/07988, 50 WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, for

instance laccases from *Scytalidium*, from *Polyporus pinsitus*, from *Myceliophthora thermophila*, from *Rhizoctonia solani* or from *Pyricularia orizae*, and variants thereof.

- 5 Laccases of microbial origin or those obtained biotechnologically will more preferentially be selected.

In one particularly preferred embodiment of the invention, the enzyme used corresponds to tyrosinase (nomenclature EC 1.14.18.1). In the present invention,
10 the term "tyrosinase" should be understood as meaning any enzyme having tyrosinase activity, this enzyme possibly having other enzymatic activities. Tyrosinase activity may be defined as the enzymatic activity that catalyses the oxidation of tyrosine to lead to the formation of the melanin precursor: dopaquinone.

15 Examples of sources of tyrosinase that may especially be mentioned include potato, fungi, microorganisms such as *Neurospora crassa*, etc.

The amount of enzyme present in the final composition may vary widely but is
20 generally from 5×10^{-3} to 5 mg and preferably from 5×10^{-2} to 0.5 mg per ml of final composition.

According to one embodiment, the said polyphenol antiperspirant-agent precursor (i) and the said enzymatic catalytic system (ii) may be conditioned in a conditioning
25 assembly that is:

- either in the form of a single compartment free of oxygen, which simultaneously contains at least the compounds (i) and (ii);
- or in the form of a kit consisting of at least two separate containers, in which compounds (i) and (ii) are not simultaneously present in the same container.

30

b) Chemical catalytic oxidation system

As chemical catalytic oxidation system, use will preferably be made of a catalytic system comprising a first constituent chosen from Mn(II) and/or Zn(II) salts and
35 oxides and mixtures thereof and a second constituent chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen carbonates, and mixtures thereof.

According to another particular mode of the invention, the cosmetic treatment
40 process for treating human perspiration comprises the application to the said skin of at least one polymer resulting from the polymerization reaction of a polyphenol (i), in particular of a compound comprising at least one aromatic ring bearing at least two hydroxyl groups borne by two consecutive carbon atoms of the aromatic ring,

45 the said polymerization reaction being performed by the placing in contact, in the presence of oxygen, of the said antiperspirant-agent precursor (i) with an effective amount of a catalytic system comprising a first constituent (ii) chosen from Mn(II) and/or Zn(II) salts and oxides and mixtures thereof and a second constituent (iii) chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen
50 carbonates, and mixtures thereof;

the said compounds (i), (ii) and (iii) being included in one to three separate cosmetic compositions before the said placing in contact, the said antiperspirant-agent precursor and the said catalytic system being placed in contact with each other in the presence of oxygen, such that the said polymerization reaction takes place at least partly on the skin, and the said polymer being present in an amount that is effective to reduce the flow of sweat.

Preferentially, the proportions of the first and of the second constituents are such that:

$$\frac{[\text{Mn(II)}]}{[\text{HCO}_3]} \leq 1 \text{ with } [\text{Mn(II)}] \neq 0$$

$$\frac{[\text{Zn(II)}]}{[\text{HCO}_3]} \leq 1 \text{ with } [\text{Zn(II)}] \neq 0$$

15

$$\frac{[\text{Mn(II)} + \text{Zn(II)}]}{[\text{HCO}_3]} \leq 1 \text{ with } [\text{Mn(II)}] \text{ and } [\text{Zn(II)}] \neq 0$$

in which $[\text{Mn(II)}]$, $[\text{Zn(II)}]$ and $[\text{HCO}_3]$ represent, respectively, the molar concentrations of Mn(II), Zn(II) and HCO_3 relative to the total volume of all of the said compositions before they are placed in contact.

20

Generally, the ratio $\frac{[\text{Mn(II)}]}{[\text{HCO}_3]}$ is chosen in the range from 10^{-5} to 10^{-1} , preferably from 10^{-3} to 10^{-2} and better still is equal to 5×10^{-3} .

In the case of Zn(II), the ratio $\frac{[\text{Zn(II)}]}{[\text{HCO}_3]}$ is generally of an order of 10 to 100 times greater than the ratio in the case of Mn(II).

25

Typically, this ratio is chosen in a range from 10^{-4} or more, for example in the range from 10^{-4} to < 1 , preferably from 10^{-3} or more, for example in the range from 10^{-3} to < 1 , and is preferably of the order of 5×10^{-1} .

30

In the case of a mixture of Mn(II) and Zn(II), the ratio $\frac{[\text{Mn(II)} + \text{Zn(II)}]}{[\text{HCO}_3]}$ is generally chosen in the range from 10^{-5} to 10^{-1} and preferably 10^{-3} to 10^{-2} , this ratio being chosen to be higher when the proportion of Zn(II) in the mixture increases.

35

Generally, the molar concentration of Mn(II), Zn(II), or Mn(II) + Zn(II) relative to the total volume of all of the compositions before they are placed in contact ranges from 10^{-3} to 10 mM/l and preferably from 10^{-2} to 1 mM/l.

When only one or more Mn(II) salts or oxides are used, the molar concentration of Mn(II) relative to the total volume of all of the compositions before they are placed in contact is typically from 10^{-3} to 10^{-1} mM/l and preferably from 10^{-2} to 10^{-1} mM/l.

5 Preferably, when only one or more Zn(II) salts or oxides are used, the molar concentration of Zn(II) relative to the total volume of all of the compositions before they are placed in contact is typically from 5×10^{-2} to 10 mM/l and better still from 5×10^{-1} to 1 mM/l.

10 Among the Mn(II) and Zn(II) salts that are suitable for use in the present invention, mention may be made of the chloride, fluoride, iodide, sulfate, phosphate, nitrate, perchlorate and carboxylic acid salts, and mixtures thereof.

15 By way of example, mention may be made of manganese chloride, manganese carbonate (for example rhodochrosite), Mn(II) difluoride, Mn(II) acetate tetrahydrate, Mn(II) lactate trihydrate, Mn(II) phosphate, Mn(II) iodide, Mn(II) nitrate trihydrate, Mn(II) bromide and Mn(II) perchlorate tetrahydrate, and Mn(II) sulfate monohydrate.

20 The Mn(II) and/or Zn(II) salt that is particularly preferred is the chloride, i.e. MnCl_2 and ZnCl_2 .

The carboxylic acid salts also include salts of hydroxylated carboxylic acids such as gluconate.

25 Among the alkali metal and alkaline-earth metal hydrogen carbonates, mention may be made of Na, K, Mg and Ca hydrogen carbonates and mixtures thereof, preferentially Na hydrogen carbonate.

30 As indicated previously, the chemical catalytic system according to the invention constitutes a pseudo-oxidase in that it oxidizes polyphenols, in the presence of oxygen, as would a natural enzymatic catalyst with polyphenol oxidase activity.

35 On the other hand, the catalytic system according to the invention has no pseudo-catalase activity, in the sense that it does not bring about the dismutation of hydrogen peroxide at 0.3% by weight (i.e. 1 volume of oxygen).

40 In addition, the pseudo-oxidase activity is associated with the use of the catalytic system according to the invention. Thus, each of the constituents of the catalytic system taken separately has no pseudo-oxidase activity. Similarly, the replacement of the Mn(II) or Zn(II) salt with another salt, Fe, Cu or even Mn(III), does not lead to a catalytic system with pseudo-oxidase activity.

45 According to one embodiment of the invention, the said antiperspirant-agent precursor (i), the said first constituent of the catalytic system (ii) and the said second constituent of the catalytic system (iii) may be conditioned in a conditioning assembly that is:

- either in the form of a single compartment free of oxygen, which simultaneously contains at least the compounds (i), (ii) and (iii);

- or in the form of a kit consisting of at least two separate containers, in which compounds (i), (ii) and (iii) are not simultaneously present in the same container.

5 **c) Enzymatic and chemical catalytic oxidation system**

According to another particular mode of the invention, the cosmetic treatment process for treating human perspiration comprises the application to the said skin of at least one polymer resulting from the polymerization reaction of a polyphenol (i), in particular of a compound comprising at least one aromatic ring bearing at least two hydroxyl groups borne by two consecutive carbon atoms of the aromatic ring, the said polymerization reaction being performed by the placing in contact, in the presence of oxygen, of the said antiperspirant-agent precursor polyphenol (i) with an effective amount of an enzymatic catalytic system (ii), of a chemical catalytic system comprising a first constituent (iii) chosen from Mn(II) and/or Zn(II) salts and oxides and mixtures thereof and a second constituent (iv) chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen carbonates, and mixtures thereof; the said compounds (i), (ii), (iii) and (iv) being included in one to four separate cosmetic compositions before the said placing in contact, the said antiperspirant-agent precursor polyphenol and the said catalytic systems being placed in contact with each other in the presence of oxygen, such that the said polymerization reaction takes place at least partly on the skin.

According to another embodiment of the invention, the said antiperspirant-agent precursor polyphenol (i), the said enzymatic system (ii), the said first constituent of the catalytic system (iii) and the said second constituent of the catalytic system (iv) may be conditioned in a conditioning assembly that is:

- either in the form of a single compartment free of oxygen, which simultaneously contains at least the compounds (i), (ii) and (iii);
- or in the form of a kit consisting of at least three separate containers, in which compounds (i), (ii), (iii) and (iv) are not simultaneously present in the same container.

According to one particular form of the invention, the said antiperspirant agent-precursor polyphenol (i) and the said enzymatic system (ii) may be present in the same container and the two catalytic constituents (iii) and (iv) in two separate containers.

40 **PHYSIOLOGICALLY ACCEPTABLE MEDIUM**

The compositions in accordance with the invention comprise a physiologically acceptable medium, i.e. a medium that is compatible with the skin and/or its integuments. It is preferably a cosmetically acceptable medium, i.e. which has a pleasant colour, odour and feel and which does not cause any unacceptable discomfort (stinging, tautness or redness) liable to discourage the consumer from using these compositions.

The physiologically acceptable medium is a solid or liquid medium that does not harm the antiperspirant properties of the polymer obtained or the catalytic effect of the catalytic system.

- 5 Advantageously, it facilitates the *in situ* polymerization of the ortho-diphenols, which gives it a bacteriostatic effect.

Among the solvents for the compounds that are required according to the invention, which are suitable for formulating the compositions in accordance with
10 the invention, mention may be made of water, alcohols, polyols and polyol ethers, and mixtures thereof.

The alcohols are preferably lower (C1-C6) alkanols such as ethanol and isopropanol, and alkanediols such as ethylene glycol, propylene glycol and
15 pentanediol.

Among the polar solvents, mention may be made of ethers, esters (in particular acetates), dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP) and ketones (in particular acetone), and mixtures thereof.
20

The physiologically acceptable medium preferably comprises water (in particular distilled or deionized water) or a water/alcohol mixture, in particular.

The amount of alcohol in the water/alcohol mixture may represent up to 80% by weight, preferably 1% to 50% by weight and better still 5% to 20% by weight of the water/alcohol mixture.
25

The compositions in accordance with the invention are advantageously suitable for topical application.

30 The compositions in accordance with the invention may be in any galenical form conventionally used for topical application and may especially be in the form of an aqueous, alcoholic or aqueous-alcoholic solution or suspension or an oily suspension, an emulsion of more or less fluid consistency and especially liquid or
35 semi-liquid consistency, obtained by dispersing a fatty phase in an aqueous phase (O/W) or, conversely, (W/O), a solid (O/W) or (W/O) emulsion, a more or less fluid or solid aqueous, aqueous-alcoholic or oily gel, a loose or compacted powder to be used in unmodified form or to be incorporated into a physiologically acceptable medium, or alternatively microcapsules, microparticles or vesicular dispersions of
40 ionic and/or nonionic type. They may thus be in the form of a solution, serum, milk, O/W or W/O cream, ointment, pomade, balm, patch, impregnated pad, stick or spray.

POLYSACCHARIDES

45 According to one particularly preferred form, in order to improve the water retention and the cosmetic properties, the compositions according to the invention also contain at least one polysaccharide.

The polysaccharides may be chosen especially from glucans, modified or unmodified starches (such as those derived, for example, from cereals, for instance wheat, corn or rice, from vegetables, for instance yellow pea, and tubers, for instance potato or cassava), amylose, amylopectin, glycogen, dextrans, 5 celluloses and derivatives thereof (methylcelluloses, hydroxyalkylcelluloses, ethylhydroxyethylcelluloses, carboxymethylcelluloses), mannans, xylans, lignins, arabans, fructans, galactans, galacturonans, chitin, chitosans, glucuronoxylans, arabinoxylans, xyloglucans, glucomannans, pectic acids and pectins, alginic acid and alginates, arabinogalactans, carrageenans, agars, glycosaminoglucans, gum 10 arabis, gum tragacanth, ghatti gums, karaya gums, carob gums, galactomannans such as guar gums and nonionic derivatives thereof (hydroxypropyl guar) and xanthan gums, and mixtures thereof.

In general, the compounds of this type that may be used in the present invention 15 are chosen from those described especially in Kirk-Othmer's *Encyclopedia of Chemical Technology*, Third Edition, 1982, volume 3, pp. 896-900, and volume 15, pp. 439-458, in *Polymers in Nature* by E.A. MacGregor and C.T. Greenwood, published by John Wiley & Sons, Chapter 6, pp. 240-328, 1980, and in *Industrial Gums – Polysaccharides and their Derivatives*, edited by Roy L. Whistler, Second 20 Edition, published by Academic Press Inc.

Use will be made more particularly of glycosaminoglucans, in particular hyaluronic acid and chitosans.

25 **ADDITIONAL ANTIPERSPIRANT ACTIVE AGENTS**

The compositions according to the invention may also contain one or more antiperspirant active agents, in particular aluminium and/or zirconium salts or complexes.

30 The antiperspirant salts or complexes in accordance with the invention are generally chosen from aluminium and/or zirconium salts or complexes. They are preferably chosen from aluminium halohydrates; aluminium zirconium halohydrates, complexes of zirconium hydroxychloride and of aluminium 35 hydroxychloride with or without an amino acid, such as those described in patent US-3 792 068.

Among the aluminium salts, mention may be made in particular of aluminium chlorohydrate in activated or unactivated form, aluminium chlorohydrate, the 40 aluminium chlorohydrate-polyethylene glycol complex, the aluminium chlorohydrate-propylene glycol complex, aluminium dichlorohydrate, the aluminium dichlorohydrate-polyethylene glycol complex, the aluminium dichlorohydrate-propylene glycol complex, aluminium sesquichlorohydrate, the aluminium sesquichlorohydrate-polyethylene glycol complex, the aluminium 45 sesquichlorohydrate-propylene glycol complex, aluminium sulfate buffered with sodium aluminium lactate.

Among the aluminium-zirconium salts, mention may be made in particular of aluminium zirconium octachlorohydrate, aluminium zirconium pentachlorohydrate, 50 aluminium zirconium tetrachlorohydrate and aluminium zirconium trichlorohydrate.

The complexes of zirconium hydroxychloride and of aluminium hydroxychloride with an amino acid are generally known as ZAG (when the amino acid is glycine). Among these products, mention may be made of the aluminium zirconium octachlorohydrate-glycine complexes, the aluminium zirconium pentachlorohydrate-glycine complexes, the aluminium zirconium tetrachlorohydrate-glycine complexes and the aluminium zirconium trichlorohydrate-glycine complexes.

The antiperspirant salts or complexes may be present in the composition according to the invention in a proportion from about 0.5% to 25% by weight relative to the total weight of the composition.

As other additional antiperspirant agents, mention may be made of perlites and preferably expanded perlites.

The perlites that may be used according to the invention are generally aluminosilicates of volcanic origin and have as the composition:

70.0-75.0% by weight of silica SiO_2
12.0-15.0% by weight of oxide of aluminium Al_2O_3
3.0-5.0% of sodium oxide Na_2O
3.0-5.0% of potassium oxide K_2O
0.5-2% of iron oxide $\text{Fe}_2\text{O}_3 \rightarrow$
0.2-0.7% of magnesium oxide MgO
0.5-1.5% of calcium oxide CaO
0.05-0.15% of titanium oxide TiO_2

The perlite is ground, dried and then calibrated in a first step. The product obtained, known as perlite ore, is grey-coloured and has a size of about 100 μm .

The perlite ore is then expanded (1000°C/2 seconds) to give more or less white particles. When the temperature reaches 850-900°C, the water trapped in the structure of the material evaporates and brings about the expansion of the material relative to its original volume. The expanded perlite particles in accordance with the invention may be obtained via the expansion process described in patent US 5 002 698.

Preferably, the perlite particles used are ground: in this case, they are known as Expanded Milled Perlite (EMP). They preferably have a particle size defined by a median diameter D_{50} ranging from 0.5 to 50 μm and preferably from 0.5 to 40 μm .

Preferably, the perlite particles used have an untamped apparent density at 25°C ranging from 10 to 400 kg/m^3 (standard DIN 53468) and preferably from 10 to 300 kg/m^3 .

Preferably, the expanded perlite particles according to the invention have a water-absorbing capacity, measured at the wet point, ranging from 200% to 1500% and preferably from 250% to 800%.

The wet point corresponds to the amount of water that needs to be added to 1 g of particle in order to obtain a homogeneous paste. This method is derived directly

from that of the oil uptake applied to solvents. The measurements are taken in the same manner by means of the wet point and the flow point, which have, respectively, the following definition:

- 5 wet point: mass expressed in grams per 100 g of product corresponding to the production of a homogeneous paste during the addition of a solvent to a powder;

flow point: mass expressed in grams per 100 g of product at and above which the amount of solvent is greater than the capacity of the powder to retain it. This is
10 reflected by the production of a more or less homogeneous mixture that flows on a glass plate.

The wet point and the flow point are measured according to the following protocol:

15 Protocol for measuring the water absorption

1) Materials used

- Glass plate (25 x 25 mm)
Spatula (wooden and partly metallic handle, 15 x 2.7 mm)
20 Silk-bristled brush
Balance

2) Procedure

- 25 The glass plate is placed on the balance and 1 g of perlite particles is weighed out. The beaker containing the solvent and the sampling pipette is placed on the balance. The solvent is gradually added to the powder, the whole being regularly blended (every 3 to 4 drops) with the spatula.
The mass of solvent needed to obtain the wet point is noted. Further solvent is
30 added and the mass required to reach the flow point is noted. The average of three tests is determined.

The expanded perlite particles sold under the trade names Optimat 1430 OR or Optimat 2550 by the company World Minerals will be used in particular.
35

DEODORANT ACTIVE AGENTS

The compositions according to the invention may also contain one or more deodorant active agents.
40

The term "deodorant active agent" refers to any substance that is capable of masking, absorbing, improving and/or reducing the unpleasant odour resulting from the decomposition of human sweat by bacteria.

- 45 The deodorant active agents may be bacteriostatic agents or bactericides that act on underarm odour microorganisms, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether (®Triclosan), 2,4-dichloro-2'-hydroxydiphenyl ether, 3',4',5'-trichlorosalicylanilide, 1-(3',4'-dichlorophenyl)-3-(4'-chlorophenyl)urea (®Triclocarban) or 3,7,11-trimethyldodeca-2,5,10-trienol (®Farnesol); quaternary
50 ammonium salts such as cetyltrimethylammonium salts, cetylpyridinium salts,

DPTA (1,3-diaminopropanetetraacetic acid), 1,2-decanediol (Symclariol from the company Symrise), glycerol derivatives, for instance caprylic/capric glycerides (Capmul MCM from Abitec), glyceryl caprylate or caprate (Dermosoft GMCY and Dermosoft GMC, respectively from Straetmans), Polyglyceryl-2 caprate
5 (Dermosoft DGMC from Straetmans), and biguanide derivatives, for instance polyhexamethylene biguanide salts. - chlorhexidine and salts thereof; 4-phenyl-4,4-dimethyl-2-butanol (Symdeo MPP from Symrise).

Among the deodorant active agents in accordance with the invention, mention may also be made of - zinc salts, for instance zinc salicylate, zinc gluconate, zinc
10 pidolate; zinc sulfate, zinc chloride, zinc lactate, zinc phenolsulfonate; salicylic acid and derivatives thereof such as 5-n-octanoylsalicylic acid.

The deodorant active agents may be odour absorbers such as zinc ricinoleate; metallic or silver or silver-free zeolites, or cyclodextrins.
15

It may also be a polyol such as glycerol or propane-1,3-diol (Zemea Propane diol sold by Dupont Tate and Lyle Bioproducts).

- alum.
20

In the event of incompatibility or to stabilize them, some of the active agents mentioned above may be incorporated into spherules, especially ionic or nonionic vesicles and/or nanoparticles (nanocapsules and/or nanospheres).

25 The deodorant active agents may be present in the composition according to the invention in a proportion from about 0.01% to 15% by weight relative to the total weight of the composition.

APPLICATION PROCESS

30 To obtain *in situ* the polymeric antiperspirant agent according to the invention, it suffices to place the antiperspirant-agent precursor polyphenol according to the invention in contact with an effective amount of the catalytic system according to the invention, in the presence of an oxidizing medium such as a medium
35 containing oxygen (for example atmospheric oxygen).

Various processes for applying the compositions in accordance with the invention may be used.

40 According to a first process, a composition comprising all the ingredients of the composition, i.e. both the antiperspirant agent-precursor polyphenol according to the invention and the catalytic system according to the invention, may be applied to the skin in the presence of oxygen, for example atmospheric oxygen, provided that these ingredients are conditioned in an oxygen-free compartment.

45 According to a second process, successive layers of composition(s) may be applied to the skin in the presence of oxygen, for example atmospheric oxygen, such that the assembly of the successive layers comprises all the ingredients required according to the invention, namely the antiperspirant agent-precursor
50 polyphenol, the enzymatic catalytic system and/or the first constituent of the

chemical catalytic system and the second constituent of the chemical catalytic system, each of the said layers not, however, simultaneously comprising all of these ingredients.

- 5 For example, a layer of a composition comprising at least one antiperspirant agent-precursor polyphenol according to the invention in a physiologically acceptable medium may first be applied to the skin, and then, on this layer, a layer comprising at least the catalytic system according to the invention in a physiologically acceptable medium, which, in the presence of oxygen, will enable
10 the *in situ* polymerization of a polymeric antiperspirant agent.

- As a variant, a layer of a composition comprising at least only one of the constituents of the chemical catalytic system according to the invention in a physiologically acceptable medium may also be applied first to the skin, and then a
15 layer comprising at least the other constituent of the chemical catalytic system according to the invention in a physiologically acceptable medium, the antiperspirant agent-precursor polyphenol according to the invention being present either in one or the other of the said layers or in a separate layer.

- 20 It is obviously possible to reverse the order of application of the successive layers.

The layers may be applied by any known means, in particular by spraying.

CONDITIONING

25

The compositions in accordance with the invention may be presented and may be conditioned in various forms.

- According to a first embodiment variant, the compositions in accordance with the
30 invention may be conditioned in a single oxygen-free compartment, for instance a pump system with only one compartment with no air intake, in which are simultaneously present at least the antiperspirant agent-precursor polyphenol according to the invention and the catalytic system(s) according to the invention.

- 35 In a second embodiment variant, the compositions in accordance with the invention may be conditioned in the form of a kit consisting of at least two separate containers, for example a kit with pumps comprising two compartments, the said kit comprising at least (i) the antiperspirant agent-precursor polyphenol according to the invention, (ii) the first constituent of the chemical catalytic system according
40 to the invention and (iii) the second constituent of the chemical catalytic system according to the invention, such that the said compounds (i), (ii) and (iii) are not simultaneously present in the same container.

- In a third embodiment variant, the compositions in accordance with the invention
45 may be conditioned in the form of a kit consisting of at least three separate containers, for example a kit with pumps comprising three compartments, the said kit comprising at least (i) the antiperspirant agent-precursor polyphenol according to the invention, (ii) the enzymatic catalytic system according to the invention, (iii) the first constituent of the chemical catalytic system according to the invention and
50 (iv) the second constituent of the chemical catalytic system according to the

invention, such that the said compounds (i), (ii), (iii) and (iv) are not simultaneously present in the same container.

5 For example, a container may contain a first composition comprising at least one antiperspirant agent-precursor polyphenol according to the invention in a physiologically acceptable medium, and another container may contain a second composition comprising at least the catalytic system according to the invention in a physiologically acceptable medium, the first and second compositions being mixed or applied successively at the time of the use.

10

As a variant, a container may contain a first composition comprising at least only one of the constituents of the catalytic system according to the invention in a physiologically acceptable medium and another container may contain a second composition comprising at least the other constituent of the catalytic system according to the invention in a physiologically acceptable medium, the antiperspirant-agent precursor according to the invention being present either in one or the other of the said compositions or in another container containing a separate composition.

15

20 In another variant, a container may contain a first composition comprising at least only one of the constituents of the chemical catalytic system according to the invention in a physiologically acceptable medium and another container may contain a second composition comprising at least the other constituent of the chemical catalytic system according to the invention in a physiologically acceptable medium, the antiperspirant agent-precursor polyphenol and optionally the enzymatic catalytic system according to the invention being present either in one or the other of the said compositions or in another container containing a separate composition.

25

30 In the embodiment variants mentioned above, use is preferably made of an extract of maritime pine (*Pinus pinaster*) bark, and in particular of an extract of maritime pine bark containing at least 60% by weight, preferably at least 65% by weight and most preferentially from 65% to 85% by weight of procyanidins.

30

35 This will be, for example, a kit consisting of at least two separate containers in which:

35

- a first container contains a first composition comprising at least one extract of maritime pine bark containing at least 60% by weight, preferably at least 65% by weight and most preferentially from 65% to 85% by weight of procyanidins and the first constituent of the catalytic system, for example Mn(II) chloride, and

40

- a second container contains the second constituent of the catalytic system, for example sodium hydrogen carbonate.

45 The examples that follow serve to illustrate the invention without, however, being limiting in nature. The compounds are, depending on the case, cited as the chemical names or as the CTFA names (International Cosmetic Ingredient Dictionary and Handbook).

45

50 The examples that follow serve to illustrate the present invention. The amounts are given as mass percentages relative to the total weight of the composition.

50

Example 1: Demonstration of the antiperspirant properties

It has been shown that the antiperspirant effect can be described by a test.

- 5 The antiperspirant effect of a product in accordance with the invention consisting of two lotions A1 and A2, the first especially containing an extract of maritime pine and MnCl_2 and the second especially containing NaHCO_3 , was first tested.

Composition A1 (invention)

10	Extract of maritime pine bark (Pycnogenol® from Biolandes Arômes)	10%
	MnCl_2	0.02%
	1N NaOH	qs pH 5-6
15	Ethanol	80%
	Distilled water	qs 100%

Composition A2:

20	NaHCO_3	8.4%
	Distilled water	qs 100 %

Mixing of the two compositions of the product in accordance with the invention is performed on a volume-for-volume basis, just before application to the specimen.

- 25 **Composition B (outside the invention): antiperspirant roll-on based on an aluminium salt**

30	Aluminium chlorohydrate (aqueous solution at 50% by weight - Chlorohydrol 50 – Summitrehis)	30% (15% AM) Dimethicone
		0.5%
	Ceteareth-33	1.25%
	Cetyl alcohol	2.5%
35	PPG-15 stearyl ether	3.0%
	Preserving agent	0.075%
	Water qs	100%

Antiperspirant test protocol

- 40 The test is performed on a panel of 22 women.

Two times 8 areas ($4 \times 5 \text{ cm}^2$) are delimited on either side of the spinal column.

- 45 Each product area has a corresponding symmetrical untreated control area.

Each composition (A1+A2) and B is applied for four days, by gentle massaging, at a rate of 75 mg on to each corresponding product area.

- 50 Single-action application: application followed by drying 15 minutes

Twofold-action application: first application - drying 15 minutes - second application - drying 15 minutes

- 5 Occlusion for 1 hour. The individuals remain throughout the occlusion period in a room maintained at 30°C and 50% relative humidity.

- 10 24 hours after the final application, the back is washed with water to remove all trace of remaining product; cellulose squares are attached to the various areas and the individuals are made to sweat in a sauna for 15 minutes at 80°C. The amount of sweat is evaluated by weighing the cellulose squares before and after sweating.

Scale of the degree of efficacy:

- | | | | |
|----|---------------------------------|-------------------|--------------------|
| 15 | - percentage efficacy reduction | $R < 10\%$ | no efficacy |
| | - percentage efficacy reduction | $10\% < R < 15\%$ | low efficacy |
| | - percentage efficacy reduction | $15\% < R < 25\%$ | moderate efficacy |
| | - percentage efficacy reduction | $25\% < R < 35\%$ | good efficacy |
| | - percentage efficacy reduction | $35\% < R < 50\%$ | high efficacy |
| 20 | - percentage efficacy reduction | $R > 50\%$ | very high efficacy |

The results obtained are as follows:

25

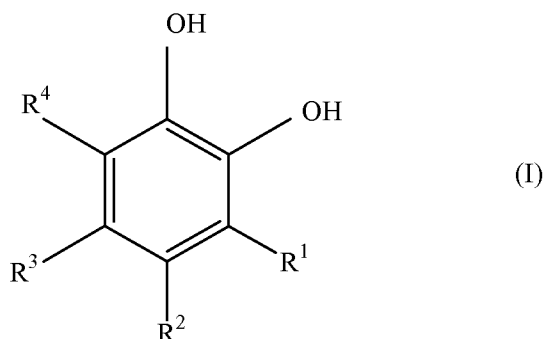
Composition tested	Percentage reduction of sweat
A1 + A2 (invention) Pycnogenol + MnCl_2 NaHCO_3	$22 \pm 9\%$
B (outside the invention) Aluminium chlorohydrate	$30 \pm 14\%$

It is observed that the application of compositions A1 and A2 according to the invention produces good antiperspirant activity equivalent to a formulation containing 15% aluminium chlorohydrate.

30

CLAIMS

1. Cosmetic process for treating human perspiration, characterized in that it comprises the application to the surface of the skin of at least one polymer resulting from the polymerization of at least one antiperspirant agent-precursor polyphenol in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a chemical catalytic oxidation system.
2. Process according to Claim 1, in which the antiperspirant agent-precursor polyphenol is a compound or compound mixture comprising at least one aromatic ring, preferably a benzene ring or a fused aromatic ring, comprising at least two hydroxyl groups (OH) borne by two consecutive carbon atoms of the aromatic ring.
3. Process according to Claim 1 or 2, in which the antiperspirant agent-precursor polyphenol is a compound of formula (I):



- in which the substituents R_1 to R_4 , which may be identical or different, represent a hydrogen atom, a halogen, hydroxyl, carboxyl, alkyl carboxylate, optionally substituted amino, optionally substituted linear or branched alkyl, optionally substituted linear or branched alkenyl, optionally substituted cycloalkyl, alkoxy, alkoxyalkyl or alkoxyaryl radical, the aryl group possibly being substituted, an aryl or substituted aryl radical, an optionally substituted heterocyclic radical, or a radical containing one or more silicon atoms, in which two of the substituents R_1 to R_4 together form a saturated or unsaturated ring optionally containing one or more heteroatoms and optionally fused with one or more saturated or unsaturated rings optionally containing one or more heteroatoms.
4. Process according to any one of Claims 1 to 3, in which the antiperspirant agent-precursor polyphenol is chosen from:
- flavanols,
 - flavonols,
 - anthocyanidins,
 - anthocyanins,
 - hydroxybenzoates,
 - flavones,
 - iridoids,
 - tannic acid,
 - ellagic acid,

- luteolin,
oleuropein and anthocyanins that may be osylated and/or in the form of oligomers
(procyanidins or proanthocyanidins),
hydroxystilbenes, optionally osylated,
5 3,4-dihydroxyphenylalanine and derivatives thereof,
2,3-dihydroxyphenylalanine and derivatives thereof,
4,5-dihydroxyphenylalanine and derivatives thereof,
4,5 dihydroxyindole and derivatives thereof,
5,6 dihydroxyindole and derivatives thereof,
10 6,7 dihydroxyindole and derivatives thereof,
2,3 dihydroxyindole and derivatives thereof,
dihydroxycinnamates,
hydroxycoumarins,
hydroxyisocoumarins,
15 hydroxycoumarones,
hydroxyisocoumarones,
hydroxychalcones,
hydroxychromones,
anthocyanins,
20 quinones,
hydroxyxanthenes,
1,2-dihydroxybenzenes,
1,2,4-trihydroxybenzenes,
1,2,3-trihydroxybenzenes,
25 2,4,5-trihydroxytoluene,
5,6-dihydroxyindoline, and
mixtures thereof.
5. Process according to any one of Claims 1 to 3, in which the antiperspirant
30 agent-precursor polyphenol is a pine extract, and especially an extract of maritime
pine bark containing at least 60% by weight, preferably at least 65% by weight and
most preferentially from 65% to 85% by weight of procyanidins.
6. Process according to Claim 5, in which the pine extract is the compound
35 referenced under the INCI name *Pinus pinaster* (bark extract) and under the CTFA
name Pine (*Pinus pinaster*) bark extract.
7. Process according to any one of Claims 1 to 6, characterized in that the said
40 antiperspirant agent-precursor polyphenol is present in a content ranging from
0.01% to 25% by weight, preferably from 0.05% to 5% by weight and especially
from 0.1% to 2% by weight relative to the total weight of the combination of
compositions before they are placed in contact.
8. Process according to any one of Claims 1 to 7, in which the enzymatic catalytic
45 oxidation system is chosen from pyranose oxidases, glucose oxidases, glycerol
oxidases, lactate oxidases, pyruvate oxidases, uricases, choline oxidases,
sarcosine oxidases, bilirubin oxidases, laccases, tyrosinases, peroxidases,
catalases and superoxide dismutases, and mixtures thereof, or from plant extracts
containing abovementioned enzymes, in the optional presence of a donor (or
50 substrate) necessary for the functioning of the said enzymes.

9. Process according to any one of Claims 1 to 8, in which the amount of enzyme present in the final composition may vary widely but is generally from 5×10^{-3} to 5 mg and preferably from 5×10^{-2} to 0.5 mg per ml of final composition.

10. Process according to any one of Claims 1 to 9, in which the chemical catalytic oxidation system comprises

a) a first constituent chosen from Mn(II) and/or Zn(II) salts and oxides and mixtures thereof, and

b) a second constituent chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen carbonates, and mixtures thereof.

11. Process according to Claim 10, in which the proportions of the first and second constituents are such that:

$$\frac{[\text{Mn(II)}]}{[\text{HCO}_3]} \leq 1 \text{ with } [\text{Mn(II)}] \neq 0$$

$$\frac{[\text{Zn(II)}]}{[\text{HCO}_3]} \leq 1 \text{ with } [\text{Zn(II)}] \neq 0$$

$$\frac{[\text{Mn(II)} + \text{Zn(II)}]}{[\text{HCO}_3]} \leq 1 \text{ with } [\text{Mn(II)}] \text{ and } [\text{Zn(II)}] \neq 0$$

in which [Mn(II)], [Zn(II)] and [HCO₃] represent, respectively, the molar concentrations of Mn(II), Zn(II) and HCO₃ relative to the total volume of all of the said compositions before they are placed in contact.

12. Process according to Claim 10 or 11, characterized in that the ratio $\frac{[\text{Mn(II)}]}{[\text{HCO}_3]}$ is chosen in the range from 10^{-5} to 10^{-1} , preferably from 10^{-3} to 10^{-2} and better still is equal to 5×10^{-3} .

13. Process according to any one of Claims 10 to 12, characterized in that the

ratio $\frac{[\text{Zn(II)}]}{[\text{HCO}_3]}$ is chosen in the range from 10^{-4} to < 1 , preferably from 10^{-3} to < 1 and better still is about 5×10^{-1} .

14. Process according to any one of Claims 10 to 13, characterized in that the

ratio $\frac{[\text{Mn(II)} + \text{Zn(II)}]}{[\text{HCO}_3]}$ is chosen in the range from 10^{-5} to 10^{-1} and preferably from 10^{-3} to 10^{-2} .

15. Process according to any one of Claims 10 to 14, characterized in that the Mn(II) and Zn(II) salts are chosen from the chlorides, fluorides, iodides, sulfates,

phosphates, nitrates, perchlorates and carboxylic acid salts, and mixtures thereof, and more particularly from the chlorides.

5 **16.** Process according to any one of Claims 1 to 15, characterized in that at least one antiperspirant active agent and/or one deodorant active agent is also used.

17. Process according to any one of Claims 1 to 16, characterized in that at least one polysaccharide chosen in particular from glycosaminoglucans and chitosans is also used.

10

18. Cosmetic use, as an agent for treating human perspiration, of at least one polymer resulting from the polymerization of at least one antiperspirant agent-precursor polyphenol as defined in any one of the preceding claims in the presence of oxygen and of an enzymatic catalytic oxidation system and/or a
15 chemical catalytic oxidation system as defined in any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/061870

A. CLASSIFICATION OF SUBJECT MATTER INV. A61K8/19 A61K8/20 A61K8/34 A61K8/49 A61K8/66 A61K8/97 A61Q15/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) A61K A61Q		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, BIOSIS, EMBASE, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
16 October 2012	29/10/2012	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Tullberg, Erik	

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/061870

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