

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
20 January 2005 (20.01.2005)

PCT

(10) International Publication Number
WO 2005/004828 A1

- (51) International Patent Classification⁷: **A61K 7/46**
- (21) International Application Number:
PCT/EP2004/006902
- (22) International Filing Date: 24 June 2004 (24.06.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0308323 8 July 2003 (08.07.2003) FR
60/490,255 28 July 2003 (28.07.2003) US
- (71) Applicant (*for all designated States except US*):
L'OREAL [FR/FR]; 14, rue Royale, F-75008 Paris (FR).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): **BARA, Isabelle** [FR/FR]; 58, bis rue St. Hilaire, 94210-La Varenne-St-Hilaire (FR).
- (74) Agent: **RENARD, Emmanuelle**; L'OREAL - D.I.P.I., 25-29, quai Aulagnier, F-92600 Asnieres (FR).
- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *with international search report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 2005/004828 A1

(54) Title: PERFUME COMPOSITION

(57) Abstract: The present invention relates to a perfume composition comprising a mixture of fragrant materials in a physiologically acceptable carrier comprising a mixture of polydimethylsiloxanes, characterized in that the said mixture of polydimethylsiloxanes consists of hexamethyldisiloxane and octamethyltrisiloxane, in a weight ratio of between 30:70 and 70:30.

PERFUME COMPOSITION

The present invention relates to novel perfume compositions comprising a mixture of fragrant materials in a physiologically acceptable carrier
5 comprising a mixture of polydimethylsiloxanes, characterized in that the said mixture of polydimethylsiloxanes consists of hexamethyldisiloxane and octamethyltrisiloxane in a hexamethyldisiloxane to octamethyltrisiloxane weight ratio ranging from 30:70 to
10 70:30.

The perfume compositions usually comprise a mixture of fragrant materials having a vapour pressure less than atmospheric pressure at 25°C and are generally liquid at 25°C, but sometimes also solid, in
15 a physiologically acceptable medium based on ethanol and optionally water.

Ethanol constitutes a good solubilizing agent for perfuming ingredients, and additionally has the advantage of being inexpensive and of allowing the
20 formulation of transparent compositions. On the other hand, it has the disadvantage of adversely affecting the olfactory characteristics of the perfuming ingredients, not only because of its potent odour but also because of its capacity to react, in the presence
25 of water, with the perfuming ingredients and to thereby modify their odour and/or their colour. It is in addition capable of chemically reacting with

atmospheric nitrogen oxides to form ozone, which constitutes, in this regard, a source of atmospheric pollution which efforts are being made to avoid.

Finally, ethanol is an irritant and may be a source of tingling when it is applied to a sensitive or damaged skin, in particular after shaving.

Several attempts have therefore been made to replace ethanol in perfume compositions with other solvents not having the above disadvantages.

10 A first route consists in replacing ethanol with aqueous compositions containing hydrophilic solubilizing agents such as polyethoxylated hydrogenated castor oils. The compositions obtained contain high percentages of these solubilizing agents
15 which may be irritating, foaming and may have a sticky effect on the skin. Another route consists in formulating perfume compositions in the form of micro- and nanoemulsions. The oily phase of these emulsions, containing the perfuming ingredients, is however
20 limited in quantity so as not to destabilize the emulsion, which reduces the perfuming effect of these compositions. Moreover, the presence of water in a large quantity is capable of causing degradation of the perfuming ingredients over time and therefore of
25 adversely affecting the olfactory characteristics of the product.

Another solution further consisted in

providing perfume compositions in which the ethanol is at least partially replaced by one or more volatile silicones which are linear - of the polydimethylsiloxane type - or cyclic. Such is the case in the document WO 99/01106 which discloses perfume compositions intended for impregnating textiles or nonwoven fabrics. The document US-6,432,912 also discloses a perfume composition containing these volatile silicones, optionally used in the form of a mixture in order to adjust the rate of evaporation of the carrier, and which are combined with cosolvents such as esters optionally combined with diesters.

However, the applicant has now discovered, surprisingly, that by choosing a particular combination of silicone compounds not described in the prior art, it was possible to obtain a perfume composition whose rate of evaporation is close to that of ethanol and possessing a flash point greater than or equal to 0°C, preferably greater than or equal to 10°C.

The subject of the present invention is therefore a perfume composition comprising a mixture of fragrant materials in a physiologically acceptable carrier comprising a mixture of polydimethylsiloxanes, characterized in that the said mixture of polydimethylsiloxanes consists of hexamethyldisiloxane and octamethyltrisiloxane in a hexamethyldisiloxane to octamethyltrisiloxane weight ratio ranging from 30:70 to

70:30.

Advantageously, the hexamethyldisiloxane to octamethyltrisiloxane weight ratio ranges from 30:70 to 40:60. More preferably, the polydimethylsiloxane mixture contains 30% by weight of hexamethyldisiloxane and 70% by weight of octamethyltrisiloxane.

The polydimethylsiloxanes according to the invention are available in particular from the company DOW CORNING under the trade name Dow Corning Fluid 200 0.65 cst and 1 cst, from the company RHODIA under the trade name Silbione Huile 70041 0.65 D, from the company WACKER under the trade name Belsil DM 0.65 and from the company GE BAYER SILICONES under the trade name hexamethyldisiloxan.

The fragrant materials contained in the perfume composition according to the invention are compounds which are customarily used by perfumers and they are described in particular in S. Arctander, Perfume and Flavor Chemicals (Montclair, N.J., 1969), in S. Arctander, Perfume and Flavor Materials of Natural Origin (Elizabeth, N.J., 1960) and in "Flavor and Fragrance Materials - 1991", Allured Publishing Co. Wheaton, III. USA.

They may be natural products (essential oils, absolutes, resinoids, resins, concretes) and/or synthetic products (hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals,

nitriles, saturated or unsaturated, aliphatic or cyclic).

Examples of essential oils comprise essential oils of lemon, orange, anise, bergamot, rose, geranium, 5 ginger, neroli, basil, rosemary, cardamom, camphor, cedar, camomile, sandalwood, sage, and mixtures thereof, without this list being limiting.

Examples of other fragrant compounds are in particular: geraniol, geranyl acetate, farnesol, 10 borneol, bornyl acetate, linalol, linalyl acetate, linalyl propionate, linalyl butyrate, tetrahydro-linalol, citronellol, citronellyl acetate, citronellyl formate, citronellyl propionate, dihydromyrcenol, dihydromyrcenyl acetate, tetrahydromyrcenol, terpineol, 15 terpinyl acetate, nopol, nopyl acetate, nerol, neryl acetate, 2-phenylethanol, 2-phenylethyl acetate, benzyl alcohol, benzyl acetate, benzyl salicylate, styrallyl acetate, benzyl benzoate, amyl salicylate, dimethyl-benzylcarbinol, trichloromethylphenylcarbinyl acetate, 20 p-tert-butylcyclohexyl acetate, isononyl acetate, vetiveryl acetate, vetiverol, alpha-hexyl-cinnamaldehyde, 2-methyl-3-(p-tert-butylphenyl)-propanal, 2-methyl-3-(p-isopropylphenyl)propanal, 3-(p-tert-butylphenyl)propanal, 2,4-dimethylcyclohex-3- 25 enylcarboxaldehyde, tricyclodecenyl acetate, tricyclodecenyl propionate, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexenecarboxaldehyde, 4-(4-methyl-3-pentenyl)-3-

cyclohexenecarboxaldehyde, 4-acetoxy-3-pentyltetra-
hydropyran, 3-carboxymethyl-2-pentylcyclopentane,
2-n-heptylcyclopentanone, 3-methyl-2-pentyl-2-cyclo-
pentenone, menthone, carvone, tagetone, geranylacetone,
5 n-decanal, n-dodecanal, 9-decen-1-ol, phenoxyethyl
isobutyrate, phenylacetaldehyde dimethyl acetal,
phenylacetaldehyde diethyl acetal, geranonitrile,
citronellonitrile, cedryl acetate, 3-isocamphylcyclo-
hexanol, cedryl methyl ether, isolongifolanone,
10 aubepine nitrile, aubepine, heliotropine, coumarin,
eugenol, vanillin, diphenyl oxide, citral, citronellal,
hydroxycitronellal, damascone, ionones, methylionones,
isomethylionones, solanone, irones, cis-3-hexenol and
its esters, indan musks, tetralin musks, isochroman
15 musks, macrocyclic ketones, macrolactone musks,
ethylene brassylate and mixtures thereof.

The composition according to the present
invention usually contains from 2 to 60% by weight, and
preferably from 5 to 40% by weight, of fragrant
20 materials. It additionally contains a sufficient
quantity of polydimethylsiloxanes to solubilize the
fragrant materials, and preferably from 20 to 99% by
weight of polydimethylsiloxanes, relative to the total
weight of the composition.

25 The perfume composition according to the
invention also generally comprises solvents, adjuvants
or additives commonly used in the perfume sector which

do not adversely affect the desired olfactory effect. Preferably, however, this composition does not contain an ester of a C₄-C₁₀ acid and of a C₄-C₁₅ alcohol.

This perfume composition may constitute an eau de Cologne, an eau de toilette, a perfume or an aftershave lotion.

Depending on its flash point, it may be packaged in an atomizer or possibly in an aerosol device. In the latter case, the composition according to the invention additionally contains a propellant gas such as dimethyl ether, propane, n-butane, isobutane, pentane, trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, 1,1,1,2-tetrafluoroethane, chloropentafluoroethane, 1-chloro-1,1-difluoroethane, 1,1-difluoroethane, and mixtures thereof. Dimethyl ether, isobutane and 1,1,1,2-tetrafluoroethane are preferably used, and preferably isobutane.

The invention will now be illustrated with the following nonlimiting examples. In these examples, the quantities are indicated as a percentage by weight.

EXAMPLES

Example 1: Comparative study of the properties of various mixtures of silicones

Various mixtures of silicones were tested in order to evaluate, on the one hand, their rate of evaporation and, on the other hand, the flash point of

a composition comprising these mixtures in combination with a perfume.

a) Protocols

Flash point

5 The test composition is heated in a closed cup of standard sizes at a temperature about 3°C less than the presumed flash point, for 60 seconds. Next, a flame of standard size is introduced into the vapours in the cup through a sliding opening. The test is
10 repeated in 1°C steps. The lowest temperature at which ignition occurs is noted as being the flash point.

The test is carried out in a SETAFLASH apparatus according to the ISO 3679 standard.

Rate of evaporation

15 15 g of solvent to be tested are introduced into a crystallizing dish (diameter: 7 cm) placed on a balance which is in a chamber of about 0.3 m³ whose temperature (25°C) and humidity (relative humidity: 50%) are regulated.

20 The solvent is allowed to evaporate freely, without stirring, while ventilating using a ventilator (PAPST-MOTOREN, reference 8550 N, revolving at 2700 revolutions/min) placed vertically above the crystallizing dish containing the solvent, the blades
25 being directed towards the crystallizing dish and at a distance of 20 cm relative to the base thereof.

The mass of solvent remaining in the

crystallizing dish is measured at regular intervals during the first thirty minutes of evaporation. The rate of evaporation is expressed in mg of solvent evaporated per unit of surface area (cm²) and per unit
5 of time (minute).

b) Results

The table below groups together the results obtained for various combinations of volatile silicones, in variable weight ratios.

10 In this table:

L2 denotes hexamethyldisiloxane

L3 denotes octmethyltrisiloxane

L4 denotes decamethyltetrasiloxane

L5 denotes dodecamethylpentasiloxane

15

Mixture of silicones		Rate of evaporation (mg/cm ² /min)	Flash point* (°C)
30/70	L2/L3	4.23	+ 11
	L2/L4	3.25	--
	L2/L5	3.39	--
40/60	L2/L3	5.39	--
55/45	L2/L3	6.98	+ 2
60/40	L2/L3	--	+ 2
70/30	L2/L3	8.97	0
	L2/L5	7.77	-1

* Compositions comprising from 12 to 17.7% by weight of perfume extract in the mixture of silicones.

By way of comparison, the rate of evaporation of ethanol, measured under the same conditions, is 5.13 mg/cm²/min. The flash point of a composition comprising 12% by weight of perfume extract in ethanol is 16°C. That of a composition comprising 12% by weight of perfume extract in hexamethyldisiloxane is -5°C.

As is evident from this table, the mixtures of silicones consisting of the silicone L2 combined with another silicone chosen from the silicones L4 and L5, in weight ratios ranging from 70:30 to 30:70, do not always make it possible to obtain compositions having a flash point greater than 0°C and a volatility at least equal to 4 mg/cm²/min, unlike the mixture of silicones according to the invention.

Example 2: Perfume compositions

The compositions below were prepared in a conventional manner for persons skilled in the art.

Composition A

Perfume extract "Noa"	12 %
Hexamethyldisiloxane	48.4 %
Octamethyltrisiloxane	39.6 %

Composition B

Perfume extract "Emporio White"	17.7 %
Hexamethyldisiloxane	24.7 %
Octamethyltrisiloxane	57.6 %

CLAIMS

1. Perfume composition comprising a mixture of fragrant materials in a physiologically acceptable carrier comprising a mixture of polydimethylsiloxanes,
5 characterized in that the said mixture of polydimethylsiloxanes consists of hexamethyldisiloxane and octamethyltrisiloxane in a hexamethyldisiloxane to octamethyltrisiloxane weight ratio ranging from 30:70 to 70:30.
- 10 2. Composition according to Claim 1, characterized in that the hexamethyldisiloxane to octamethyltrisiloxane weight ratio ranges from 30:70 to 40:60.
- 15 3. Composition according to Claim 1 or 2, characterized in that the said mixture of polydimethylsiloxanes contains 30% by weight of hexamethyldisiloxane and 70% by weight of octamethyltrisiloxane.
- 20 4. Composition according to any one of Claims 1 to 3, characterized in that it contains from 5 to 40% by weight of fragrant materials.
5. Composition according to any one of Claims 1 to 4, characterized in that it contains from 20 to 99% by weight of a mixture of polydimethylsiloxanes.
- 25 6. Composition according to any one of Claims 1 to 5, characterized in that it does not contain an ester of a C₄-C₁₀ acid and of a C₄-C₁₅

alcohol.

7. Composition according to any one of the preceding claims, characterized in that it is packaged in an aerosol device.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/006902

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A61K7/46				
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) IPC 7 A61K				
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 practical, search terms used) EPO-Internal, WPI Data, CHEM ABS Data, PAJ				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	WO 01/00141 A (UNILEVER PLC ;LEVER HINDUSTAN LTD (IN); UNILEVER NV (NL)) 4 January 2001 (2001-01-04) page 12, line 14 - page 13, line 29; claim 1 Formulations Q,R,S on page 35	1-3,5,6		
X	FR 2 791 886 A (CASTER) 13 October 2000 (2000-10-13) page 1, lines 1-4; examples 1,4-6 page 3, line 20 - page 4, line 18; claims 1-3 page 2, line 10 - line 21	1-7		
-/--				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.				
<input checked="" type="checkbox"/> Patent family members are listed in annex.				
° Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document 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 </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> *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 </td> </tr> </table>			*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document 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
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document 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			
6 October 2004	26/10/2004			
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Loloiu, C			

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/EP2004/006902

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 566 240 A (DOW CORNING) 20 October 1993 (1993-10-20) page 2, lines 1-4; claims; examples III,E,K page 2, line 48 - page 3, line 5 page 3, line 52 - page 5, line 4 -----	1-7
A	WO 99/06017 A (RHODIA CHIMIE) 11 February 1999 (1999-02-11) page 1, lines 10-37; claim 14; examples 3,4 page 6, line 34 - page 7, line 4 page 7, lines 9-27 -----	1-7
A	DE 43 41 652 A (KAO CORP GMBH) 30 June 1994 (1994-06-30) page 2, line 31 - line 62; claim 1; table I -----	1
A	EP 0 527 496 A (WERNER & MERTZ GMBH) 17 February 1993 (1993-02-17) page 2, line 56 - page 3, line 5; claims 1-3,12; examples 1,4 page 4, line 20 - page 5, line 3 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/006902

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0100141	A	04-01-2001	US 6685952 B1	03-02-2004
			AU 766608 B2	16-10-2003
			AU 5811000 A	31-01-2001
			BR 0011883 A	05-03-2002
			CA 2376864 A1	04-01-2001
			CN 1370062 T	18-09-2002
			WO 0100141 A1	04-01-2001
			EP 1198217 A1	24-04-2002
			JP 2003503327 T	28-01-2003
			PL 353167 A1	03-11-2003
			ZA 200110466 A	20-12-2002
FR 2791886	A	13-10-2000	FR 2791886 A1	13-10-2000
			EP 1043015 A2	11-10-2000
			US 6432912 B1	13-08-2002
EP 0566240	A	20-10-1993	US 5160494 A	03-11-1992
			CA 2091664 A1	15-10-1993
			DE 69302124 D1	15-05-1996
			DE 69302124 T2	24-10-1996
			EP 0566240 A1	20-10-1993
			JP 6009361 A	18-01-1994
WO 9906017	A	11-02-1999	FR 2766704 A1	05-02-1999
			FR 2777287 A1	15-10-1999
			AU 8985798 A	22-02-1999
			DE 69815352 D1	10-07-2003
			DE 69815352 T2	29-04-2004
			EP 1003472 A1	31-05-2000
			ES 2195377 T3	01-12-2003
			WO 9906017 A1	11-02-1999
			US 6395704 B1	28-05-2002
			AU 8985698 A	01-11-1999
			AU 8985898 A	22-02-1999
			DE 69813306 D1	15-05-2003
			DE 69813306 T2	12-02-2004
			EP 1068256 A1	17-01-2001
			EP 0988027 A1	29-03-2000
			WO 9952965 A1	21-10-1999
			WO 9906018 A1	11-02-1999
			JP 2001511437 T	14-08-2001
			JP 2002511510 T	16-04-2002
			US 6509023 B1	21-01-2003
US 6437163 B1	20-08-2002			
DE 4341652	A	30-06-1994	JP 6199640 A	19-07-1994
			DE 4341652 A1	30-06-1994
			DE 9318715 U1	28-04-1994
EP 0527496	A	17-02-1993	DE 4126975 A1	18-02-1993
			AT 153048 T	15-05-1997
			DE 59208477 D1	19-06-1997
			EP 0527496 A1	17-02-1993