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(54) Perfume compositions

(57) Perfume compositions, eg for use in particulate cleaning materials such as laundry powers, comprise silica particles having a mean particle size greater than 50 micron, bearing perfume at a loading of at least 30% by weight.

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Description

Field of Invention

This invention concerns perfume compositions and their use in particulate products, particularly, but not exclusively, particulate cleaning materials such as laundry powders.

Background to the Invention

It is common practice to incorporate perfumes into solid products, eg particulate products such as laundry powders. For this purpose, the perfume may be loaded onto a particulate carrier material.

For example, GB 1306924 discloses perfume concentrates in free-flowing powder form comprising perfume absorbed on particulate silica, particularly silica having an average particle size less than 10 micron.

EP 332259 and EP 332260 detail the use of silica perfume carriers in detergent powders and fabric softeners, respectively. The silicas span a wide range of types, with particle size of from 0.001 micron (fumed silica) through to 15 micron (silica gel), with a surface area of 100 - 800 m^2/g. For laundry detergent powders the preferred silica is a fumed type, with particle size in the range 0.007 micron to 0.025 micron, although silica gels may also be used, the preferred particle size being 1 to 8 micron. These silica carriers are optimised for application in detergent compositions providing perfume at a level of 0.01 to 0.5%, and where the perfume includes components which require protection from hostile bleaching agents present in the detergent composition. It is stated in EP 332259, on page 3 lines 6 to 8, that "the perfume oil adsorption is affected by particle size (microns) and surface area (m^2/g). In general, the amount of perfume that can be adsorbed per unit weight of silica is greater for small particle sizes".

EP 535942 discloses porous inorganic carrier particles, eg of silica, having at least a pore volume of 0. 1ml/g consisting of pores with a diameter of 7 to 50Å and having perfume absorbed into the particle. The particles may be used, for instance, in laundry detergent products. Be weight ratio of perfume to carrier is at most 3:1, ie 25% by weight pefume.

WO94/16046 discloses perfume-on-carrier systems for concentrated laundry detergent powders, comprising an inert carrier with a mean particle diameter in the range 5 to 50 micron. The carrier is typically amorphous silica, with specific examples of useful silicas used being the precipitated silicas Neosyl GP and HP39 (Neosyl GP and HP39 are Trade Marks) both from Crosfield and having respective weight mean particle sizes (determined using a Malvern Particlesizer - Particlesizer is a Trade Mark) of 18 and 11 micron.

Summary of the Invention

In one aspect the present invention provides a perfume composition comprising silica particles having a mean particle size (determined using a Malvern Mastersizer) greater than 50 micron, bearing perfume at a loading of at least 30% by weight.

The silica particles preferably have a mean particle size in the range 50 to 500 micron, more preferably 100 to 400 micron. Particularly good results have been obtained with silicas having mean particle sizes of about 100 and about 250, respectively.

The silica particles preferably have a perfume absorption of at least 30%, more preferably at least 50%, most preferably at least 60% as determined by the following perfume absorption test procedure. A precisely measured weight, for instance 1g, of silica is placed into a glass vial. Perfume is added dropwise, with stirring, until the silica is no longer a dry free flowing powder. The silica is reweighed and the weight of the added perfume calculated. The weight of perfume expressed as a precentage of the weight of silica is the perfume absorption value.

The actual perfume loading of the silica particles is preferably somewhat less than the maximum achievable, ie the pefume absorption as discussed above. Loading levels of about 80% of the perfume absorption values are suitable for manufacture. For example, for a silica with a perfume absorption of 60%, loading at 80% of this value gives an actual perfume loading of about 50% by weight.

In accordance with the invention, the actual perfume loading of the silica particles is at least 30% by weight, and is preferably at least 40%, more preferably at least 50%.

Suitable perfume loadings are conveniently achieved by use of silica particles having mean pore diameters greater than 50Å.

The silica particles conveniently have a surface area in the range 100 to 450 m^2/g, more conveniently in the range 100 to 350m^2/g, most conveniently in the range 100 to 300m^2/g.

The silica is suitably in the form of amorphous silica, including silica gels and precipitated silica.

The perfume generally comprises a substantially water-insoluble composition of matter consisting of one or more perfume components optionally mixed with a suitable solvent or diluent.

Perfume components are those constituents of a perfume which are added thereto only or primarily for their olfactive contribution or for their deodorant properties. Perfume components may be natural products such as extracts, essential oils, absolutes, resinoids, resins, concretes etc., but also synthetic materials such as hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals, nitriles, etc., including saturated and unsaturated compounds, aliphatic, carbocyclic and heterocyclic compounds. Such perfume components are mentioned, for example, 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, Ill. USA.

Examples of perfume components are: geraniol, geranyl acetate, linalol, linalyl acetate, tetrahydrolinalol, citronellol, citronellyl acetate, dihydromyrcenol, dihydromyrcenyl acetate, tetrahydromyrcenol, terpineol, terpinyl acetate, nopol, nopyl acetate, 2-phenylethanol, 2-phenyl-ethyl acetate, berzyl alcohol, benyl acetate, benzyl salicylate, styrallyl acetate, benzyl benzoate, amyl salicylate, dimethylberizyl carbinol, trichloromethylphenyl- carbinyl acetate, p-tert-butyl cyclohexyl acetate, isononyl acetate, vetiveryl acetate, vetiverol, α-hexylcinnam-aldehyde, 2-methyl-3-(p-tert-butylphenyl)propanal, 2-methyl-3-(p-isopropylphenyl)propanal, 3-(p-tert-butyl-phenyl)propanal, tricyclodecenyl acetate, tricyclodencenyl propionate, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-carbaldehyde, 4-(4-methyl-3-pentenyl)-3-cyclohexene-carbaldehyde, 4-acetoxy-3-pentyltetrahydropyran, 3-carboxymethyl-2-pentycyclopentane, 2-n-heptylcyclopentanone, 3-methyl-2-pentyl-2-cyclopentenone, n-decanal, n-dodecanal, 9-decenol-1, phenoxyethyl isobutyrate, phenyl-acetaldehyde dimethylacetal, phenylacetaldehyde diethyl-acetal, geranyl nitrile, citronellyl nitrile, cedryl acetate, 3-isocamphylcyclohexanol, cedryl methyl ether, isolongifolanone, aubepine nitrile, aubepine, heliotropin, coumarin, eugenol, vanillin, diphenyl oxide, hydroxy-citronellal, ionones, methylionones, isomethylionones, irones, cis-3-hexanol and esters thereof, indan musks, tetralin musks, isochroman musks, macrocyclic ketones, macrolactone musks, ethylene brassylate, aromatic nitromusks, etc.

Suitable solvents and diluents for perfumes as mentioned above are, for example, diethyl phthalate, triethyl citrate, ethanol, isopropanol, dipropylene glycol, etc.

The perfume composition is conveniently prepared by mixing the perfume with the silica particles. The mixing of the perfume and the silica may be carried out in a variety of ways known to the practitioner in the art, for example by spraying the perfume onto the particles contained in a rotary drum or positioned on a conveyor belt. A non-limiting example of a suitable procedure involves the use of a Tatham-Forberg mixer in a low speed, short duration operation. Be equipment comprises a twin-drum assembly with a rotary twin-shaft arrangement. Attached to each shaft is a set of carefully profiled paddles positioned at specific angles. The powder charge is fluidised by the paddle rotation and the perfume oil is sprayed on and mixing is continued until perfume take up is complete. The perfumed particle mass is then dropped through the bottom of the mixer into a suitable container.

Be perfume compositions of the invention find use in particulate products generally, particularly particulate, granular or powdered cleaning materials, such as laundry powders, particularly concentrated laundry detergent powders, dishwashing powders, scouring powders, carpet cleaners etc.

In a further aspect the present invention thus provides a particulate product comprising a perfume composition in accordance with the invention.

The perfume composition of the present invention may be incorporated into a particulate product using standard powder handling equipment known in the art, eg. by utilisation of weigh-belts.

In a preferred aspect the invention provides a laundry detergent powder comprising a perfume composition in accordance with the invention.

The laundry detergent powder can otherwise be generally of conventional composition.

Detergent powders for laundry use span a wide range of compositions. Traditional (or "regular") products are typified by a detergent surfactant level of between 8% and 20% by weight in total, more commonly 10% to 15%. Be surfactant may be anionic, non-ionic, cationic, zwitterionic or amphoteric in nature, and commercial products may contain all classes of surfactant, but the predominant form is generally anionic (ie. anionic surfactant typically account for 50% or more of the total surfactants). Typical detergent surfactants are described in detail in "Surfactant Surface Agents and Detergents", volume II by Schwartz, Perry and Birch, Interscience Publishers (1958). The remainder of a laundry detergent composition generally comprises builders, fillers, moisture, soil release and soil suspension and anti-redeposition agents, and other optional adjuncts such as processing aids, optical brighteners, dyes, foam control agents, anti-corrosion agents, perfumes, pH control agents, enzymes, stabilisers, bleaches and bleach activators. The level of solid components in regular laundry detergent compositions is high, usually above 75%, often above 85%. Perfume loadings for such compositions are generally within the range 0.05% to 0.4%, more commonly 0.1% to 0.3%, and the ratio of solid constituents to organic liquid constituents in a regular detergent composition is usually at least 30:1, and is likely in practice to be considerably higher, eg. at least 150:1 and up to 500:1.

Laundry detergent powder concentrates and hyperconcentrates (for the purposes of this specification further referred to as "concentrates") represent a relatively new product segment which is assuming increasing commercial importance world-wide. These concentrated products have a rather different composition to the described above.

The total level of detergent surfactant in concentrates generally lies within the range 15% to 60% by weight of the powder, more usually 20% to 40%. In addition to the difference in the level of surfactants another major point of difference concerns the level of low-functionality material such as fillers. In concentrates the level of sodium sulphate, for example, is rarely above 6% or even 2% by weight, whereas in regular powders levels of 20% to 30% are common. The composition of the actives may be similar to that in regular products, ie predominantly anionics, but not restricted to this and, for example, a high proportion of non-ionics may be used advantageously. The use of higher proportions of non-ionic surfactants is reported to be a significant trend in the detergent industry, at least for Europe, as reported by Smulders and Krings (Chemistry and Industry, March 1990, pages 160 to 163). Examples of detergent powder formulations with high non-ionics levels are disclosed in EP 228011, EP 168102, EP 425277, and EP 120492. Many non-ionic surfactant are liquid at ambient temperatures. Yet another difference between "regulars" and concentrates is that the percentage of perfume incorporated into concentrates tends to be higher than that for regular powder use, and lies generally above 0.1% by weight, normally within the range 0.2% to 2.5% by weight of the powder, more typically 0.4% to 1.5%.

The amount of perfume composition of the invention used in laundry detergent powders will typically be to produce perfume levels in the powder in the ranges given above, ie 0.05 to 2.5% by weight, with a typical perfume content being about 0.4% by weight.

For use in product formulations containing bleaching agents (which are particularly hostile to perfume components) the perfume is preferably one which is resistant to such attack and retains high performance even when stored in the presence of such hostile ingredients. Non-limiting examples of suitable perfumes are disclosed in EP 299561 and US 4663068.

It is found that certain handling advantages arise from use of larger than conventional silica particles bearing perfume.

1. Be particles have better flow properties, as indicated by higher angles of repose (cot ϕ), and so are easier to handle.

2. There is less risk of forming an undesirable dust cloud.

3. Be particles have a higher bulk density, which is closer to that of particulate products such as laundry powders, so the particles are less likely to settle out.

Comparative tests have shown that the performance of perfume compositions in accordance with the invention incorporated into laundry powders, in terms of perfume stability, perfume release and perfume delivery, is not significantly different from smaller, conventional silica particles bearing perfume.

The invention will be further described, by way of illustration, in the following Examples. The Examples refer to various precipated silicas, details of which are given in the following table.

Identification of silicas	Mean Particle size (μ)	Perfume absorption (w/w%)	Surface area (m^2/g)
Silica 1	100	65	ND
Silica 2	250	61	ND
Silica 3	80	61	ND
Silica 4	300	38	ND
Silica 5	18	65	200

Mean particle sizes were determined using a Malvern Mastersizer (Mastersizer is a Trade Mark).
Silica 5 is outside the scope of the invention, and is equivalent to Neosyl GP. ND = not determined.

Certain Examples also refer to a concentrated laundry powder, which has the following composition:

Concentrated Laundry Powder	%w/w
Zeolite 4A	29.8
Sodium perborate*	15.6
Sodium carbonate	9.7
TAED granules **	8.2
Dobanol 23 - 3	8.7
Dobanol 23 -6.5	7.3
Sodium LAS	5.1
Polyacrylate (mw 3000 - 4000)	3.1
Sodium sulphate	1.6
Perfume/silica particles	1.0
Sodium soap	1.5
Sodium silicate	1.5
Enzymes	0.8
Anti-redeposition agent	0.4
Sodium EDTA	0.3
Antifoam	0.3
Water, dye, minor components	5.1
	100

* monohydrate

** tetraacetylethylene diamine sodium salt

Example 1

Equal weights of silica particles and perfume were mixed together to produce perfume-loaded particles comprising 50% perfume. On a laboratory scale, this was carried out by adding equal weights of silica particles and perfume to a vial and stirring with a spatula until homogeneous. The particles/perfume were left overnight to equilibrate, were stirred again and then were ready for use. Three types of silica particles were treated in this way: Silica 1, Silica 2 and Silica 5 as identified in the Table above. Details of the resulting silica adsorbates are as follows:

	Silica 5	Silica 1	Silica 2
Angle of repose (cot ϕ)	0.93	2.44	1.60
Bulk density (kg/l)	0.29	0.57	0.57
Average particle size (microns)	18	250	100

The larger particle size reduces the possibility of dust cloud formation. The larger particle size also increases the bulk density, an advantage for concentrated laundry powders having a similar bulk density, and gives improved flow characteristics, as shown by the much higher angle of repose. The two silicas are otherwise generally similar in terms of perfume stability, perfume release and perfume delivery.

Example 2

A series of generally conventional concentrated laundry powders (with the composition given above) were made

up incorporating various different perfume-loaded silicas, prepared generally as described in Example 1. The silicas used included Silica 5 (for comparison) and Silicas 1 and 2 as in Example 1, and also 2 further large particle size silicas, Silica 3 and Silica 4. Perfume loading levels were approximately 80% of the perfume absorption levels, which are suitable levels for manufacture.

Various measurements were made on the laundry powders, including the following:

1. % of fines, ie the amount of material passing through a 180 micron sieve. Laundry powders including silicas of the invention produced lower levels of fines than those including the smaller Silica 5.

2. Deposition on black cloth: This is a test to determine if the silicas deposit onto cloth and are visible to the naked eye, which is a possible problem if the particles are too big. Pieces of black cotton cloth were put through the normal wash cycle in a tergotometer (laboratory scale washing machine) five times using concentrated laundry powder dosed with the appropriate perfume/silica. The cloths were dried and then inspected visually for silica particles. Only the largest particle size silica (Silica 4) produced a visible deposit (more than the control), and this was very slight. (A C = as control, VSl = very slight.

3. Deposition of perfume: Cloths (terry towelling) were washed in a conventional automatic machine using concentrated laundry powder dosed with the appropriate perfume/silica. The cloths were evaluated by experienced personnel for the odour strength of the perfume, using a scale 0 to 5, where 0 is odourless. The cloths were evaluated damp and after drying, either tumble dried or line dried. There were no large differences in odour strength between the neat essence and any of the silica systems. Silica 1 produced a slightly greater odour intensity on line dried cloth.

4. Stability: Perfume/silica were mixed as described in Example 1 and stored in a glass jar for one week at 50°C. At the end of this period the perfume was extracted from the silica with solvent (ethyl acetate) and the perfume content determined using a standard gas chromatographic technique. Perfume has 90% or greater stability in all the silicas.

Detailed results are given in the following Table.

Sample	Perfume Loading (%)	Particle Size (um)	Fines in Laundry Powder (%)	Deposition on Black Cloth		Deposition of perfume			Stability (%)
				Tergo	Machine	Line Dried	Tumble dried	Damp	
Neat	100	N/A	14.9	Control	Control	1.0	1.0	4.2	
Silica 5	50	18	18.4	-	-	0.8	0.5	4.0	98
Silica 1	50	150	16.6	AC	AC	2.0	1.0	4.0	97
Silica 2	50	100	16.4	AC	AC	0.6	1.0	4.2	94
Silica 3	50	80	16.1	AC	AC				90
Silica 4	30	200-425	16.4	V Sl	V Sl	0.5	1.5	3.5	100

Of the silicas tested, Silica 1 may provide slightly enhanced perfume deposition and this was most favoured, with Silica 2 being the second favoured.

Example 3

Wash trials and stability testing was perfomed on the concentrated laundry powder described above, with and without perfume-loaded Silica 1 and Silica 2, prepared as described in Example 1, ie equal weights of silica and perfume. Where present, the perfume constituted 0.5% by weight of the laundry powder.

Initial wash trials showed comparable performance in laundry powders with and without perfume-loaded silica.

For stability testing, the samples were stored in glass jars at 37°C for 12 weeks and then the perfume content determined by extraction and gas chromatography by the following technique.

4.0g of laundry powder and 0.02g of C_{13} standard were accurately weighed out into a suitable large glass vial.

10mls of high purity ethyl acetate was added. After securely capping the vial the whole was shaken vigorously for 15 minutes followed by centrifugation to settle the solids.

The results were expressed as a percentage of the perfume concentration of similarly treated concentrated laundry powder containing pefume doesed as neat essence. After storage the perfume content of the samples in silica was within 5% of the similar samples containing neat essence. Results were as follows:

Storage Period	Silica 1 Total Perfume Content (% theory)	Silica 2 Total Perfume Content (% theory)
12 weeks	105	97

Claims

1. A perfume composition comprising silica particles having a mean particle size (determined using a Malvern Mastersizer) greater than 50 micron, bearing perfume at a loading of at least 30% by weight.

2. A perfume composition according to claim 1, wherein the silica particles have a mean particle size in the range of 50 to 500 micron, preferably 100 to 400 micron.

3. A perfume composition according to claim 1 or 2, wherein the silica particles have a perfume absportion of a least 30%, preferably at least 50%, most preferably at least 60%.

4. A perfume composition according to claim 1, 2 or 3, wherein the silica particles have mean pore diameters greater than 50Å.

5. A perfume composition according to any one of the preceding claims, wherein the silica particles have a surface area in the range 100 to 450 m^2/g, more preferably 100 to 350 m^2/g, most preferably 100 to 300 m^2/g.

6. A perfume composition according to any one of the preceding claims, wherein the silica comprises amorphous silica.

7. A perfume composition according to claim 6, wherein the silica comprises precipitated silica or silica gel.

8. A perfume composition according to any one of the preceeding claims, comprising at least 40% w/w of perfume, preferably at least 50%.

9. A particulate product comprising a perfume composition in accordance with any one of the preceeding claims.

10. A laundry detergent powder comprising a perfume composition in accordance with any one of claims 1 to 8.

11. A laundry detergent powder according to claim 10, wherein the amount of perfume is in the range 0.05 to 2.5% by weight.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 5173

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	GB-A-2 024 014 (P.GUALANDI) * page 2, line 9-14; claims 1,4,6,10 *	1,2,6-9	A61K7/46 C11D3/50
Y	* page 1, line 55-60 *	4,5	
Y	EP-A-0 535 942 (UNILEVER) * claims *	4,5	
X	EP-A-0 294 206 (UNILEVER) * claims 1-6 *	1-11	
D,A	EP-A-0 332 259 (PROCTER & GAMBLE) * claims *	1-11	
D,A	EP-A-0 332 260 (PROCTER & GAMBLE) * claims *	1-11	
D,A	GB-A-1 306 924 (ZIMMERMANN) * the whole document *	1-11	
A	DATABASE WPI Section Ch, Week 8634 Derwent Publications Ltd., London, GB; Class A97, AN 86-223138 XP002021563 & JP-A-61 155 307 (LION CORP) , 15 July 1986 * abstract *	1-11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) A61K A23L C11D
A	DATABASE WPI Section Ch, Week 9238 Derwent Publications Ltd., London, GB; Class A97, AN 92-312565 XP002021564 & JP-A-04 218 583 (SHOHKOH KAGAKU KENKYUUSHO KK) , 10 August 1992 * abstract *	1-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 December 1996	Van Moer, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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