

A METHOD OF COUNTERING MALODOUR IN A WASHING MACHINE COMPRISING THE ADDITION OF A FRAGRANCE PRECURSOR

This disclosure relates to fragrance compositions, and more particularly to fragrance compositions for use in washing machines, both for fabrics and dishes/cutlery.

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It is a well-known phenomenon that, when a washing machine has finished a wash cycle and has been emptied and left open for a prolonged period, an undesirable odour may emanate from the machine, this resulting from a combination of residual water in the machine and bacteria that have not been killed during the wash cycle. One possibility is to run the machine with a bactericidal preparation, and some washing machine manufacturers have made available such a product. Another possibility is to run a washing cycle at elevated temperature to destroy the bacteria, but this is wasteful of energy. A further possibility has been the addition of fragrance to mask this odour.

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15 It has now been found that there is a particularly effective counter to this malodour problem without the need for the purchase of special cleaning preparations or additional hot water washes. There is therefore provided a method of countering malodour in a washing machine at the end of a wash cycle, comprising the addition thereto of a fragrance precursor.

20 By "fragrance precursor" is meant a compound that, under particular circumstances, will break down to provide a fragrant material. The circumstances will depend on the nature of the compound – for example, some precursors will break down in the presence of humidity, others in the presence of oxygen. However, the common factor is that, on breakdown, they produce a fragrant material.

25 By "at the end of a wash cycle" is meant that part of the wash cycle after the actual detergent wash is completed. This typically includes at least one rinse step, during which step a fabric softener may be introduced. The fragrance precursor may be included with the fabric softener, either as part of a fragrance formulation included in the fabric softener, or it may be added independently to a fabric softener as a solution in a suitable solvent, or as part of a fragrance.

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Fragrance precursors are well known in the art, and any suitable fragrance precursor may be used. In a particular embodiment, the fragrance precursor is selected from the class of fragrance precursors that break down under the influence of humidity or in the presence of oxygen. Typical examples of such fragrance precursors may be found in, for example, International Publications
35 WO 2007/143873 and WO 2018/096176 (humidity cleavage), and WO 2012/085287 (oxygen cleavage).

In a particular embodiment the precursor is selected from the group consisting of
ethyl (Z)-2-acetyl-4-methyltridec-2-enoate;

40 ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate;

4-(dodecylthio)-4-methylpentan-2-one;
 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene;
 2-ethoxy-4-((1E,4Z)-hepta-1,4-dien-1-yl)phenol;
 and mixtures thereof.

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More than one such precursor may be used, and the use of the singular in the following description also includes the plural. The number and nature of precursors will depend entirely on the extent of the odour counteraction and/or hedonic effect desired.

- 10 Certain fragrance precursors provide a surprisingly long-lasting fragrance in the circumstances hereinabove described, such that a washing machine thus treated will remain free of undesirable odour for a prolonged period, six days or more.

The precursor may be used alone, or it may be combined with other common fragrance ingredients to provide a complete fragrance formulation. As the precursors hereinabove defined release aldehydes and/or ketones, highly volatile materials that are what the fragrance industry knows as "top notes", their presence in a perfume formulation must be compensated by an increase in the proportions of "middle notes" and "bass notes", fragrance materials that evaporate more slowly, but whose presence is essential to an overall hedonic effect.

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Typical, non-limiting examples of "top note" fragrance materials useful in the compositions of this disclosure include:

- ethyl isobutyrate butyl acetate, (+)-ethyl 2-methylbutanoate, (+)-isopropyl methylbutanoate, (+)-ethyl 2-methylpentanoate, (2E)-2hexenal 3-methyl-2-buten-1-yl acetate, 2-heptanone methyl hexanoate, 7-methyl-3-methylene-1,6-octadiene, 5-methyl-3-heptanone, (+)-limonene, (+)-4-methyl-4-penten-2-yl 2-methylpropanoate, (Z)-3-hexenyl formate, 1-methoxy-4-propylbenzene, (+)-3-methoxy-2-methylpropylbenzene, 2-phenylethyl formate, (+)-2-pentylcyclopentanone, methyl phenylacetate, (+)-(1R)-1,7,7-trimethyl-bicyclo[2.2.1] heptan-2-one, 3-(2,2-dimethylpropyl)pyridine benzyl acetate, cyclohexyl ethyl acetate, ethyl 2-methyl-1,3-dioxolane-2-yl-phenyl-1-ethanol, 2-methylpentyl-2-methylpentanoate, (+)-2-propylheptanenitrile, (+)-3-mercaptohexyl acetate, (+)-1,5-dimethyl-1-vinyl-4-hexenyl acetate, (1R,2R)-2-(2-methyl-2-propanyl)cyclohexyl acetate, (+)-1-phenylethyl acetate, ethyl 2,6,6-trimethyl-1,3-cyclohexadiene-1-carboxylate, (+)-1,5-dimethyl-1-vinyl-4-hexenyl acetate, (+)-3,7 dimethyl-6-octen-1-yl formate, (+)-ethyl 2-acetyl-4-methyl-4-pentenoate, *cis*-4-(2-methyl-2-propanyl)cyclohexyl acetate, *trans*-4-(2-methyl-2-propanyl)cyclohexyl acetate, ethyl phenylacetate, (+)-2,2,5-trimethyl-5-pentylcyclopentanone, methyl (2E)-2-nonenoate, (+)-2,4-dimethyl-4-phenyltetrahydrofuran, (+)-3,7-dimethyl-6-octenyl formate, allyl (3-methylbutoxy)acetate, (+)-allyl (2-methylbutoxy)acetate, hexyl (2E)-2-methyl-2-butenolate, (2R,5S)-6-ethyl-2,10,10-trimethyl-1-oxaspiro [4.5] deca-3,6-diene, ((2R,5S)-6-ethyl-2,10,10-trimethyl-1-oxaspiro [4.5] deca-3,6-diene, *cis*-4-(2-methyl-2-propanyl)cyclohexyl acetate, *trans*-4-(2-methyl-2-propanyl)cyclohexyl acetate, ((3Z)-3-hexen-1-yl

- (3Z)-3-hexenoate, (z)-3,7-dimethyl-2,6-octadienal, (e)-3,7-dimethyl-2,6-octadienal, 2-phenylethyl acetate, 1,1-dimethyl-2-phenylethyl acetate, 1-methoxy-4-[(1e)-1-propen-1-yl] benzene, 4-phenyl-2-butanone, 4-methylphenyl isobutyrate, 2-phenylethanol, (1R,4R)-8-mercapto-3-p-menthanone, (+)-(e)-1-(2,2-dimethyl-6-methylene-1-cyclohexyl)-2-buten-1-one, (2E)-1-[(1R,2SR)-2,6,6-trimethyl-3-cyclohexen-1-yl]-2-buten-1-one, [2-(1-ethoxyethoxy)ethyl]benzene, 1,1-bis(2-phenylethoxy)-ethane, 3,7-dimethyl-6-octenyl acetate, 5-methyl-3-heptanone, (2Z)-3,7-dimethyl-2,6-octadien-1-yl acetate, (2E)-1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one, 2,4,6-trimethyl-4-phenyl-1,3-dioxane, benzyl propanoate, (+)-(2e)-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one, ethyl tricyclo[5.2.1.0.(2,6)]decane carboxylate, (+)-(2e)-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one, 3-methylbutyl-2-phenylethyl ether, (+)-4-octanolide hexyl hexanoate, (+)-3,7-dimethyl-1,6-octadien-3-ol, (+)-3,7-dimethyl-1,6-octadien-3-ol, (e)-4-decenal octyl acetate, (+)-3,5,6,6-tetramethyl-4-methylidene-2-heptanone, (+)-(4e)-3,4,5,6,6-pentamethyl-4-hepten-2-one, (+)-(M3Z)-3,4,5,6,6-pentamethyl-3-hepten-2-one, (+-M3E)-3,4,5,6,6-pentamethyl-3-hepten-2-one, (+)-(3-methoxy-2-methylpropyl)benzene, 2-phenylethyl formate,
- 15 (+)-2-propylheptanenitrile, (+)-1,5-dimethyl-1-vinyl-4-hexenyl acetate, (+)-1-phenylethyl-1,5-dimethyl-1-vinyl-4-hexenylacetate, *cis*-4-(2-methyl-2-propanyl)cyclohexyl acetate, *trans*-4-(2-methyl-2-propanyl)cyclohexyl acetate, (Z)-3,7-dimethyl-2,6-octadienal, (E)-3,7-dimethyl-2,6-octadienal, (+)-2,6-dimethyl-5-heptenal, (2E,6Z)-2,6-nonadienal, methyl 2-octynoate, decanal, (+)-2-methyldecanal, undecanal, dodecanal, 10-undecenal, (9E)-9-undecenal, (9Z)-9-undecenal, 8-
- 20 isopropyl-6-methyl-bicyclo[2.2.2] oct-5-ene-2-carbaldehyde, (2Z)-3,7-dimethyl-2,6-octadien-1-yl acetate, ethyl isobutyrate, butyl acetate, (+)-ethyl 2-methylbutanoate, (+)-isopropyl 2-methylbutanoate, (+)-ethyl 2-methylpentanoate, (2E)-2-hexenal 3-methyl-2-buten-1-yl acetate, 2-heptanone, methyl hexanoate, 7-methyl-3-methylene-1,6-octadiene, 5-methyl-3-heptanone, (+)-limonene, (+)-4-methyl-4-penten-2-yl-2-(Z)-3-hexenyl formate, ethyl hexanoate, 3-octanone, (+)-methyl 2-ethylhexanoate, 2-octanone, (1R,5R)-4,7,7-trimethyl-6-thiabicyclooct-3-ene-(1R,4R,5R)-4,7,7-trimethyl-6-thiabicyclo[3.2.1] octane, (E)-2-hexenyl acetate, 6-methyl-5-hepten-2-one, 1-isobutyl-3-methylbutyl acetate, (+)-2,6-dimethyl-7-octen-4-one, (2Z)-3-methyl-2-hexen-1-yl acetate, ((2E)-3-methyl-2-hexen-1-yl acetate, 3,7-dimethyl-1,3,6-octatriene, ethyl heptanoate, ethyl 3-oxobutanoate, (2Z)-ethyl 3-hydroxy-2-butenate, heptyl acetate, 3-methylbutyl
- 25 butanoate, methylbutyl butanoate, (+)-4-pentanolide, hexyl acetate, (+)-2,6-dimethyl-5-heptenal, (3Z)-3-hexen-1-yl butyrate, hexyl 2-methylpropanoate, ethyl (2E)-2,4-dimethyl-2-pentenoate, 3-methylbutanoic acid, (+-H)-pentyl-2-propenyl acetate, (3Z)-hex-3-en-1-yl methyl carbonate, 3,5,5-trimethylhexyl acetate, ethyl benzoate, allyl heptanoate, 1-(3,3-dimethyl-1-cyclohexyl)ethyl formate, (+)-methyl 2,2-dimethyl-6-methylidenecyclohexanecarboxylate, (Z)-3-hexenyl
- 35 isobutyrate, (-)-propyl (S)-2-dimethylpropoxy allyl hexanoate, (+)-3,7-dimethyl-1,6-octadien-3-ol, (+)-(Z)-3-hexenyl 2-methylbutanoate, octyl acetate, (+)-1S,2,3,5,6,6-tetramethyl-4-methylidene-2-heptanone, (+)-(4e)-3,4,5,6,6-pentamethyl-4-hepten-2-one, 1-methoxy-4-propylbenzene, (+)-(3-methoxy-2-methylpropyl)benzene, 2-phenylethyl formate, (+)-2-pentylcyclopentanone, methyl phenylacetate, (+)-(1R)-1,7,7-trimethyl-bicyclo[2.2.1] heptan-2-one, 3-(2,2-dimethyl-
- 40 propyl)pyridine, benzyl acetate, hexanolide, (+)-2-pentylcyclopentanone, methyl

- phenylacetate, 2-cyclohexyl ethyl acetate, ethyl-2-methyl-1,3-dioxolane-2-acetate, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 2-methoxy-4-methylphenol heptanolide, (3Z)-3-hexen-1-yl (2E)-2-methyl-2-butenolate, (3Z)-3-hexen-1-yl (3Z)-3-hexenoate, 2-phenylethyl acetate, hexanoic acid, 1-methoxy-4-[1E]-1-propen-1-yl] benzene phenylethanol, (+)-(e)-1-(2,2-dimethyl-6-methylene-1-
- 5 cyclohexyl)-2-buten-1-one, (2E)-1-[(1RS,2SR)-2,6,6-trimethyl-3-cyclohexen-1-yl]-2-buten-1-one, [2-(1-ethoxyethoxy)ethyl]benzene, (1,1-bis(2-phenylethoxy)ethane 5-methyl-3-heptanone oxime, (+)-(2E)-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one, 3-methylbutyl-2-phenylethyl ether butyl acetate, (+)-3-hydroxy-2-butanone, 1-butanol, (+)-4-methyl-4-penten-2-yl 2-methyl-
- 10 propanoate, ethyl hexanoate, diallyl disulfide, allyl heptanoate, (+)-2-pentylcyclopentanone, methyl phenylacetate, 2-cyclohexyl ethyl acetate, ethyl 2-methyl-1,3-dioxolane-2-acetate, (3Z)-3-hexen-1-yl (3Z)-3-hexenoate, 2-phenylethyl acetate, hexanoic acid, 1-methoxy-4-[1E]-1-propen-1-yl] benzene, 2-phenylethanol, (+)-(E)-1-(2,2-dimethyl-6-methylene-1-
- 15 cyclohexyl)-2-buten-1-one, (2E)-1-[(1RS,2SR)-2,6,6-trimethyl-3-cyclohexen-1-yl]-2-buten-1-one, 1,1-bis(2-phenylethoxy)ethane, 5-methyl-3-heptanone oxime, 3-methylbutyl-2-phenylethyl ether, (+)-4-octanolide, 1-butanol, (+)-methyl 2-ethylhexanoate, 3-methylbutanoic acid, 6,6-dimethoxy-2,5,5-trimethyl-2-hexene, 4-(2-methyl-2-propenyl)cyclohexanone, (+)-(3Z)-3,4,5,6,6-
- 20 pentamethyl-3-hepten-2-one, (1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylpropanoate, (+)-(2-tert-butyl-1-cyclohexyloxy)-2-butanol, (+)-alpha-terpineol, (+)-2-ethoxy-2,6,6-trimethyl-9-methylene-bicyclo[3.3.1] nonane, (+)-(2E)-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one,
- 25 (+)-(E)-3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one, 3-octanone, (+)-methyl 2-ethylhexanoate, ethyl acetate, ethyl butanoate, 2-octanone, (E)-2-hexenyl acetate, 6-methyl-5-hepten-2-one, 1-isobutyl-3-methylbutyl acetate, (+)-2,6-dimethyl-7-octen-4-one, (+)-3,7-dimethyl-1,6-octadien-3-ol, (+)-3,7-dimethyl-1,6-octadien-3-ol, 2-phenylethyl formate, (+)-2-propylheptanenitrile, (+)-1,5-dimethyl-1-vinyl-4-hexenyl acetate, (+)-1-phenylethyl acetate, (+)-1,5-
- 30 dimethyl-1-vinyl-4-hexenyl acetate, *cis*-4-(2-methyl-2-(Z)-3,7-dimethyl-2,6-octadienal, (E)-3,7-dimethyl-2,6-octadienal, ethyl butanoate, (+)-ethyl 2-methylbutanoate, hexanal, (1)-ethyl-2-methylpentanoate, (-)-(1S,9-2,6,6-trimethyl-bicyclo[3,1,1] hept-2-ene, alpha-pinene, beta-pinene, (2E)-2-hexenal, (+)-3-hydroxy-2-butanone, 3-methyl-2-buten-1-yl acetate, methyl hexanoate, (+)-2-ethenyl-2,6,6-trimethyl tetrahydro-2H-furan, heptanal, 1-butanol, ethyl hexanoate, benzaldehyde,
- 35 (E)-2-hexenyl acetate, (Z)-3-hexenol, 3,7-dimethyl-1,3,6-octatriene, (Z)-3-hexenyl acetate, (+)-1-octen-3-ol, ethyl 3-oxobutanoate, ethyl 3-hydroxy-2-butenolate, nonanal, dibutyl sulfide, (+)-1-methoxy-3-hexanethiol, tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-2H-pyran, (Z)-6-nonenal, (+)-ethyl 3-methyl-2-oxopentanoate, 1-hexanol, (+)-methyl trimethyl-2-cyclohexene-1-carboxylate, (3Z)-hex-3-en-1-yl methyl carbonate, benzyl formate, (3E,5Z)-1,3,5-undecatriene, (2-methoxy-
- 40 ethyl)benzene, allyl heptanoate, (Z)-3-hexenyl formate, (+)-(Z)-3-hexenyl 2-ethyl octanoate, 2-methyl-3-hexanone oxime, (2E,6Z)-2,6-nonadienal, (Z)-4-decenal, (+)-(3-methoxy-2-methylpropyl)benzene, 2-phenylethyl formate, ethyl 2-ethyl-1,3-dioxolane-2-acetate, methyl 2-octynoate, (2,2-dimethoxyethyl)benzene, 2-methylpentyl 2-methylpentanoate, (+)-3,7-dimethyl-3-octanol, (+)-3-mercaptohexyl acetate, 3-(4,4-dimethyl-1-cyclohexen-1-yl)propanal, 1,1-dimethoxy-

- pentenoate, (+-)-(4Z)-4-cycloocten-1-yl, methyl carbonate, methyl (2E)-2-nonenoate, (+-)-2,4-dimethyl-4-phenyltetrahydrofuran, (+-)-3-phenylbutanal, (3Z)-3-hexen-1-yl (3Z)-3-hexenoate, hexanoic acid, 2-methoxy-3-(4-methylpentyl)pyrazine, 2-methoxy-4-propyl-1-cyclohexanol, 4-phenyl-2-butanone, (3Z)-3-hexen-1-yl (2E)-2-methyl-2-buten-1-ol, 8-isopropyl-6-ethyl-
- 5 bicyclo[2.2.2]oct-5-ene-2-carbaldehyde, 5-methyl-3-heptanone oxime, benzyl propanoate, ethyl tricyclo[5.2.1.0.(2,6)]decane-2-carboxylate, (+-)-(2E)-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one, (±)-isopropyl-2-methylbutanoate, (+)-limonene, 1-methyl-4-(2-propanyl)-1,4-cyclohexadiene, (±)-2,6-dimethyl-7-octen-4-one, heptyl acetate, nonanal, (±)-4-pentanolide, 1-(3,3-dimethyl-1-cyclohexyl) ethyl formate, ethyl acetate, butyl acetate, (±)-3-hydroxy-2-butanone, 2-
- 10 furanmethanethiol, 1-butanol, diallyl disulphide, 1-phenylethanone, allyl heptanoate, ethyl hexanoate and benzaldehyde,

Typical, non-limiting examples of "middle note" fragrance materials useful in the compositions of this disclosure include:

- 15 methyl 2-nonynoate, 7-methyl-2H-1,5-benzodioxepin-3(4H)-one, (+-)-tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol, (+-)-2-methylundecanal, 7-methyl-2H-1,5-benzodioxepin-3(4H)-one, 7-isopropyl-2H,4H-1,5-benzodioxepin-3-one, dodecanenitrile, (2E,6Z)-2,6-nonadien-1-ol, 4-methoxybenzaldehyde, 4-methyl 2-nonynoate, (4-methylphenoxy) acetaldehyde, 7-methyl-2H-1,5-benzodioxepin-3(4H)-one, (E)-3,7-dimethyl-2,6-octadienyl acetate
- 20 (+-)-(3E)-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one, (+-)-(E)-4-methyl-3-decen-5-ol, 6(8)-isopropylquinoline, 1-phenyl-2-(1-propoxyethoxy)ethane, (+-)-1,3-dimethyl-3-phenylbutyl acetate, 1-(4-methoxyphenyl)-1-ethanone, 3-hydroxy-2-methyl-4(4H)-pyranone, (2E)-1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one, (E)-3,7-dimethyl-2,6-octadienyl acetate, (2E)-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-buten-1-one, 4-cyclohexyl-2-
- 25 methyl-2-butanol, (E)-3,7-dimethyl-2,6-octadienyl acetate, allyl 3-cyclohexylpropanoate, 2-phenylethyl pivalate, 2-phenylethyl isobutyrate, (+-)-(E)-4-methyl-3-decen-5-ol, benzyl 3-methylbutanoate, ethyl (E)-3-phenyl-2-propenoate, (+-)-6-propyltetrahydro-2H-pyran-2-one, (+-)-1,3-dimethyl-3-phenylbutyl acetate, 3,7-dimethyl-2,6-octadien-1-ol, (E)-3,7-dimethyl-2,6-octadien-1-ol, (E)-3,7-dimethyl-2,6-octadien-1-ol, (Z)-3,7-dimethyl-2,6-octadien-1-ol, 4-cyclohexyl-2-methyl-
- 30 2-butanol, (+-)-3,7-dimethyl-1-octanol, 3,7-dimethyl-2,6-octadien-1-ol, (+-)-6-propyltetrahydro-2H-pyran-2-one, allyl 3-cyclohexylpropanoate, (3S,3aS,6R,7aR)-3,6-dimethyl-hexahydro-1-benzofuran-2(3H)-one, 2-phenylethyl 2-phenylethyl isobutyrate, 1-oxaspiro[4.5] decan-2-one, benzo[d][1,3]dioxole-5-carbaldehyde, 3-methyl-2-[(2Z)-2-penten-1-yl]-2-cyclopenten-1-one, 2-methoxynaphthalene, (2E)-1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-
- 35 one, (5R,6R)-2,6,10,10-tetramethyl-1-oxaspiro[4.5]decan-6-ol, 2-tert-butyl-dimethoxy-benzene (2E)-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-buten-1-one, (E)-3-phenyl-2-propenal, (E)-3-phenylpropenenitrile, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone, and 2-(6,6-dimethyl-bicyclo[3.1.1] hept-2-en-2-yl)ethyl acetate.

Typical, non-limiting examples of "bass note" fragrance materials useful in the compositions of this disclosure include:

- 7-methyl-2H-1,5-benzodioxepin-3(4H)-one, (+-)-1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carbaldehyde, (+-)-3-(4-isopropylphenyl)-2-methylpropanal,
- 5 (+-)-3-(4-methoxyphenyl)-2-methylpropanal, (+-)-2,6,10-trimethyl-9-undecenal, 1,5,9-trimethyl-4,8-decadienyl acetate, (+-)-3-(3-isopropyl-1-phenyl)butanal, (+-)-2-methyl-3-[4-(2-methyl-2-propenyl)phenyl]propanal, (+-)-7-hydroxy-3,7-dimethyloctanal, (z)-6-nonen-1-ol, 8(9)-methoxy-tricyclo[5.2.1.0(2,6)]decane-3(4)-carbaldehyde, (+-)-2,5-dimethyl-2-indanmethanol, 7-propyl-2H,4H-1,5-benzodioxepin-3-one, 7-(2-methyl-2-propenyl)-2H-1,5-benzodioxepin-3(4H)-one,
- 10 (+-)-3-(1,3-benzodioxol-5-yl)-2-methylpropanal, methyl 2,4-dihydroxy-3,6-dimethylbenzoate, 2-ethyl-3-hydroxy-4(4H)-pyranone, allyl (cyclohexyl oxy)acetate, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one, (+-)-2-phenylethyl-2-methylbutanoate, ethyl (2e,4z)-2,4-decadienoate, (+-)-3,4'-dimethylspiro [oxirane-2,9'-tricyclo[6.2.1.0-2,7~]undec[4]ene,(+)-(e)-3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one,1,1-dimethyl-2-phenylethyl butanoate, benzyl (e)-2-methyl-2-
- 15 butenoate, (+-)-4-nonanolide, 9-decen-1-ol, ethyl (2e)-2,4,7-decatrienoate, 5-nonanolide, ethyl (e)-3-phenyl-2-propenoate, (e)-3-phenyl-2-propenyl acetate, 4-methoxybenzyl acetate, 1,5,9-trimethyl-4,8-decadienyl acetate, ethyl 2,3-epoxy-3-phenylbutanoate, (+-)-2,2,2-trichloro-1-phenylethyl acetate, (3z)-3-hexen-1-yl benzoate, (+-)-4-decanolide, 2-phenoxyethyl 2-methylpropanoate, allyl phenoxyacetate, (+-)-6-pentyltetrahydro-2H-pyran-2-one, (e)-3-phenyl-2-propenyl
- 20 propanoate, 8(9)-methoxy-tricyclo[5.2.1.0(2,6)]decane-3(4)-carbaldehyde, 4-(4-methoxyphenyl)-2-butanone, 6-hexyltetrahydro-2H-pyran-2-one, (+)-(1S,1'R)-2-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxy]-2-methylpropyl propanoate, (+)-(1S,2S,3S,5R)-2,6,6-trimethylspiro [bicyclo[3.1.1]heptane-3,1'-cyclohexane]-2'-en-4'-one, hexyl 2-hydroxybenzoate, (+-)-5-heptyldihydro-2(3H)-furanone, (1'R)-2-[2-(4'-methyl-3'-cyclohexen-1'-yl)propyl]-
- 25 cyclopentanone, (e)-2-methoxy-4-(1-propenyl)phenyl acetate, (+)-4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene, methyl { (1RS,2RS)-3-oxo-2-[(2Z)-2-penten-1-yl]cyclopentyl } acetate, (+-)-5-octyldihydro-2(3H)-furanone, (2e)-2-benzylideneoctanal, 4-formyl-2-methoxyphenyl 2-methylpropanoate, (+-)-6-heptyltetrahydro-2H-pyran-2-one, benzyl benzoate(10e)-oxacycloheptadec-10-en-2-one, (e)-2-pentyl-3-phenyl-2-propenal, 4-(4-hydroxy-1-
- 30 phenyl)-2-butanone, 2-phenylethyl phenylacetate, 9-decen-1-ol, 2-ethoxynaphthalene, (+-)-2,2,2-trichloro-1-phenylethyl acetate, (3z)-3-hexen-1-yl benzoate, 8(9)-methoxy-tricyclo[5.2.1.0(2,6)]decane-3(4)-carbaldehyde, (+-)-(3,7-dimethyl-6-octenyloxy)acetaldehyde, (+-)-(3,7-dimethyl-6-octenyloxy)acetaldehyde, hexyl 2-hydroxybenzoate, methyl 2-((1RS,2RS)-3-oxo-2-pentylcyclopentyl) acetate, (e)-2-methoxy-4-(1-propenyl)phenyl acetate, benzyl benzoate, (10e)-
- 35 oxacycloheptadec-10-en-2-one, (e)-2-pentyl-3-phenyl-2-propenal, 2-phenylethyl phenylacetate, (+-)-7-methoxy-3,7-dimethyl-2-octanol, (3e)-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one, benzyl (e)-2-methyl-2-butenate, 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4-indenone, (e)-3-methyl-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol,5,5,8a-trimethyldecahydro-2-naphthalenyl acetate, (2RS,4aRS,8aRS)-5,5,8a-trimethyldecahydro-2-naphthalenyl acetate, (+-)-
- 40 3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-ol, 3aRS,5aSR,9aSR, 9bSR)-3a,6,6,9a-

- tetramethyldodecahydronaphtho [2, 1-b]furan, 1RS,6RS, 11RS)-2,2,9,11- tetramethylspiro [5.5]undec-8-en-1-yl acetate, (-)- (3aR,5aS,9aS,9bR)-3a,6,6,9a- tetramethyldodecahydronaphtho [2,1-b]furan, (ethoxymethoxy)cyclododecane, (+)-3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-pentanol, (+)--(1-ethoxyethoxy)cyclododecane, (+)-(1R,7R)-10,10-dimethyl-
- 5 tricyclo[7.1.1 .0(2,7)]undec-2-en-4-one, (+)-(1S,2S,3S,5R)-2,6,6-trimethylspiro bicyclo-[3.1.1]heptane-3,1'-cyclohexane]-2'- en-4'-one, 2-(2,4-dimethyl-3-cyclohexen-1-yl)-5-methyl-5-(1-methylpropyl)-1,3-dioxane, (+)-2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, (+)-11(2,2,3,6-tetramethyl- cyclohexyl)-3-hexanol, (-)-(2e)-2-ethyl-4-[(1R)-2,2,3-trimethyl-3-cyclopenten-1-yl]-2-buten-1-ol, 1-[(1RS,6SR)-2,2,6-trimethylcyclohexyl]-3-hexanol, (-)- (3aR,5aS,9aS,9b,R)-
- 10 3a,6,6,9a-tetramethyldodecahydronaphtho [2,1-b]furan, (-)- (3aR,5aS,9aS,9b,R)-3a,6,6,9a-tetramethyldodecahydronaphtho [2,1-b]furan, (1'S,3'R)-{1-methyl-2- [(1',2',2'-trimethyl-bicyclo[3.1.0]hex-3-yl)methyl]cyclopropyl} methanol, and (+)-methyl (1R)-cis-3-oxo-2-pentyl-1-cyclopentane acetate

- In a particular embodiment, when used as part of a fragrance formulation, the fragrance precursor
- 15 is present at a proportion of from 0.1% to 30 % by weight of the formulation. In a particular embodiment, it is present in the proportion of from 0.5 -20%, more particularly from 0.5 – 17%, and even more particularly from 5-17% and even more particularly from 15-17%. These proportions are valid also for blends of precursors.

- In particular embodiments, the precursor is selected from ethyl (Z)-2-acetyl-4-methyltridec-2-enoate
- 20 and a blend of ethyl (Z)-2-acetyl-4-methyltridec-2-enoate with ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate. In the blend, the weight ratio of ethyl (Z)-2-acetyl-4-methyltridec-2-enoate to ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate is from 5:1 to 20:1, particularly from 8:1 to 10:1.

- 25 In a further particular embodiment, the fragrance precursor may be added as part of a fragrance formulation, but not as a component of a washing product such as a fabric conditioner/softener. Alternatively, it may be added separate from a perfume formulation, typically as a solution in a suitable solvent, such as dipropylene glycol, isopropyl myristate, triethyl citrate (TEC), pentane-1,2-diol, and ethanol. Such a solution (or a fragrance, in the case of addition as part of a fragrance) will
- 30 typically contain from 10% to 80 weight % precursor. The quantity of precursor solution is entirely dependent on individual taste, but a typical quantity of solution in an average-sized washing machine will deliver the same proportion of precursor as would a precursor-containing perfume formula in a standard dose of fabric softener added to a washing machine, the fabric softener typically containing from 1-2% by weight of fragrance.

35

The disclosure is further described with reference to the following example, which describes a particular embodiment, and which is not intended to be in any way limiting.

Example: Fragrance suitable for fabric softener

	Compound / Ingredient	parts by weight 1/1000
	AGRUMEX (2-TERT-BUTYLCYCLOHEXYL ACETATE)	30
5	DODECANAL	2
	2-METHYLUDECANAL	1
	AMBROFIX (3A,6,6,9A-TETRAMETHYLDODECAHYDRONAPHTHO[2,1-B]FURAN)	5
	BENZYL ACETATE	20
	CASHMERAN (6,7-DIHYDRO-1,1,2,3,3-PENTAMETHYL-4(5H)-INDANONE)	10
10	CITRONELLOL	40
	CYCLOGALBANATE (2-PROPENYL (CYCLOHEXYLOXY)ACETATE)	5
	DAMASCONE DELTA (1-(2,6,6-TRIMETHYL-3-CYCLOHEXEN-1-YL)-2-BUTEN-1-ONE)	10
	DIHYDRO MYRCENOL (2,6-DIMETHYL-7-OCTEN-2-OL)	80
	ETHYL VANILLIN (3-ETHOXY-4-HYDROXYBENZALDEHYDE)	15
15	GARDENOL (1-PHENYLETHYL ACETATE)	5
	GERANIOL (2-TRANS-3,7-DIMETHYL-2,6-OCTADIEN-1-OL)	30
	GERANYL ACETATE (3,7-DIMETHYLOCTA-2,6-DIENYL ACETATE)	15
	HEDIONE (METHYL 3-OXO-2-PENTYLCYCLOPENTANEACETATE)	60
	HEXYL ACETATE	15
20	HEXYL CINNAMIC ALDEHYDE (2-HEXYL-3-PHENYL-2-PROPENAL)	60
	HEXYL SALICYLATE (HEXYL 2-HYDROXYBENZOATE)	90
	IONONE BETA (4-(2,6,6-TRIMETHYL-1-CYCLOHEXEN-1-YL)-3-BUTEN-2-ONE)	15
	ISO E SUPER	
	(2-ACETYL-1,2,3,4,5,6,7,8-OCTAHYDRO-2,3,8,8-TETRA-METHYLNAPHTALENE)	50
25	JASMACYCLENE	
	(3A,4,5,6,7,7A-HEXAHYDRO-4,7-METHANO-1-INDEN-5(6)-YL ACETATE)	30
	JAVANOL ¹⁾	5
	LAVANDIN GROSSO OIL	30
	MANZANATE (ETHYL 2-METHYLPENTANOATE)	4
30	MEFROSOL (3-METHYL-5-PHENYL-1-PENTANOL)	30
	METHYL ANTHRANILATE(METHYL 2-AMINOBENZOATE)	5
	NEROLINE CRYSTALS (NAPHTALENE, 2-ETHOXY-)	15
	NYMPHEAL (3-(4-ISOBUTYL-2-METHYLPHENYL)PROPANAL)	20
	PATCHOULI OIL	10
35	PEACH PURE (4-UNDECANOLIDE)	15
	PEONILE (2-CYCLOHEXYLIDENE-2-PHENYLACETONITRILE)	40
	PETALIA (CYCLOHEXYLIDENE-O-TOLYL-ACETONITRILE)	15
	PHENYL ETHYL ACETATE (2-PHENYLETHYL ACETATE)	5
	PHENYL ETHYL ALCOHOL (2-PHENYLETHANOL)	40
40	RADJANOL ²⁾	30

	RASPBERRY KETONE (4-(4-HYDROXYPHENYL)-2-BUTANONE)	5
	ROSE OXIDE (4-METHYL-2-(2-METHYL-1-PROPENYL)TETRAHYDRO-2H-PYRAN)	3
	ROSYFOLIA ((1-METHYL-2-(5-METHYLHEX-4-EN-2-YL)CYCLOPROPYL)METHANOL)	10
	TRICYCLAL (2,4-DIMETHYL-3-CYCLOHEXENE-1-CARBALDEHYDE)	5
5	UNDECAVERTOL (4-METHYL-3-DECEN-5-OL)	15
	<u>DIPROPYLENE GLYCOL</u>	<u>110</u>

Total: 1000

- 10 1) Javanol = ((1-METHYL-2-(1,2,2-TRIMETHYLBICYCLO(3.1.0)-HEX-3-YLMETHYL)-CYCLOPROPYL)METHANOL)
- 2) Radjanol = 2-ETHYL-4-(2,2,3-TRIMETHYL-3-CYCLOPENTEN-1-YL)-2-BUTEN-1-OL

This accord was characterized as having a fresh, floral fruity character[CN1]. This was designated

15 Accord 1.

A fragrance accord was created by replacing 70 parts of the DPG of this accord above by ethyl (Z)-2-acetyl-4-methyltridec-2-enoate. This was designated Accord 2.

- 20 A third accord was prepared by replacing the DPG completely with an equal amount of a blend of ethyl (Z)-2-acetyl-4-methyltridec-2-enoate (60 parts), ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate (40 parts) and 4-(dodecylthio)-4-methylpentan-2-one (10 parts). This was designated Accord 3.

- 25 All of these accords were incorporated into samples of a fabric softener base at a dosage of 1.5% by weight, and each of these fabric softeners was then tested in the wash cycles described below. The fabric softener samples were prepared one day before testing.

- In order to emulate the operation of a normal washing machine in everyday use, 11 washes were
- 30 made with a washing load consisting of one towel and 4 T-shirts, two 5% polyester and two 100% polyester. The cycle was 38 minutes at 30°C with a spin of 1200 rpm. 4 washes per day were performed. The machine door was left partially open for 1 hour before the next wash.

- On the third day, when the washed had been completed, the odour in the machine was assessed
- 35 by trained perfumers, who gave an assessment of the perfume odour on a scale of from 0 (no perfume odour) to 5 (very strong perfume odour).

The results, with tester comments, were as follows:

- 40 Accord 1 – average score 1.75 – not very strong, less fresh, less powerful, less pleasant

Accord 2 – average score 4 – more chypre, aldehydic, cleaner odour, stronger, more pleasant

Accord 3 – average score 3 – floral, rosy, softer, original fragrance detectable.

5

The fabric softener with only ethyl (Z)-2-acetyl-4-methyltridec-2-enoate added to the fragrance gave the best results, not only from a durability standpoint, but also from an olfactory standpoint.

Claims:

1. A method of countering malodour in a washing machine at the end of a wash cycle,
comprising the addition thereto of a fragrance precursor,
5 wherein the fragrance precursor comprises ethyl (Z)-2-acetyl-4-methyltridec-2-enoate.
2. The method according to claim 1, wherein the fragrance precursor further comprises
ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate and
4-(dodecylthio)-4-methylpentan-2-one.
10
3. The method according to claim 1 or 2, in which the fragrance precursor is added in the
form of a solution in a solvent.
4. The method according to any one of claims 1 to 3, in which the fragrance precursor is
15 added as part of a fragrance formulation.
5. The method according to claim 4, in which the fragrance formulation forms part of a fabric
conditioner/softener formulation.
- 20 6. The method according to any one of claims 2 to 5, in which the weight ratio of ethyl (Z)-2-
acetyl-4-methyltridec-2-enoate to ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-
yl)butan-2-yl)cysteinate is from 5:1 to 20:1.
7. The method according to claim 6, in which the weight ratio is from 8:1 – 10:1.
25
8. The method according to any one of claims 3 to 7, in which the weight proportion of
fragrance precursor in the solution is from 10-80% by weight.