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(54) USE OF COMPOSITIONS COMPRISING TANNINS

(57) The invention relates to the use of cleaning and/or treatment compositions comprising tannins to inhibit or reduce malodour. Malodour reduction of inhibition may be by reduction or inhibition of the oxidation of fatty soils thereby reducing formation of malodourous species. The invention relates to the use of cleaning and/or treatment compositions comprising selected condensed tannins to trap malodourous species residual on fabrics. Such cleaning and/or treatment compositions can mitigate malodors without imparting color to an article that is treated with such cleaning and/or treatment composition. In addition, the appearance of such compositions is not adversely impacted by the tannins that they contain.

Description

FIELD OF INVENTION

⁵ **[0001]** The invention relates to the use of cleaning and/or treatment compositions comprising a tannin, particularly a condensed tannin and methods of making and using same to inhibit malodor.

[0002] The invention also relates to the use of cleaning and/or treatment compositions comprising a tannin, preferably a condensed tannin and methods of making and using same to trap malodourous species residual on fabrics.

10 BACKGROUND OF THE INVENTION

[0003] Manufacturers of unscented or scented products rely on malodor reduction ingredients or other technologies (e.g. filters) to reduce malodors.

- [0004] Malodourous species may be formed by any number of mechanisms for example, by the enzymatic oxidation
- ¹⁵ of fatty acids present in domestic soils. The present inventors have found that [OL1]tannins, particularly condensed tannins reduce malodour, in particular malodour from fatty acids. Whilst not wishing to be bound by theory, the mechanism for achieving this is considered to be by reducing the formation of and/or reducing the presence of (for example by entrapment) and/or by reducing the detection by the nose of malodor. The Applicants believe that when tannins, particularly condensed tannins deposit on fabrics during the laundry process malodour is inhibited for example, by the inhibition of oxidative
- 20 activity of enzymes, such as lipoxygenase, which may act on polyunsaturated fatty acids present in domestic soils, and that have a cis,cis-1,4-pentadiene moiety (e.g. linoleic or linolenic acid) to generate malodorous species. Thus, tannins may inhibit malodour by reducing the malodourous species formed by oxidation of polyunsaturated fatty acids present in domestic soils, and that have a cis,cis-1,4-pentadiene moiety (e.g. linoleic or linolenic acid).
- [0005] Without wishing to be bound by theory, the Applicants also believe that when tannins, particularly condensed tannins deposit on fabrics during the laundry process, thanks to π-stacking, they trap the malodourous species residual on fabrics.

[0006] Tannins can be used at low levels to control malodor via applications that include through-the-wash and rinse applications.

[0007] Tannins are polyphenolic compounds that are found in products such as red wine. Materials like tannins are generally avoided in through-the-wash, spray-on and dryer-added laundry applications as they can stain fabrics.

[0008] With most benefit agents, as the level of an active is increased the benefit of the active increases. Here, Applicants recognized that low levels of tannins can be used in cleaning and/or treatment compositions to mitigate /neutralize malodors without imparting significant color to a cleaning and/or treatment composition, i.e. without staining. Thus, low tannins level rather than higher levels are effective and preferred.

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SUMMARY OF THE INVENTION

[0009] The invention relates to the use of a cleaning and/or treatment composition comprising a cleaning and/or treatment adjunct and a tannins to inhibit or reduce malodour. Preferably the tannin comprises a condensed tannin.

40 **[0010]** Preferably the tannin has a weight average molecular weight of 0, 100 to 10000 Daltons. Preferably the tannin has a ratio of aromatic to aliphatic hydroxyls greater than 1.8.

[0011] Reduction or inhibition of malodour may be by reduction of the formation of malodourous species, for example by reducing formation and/or release of malodourous species from fatty soils; by reduction of the presence of malodourous species, for example by entrapment; or by reduction of detection of malodourous species, for example by masking.

- ⁴⁵ Thus, the invention also relates to the use of a cleaning and/or treatment composition comprising a tannin to trap malodourous species residual on fabrics. Preferably the tannin will be used at a low level, for example in the cleaning and/or treatment composition in an amount from 0.0001 to 3 wt% based on the weight of the cleaning and/or treatment composition. Such cleaning and/or treatment compositions can reduce or inhibit malodour, for example by reducing the malodour originating from fatty soils and/or entrapment of malodourous species residual on surfaces, particularly fabrics,
- ⁵⁰ without imparting significant color to an article, i.e. without staining an article, that is treated with such cleaning and/or treatment composition. In addition, the appearance of such compositions is not adversely impacted by the tannins that they contain.

DETAILED DESCRIPTION OF THE INVENTION

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Definitions

[0012] As used herein, the term "cleaning and/or treatment composition" includes, unless otherwise indicated, fabric

and home care products. Such products are preferably products for cleaning and/or treating fabrics, hard surfaces and any other surfaces in the area of fabric and home care, including: air care including air fresheners and scent delivery systems, car care, dishwashing, fabric conditioning (including softening and/or freshening), laundry detergency, laundry and rinse additive and/or care, hard surface cleaning and/or treatment including floor and toilet bowl cleaners, granular

- ⁵ or powder-form all-purpose or "heavy-duty" washing agents, especially cleaning detergents; liquid, gel or paste-form allpurpose washing agents, especially the so-called heavy-duty liquid types; liquid fine-fabric detergents; hand dishwashing agents or light duty dishwashing agents, especially those of the high-foaming type; machine dishwashing agents, including the various tablet, granular, liquid and rinse-aid types for household and institutional use; cleaning auxiliaries such as bleach additives and "stain-stick" or pre-treat types, substrate-laden products such as dryer added sheets, dry and
- ¹⁰ wetted wipes and pads, nonwoven substrates, and sponges; as well as sprays and mists all for consumer or/and institutional use. The invention is particularly directed to use for cleaning and/or treating compositions for fabric surfaces. [0013] As used herein, the term "fabric cleaning and/or treatment composition" is a subset of cleaning and/or treatment compositions comprising unless otherwise indicated, particulate including granular or powder-form, liquid, gel or pasteform all-purpose washing agents, especially the so-called heavy-duty types; liquid fine-fabric detergents; fabric condi-
- ¹⁵ tioning products including softening and/or freshening that may be in liquid, solid and/or dryer sheet form ; as well as cleaning auxiliaries such as bleach additives and "stain-stick" or pre-treat types, substrate-laden products such as dryer added sheets, dry and wetted wipes and pads, nonwoven substrates, and sponges; as well as sprays and mists.
 [0014] As used herein, articles such as "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.
- 20 [0015] As used herein, the terms "include", "includes" and "including" are meant to be non-limiting.
 - [0016] As used herein, the term "solid" includes granular, powder, bar and tablet product forms.
 - [0017] As used herein, the term "fluid" includes liquid, gel, paste and gas product forms, preferably liquid.

[0018] Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

[0019] All percentages and ratios are calculated by weight unless otherwise indicated. All percentages and ratios are calculated based on the total cleaning and/or treatment composition unless otherwise indicated.

[0020] It should be understood that every maximum numerical limitation given throughout this specification includes every lower numerical limitation, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this specification will include every higher numerical limitation, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

35 Compositions

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[0021] A cleaning and/or treatment composition or product for use herein comprises tannin, preferably condensed tannin. Preferably based on total cleaning and/or treatment product weight, the tannin is present in an amount from about 0.0001 % to about 3%, preferably from about 0.001 % to about 1.5%, more preferably from 0.01% to 0.5% by weight of the composition. Preferably the tannin comprises a condensed tannin, preferably having a Weight Average Molecular Weight Mw of 100, to 10,000 Daltons, preferably of 200to 8,000 Daltons, even more preferably of 300to 7,000

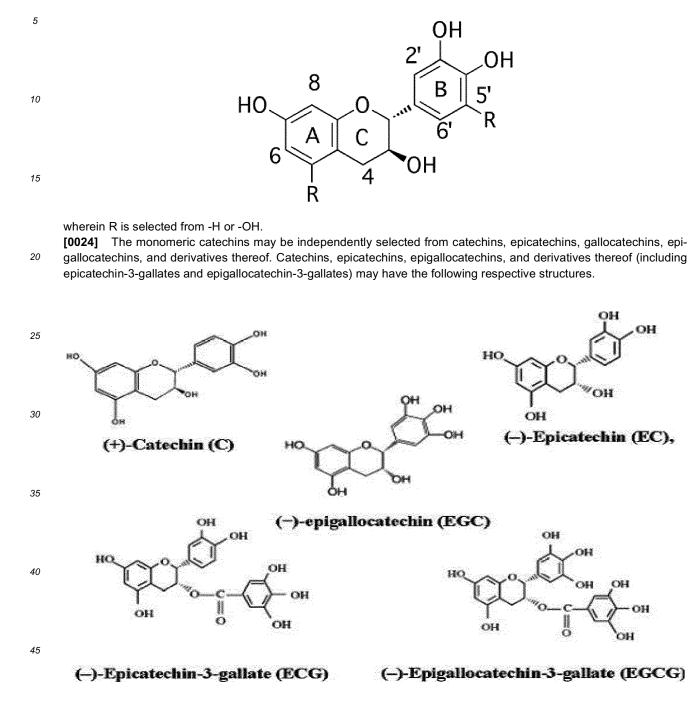
Daltons. Preferably the tannin comprises a ratio of aromatic to aliphatic hydroxyls >1.8 [0022] Condensed tannins comprise proanthocyanidins, polyflavonoid tannins, catechol-type tannins, pyrocatecollic type tannins, non-hydrolyzable tannins or flavolans - polymers formed by the condensation of flavans. Preferred tannins are condensed tannins comprising oligomeric and polymeric proanthocyanidins formed by linkage of C-4 of one catechin with C-8 or C-6 of the next monomeric catechin. Condensed tannins may be linear, branched, or a mixture thereof.

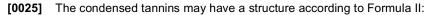
[0023] The condensed tannins may comprise monomeric catechins. The monomeric catechins may independently have a structure according to Formula 1:

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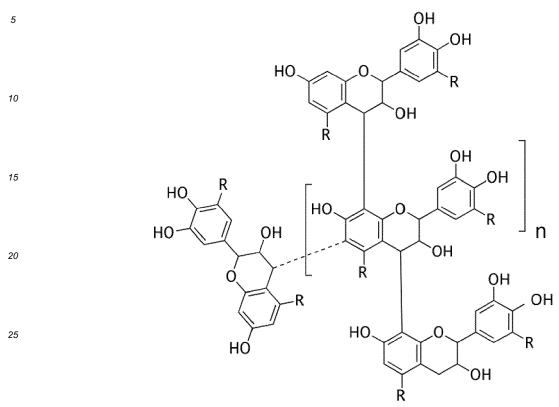
Formula 1





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wherein each R is independently selected from -H and -OH, and wherein n is from about 2 to about 200. [0026] Tannins of the present disclosure may be derived or extracted from any suitable source. Table 1 shows condensed tannins that may be found in common higher plants.

35		Т	able 1	
	COMMON NAME	FAMILY	<u>GENUS</u>	SPECIES (example of species studied)
	Willow leaf	Anacardiacee	Shinopsis	balansae
40	Red Quebracho	Anacardiacee	Shinopsis	lorentzii
40	Grape seeds	Vitaceae	Vitis	vinifera
	Mimosa bark	Fabaceae Mimosoideae	acacia	mollissima
	(black wattle)	Fabaceae Mimosoideae	Acacia	mearnsii
45	Quechua	Fabaceae	Sesbania	
	Trefoil	Fabaceae	Lotus	
	sainfoin	Fabaceae	Onobrychis sp.	
50		Fabaceae	Vicia	faba
50	chestnut	Fagaceae	Lithocarpus	
		Beech	<i>glaber</i> sp.	
	Pine bark	Pinaceae	Pinus	
55		Pinoidaea		
	Spruce bark	Pinaceae	Picea	
			Sorghum	

	COMMON NAME	FAMILY	GENUS	SPECIES (example of species studied)
		Rhizophoraceae	mangrove	
,		Myrtaceae	Eucalyptus	
	Myrtan or black marlock	Myrtaceae	Eucalyptus	redunca
	Myrtle	Myrtaceae	Mirtus	
0	Myrabolan	Rosaceae	<i>Prunus</i> sp.	
		Rosaceae	<i>Malus</i> sp.	
	Betel	Arecaceae	Areca	catechu
5		Burseraceae	Commiphora	
-		Burseraceae	Angolensissp.	
		Burseraceae	Canarium sp.	

(continued)

[0027] Preferred condensed tannins are selected from the group consisting of tannins extracted from bark pine, quebracho, mimosa bark, spruce bark, grape seeds, more preferably said condensed tannins are selected from the group consisting of tannins extracted from bark pine and quebracho.

[0028] Preferably said a cleaning and/or treatment product comprises, based on total cleaning and/or treatment product weight, from about 1% to about 97%, preferably from about 5% to about 90%, more preferably from about 8% to about 80% water.

[0029] The cleaning and/or treatment composition additionally comprises a cleaning and/or treatment adjunct, preferably comprising one or more adjuncts selected from the group consisting of surfactants, softener actives, chelants, builders, fatty acids, perfumes, perfume delivery systems, silicones and mixtures thereof. Preferably said adjunct comprises an adjunct selected from the group consisting of surfactants and fabric softener actives and mixtures thereof. Preferably said adjunct comprises an adjunct selected from the group consisting of perfumes and perfume delivery

30 Preferably systems.

[0030] Preferably the composition comprises, based on total composition weight, 0.05 wt % to 50 wt %, advantageously 1 to 40 wt %, 3 to 30 wt % or 5 wt % to 20 wt % surfactant selected from the groups of anionic surfactants, nonionic surfactants, cationic, zwitterionic and/or amphoteric surfactants. Preferred compositions comprise anionic surfactant, in

- particular where the cleaning and/or treatment composition is for contact with the surface during a washing step and the tannin is contacted with the surface from a cleaning composition. Most preferably the anionic surfactant comprises linear alkylbenzene sulphonate anionic surfactant. Anionic and nonionic surfactants are typically employed if the fabric care product is a laundry detergent. On the other hand, cationic surfactants are typically employed if the fabric care product is a fabric softener.
- **[0031]** In addition to the anionic surfactant, the fabric care compositions of the present invention may further contain a nonionic surfactant.

[0032] Preferably the composition contains, based on total composition weight, a nonionic surfactant, in one aspect, said composition contains, based on total composition weight, from 0.01 or 0.1 to 30 or 25 wt %, from 1 to 20 wt %, or from 3 to 15 or 10 wt %, nonionic surfactant. In one embodiment, the nonionic surfactant may comprise an ethoxylated

⁴⁵ nonionic surfactant. Suitable for use herein are the ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC₂H₄)n OH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 20 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15.

[0033] Suitable nonionic surfactants are those of the formula $R1(OC_2H_4)nOH$, wherein R1 is a $C_{10} - C_{16}$ alkyl group or a Cs -C₁₂ alkyl phenyl group, and n is from 3 to about 80. In one aspect, particularly useful materials are condensation products of C₉-C₁₅ alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol.

[0034] The fabric cleaning and/or treatment composition for use in the present invention may be a fabric treatment or softening composition, particularly a post-wash composition, for contacting with the surface in a rinse or drying step of a washing process. Preferably such compositions comprise a fabric softener active, most preferably such compositions comprise a quaternary ammonium ester softening active.

⁵⁵ comprise a quaternary ammonium ester softening active.
 [0035] The fabric softener composition for use in the present invention preferably comprises from 3.0% to 25.0% of a quaternary ammonium ester softening active (Fabric Softening Active, "FSA"). In preferred fabric softener composition, the quaternary ammonium ester softening active is present at a level of from 4.0% to 20%, more preferably from 5.0%

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to 15%, even more preferably from 7.0% to 12% by weight of the composition. The level of quaternary ammonium ester softening active may depend of the desired concentration of total softening active in the composition (diluted or concentrated composition) and of the presence or not of other softening active.

- **[0036]** Preferably the iodine value (see Methods) of the parent fatty acid from which the quaternary ammonium fabric softening active is formed is from 0 to 100, preferably from 10 to 60, more preferably 15 to 45.
- **[0037]** Suitable quaternary ammonium ester softening actives include but are not limited to, materials selected from the group consisting of monoester quats, diester quats, triester quats and mixtures thereof. Preferably, the level of monoester quat is from 2.0% to 40.0%, the level of diester quat is from 40.0% to 98.0%, the level of triester quat is from 0.0% to 25.0% by weight of total quaternary ammonium ester softening active.
- ¹⁰ [0038] Said quaternary ammonium ester softening active may comprise compounds of the following formula:

$$\{{\sf R^2}_{(4\text{-}m)}\text{-}{\sf N}\text{+}\text{-}[{\sf X}\text{-}{\sf Y}\text{-}{\sf R}^1]_m\}\,{\sf A}\text{-}$$

wherein:

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m is 1, 2 or 3 with proviso that the value of each m is identical;

each R¹ is independently hydrocarbyl, or branched hydrocarbyl group, preferably R¹ is linear, more preferably R¹ is partially unsaturated linear alkyl chain;

each R^2 is independently a C_1 - C_3 alkyl or hydroxyalkyl group, preferably R^2 is selected from methyl, ethyl, propyl, hydroxyethyl, 2-hydroxypropyl, 1-methyl-2-hydroxyethyl, poly(C_{2-3} alkoxy), polyethoxy, benzyl;

each X is independently (CH₂)n, CH₂-CH(CH₃)- or CH-(CH₃)-CH₂- and

each n is independently 1, 2, 3 or 4, preferably each n is 2;

each Y is independently -O-(O)C- or -C(O)-O-;

A- is independently selected from the group consisting of chloride, methylsulfate, and ethylsulfate, preferably A- is selected from the group consisting of chloride and methylsulfate;

with the proviso that when Y is -O-(O)C-, the sum of carbons in each R¹ is from 13 to 21, preferably from 13 to 19. [0039] Examples of suitable guaternary ammonium ester softening actives are commercially available from KAO

- Chemicals under the trade name Tetranyl AT-1 and Tetranyl AT-7590, from Evonik under the tradename Rewoquat
 WE16 DPG, Rewoquat WE18, Rewoquat WE20, Rewoquat WE28, and Rewoquat 38 DPG, from Stepan under the tradename Stepantex GA90, Stepantex VR90, Stepantex VK90, Stepantex VA90, Stepantex DC90, Stepantex VL90A.
 [0040] These types of agents and general methods of making them are disclosed in U.S.P.N. 4,137,180. Typically such fabric softener compositions will be substantially free of anionic surfactant.
- ³⁵ Method of measuring iodine value of a quaternary ammonium ester fabric softening active:

[0041] The iodine value ("IV") of a quaternary ammonium ester fabric softening active is the iodine value of the parent fatty acid from which the fabric softening active is formed, and is defined as the number of grams of iodine which react with 100 grams of parent fatty acid from which the fabric softening active is formed.

- 40 [0042] First, the quaternary ammonium ester fabric softening active is hydrolysed according to the following protocol: 25 g of fabric softener composition is mixed with 50 mL of water and 0.3 mL of sodium hydroxide (50% activity). This mixture is boiled for at least an hour on a hotplate while avoiding that the mixture dries out. After an hour, the mixture is allowed to cool down and the pH is adjusted to neutral (pH between 6 and 8) with sulfuric acid 25% using pH strips or a calibrated pH electrode.
- ⁴⁵ [0043] Next the fatty acid is extracted from the mixture via acidified liquid-liquid extraction with hexane or petroleum ether: The sample mixture is diluted with water/ethanol (1:1) to 160 mL in an extraction cylinder, 5 grams of sodium chloride, 0.3 mL of sulfuric acid (25% activity) and 50 mL of hexane are added. The cylinder is stoppered and shaken for at least 1 minute. Next, the cylinder is left to rest until 2 layers are formed. The top layer containing the fatty acid in hexane is transferred to another recipient. The hexane is then evaporated using a hotplate leaving behind the extracted for fatty acid.

[0044] Next, the iodine value of the parent fatty acid from which the fabric softening active is formed is determined following ISO3961:2013. The method for calculating the iodine value of a parent fatty acid comprises dissolving a prescribed amount (from 0.1-3g) into 15mL of chloroform. The dissolved parent fatty acid is then reacted with 25 mL of iodine monochloride in acetic acid solution (0.1M). To this, 20 mL of 10% potassium iodide solution and 150 mL deionised

⁵⁵ water is added. After the addition of the halogen has taken place, the excess of iodine monochloride is determined by titration with sodium thiosulphate solution (0.1M) in the presence of a blue starch indicator powder. At the same time a blank is determined with the same quantity of reagents and under the same conditions. The difference between the volume of sodium thiosulphate used in the blank and that used in the reaction with the parent fatty acid enables the

iodine value to be calculated. Preferred compositions are in liquid form.

[0045] It will be understood that combinations of softener actives disclosed above are suitable for use herein.

[0046] It may be preferred for the composition to contain, based on total composition weight, from 0.1 to 80 wt %, 1 to 60 wt %, or 5 to 50 wt % builders. Preferably the builder comprises a soluble builder system, for example comprising soda, i.e carbonate or bicarbonate, silicate, citrate and/or polycarboxylates.

- ⁵ soda, i.e carbonate or bicarbonate, silicate, citrate and/or polycarboxylates. [0047] Preferred compositions for use in the present invention comprise chelant. Where present, preferably the chelant is present in amounts from 0.001 to less than 10 or 7 or 5 %, or from 0.01 % to 3% of a chelant such as nitrogen-containing, P-free aminocarboxylates such as EDDS, EDTA and DTPA; aminophosphonates such as diethylenetriamine pentamethylenephosphonic acid and, ethylenediamine tetramethylenephosphonic acid; nitrogen-free phosphonates
- e.g., HEDP; and nitrogen or oxygen containing, P-free carboxylate-free chelants such as compounds of the general class of certain macrocyclic N-ligands such as those known for use in bleach catalyst systems.
 [0048] Preferably the composition comprises a perfume and a perfume delivery system. This perfume delivery system comprises a material selected from the group consisting of microcapsules, a polymer assisted delivery system; a molecule-assisted delivery system; a fiber-assisted delivery system; a cyclodextrin delivery system; a starch encapsulated
- ¹⁵ accord; and/or an inorganic carrier delivery system. [0049] Preferably the perfume microcapsule comprises a material selected from the group consisting of melamine-formaldehyde polymers, melamine-urea polymers, polyurea, polyurethane, polyacrylate, polymethylmethacylate and polyacrylate esters. The microcapsules preferably contain aromatic substances.
- [0050] The compositions for use in the present invention may be made by a method comprising mixing for example by stirring the tannin into a composition or by continuously adding the tannin into a composition and mixing the ingredients by means of static mixing elements.

[0051] The tannin may be introduced into the cleaning and/or treatment composition in the form of powder (100% active) or as a water-solvent solution for example: water:ethanol: ethylene glycol=1:1:1 solution.

[0052] Preferably the tannin is mixed with surfactant prior to mixing with the remaining components in the composition in any convenient order. Preferred compositions are liquids. When manufacturing a solid cleaning and/or treatment composition, the tannin may be in the form of a granule or other supported form which may be mixed with the remaining components of the composition in any convenient order, this the method may comprise the steps of mixing said tannin in dried, granulated or supported form into a solid composition. The tannins are stable within the detergent or cleaning agent matrix. During use of the detergent or cleaning agent, for example when washing laundry, the tannins are deposited on the item to be cleaned and provide reduced malodor.

Further Optional Adjunct Materials

- [0053] The disclosed compositions may include additional adjunct ingredients that include: fabric hueing agents, bleach activators, surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, and enzyme stabilizers, catalytic metal complexes, polymeric dispersing agents, clay and soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, additional perfumes and perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids and/or pigments. Other embodiments of Applicants' compositions do not contain one or more of the following adjuncts materials: fabric hueing agents, bleach activators, surfactants, builders,
- 40 chelating agents, dye transfer inhibiting agents, dispersants, enzymes, and enzyme stabilizers, catalytic metal complexes, polymeric dispersing agents, clay and soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, ad-ditional perfumes and perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids and/or pigments. The precise nature of these additional components, and levels of incorporation thereof, will depend on the physical form of the composition and the nature of the operation for which it is to be used. However,
- ⁴⁵ when one or more adjuncts are present, such one or more adjuncts may be present as detailed below. The following is a non-limiting list of suitable additional adjuncts.

[0054] Fabric Hueing Agents - The composition may comprise a fabric hueing agent (sometimes referred to as shading, bluing or whitening agents). Typically the hueing agent provides a blue or violet shade to fabric. Hueing agents can be used either alone or in combination to create a specific shade of hueing and/or to shade different fabric types. This may

- ⁵⁰ be provided for example by mixing a red and green-blue dye to yield a blue or violet shade. Hueing agents may be selected from any known chemical class of dye, including but not limited to acridine, anthraquinone (including polycyclic quinones), azine, azo (e.g., monoazo, disazo, trisazo, tetrakisazo, polyazo), including premetallized azo, benzodifurane and benzodifuranone, carotenoid, coumarin, cyanine, diazahemicyanine, diphenylmethane, formazan, hemicyanine, indigoids, methane, naphthalimides, naphthoquinone, nitro and nitroso, oxazine, phthalocyanine, pyrazoles, stilbene,
- ⁵⁵ styryl, triarylmethane, triphenylmethane, xanthenes and mixtures thereof. [0055] Suitable fabric hueing agents include dyes, dye-clay conjugates, and organic and inorganic pigments. Suitable dyes include small molecule dyes and polymeric dyes. Suitable small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour Index (C.I.) classifications of Acid, Direct, Basic, Reactive or

hydrolysed Reactive, Solvent or Disperse dyes for example that are classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of Colour Index (Society of Dyers and Colourists, Bradford, UK) numbers Direct Violet dyes such as 9, 35, 48, 51, 66, and 99, Direct Blue dyes such as 1, 71, 80 and 279, Acid Red

- ⁵ dyes such as 17, 73, 52, 88 and 150, Acid Violet dyes such as 15, 17, 24, 43, 49 and 50, Acid Blue dyes such as 15, 17, 25, 29, 40, 45, 75, 80, 83, 90 and 113, Acid Black dyes such as 1, Basic Violet dyes such as 1, 3, 4, 10 and 35, Basic Blue dyes such as 3, 16, 22, 47, 66, 75 and 159, Disperse or Solvent dyes US 8,268,016 B2, or dyes as disclosed in US 7,208,459 B2, and mixtures thereof. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of C. I. numbers Acid Violet 17, Acid Blue 80, Acid Violet 50, Direct Blue 71, Direct
- Violet 51, Direct Blue 1, Acid Red 88, Acid Red 150, Acid Blue 29, Acid Blue 113 or mixtures thereof. [0056] Suitable polymeric dyes include polymeric dyes selected from the group consisting of polymers containing covalently bound (sometimes referred to as conjugated) chromogens, (dye-polymer conjugates), for example polymers with chromogens co-polymerized into the backbone of the polymer and mixtures thereof. Polymeric dyes include those described in US 7,686,892 B2.
- ¹⁵ **[0057]** In another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of fabricsubstantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA), dye-polymer conjugates formed from at least one reactive dye and a polymer selected from the group consisting of polymers comprising a moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and mixtures thereof. In still another aspect, suitable polymeric dyes include polymeric dyes selected from
- 20 the group consisting of Liquitint® Violet CT, carboxymethyl cellulose (CMC) covalently bound to a reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC, alkoxylated triphenyl-methane polymeric colourants, alkoxylated thiophene polymeric colourants, and mixtures thereof.
- [0058] Suitable dye clay conjugates include dye clay conjugates selected from the group comprising at least one cationic/basic dye and a smectite clay, and mixtures thereof. In another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of one cationic/basic dye selected from the group consisting of C.I. Basic Yellow 1 through 108, C.I. Basic Orange 1 through 69, C.I. Basic Red 1 through 118, C.I. Basic Violet 1 through 51, C.I. Basic Blue 1 through 164, C.I. Basic Green 1 through 14, C.I. Basic Brown 1 through 23, CI Basic Black 1 through 11, and a clay selected from the group consisting of Montmorillonite clay, Hectorite clay, Saponite clay and mixtures
- ³⁰ thereof. In still another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of: Montmorillonite Basic Blue B7 C.I. 42595 conjugate, Montmorillonite Basic Blue B9 C.I. 52015 conjugate, Montmorillonite Basic Violet V3 C.I. 42555 conjugate, Montmorillonite Basic Green G1 C.I. 42040 conjugate, Montmorillonite Basic Red R1 C.I. 45160 conjugate, Montmorillonite C.I. Basic Black 2 conjugate, Hectorite Basic Blue B7 C.I. 42595 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic B1 C.I. 42555 conjugate, Hectorite B1 C.I. 42555
- ³⁵ Green G1 C.I. 42040 conjugate, Hectorite Basic Red R1 C.I. 45160 conjugate, Hectorite C.I. Basic Black 2 conjugate, Saponite Basic Blue B7 C.I. 42595 conjugate, Saponite Basic Blue B9 C.I. 52015 conjugate, Saponite Basic Violet V3 C.I. 42555 conjugate, Saponite Basic Green G1 C.I. 42040 conjugate, Saponite Basic Red R1 C.I. 45160 conjugate, Saponite C.I. Basic Black 2 conjugate and mixtures thereof.
- [0059] The hueing agent may be incorporated into the detergent composition as part of a reaction mixture which is 40 the result of the organic synthesis for a dye molecule, with optional purification step(s). Such reaction mixtures generally comprise the dye molecule itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route.

[0060] Suitable polymeric hueing agents may be alkoxylated. As with all such alkoxylated compounds, the organic synthesis may produce a mixture of molecules having different degrees of alkoxylation. Such mixtures may be used

- ⁴⁵ directly to provide the hueing agent, or may undergo a purification step to increase the proportion of the target molecule. Suitable pigments include pigments selected from the group consisting of flavanthrone, indanthrone, chlorinated indanthrone containing from 1 to 4 chlorine atoms, pyranthrone, dichloropyranthrone, monobromodichloropyranthrone, dibromodichloropyranthrone, tetrabromopyranthrone, perylene-3,4,9,10-tetracarboxylic acid diimide, wherein the imide groups may be unsubstituted or substituted by C1-C3 -alkyl or a phenyl or heterocyclic radical, and wherein the phenyl
- ⁵⁰ and heterocyclic radicals may additionally carry substituents which do not confer solubility in water, anthrapyrimidinecarboxylic acid amides, violanthrone, isoviolanthrone, dioxazine pigments, copper phthalocyanine which may contain up to 2 chlorine atoms per molecule, polychloro-copper phthalocyanine or polybromochloro-copper phthalocyanine containing up to 14 bromine atoms per molecule and mixtures thereof. In another aspect, suitable pigments include pigments selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15), Monastral Blue and mixtures thereof.
 - Violet 15), Monastral Blue and mixtures thereof. [0061] The aforementioned fabric hueing agents can be used in combination (any mixture of fabric hueing agents can be used).

[0062] Deposition Aid - In one aspect, the fabric treatment composition may comprise from about 0.01% to about 10%,

from about 0.05 to about 5%, or from about 0.15 to about 3% of a deposition aid. In one aspect, the deposition aid may be a cationic or amphoteric polymer. In another aspect, the deposition aid may be a cationic polymer. Cationic polymers in general and their method of manufacture are known in the literature. In one aspect, the cationic polymer may have a cationic charge density of from about 0.005 to about 23 meg/g, from about 0.01 to about 12 meg/g, or from about 0.1

- ⁵ to about 7 meq/g, at the pH of the composition. For amine-containing polymers, wherein the charge density depends on the pH of the composition, charge density is measured at the intended use pH of the product. Such pH will generally range from about 2 to about 11, more generally from about 2.5 to about 9.5. Charge density is calculated by dividing the number of net charges per repeating unit by the molecular weight of the repeating unit. The positive charges may be located on the backbone of the polymers and/or the side chains of polymers.
- 10 [0063] In another aspect, the deposition aid may comprise a cationic acrylic based polymer. In a further aspect, the deposition aid may comprise a cationic polyacrylamide. In another aspect, the deposition aid may comprise a polymer comprising polyacrylamide and polymethacrylamidopropyl trimethylammonium cation. In another aspect, the deposition aid may comprise poly(acrylamide-N-dimethyl aminoethyl acrylate) and its quaternized derivatives.
- [0064] In another aspect, the deposition aid may be selected from the group consisting of cationic or amphoteric polysaccharides. In one aspect, the deposition aid may be selected from the group consisting of cationic and amphoteric cellulose ethers, cationic or amphoteric galactomannan, cationic guar gum, cationic or amphoteric starch, and combinations thereof

[0065] Another group of suitable cationic polymers may include alkylamine-epichlorohydrin polymers which are reaction products of amines and oligoamines with epichlorohydrin. Another group of suitable synthetic cationic polymers may

²⁰ include polyamidoamine-epichlorohydrin (PAE) resins of polyalkylenepolyamine with polycarboxylic acid. The most common PAE resins are the condensation products of diethylenetriamine with adipic acid followed by a subsequent reaction with epichlorohydrin.

[0066] The weight-average molecular weight of the polymer may be from about 500 Daltons to about 5,000,000 Daltons, or from about 1,000 Daltons to about 2,000,000 Daltons, or from about 2,500 Daltons to about 1,500,000 Daltons, as determined by size exclusion chromatography relative to polyethylene oxide standards with RI detection. In

- Daltons, as determined by size exclusion chromatography relative to polyethylene oxide standards with RI detection. In one aspect, the MW of the cationic polymer may be from about 500 Daltons to about 37,500 Daltons.
 [0067] Builders The compositions may also contain from about 0.1% to 80% by weight of a builder. Compositions in liquid form generally contain from about 1% to 10% by weight of the builder component. Compositions in granular form generally contain from about 1% to 50% by weight of the builder component. Detergent builders are well known in the
- 30 art and can contain, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric
- acid. Other polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate. Builders for use in liquid detergents include citric acid. Suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates, such as sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of SiO2 to alkali metal oxide of from about 0.5 to about 4.0, or from about 1.0 to about 2.4. Also useful are aluminosilicates including zeolites.

[0068] Dispersants - The compositions may contain from about 0.1%, to about 10%, by weight of dispersants Suitable water-soluble organic materials are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid may contain at least two carboxyl radicals separated from each other by not more than two carbon atoms. The dispersants may also be alkoxylated derivatives of polyamines, and/or quaternized derivatives.

- ⁴⁵ [0069] Enzymes The compositions may contain one or more detergent enzymes which provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A typical combination may be a cocktail of
- 50 conventional applicable enzymes like protease, lipase, cutinase and/or cellulase in conjunction with amylase. Enzymes can be used at their art-taught levels, for example at levels recommended by suppliers such as Novozymes and Genencor. Typical levels in the compositions are from about 0.0001% to about 5%. When enzymes are present, they can be used at very low levels, e.g., from about 0.001% or lower; or they can be used in heavier-duty laundry detergent formulations at higher levels, e.g., about 0.1% and higher. In accordance with a preference of some consumers for "non-biological"
- ⁵⁵ detergents, the compositions may be either or both enzyme-containing and enzyme-free. [0070] Dye Transfer Inhibiting Agents - The compositions may also include from about 0.0001%, from about 0.01%, from about 0.05% by weight of the compositions to about 10%, about 2%, or even about 1% by weight of the compositions of one or more dye transfer inhibiting agents such as polyvinylpyrrolidone polymers, polyamine N-oxide polymers,

copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinyloxazolidones and polyvinylimidazoles or mixtures thereof.

[0071] Brighteners - The compositions may also comprise a brightener (also referred to as "optical brightener") and may include any compound that exhibits fluorescence, including compounds that absorb UV light and reemit as "blue"

- 5 visible light. Non-limiting examples of useful brighteners include: derivatives of stilbene or 4,4'-diaminostilbene, biphenyl, five-membered heterocycles such as triazoles, pyrazolines, oxazoles, imidiazoles, etc., or six-membered heterocycles (coumarins, naphthalamide, s-triazine, etc.). Cationic, anionic, nonionic, amphoteric and zwitterionic brighteners can be used. Suitable brighteners include those commercially marketed under the trade name Tinopal-UNPA-GX® by Ciba Specialty Chemicals Corporation (High Point, NC).
- 10 [0072] Bleach system - Bleach systems suitable for use herein contain one or more bleaching agents. Non-limiting examples of suitable bleaching agents include catalytic metal complexes; activated peroxygen sources; bleach activators; bleach boosters; photobleaches; bleaching enzymes; free radical initiators; H2O2; hypohalite bleaches; peroxygen sources, including perborate and/or percarbonate and combinations thereof. Suitable bleach activators include perhydrolyzable esters and perhydrolyzable imides such as, tetraacetyl ethylene diamine, octanoylcaprolactam, benzoyloxybenzenesul-
- 15 phonate, nonanoyloxybenzene¬sulphonate, benzoylvalerolactam, dodecanoyloxybenzenesulphonate. Other bleaching agents include metal complexes of transitional metals with ligands of defined stability constants.

Structurant / Thickeners

20 1 Di-benzylidene Polyol Acetal Derivative

[0073] The fluid detergent composition may comprise from about 0.01% to about 1% by weight of a dibenzylidene polyol acetal derivative (DBPA), or from about 0.05% to about 0.8%, or from about 0.1% to about 0.6%, or even from about 0.3% to about 0.5%. Non-limiting examples of suitable DBPA molecules are disclosed in US 61/167604. In one 25 aspect, the DBPA derivative may comprise a dibenzylidene sorbitol acetal derivative (DBS). Said DBS derivative may be selected from the group consisting of: 1,3:2,4-dibenzylidene sorbitol; 1,3:2,4-di(p-methylbenzylidene) sorbitol; 1,3:2,4di(p-chlorobenzylidene) sorbitol; 1,3:2,4-di(2,4-dimethyldibenzylidene) sorbitol; 1,3:2,4-di(p-ethylbenzylidene) sorbitol; and 1,3:2,4-di(3,4-dimethyldibenzylidene) sorbitol or mixtures thereof. These and other suitable DBS derivatives are disclosed in US 6,102,999, column 2 line 43 to column 3 line 65.

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2 Bacterial Cellulose

[0074] The fluid detergent composition may also comprise from about 0.005 % to about 1 % by weight of a bacterial cellulose network. The term "bacterial cellulose" encompasses any type of cellulose produced via fermentation of a 35 bacteria of the genus Acetobacter such as CELLULON® by CPKelco U.S. and includes materials referred to popularly as microfibrillated cellulose, reticulated bacterial cellulose, and the like. Some examples of suitable bacterial cellulose can be found in US 6,967,027; US 5,207,826; US 4,487,634; US 4,373,702; US 4,863,565 and US 2007/0027108. In one aspect, said fibres have cross sectional dimensions of 1.6 nm to 3.2 nm by 5.8 nm to 133 nm. Additionally, the bacterial cellulose fibres have an average micro fibre length of at least about 100 nm, or from about 100 to about 1,500

40 nm. In one aspect, the bacterial cellulose microfibres have an aspect ratio, meaning the average microfibre length divided by the widest cross sectional microfibre width, of from about 100:1 to about 400:1, or even from about 200:1 to about 300:1.

3 Coated Bacterial Cellulose

- 45 [0075] In one aspect, the bacterial cellulose is at least partially coated with a polymeric thickener. The at least partially coated bacterial cellulose can be prepared in accordance with the methods disclosed in US 2007/0027108 paragraphs 8 to 19. In one aspect the at least partially coated bacterial cellulose comprises from about 0.1 % to about 5 %, or even from about 0.5 % to about 3 %, by weight of bacterial cellulose; and from about 10 % to about 90 % by weight of the polymeric thickener. Suitable bacterial cellulose may include the bacterial cellulose described above and suitable poly-50 meric thickeners include: carboxymethylcellulose, cationic hydroxymethylcellulose, and mixtures thereof.

4 Cellulose fibers non-bacterial cellulose derived

[0076] In one aspect, the composition may further comprise from about 0.01 to about 5% by weight of the composition 55 of a cellulosic fiber. Said cellulosic fiber may be extracted from vegetables, fruits or wood. Commercially available examples are Avicel® from FMC, Citri-Fi from Fiberstar or Betafib from Cosun.

5 Non-Polymeric Crystalline Hydroxyl-Functional Materials

[0077] In one aspect, the composition may further comprise from about 0.01 to about 1% by weight of the composition of a non-polymeric crystalline, hydroxyl functional structurant. Said non-polymeric crystalline, hydroxyl functional structurants generally may comprise a crystallizable glyceride which can be pre-emulsified to aid dispersion into the final fluid detergent composition. In one aspect, crystallizable glycerides may include hydrogenated castor oil or "HCO" or derivatives thereof, provided that it is capable of crystallizing in the liquid detergent composition.

6 Polymeric Structuring Agents

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[0078] Fluid detergent compositions of the present invention may comprise from about 0.01 % to about 5 % by weight of a naturally derived and/or synthetic polymeric structurant. Examples of naturally derived polymeric structurants of use in the present invention include: hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, carboxymethyl cellulose, polysaccharide derivatives and mixtures thereof. Suitable polysaccharide derivatives include: pectine, alginate,

¹⁵ arabinogalactan (gum Arabic), carrageenan, gellan gum, xanthan gum, guar gum and mixtures thereof. Examples of synthetic polymeric structurants of use in the present invention include: polycarboxylates, polyacrylates, hydrophobically modified ethoxylated urethanes, hydrophobically modified non-ionic polyols and mixtures thereof. In one aspect, said polycarboxylate polymer is a polyacrylate, polymethacrylate or mixtures thereof. In another aspect, the polyacrylate is a copolymer of unsaturated mono- or di-carbonic acid and C₁-C₃₀ alkyl ester of the (meth)acrylic acid. Said copolymers

²⁰ are available from Noveon inc under the tradename Carbopol Aqua 30.

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- [0079] Silicones Suitable silicones comprise Si-O moieties and may be selected from (a) non-functionalized siloxane polymers, (b) functionalized siloxane polymers, and combinations thereof. The molecular weight of the organosilicone is usually indicated by the reference to the viscosity of the material. In one aspect, the organosilicones may comprise a viscosity of from about 10 to about 2,000,000 centistokes at 25°C. In another aspect, suitable organosilicones may have a viscosity of from about 10 to about 800,000 centistokes at 25°C.
 - [0080] Suitable organosilicones may be linear, branched or cross-linked.
- 30 [0081] In one aspect, the organosilicone may comprise a cyclic silicone. The cyclic silicone may comprise a cyclomethicone of the formula [(CH₃)₂SiO]_n where n is an integer that may range from about 3 to about 7, or from about 5 to about 6.

[0082] In one aspect, the organosilicone may comprise a functionalized siloxane polymer. Functionalized siloxane polymers may comprise one or more functional moieties selected from the group consisting of amino, amido, alkoxy,

- ³⁵ hydroxy, polyether, carboxy, hydride, mercapto, sulfate phosphate, and/or quaternary ammonium moieties. These moieties may be attached directly to the siloxane backbone through a bivalent alkylene radical, (i.e., "pendant") or may be part of the backbone. Suitable functionalized siloxane polymers include materials selected from the group consisting of aminosilicones, amidosilicones, silicone polyethers, silicone-urethane polymers, quaternary ABn silicones, amino ABn silicones, and combinations thereof.
- ⁴⁰ **[0083]** In one aspect, the functionalized siloxane polymer may comprise a silicone polyether, also referred to as "dimethicone copolyol." In general, silicone polyethers comprise a polydimethylsiloxane backbone with one or more polyoxyalkylene chains. The polyoxyalkylene moieties may be incorporated in the polymer as pendent chains or as terminal blocks. In another aspect, the functionalized siloxane polymer may comprise an aminosilicone.

[0084] In one aspect, the organosilicone may comprise amine ABn silicones and quat ABn silicones. Such organosilicones are generally produced by reacting a diamine with an epoxide.

[0085] In another aspect, the functionalized siloxane polymer may comprise silicone-urethanes. These are commercially available from Wacker Silicones under the trade name SLM-21200®.

[0086] Perfume: The optional perfume component may comprise a component selected from the group consisting of

- 50 (1) a perfume microcapsule, or a moisture-activated perfume microcapsule, comprising a perfume carrier and an encapsulated perfume composition, wherein said perfume carrier may be selected from the group consisting of cyclodextrins, starch microcapsules, porous carrier microcapsules, and mixtures thereof; and wherein said encapsulated perfume composition may comprise low volatile perfume ingredients, high volatile perfume ingredients, and mixtures thereof;
- ⁵⁵ (2) a pro-perfume;

(3) a low odor detection threshold perfume ingredients, wherein said low odor detection threshold perfume ingredients may comprise less than about 25%, by weight of the total neat perfume composition; and
(4) mixtures thereof; and

[0087] Porous Carrier Microcapsule - A portion of the perfume composition can also be absorbed onto and/or into a porous carrier, such as zeolites or clays, to form perfume porous carrier microcapsules in order to reduce the amount of free perfume in the multiple use fabric conditioning composition.

[0088] Pro-perfume - The perfume composition may additionally include a pro-perfume. Pro-perfumes may comprise nonvolatile materials that release or convert to a perfume material as a result of, e.g., simple hydrolysis, or may be pHchange-triggered pro-perfumes (e.g. triggered by a pH drop) or may be enzymatically releasable pro-perfumes, or lighttriggered pro-perfumes. The pro-perfumes may exhibit varying release rates depending upon the pro-perfume chosen.

Tannin Concentration Test Method

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[0089] UV-Spectroscopy is used to determine the concentration of tannins in a liquid test composition, or in a solid or unit dose test composition, or in the wash water liquor of a test composition. One suitable UV-spectrophotometer instrument is the model UV1800, manufactured by Shimadzu Corporation in Kyoto, Japan. Samples of the test composition material are prepared in order to generate a liquid test sample which is the solution that is measured spectroscopically.

- ¹⁵ The UV-spectroscopy analysis is conducted in transmission mode, with an optical path length of 0.4 cm, and the absorbance measured at a wavelength of 280 nm. Two standard reference materials of known tannins are prepared in dilution series in order to create two internal-spike calibration curves for determining tannin concentration. These two standard reference material tannins are: tannic acid and (-)-epigallocatechin gallate, (available as catalogue numbers 16201 and 93894, respectively, from Sigma Aldrich Co. LLC in St. Louis, MO, USA).
- 20 [0090] Samples of solid or unit dose test compositions are first dissolved in a known mass of deionized water that is sufficient to fully dissolve the solid composition at 25°C. Samples of solid or unit dose test compositions are initially dissolved in an equal mass of deionized water, to create a 50% (wt/wt) solution. Agitation and heating to a temperature of 25°C may be required to achieve dissolution within 30 mins. If additional water is required to fully dissolve the solid composition mass of deionized water are added, with each sequential addition having
- the same mass as the first addition of water. A minimum number of water additions are used in order to achieve full dissolution of the composition. The resultant solution is the liquid test sample to be analysed for the solid or unit dose composition being tested.

[0091] Samples of liquid test compositions are diluted with an equal volume of deionized water to create a 50% (v/v) solution. The resultant solution is the liquid test sample to be analysed for the fluid composition being tested.

[0092] Samples of wash water liquor are generated according to the procedure below.

Preparation of Tannin Solvent

[0093] Tannin solvent is prepared by making a 1:1:1 solution water:ethanol:ethylene glycol. A glass jar is tared on a scale and 25 mg of water is added to the jar. The scale is then re-zeroed and 25 g of ethanol is added to the jar containing water. The scale is re-zeroed and 25 g of ethylene glycol is added to the water:ethanol mixture. The jar is then sealed with a lid and shaken to mix.

Preparation of Tannin Working Solution

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[0094] Tannin working solution is prepared by making a 2% mixture of tannin material in Tannin Solvent. A glass jar is tared on a scale and 0.4 g of tannin extract is added to the jar. Next, Tannin Solvent is added to the jar until the measured weight reaches 20 g. The jar is sealed with a lid and placed in a ultrasonicator where the mixture is sonicated for 30 minutes.

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Preparation of Liquid Laundry Detergent + Tannin

[0095] A mixture of liquid laundry detergent containing 0.2% Tannin Working Solution is prepared by taring a glass jar on a scale and adding 0.2 g of Tannin Working Solution to the jar. Liquid Laundry Detergent is then added to the jar until the measured weight reaches 100g.

Preparation of Wash Liquor

[0096] Prepare a mixture of water containing 0.095% liquid laundry detergent comprising tannin. A pail is tared on a scale and 7.2 g of liquid laundry detergent + tannin is added to the pail. The scale is then re-zeroed and 7.57 kg of 32°C, 7 gpg water is added to the pail. The Wash liquor is then blended to mix by using and overhead mixer with a pitched impeller to stir.

[0097] The resultant solution is the liquid test sample to be analysed to determine tannin concentration in the wash

water liquor of the composition being tested.

[0098] The two internal calibration curves are created by generating two separate tannin-spiked sample solutions, one from each of the two standard reference tannins. Each tannin-spiked sample solution comprises a final concentration of 1% standard reference tannin (wt/v), in an aliquot of liquid test sample prepared according to the instructions given

- ⁵ herein. Each of the resulting two tannin-spiked sample solutions is then subsequently used to create a dilution series. [0099] A dilution series is created from each prepared liquid test sample or tannin-spiked sample solution. Each dilution series is prepared with buffer and deionized water to yield a series of five dilution solutions each having a different final concentration. The final concentration of liquid test solution or tannin-spiked sample solution (as appropriate) in each of the five solutions in the dilution series is as follows: 100 ppm; 50 ppm; 25 ppm; 10 ppm; and 0 ppm. Each solution in
- ¹⁰ the dilution series has a final volume of 1 mL and comprises 990 uL of 20 mM MOPS (3-(N-morpholino)propanesulfonic acid) buffer at pH 7.1. The remaining volumes of deionized water, and either liquid test sample or tannin stock solution, are adjusted as needed in order to achieve the five specified concentrations. [0100] Each material being tested yields a total of 15 fluids, resulting from 5 dilutions in 3 series (i.e., liquid test sample;
- the first tannin-spiked reference sample; and the second tannin-spiked reference sample). Each of the 15 fluids is
 measured in the UV-spectrophotometer and the absorbance value at 280 nm is measured three times. The average of the three measurements is the absorbance value recorded for that fluid.
 [0101] The measured absorbance values from the three series are plotted on a graph and linear line fit to each of the

three data series. The slopes of the lines from the two tannin-spiked reference samples are then compared to the slope of the line from the liquid test sample. The tannin-spike reference sample having a slope most similar to the liquid test

- 20 sample slope is identified and selected for further analysis. The least similar slope is discarded. Of the most similar tannin-spiked reference line, if the range of absorbance values does not overlap with the range of absorbance values of the liquid test sample, then an additional calibration dilution series is prepared and measured. This new dilution series is prepared at modified concentrations such that the new linear calibration curve overlaps with the linear line fit through the absorbance values from the liquid test sample series. The point at which the two lines intersect indicates the con-
- 25 centration of tannin in the liquid test sample, and is used to back calculate the concentration of tannin present in the original test material.
 101021 Method of measuring M and M : The number everage melocular weight, M as well as the weight everage.

[0102] Method of measuring \overline{M}_n and \overline{M}_w : The number average molecular weight, \overline{M}_n , as well as the weight average molecular weight, \overline{M}_w , can be determined using gel permeation chromatography (GPC). Prior to analysis, representative tannin samples are acetobrominated as reported in archival literature (J. Asikkala, T. Tamminen, D. S. Argyropoulos,

- ³⁰ J. Agric. Food Chem. 2012, 60, 8968-8973.) to ensure complete solubilisation in tetrahydrofuran (THF). 5mg tannin is suspended in 1mL glacial acetic acid/acetyl bromide (9:1 v/v) for 2 h. The solvent is then removed under reduced pressure, and the residue is dissolved in HPLC-grade THF and filtered over a 0.45 μm syringe filter prior to injection into a 20 μL sample loop. Typical analysis set-ups resemble the following specific example: GPC-analyses are performed using a Shimadzu instrument consisting of a controller unit (CBM-20A), a pumping unit (LC 20AT), a degasser unit
- ³⁵ (DGU-20A3), a column oven (CTO-20AC), a diode array detector (SPD-M20A), and a refractive index detector (RID-10A); the instrumental set-up is controlled using the Shimadzu LabSolution software package (Version 5.42 SP3). Three analytical GPC columns (each 7.5 x 30 mm) are connected in series for analyses: Agilent PLgel 5 μm 10000 Å, followed by Agilent PLgel 5 μm 1000 Å and Agilent PLgel 5 μm 500 Å. HPLC-grade THF (Chromasolv®, Sigma-Aldrich) is used as eluent (isocratic at 0.75 mL min 1, at 40 °C). Standard calibration is performed with polystyrene standards (Sigma
- ⁴⁰ Aldrich, MW range 162 5 x 106 g mol 1), and lower calibration limits are verified / adjusted by the use of synthesized dimeric and trimeric lignin models. Final analyses of each sample is performed using the intensities of the UV signal at $\lambda = 280$ nm employing a tailor-made MS Excel-based table calculation, in which the number average molecular weight (\overline{M}_{w}) is calculated based on the measured absorption (in a.u.) at a given
- $\frac{1}{45}$ time (min) after corrections for baseline drift and THF-stemming artifacts.
- \overline{M}_n is calculated according to the formula

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$$\overline{M}_{n} = \frac{\sum w_{i}}{\sum \frac{w_{i}}{M_{i}}}$$

in which \overline{M}_n is the number average molecular weight

$$_{55}$$
 w_i is obtained via $w_i = - \, h_i \; \frac{dV}{d(\log M)}$ with M being molecular weight

hi being the signal intensity of a given logM measurement point

V being the volume of the curve over a given logM interval d(logM).

M_i is a given molecular weight.

The analysis is run in triplicate, and final values are obtained as the standard average. \overline{M}_w is calculated according to the formula

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$$\overline{M}_{w} = \frac{\sum w_{i}M_{i}}{\sum w_{i}}$$

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in which \overline{M}_{w} is the number average molecular weight

 w_i is obtained via $\,\mathsf{w}_i = -\,h_i\,\,\frac{dV}{d(\log M)}\,$ with M being the molecular weight

hi being the signal intensity of a given logM measurement point

V being the volume of the curve over a given logM interval d(logM).

M_i is a given molecular weight.

The analysis is run in triplicate, and final values are obtained as the standard average.

[0103] Eventually necessary adjustment of \overline{M}_n and \overline{M}_w with respect to the desired applications is achieved by mechanical breaking of polymeric lignin using a ball mill, by chemically or enzymatically polymerising oligomeric lignin.

- [0104] Method of measuring aromatic hydroxyl and aliphatic hydroxyl content: Typically, a procedure similar to the one originally published can be used (A. Granata, D. S. Argyropoulos, J. Agric. Food Chem. 1995, 43, 1538-1544). A solvent mixture of pyridine and (CDCl3) (1.6:1 v/v) is prepared under anhydrous conditions. The NMR solvent mixture is stored over molecular sieves (4 Å) under an argon atmosphere. Cholesterol is used as internal standard at a concen-
- ²⁵ tration of 0.1 mol/L in the aforementioned NMR solvent mixture. 50 mg of Cr(III) acetyl acetonate are added as relaxation agent to this standard solution. **104021** Oct 200 mm of the limit are accessed by the second solution.

[0105] Ca. 30 mg of the lignin are accurately weighed in a volumetric flask and suspended in 400 μ L of the above prepared solvent solution. One hundred microliters of the internal standard solution are added, followed by 100 μ L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (CI-TMDP). The flask is tightly closed, and the mixture is stirred

- ³⁰ for 120 min at ambient temperature. 31P NMR spectra are recorded using suitable equipment, similar or identical to the following example: On a Bruker 300 MHz NMR spectrometer, the probe temperature is set to 20 °C. To eliminate NOE effects, the inverse gated decoupling technique is used. Typical spectral parameters for quantitative studies are as follows: 90° pulse width and sweep width of 6600 Hz. The spectra are accumulated with a delay of 15 s between successive pulses. Line broadening of 4 Hz is applied, and a drift correction is performed prior to Fourier transform.
- ³⁵ Chemical shifts are expressed in parts per million from 85 % H3PO4 as an external reference. All chemical shifts reported are relative to the reaction product of water with CI-TMDP, which has been observed to give a sharp signal in pyridine/CDCI3 at 132.2 ppm. To obtain a good resolution of the spectra, a total of 256 scans are acquired. The maximum standard deviation of the reported data is 0.02 mmol/g, while the maximum standard error is 0.01 mmol/g. (A. Granata, D. S. Argyropoulos, J. Agric. Food Chem. 1995, 43, 1538-1544). Quantification on the basis of the signal areas at the
- ⁴⁰ characteristic shift regions (in ppm, as reported in A. Granata, D. S. Argyropoulos, J. Agric. Food Chem. 1995, 43, 1538-1544) is done using a tailor-made table calculation in which the abundances, given in mmol/g, of the different delineable phosphitylated hydroxyl groups are determined on the basis of the integral obtained for the signal of the internal standard, that is present in the analysis sample at a concentration of 0.1 m, creating a signal at the interval ranging from 144.5 ppm to 145.3 ppm. The area underneath the peak related to the internal standard is set to a value
- ⁴⁵ of 1.0 during peak integration within the standard processing of the crude NMR data, allowing for determining abundances using simple rule-of-proportion mathematics under consideration of the accurate weight of the sample used for this analysis. The analysis is run in triplicate, and final values are obtained as the standard average.

Method of Use

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[0106] A method of reducing malodor comprising contacting a surface, preferably a fabric surface, with a composition or product as described herein in a , washing, rinsing and/ or drying step of a cleaning and/or treatment process for a surface. Where the surface is contacted with the composition in a washing step, preferably the composition comprising tannin is a cleaning composition. Where the surface is contacted with the composition in a rinse step, the composition comprising tannin is a fabric treatment composition, preferably a fabric softening composition. Where the surface is contacted with the composition comprising tannin is a fabric treatment composition, preferably a fabric softening composition. Where the surface is contacted with the composition comprising tannin is in the form of a dryer-

additive, such as a dryer sheet. A drying step may comprise passive and/or active drying..

[0107] Preferably said surface, preferably a fabric surface is sufficiently treated to provide said surface with, based on total surface weight, from about 0.001 ppm to about 100ppm of a tannin.

Treatment Liquor

[0108] A treatment liquor comprising based on total treatment liquor weight, from about 0.001 ppm to about 500 ppm, from about 0.01 ppm to about 100 ppm, more preferably from about 0.1 ppm to about 50 ppm of a tannin is disclosed.

EXAMPLES

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- [0109]
 - I. Synthesis examples:
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Bark pine was air dried. After wiley milling it was submitted to extraction in 2% Na2CO3-in a 1:5 liquor. The mixture was refluxed during two hours. The solid residue was filtered off and the solvent removed by rotary evaporation after careful neutralization with HCI.

Examples of use

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[0110] Granular laundry detergent compositions for hand washing or washing machines, typically top-loading washing machines.

25		A (wt %)	B (wt %)	C (wt %)	D (wt %)	E (wt %)	F (wt %)
25	Linear alkylbenzenesulfonate	20	22	20	15	19.5	20
	C ₁₂₋₁₄ Dimethylhydroxyethyl ammonium chloride	0.7	0.2	1	0.6	0.0	0
	AE3S	0.9	1	0.9	0.0	0.4	0.9
30	AE7	0.0	0.0	0.0	1	0.1	3
	Sodium tripolyphosphate	5	0.0	4	9	2	0.0
	Zeolite A	0.0	1	0.0	1	4	1
35	1.6R Silicate (SiO ₂ :Na ₂ O at ratio 1.6:1)	7	5	2	3	3	5
30	Sodium carbonate	25	20	25	17	18	19
	Polyacrylate MW 4500	1	0.6	1	1	1.5	1
	Random graft copolymer ¹	0.1	0.2	0.0	0.0	0.05	0.0
40	Carboxymethyl cellulose	1	0.3	1	1	1	1
	Stainzyme® (20 mg active/g)	0.1	0.2	0.1	0.2	0.1	0.1
	Protease (Savinase®, 32.89 mg active/g)	0.1	0.1	0.1	0.1		0.1
45	Amylase - Natalase® (8.65 mg active /g)	0.1	0.0	0.1	0.0	0.1	0.1
10	Lipase - Lipex® (18 mg active /g)	0.03	0.07	0.3	0.1	0.07	0.4
	Fluorescent Brightener 1	0.06	0.0	0.06	0.18	0.06	0.06
50	Fluorescent Brightener 2	0.1	0.06	0.1	0.0	0.1	0.1
	DTPA	0.6	0.8	0.6	0.25	0.6	0.6
55	MgSO ₄	1	1	1	0.5	1	1
	Sodium Percarbonate	0.0	5.2	0.1	0.0	0.0	0.0
	Sodium Perborate Monohydrate	4.4	0.0	3.85	2.09	0.78	3.63
	NOBS	1.9	0.0	1.66	0.0	0.33	0.75

(continued)

		A (wt %)	B (wt %)	C (wt %)	D (wt %)	E (wt %)	F (wt %)
5	TAED	0.58	1.2	0.51	0.0	0.015	0.28
0	Sulphonated zinc phthalocyanine	0.0030	0.0	0.0012	0.0030	0.0021	0.0
	S-ACMC	0.1	0.0	0.0	0.0	0.06	0.0
	Direct Violet Dye (DV9 or DV99 or DV66)	0.0	0.0	0.0003	0.0001	0.0001	0.0
10	Additional Neat Perfume	0.5	0.5	0.5	0.5	0.5	0.5
	Tannin	0.07	0.004	0.0001	0.05	1	0.08
15							
	Sulfate/Moisture	Balance					

II.2 Granular laundry detergent compositions typically for front-loading automatic washing machines. The typical pH is about 10

[0111]

		A (wt%)	B (wt%)	C (wt%)	D (wt%)	E (wt%)	F (wt%)
5	Linear alkylbenzenesulfonate	8	7.1	7	6.5	7.5	7.5
	AE3S	0	4.8	1.0	5.2	4	4
	C12-14 Alkylsulfate	1	0	1	0	0	0
-	AE7	2.2	0	2.2	0	0	0
)	C ₁₀₋₁₂ Dimethyl hydroxyethylammonium chloride	0.75	0.94	0.98	0.98	0	0
	Crystalline layered silicate (-Na ₂ Si ₂ O ₅)	4.1	0	4.8	0	0	0
5	Zeolite A	5	0	5	0	2	2
	Citric Acid	3	5	3	4	2.5	3
	Sodium Carbonate	15	20	14	20	23	23
	Silicate 2R(SiO ₂ :Na ₂ O at ratio 2:1)	0.08	0	0.11	0	0	0
)	Soil release agent	0.75	0.72	0.71	0.72	0	0
	Acrylic Acid/Maleic Acid Copolymer	1.1	3.7	1.0	3.7	2.6	3.8
	Carboxymethylcellulose	0.15	1.4	0.2	1.4	1	0.5
ō	Protease - Purafect® (84 mg active/g)	0.2	0.2	0.3	0.15	0.12	0.13
	Amylase - Stainzyme Plus® (20 mg active/g)	0.2	0.15	0.2	0.3	0.15	0.15
	Lipase - Lipex® (18.00 mg active/g)	0.05	0.15	0.1	0	0	0
	Amylase - Natalase® (8.65 mg active/g)	0.1	0.2	0	0	0.15	0.15
	Cellulase - Celluclean™ (15.6 mg active/g)	0	0	0	0	0.1	0.1
	TAED	3.6	4.0	3.6	4.0	2.2	1.4
	Percarbonate	13	13.2	13	13.2	16	14
	Na salt of Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer (EDDS)	0.2	0.2	0.2	0.2	0.2	0.2
	Hydroxyethane di phosphonate (HEDP)	0.2	0.2	0.2	0.2	0.2	0.2

(continued)

		A (wt%)	B (wt%)	C (wt%)	D (wt%)	E (wt%)	F (wt%)
5 N	MgSO ₄	0.42	0.42	0.42	0.42	0.4	0.4
	Perfume	0.5	0.6	0.5	0.6	0.6	0.6
S	Suds suppressor agglomerate	0.05	0.1	0.05	0.1	0.06	0.05
S	Soap	0.45	0.45	0.45	0.45	0	0
) s	Sulphonated zinc phthalocyanine (active)	0.0007	0.001 2	0.0007	0	0	0
S	S-ACMC	0.01	0.01	0	0.01	0	0
D	Direct Violet 9 (active)	0	0	0.0001	0.0001	0	0
A	Additional Neat Perfume	0.5	0.5	0.5	0.5	0.5	0.5
	Fannin	0.2	1.5	0.9	0.005	1.5	0.08
° s	Sulfate/ Water & Miscellaneous	Balance					

II.3 Heavy Duty Liquid laundry detergent compositions

₂₅ [0112]

		A (wt%)	B (wt%)	C (wt%)	D (wt%)	E (wt%)	F (wt%)	G (wt%)
0.0	AES C ₁₂₋₁₅ alkyl ethoxy (1.8) sulfate	11	10	4	6.32	0	0	0
30	AE3S	0	0	0	0	2.4	0	0
	Linear alkyl benzene sulfonate/sulfonic acid	1.4	4	8	3.3	5	8	19
	HSAS	3	5.1	3	0	0	0	0
35	Sodium formate	1.6	0.09	1.2	0.04	1.6	1.2	0.2
	Sodium hydroxide	2.3	3.8	1.7	1.9	1.7	2.5	2.3
	Monoethanolamine	1.4	1.49	1.0	0.7	0	0	To pH 8.2
40	Diethylene glycol	5.5	0.0	4.1	0.0	0	0	0
	AE9	0.4	0.6	0.3	0.3	0	0	0
	AE8	0	0	0	0	0	0	20.0
45	AE7	0	0	0	0	2.4	6	0
	Chelant (HEDP)	0.15	0.15	0.11	0.07	0.5	0.11	0.8
	Citric Acid	2.5	3.96	1.88	1.98	0.9	2.5	0.6
	C ₁₂₋₁₄ dimethyl Amine Oxide	0.3	0.73	0.23	0.37	0	0	0
50	C ₁₂₋₁₈ Fatty Acid	0.8	1.9	0.6	0.99	1.2	0	15.0
	4-formyl-phenylboronic acid	0	0	0	0	0.05	0.02	0.01
	Borax	1.43	1.5	1.1	0.75	0	1.07	0
55	Ethanol	1.54	1.77	1.15	0.89	0	3	7

(continued)

	A (wt%)	B (wt%)	C (wt%)	D (wt%)	E (wt%)	F (wt%)	G (wt%)
A compound having the following general structure: $bis((C_2H_5O)(C_2H_4O)n)$ (CH ₃)-N ⁺ -C _x H _{2x} -N ⁺ -(CH ₃)-bis((C ₂ H ₅ O)(C ₂ H ₄ O) n), wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof	0.1	0	0	0	0	0	2.0
Ethoxylated (EO ₁₅) tetraethylene pentamine	0.3	0.33	0.23	0.17	0.0	0.0	0
Ethoxylated Polyethylenimine	0	0	0	0	0	0	0.8
Ethoxylated hexamethylene diamine	0.8	0.81	0.6	0.4	1	1	
1,2-Propanediol	0.0	6.6	0.0	3.3	0.5	2	8.0
Fluorescent Brightener	0.2	0.1	0.05	0.3	0.15	0.3	0.2
Hydrogenated castor oil derivative structurant	0.1	0	0	0	0	0	0.1
Perfume	1.6	1.1	1.0	0.8	0.9	1.5	1.6
Protease (40.6 mg active/g)	0.8	0.6	0.7	0.9	0.7	0.6	1.5
Mannanase: Mannaway® (25 mg active/g)	0.07	0.05	0.045	0.06	0.04	0.045	0.1
Amylase: Stainzyme® (15 mg active/g)	0.3	0	0.3	0.1	0	0.4	0.1
Amylase: Natalase® (29 mg active/g)	0	0.2	0.1	0.15	0.07	0	0.1
Xyloglucanase (Whitezyme®, 20mg active/g)	0.2	0.1	0	0	0.05	0.05	0.2
Lipex® (18 mg active/g)	0.4	0.2	0.3	0.1	0.2	0	0
Additional Neat Perfume	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tannin	0.25	0.004	0.5	0.05	0.007	1.0	0.08
*Water, dyes & minors	Balance						

Examples II.4 Unit Dose Compositions

[0113]

Example of Unit Dose detergents	А	В
C ₁₄₋₁₅ alkyl poly ethoxylate (8)	12	-
C ₁₂₋₁₄ alkyl poly ethoxylate (7)	1	14
C ₁₂₋₁₄ alkyl poly ethoxylate (3) sulfate Mono EthanolAmine salt	8.4	9
Linear Alkylbenzene sulfonic acid	15	16
Citric Acid	0.6	0.5
C ₁₂₋₁₈ Fatty Acid	15	17
Enzymes	1.5	1.2
PEI 600 EO20	4	-
Diethylene triamine penta methylene phosphonic acid or HEDP	1.3	-
Fluorescent brightener	0.2	0.3

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(continued)

Example of Unit Dose detergents	А	В
Hydrogenated Castor Oil	0.2	0.2
1, 2 propanediol	16	12
Glycerol	6.2	8.5
Sodium hydroxide	-	1
Mono Ethanol Amine	7.9	6.1
Dye	Present	Presen
PDMS	-	2.7
Potassium sulphite	0.2	0.2
Tannin	0.005	0.09
Water	Up to 100p	Up to 10
(1)		

²⁵ Raw Materials and Notes For Composition Examples

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[0114] LAS is linear alkylbenzenesulfonate having an average aliphatic carbon chain length C_9 - C_{15} supplied by Stepan, Northfield, Illinois, USA or Huntsman Corp. (HLAS is acid form).

- ³⁰ C₁₂₋₁₄ Dimethylhydroxyethyl ammonium chloride, supplied by Clariant GmbH, Germany AE3S is C₁₂₋₁₅ alkyl ethoxy (3) sulfate supplied by Stepan, Northfield, Illinois, USA
 - AE7 is C₁₂₋₁₅ alcohol ethoxylate, with an Javerage degree of ethoxylation of 7, supplied by Huntsman, Salt Lake City, Utah, USA

AES is C₁₀₋₁₈ alkyl ethoxy sulfate supplied by Shell Chemicals.

 35 AE9 is C₁₂₋₁₃ alcohol ethoxylate, with an average degree of ethoxylation of 9, supplied by Huntsman, Salt Lake City, Utah, USA

HSAS or HC1617HSAS is a mid-branched primary alkyl sulfate with average carbon chain length of about 16-17 Sodium tripolyphosphate is supplied by Rhodia, Paris, France

Zeolite A is supplied by Industrial Zeolite (UK) Ltd, Grays, Essex, UK

- 1.6R Silicate is supplied by Koma, Nestemica, Czech Republic
 Sodium Carbonate is supplied by Solvay, Houston, Texas, USA
- Polyacrylate MW 4500 is supplied by BASF, Ludwigshafen, Germany Carboxymethyl cellulose is Finnfix® V supplied by CP Kelco, Arnhem, Netherlands Suitable chelants are, for example, diethylenetetraamine pentaacetic acid (DTPA) supplied by Dow Chemical, Midland, Michigan, USA or Hydroxyethane di phosphonate (HEDP) supplied by Solutia, St Louis, Missouri, USA Bagsvaerd, Denmark

⁴⁵ Savinase®, Natalase®, Stainzyme®, Lipex®, Celluclean[™], Mannaway® and Whitezyme® are all products of Novozymes, Bagsvaerd, Denmark. Proteases may be supplied by Genencor International, Palo Alto, California, USA (e.g. Purafect Prime®) or by Novozymes, Bagsvaerd, Denmark (e.g. Liquanase®, Coronase®). Fluorescent Brightener 1 is Tinopal® AMS, Fluores-

cent Brightener 2 is Tinopal® CBS-X, Sulphonated zinc phthalocyanine and Direct Violet 9 is Pergasol® Violet BN-Z all supplied by Ciba Specialty Chemicals, Basel, Switzerland
 Sodium percarbonate supplied by Solvay, Houston, Texas, USA
 Tannin is from pine bark or grape seeds

Sodium perborate is supplied by Degussa, Hanau, Germany

- ⁵⁵ NOBS is sodium nonanoyloxybenzenesulfonate, supplied by Future Fuels, Batesville, USA. TAED is tetraacetylethylenediamine, supplied under the Peractive® brand name by Clariant GmbH, Sulzbach, Germany S-ACMC is carboxymethylcellulose conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under
 - S-ACMC is carboxymethylcellulose conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC.

Soil release agent is Repel-o-tex® PF, supplied by Rhodia, Paris, France Acrylic Acid/Maleic Acid Copolymer is molecular weight 70,000 and acrylate:maleate ratio 70:30, supplied by BASF, Ludwigshafen, Germany

Na salt of Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer (EDDS) is supplied by Octel, Ellesmere Port, UK

Hydroxyethane di phosphonate (HEDP) is supplied by Dow Chemical, Midland, Michigan, USA

Suds suppressor agglomerate is supplied by Dow Coming, Midland, Michigan, USA

HSAS is mid-branched alkyl sulfate as disclosed in US 6,020,303 and US 6,060,443

 C_{12-14} dimethyl Amine Oxide is supplied by Procter & Gamble Chemicals, Cincinnati, USA

[0115] Random graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is about 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is about 40:60 and no more than 1 grafting point per 50 ethylene oxide units.

- [0116] Ethoxylated polyethyleneimine is polyethyleneimine (MW = 600) with 20 ethoxylate groups per -NH.
- [0117] Cationic cellulose polymer is LK400, LR400 and/or JR30M from Amerchol Corporation, Edgewater NJ
- [0118] Note: all enzyme levels are expressed as % enzyme raw material.

Performance Data

- [0119] The Applicants conducted a small scale wash test comparing a commercially available liquid detergent and the same liquid detergent also comprising the condensed tannin. A 90°F (32°C) wash cycle for 12 minutes was performed followed by a 2 minute, 60°F (15.5°C) rinse cycle. Water hardness for the wash and rinse was 7 gpg. The wash ballast consisted of 250 g of cotton terry cloth. 3 swatches treated with a malodor cocktail were included in the wash experiments. After wash, ballast and swatches treated with malodor were dried in an electric clothes dryer on high/cotton setting for 50 minutes.
- ²⁵ **[0120]** A panel of experienced evaluators assesses malodor intensity of the dry swatches which were originally treated with malodor and then washed. Malodor intensity is assessed on a 0-100 scale, where 0 means absence of malodor and 100 means a very high a noticeable malodor intensity. A difference of 5 points is consumer noticeable. After washing and drying the swatches treated with the liquid detergent containing the condensed tannin have a lower malodor intensity than the swatches treated only with the liquid detergent.
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Product	Malodor intensity (Scale 0-100)
Liquid detergent	50
Liquid detergent + 0.2% of a solution containing 2% tannin (bark pine extract)	30
Liquid detergent + 1% of a solution containing tannin 2% (bark pine extract)	40

[0121] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

Claims

- **1.** Use of a cleaning and/or treatment composition comprising a cleaning and/or treatment adjunct and a tannin to inhibit malodour..
- 2. Use according to calim 1 wherein the tannin comprises a condensed tannin.

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- **3.** Use according to claim 1 or claim 2 wherein the tannin has a weight average molecular weight of 100,Daltons to 10,000 Daltons.
- 4. Use according to any preceding claim wherein the tannin has a ratio of aromatic to aliphatic hydroxyls greater than 1.8.
 - 5. Use according to any preceding claim wherein the tannin is present in the cleaning and/or treatment composition in an amount from 0.0001 to 3 wt%.

- 6. Use according to any preceding claim wherein said tannin is selected from the group consisting of tannins extracted from bark pine, quebracho, mimosa bark, spruce bark, grape seeds and mixtures thereof.
- 7. Use according to any preceding claim wherein said cleaning and/or treatment adjunct comprises an anionic surfactant, preferably comprising a linear alkylbenzene sulphonate surfactant.
 - 8. Use according to any preceding claim wherein the cleaning and/or treatment adjunct comprises a fabric softener active material, preferably a quaternary ammonium ester softener active.
- Use according to any preceding claim wherein the cleaning and/or treatment adjunct is selected from the group consisting of perfumes, perfume delivery systems and mixtures thereof.
 - **10.** Use according to any preceding claim wherein said cleaning and/or treatment adjunct comprises a chelant.

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EUROPEAN SEARCH REPORT

Application Number EP 17 18 3798

		DOCUMENTS CONSID	ERED TO BE RELEVANT]
	Category	Citation of document with in of relevant pass	ndication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
10	Х,Р	WO 2016/130288 A1 (18 August 2016 (201 * the whole documer	6-08-18)	1-10	INV. C11D3/00 C11D3/20 C11D3/382
15	x	DE 20 2015 100862 U GMBH) 30 May 2016 (* paragraph [0002] claims *		1-10	C11D7/26 C11D7/44
20	X	19 August 2010 (201	 FURNO FRANCK ET AL) [0-08-19) , [0016] - [0025];	1-10	
25	X	US 2014/234234 A1 (FRANCISCO) 21 Augus * paragraphs [0004] [0017]; claims; exa	t 2014 (2014-08-21) - [0007], [0015] -	1-10	
	x	JP H02 102299 A (05 KK) 13 April 1990 (SAKA YAKUHIN KENKYUSHO	1-10	TECHNICAL FIELDS
30		* abstract *			SEARCHED (IPC) C11D
35					
40					
45					
	1	The present search report has been drawn up for all claims			
50	(co1)	Place of search Munich	Date of completion of the search 19 September 201	.7 Hil	Examiner lebrecht, Dieter
	C C	ATEGORY OF CITED DOCUMENTS	T : theory or princip E : earlier patent do	le underlying the i	nvention
	X : par X : par Y : par	ticularly relevant if taken alone ticularly relevant if combined with anot	after the filing da her D : document cited	te in the application	onea on, or
55	A:tec 이 O:noi	ument of the same category nnological background n-written disclosure rrmediate document	L : document cited f & : member of the s document		, corresponding

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 17 18 3798

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

way hable for these particulars which are merely given for the purpose of information. 19-09-2017

10	Patent document cited in search report	Publication date	Patent family member(s)	Publication date
15	WO 2016130288 A1	18-08-2016	CA 2974200 A1 US 2016230122 A1 US 2017088798 A1 WO 2016130288 A1	16-08-2016 11-08-2016 30-03-2017 18-08-2016
	DE 202015100862 U1	30-05-2016	NONE	
20 25	US 2010209379 A1	19-08-2010	CN 101407638 A DE 102007045724 A1 EP 2176325 A2 JP 2010540685 A KR 20100074230 A TW 200930725 A US 2010209379 A1 WO 2009040106 A2	$\begin{array}{c} 15-04-2009\\ 02-04-2009\\ 21-04-2010\\ 24-12-2010\\ 01-07-2010\\ 16-07-2009\\ 19-08-2010\\ 02-04-2009 \end{array}$
	US 2014234234 A1	21-08-2014	BR PI1101172 A2 US 2014234234 A1 WO 2012129630 A1	04-06-2013 21-08-2014 04-10-2012
30	JP H02102299 A	13-04-1990	NONE	
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55	For more details about this annex : see 0	Dfficial Journal of the Euror	pean Patent Office, No. 12/82	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 4137180 A [0040]
- US 8268016 B2 [0055]
- US 7208459 B2 [0055]
- US 7686892 B2 [0056]
- US 61167604 B [0073]
- US 6102999 A [0073]
- US 6967027 B [0074]

- US 5207826 A [0074]
- US 4487634 A [0074]
- US 4373702 A [0074]
- US 4863565 A [0074]
- US 20070027108 A [0074] [0075]
- US 6020303 A [0114]
- US 6060443 A [0114]

Non-patent literature cited in the description

- J. ASIKKALA; T. TAMMINEN; D. S. ARGYRO-POULOS. J. Agric. Food Chem., 2012, vol. 60, 8968-8973 [0102]
- A. GRANATA ; D. S. ARGYROPOULOS. J. Agric. Food Chem., 1995, vol. 43, 1538-1544 [0104] [0105]