



(51) International Patent Classification:

A61L 9/01 (2006.01) C11D 3/50 (2006.01)  
A61L 101/32 (2006.01) A61L 15/46 (2006.01)  
C11D 3/00 (2006.01) A61L 101/20 (2006.01)  
A61L 9/014 (2006.01) A61L 101/36 (2006.01)

(21) International Application Number:

PCT/US2012/020884

(22) International Filing Date:

11 January 2012 (11.01.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/006,644 14 January 2011 (14.01.2011) US

(71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **WOO, Ricky, Ah-Man** [US/US]; 6940 Van Gordon Road, Hamilton, Ohio 45011 (US). **EYLEM, Cahit** [US/US]; 7470 Oakleaf Lane, West Chester, Ohio 45069 (US). **AZIRBAYEVA, Larissa** [US/US]; 6796 Grand Oaks Court, Mason, Ohio 45040 (US). **LIU, Zaiyou** [US/US]; 8040 Stonebarn Drive, West Chester, Ohio 45069 (US). **NAIR, Radhakrishnan, Janardanan** [IN/JP]; 5-11-501-1508, Koyo-Cho Naka, Higashinada-KU, Kobe, 658-0032 (JP). **JOHNSTONE, Kevin, Robert** [US/US]; 1433 Covered Bridge Road, Cincinnati, Ohio 45231 (US).

(74) Common Representative: **THE PROCTER & GAMBLE COMPANY**; c/o Eileen L. Hughett, Global Patent Services, 299 East Sixth Street, Sycamore Building, 4th Floor, Cincinnati, Ohio 45202 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: COMPOSITIONS COMPRISING METALLATED MALODOR CONTROL POLYMERS

(57) Abstract: Compositions comprising a metallated malodor control polymer, a malodor counteractant comprising a perfume material, an aqueous carrier, and a pH of about 5 to about 10; and methods thereof are provided. Such compositions may be used to reduce or neutralize malodors on surfaces or in the air.



WO 2012/097033 A1

## COMPOSITIONS COMPRISING METALLATED MALODOR CONTROL POLYMERS

### FIELD OF THE INVENTION

The present invention relates to compositions comprising metallated malodor control  
5 polymers and methods thereof.

### BACKGROUND OF THE INVENTION

Products for reducing or masking malodors are currently available and are widely  
described in patent literature. These products may be designed to work specifically in air, on  
10 fabrics, or on other surfaces. However, not all malodors are effectively controlled by products in  
the market. Amine-based malodors such as fish and urine malodors and sulfur-based malodors  
such as garlic, onion, foot, and fecal malodors are difficult to combat. Further, the time required  
for a product to noticeably combat malodors may create consumer doubt as to a product's  
efficacy on malodors. For example, a consumer may leave the treated space before the product  
15 begins to noticeably reduce the malodors. Even further, certain compositions may cause fabrics  
on surrounding surfaces to turn yellow or brown under natural light and/or make fabrics  
susceptible to soiling, particularly compositions that contain certain types or amounts of  
aldehydes and/or surfactants. The difficulty in overcoming a broad range of malodors has  
spawned a diverse assortment of products to neutralize, mask, or contain malodors.

20 There remains a continuing need for a malodor control composition that neutralizes a  
broad range of malodors, including amine-based and sulfur-based malodors, while not  
overpowering malodors with an overwhelming perfume and while not soiling and staining  
fabrics.

### 25 SUMMARY OF THE INVENTION

According to one embodiment of the present invention, there is provided a composition  
for reducing malodor comprising: (a) an effective amount of a metallated malodor control  
polymer comprising a water-soluble metal ion and a polymer selected from the group consisting  
of: partially hydrolyzed polyvinylamine (PVam), partially hydrolyzed hydrophobically modified  
PVam, polyethyleneimine (PEI), hydrophobically modified (PEI), polyamidoamine (PAam),  
hydrophobically modified PAam, polyallyamine (PAam), hydrophobically modified (PAam),  
polyetheramine (PEam), hydrophobically modified PEam, and mixtures thereof; (b) a malodor

counteractant comprising a perfume material; and (c) an aqueous carrier; wherein said composition comprises a pH of about 5 to about 10.

According to another embodiment, there is provided a method of reducing malodor comprising the steps of: (a) providing a composition comprising an effective amount of a metallated malodor control polymer comprising a water-soluble metal ion and a polymer selected from the group consisting of: partially hydrolyzed PVam, partially hydrolyzed hydrophobically modified PVam, PEI, hydrophobically modified PEI, PAMam, hydrophobically modified PAMam, PAam, hydrophobically modified PAam, PEam, hydrophobically modified PEam, and mixtures thereof; a malodor counteractant comprising a perfume material; and an aqueous carrier; wherein said composition comprises a pH of about 5 to about 10; and (b) dispersing an effective amount of said composition on an inanimate surface or in the air.

#### DETAILED DESCRIPTION OF THE INVENTION

The composition of the present invention is designed to deliver genuine malodor reduction and not function merely by using perfume to cover up or mask odors. A genuine malodor reduction provides a sensory and analytically measurable (e.g. gas chromatograph) malodor reduction. Malodors may include odors from food such as fish, onion, and garlic; odors from grease, body, mold/mildew, smoke, pet urine, sewage; and bathroom based odors. Thus, if the composition delivers a genuine malodor reduction, the composition will neutralize malodors in the air, on fabrics, and/or on other surfaces.

“Neutralize” or “neutralization” as used herein means chemically reacting with malodor components (e.g. the reaction of primary amines with aldehydes to form imines, reductive alkylation of amines, protonation and deprotonation of amines, polymerization or depolymerization); or suppressing the volatility of malodorous components such that other parts of the composition may react (e.g. acid – base neutralization); or physically entrapping odorous molecules such that they are not re-released into the air (e.g. cyclodextrin inclusion complexes as described herein).

The composition may also act as a barrier to prevent malodors from adhering to or penetrating a surface.

#### I. Composition

The composition for reducing malodor comprises an effective amount of a malodor control polymer, a malodor counteractant comprising a perfume material, and an aqueous carrier.

In one embodiment, the composition may be free of ingredients that soil or stain fabrics treated with or surrounding the treated surface. In such embodiments, the total amount of surfactants (e.g. solubilizer, wetting agent) in the composition is from 0% to about 3% or no more than about 3%, alternatively from 0% to about 1% or no more than about 1%, alternatively from 0% to about 0.9% or no more than about 0.9%, alternatively from 0% to about 0.7% or no more than 0.7%, alternatively from 0% to about 0.5% or no more than about 0.5%, alternatively from 0% to about 0.3% or no more than about 0.3%, by weight of the composition.

Compositions with higher concentrations may make fabrics susceptible to soiling and/or leave unacceptable visible stains on fabrics as the solution evaporates.

A. Hydrophobically Modified Malodor Control Polymers

The composition of the present invention includes a hydrophobically modified malodor control polymer (HMP). A HMP is formed from a polyamine polymer having a primary, secondary, and/or tertiary amine group that is modified with a hydrophobic group such as an alkyl, alkyloxy, or amide. Although the amine group has been modified, a HMP has at least one free and unmodified primary, secondary, and/or tertiary amine group, to react with malodorous components. Not wishing to be bound by theory, hydrophobic modification may increase a polymer's affinity for hydrophobic odors, thus enabling interactions between the odor molecules and active amine sites.

A HMP of the present invention has the general formula (I):



wherein:

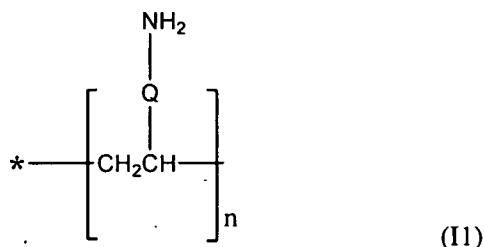
P is a polyamine polymer;

R is a C2 to C26 hydrophobic group; and

x is the total degree of substitution, which is less than 100%, of amine sites on the polymer.

1. Polyamine Polymer

HMPs may include a polyamine polymer backbone that can be either linear or cyclic. HMPs can also comprise polyamine branching chains to a greater or lesser degree. The polyamine polymer has a general formula (I1):

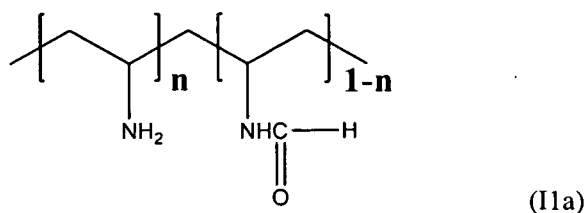


5 where Q is an integer having values between 0-3.

Non-limiting examples of polyamine polymers include polyvinylamines (PVams), polyethyleneimines (PEIs) that are linear or branched, polyamidoamines (PAMams), polyallylamines (PAams), polyetheramines (PEams) or other nitrogen containing polymers, such as lysine, or mixtures of these nitrogen containing polymers.

a. PVams

In one embodiment, the HMP includes a PVam backbone. A PVam is a linear polymer with pendent, primary amine groups directly linked to the main chain of alternating carbons. PVams are manufactured from hydrolysis of poly(N-vinylformamide) (PVNF) which results in the conversion of formamide units to amino groups as described by the following formula (I1a):



where n is a number from 0.1 to 0.99 depending on the degree of hydrolysis. For instance, in 95% hydrolyzed PVam polymer, n will be 0.95 while 5% of the polymer will have formamide units.

20 PVams may be partially hydrolyzed meaning that 1% to 99%, alternatively 30% to 99%, alternatively 50% to 99%, alternatively 70% to 99%, alternatively 80% to 99%, alternatively 85% to 99%, alternatively 90% to 99%, alternatively 95% to 99%, alternatively 97% to 99%, alternatively 99% of the PVam is hydrolyzed. It has been found that high degree of hydrolysis of PVam increases the resulting polymer's ability to mitigate the odors.

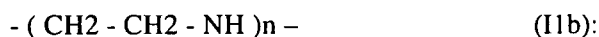
PVams that can be hydrolyzed may have an average molecular weight (MW) of 5,000 to 350,000. Suitable hydrolyzed PVams are commercially available from BASF. Some examples include Lupamin™ 9095, 9030, 5095, and 1595.

Such hydrolyzed PVams may then be hydrophobically modified. Hydrophobic  
5 modification, as described herein, may further improve malodor removal efficacy.

b. Polyalkylenimine/PEIs

In another embodiment, the HMP includes a polyalkylenimine backbone. Polyalkylenimines include PEIs and polypropylenimines as well as the C4-C12 alkylenimines.

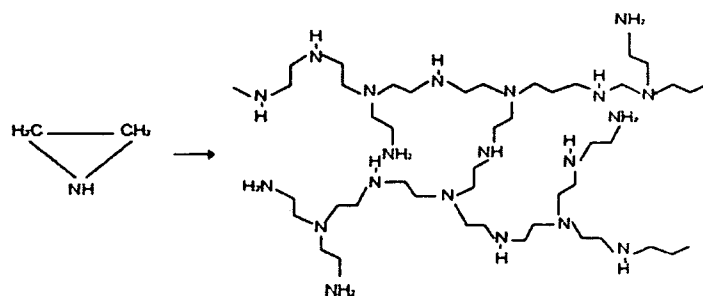
PEI is a suitable polyalkylenimine. The chemical structure of a PEI follows a simple  
10 principle: one amine function and two carbons. PEIs have the following general formula (I1b):



where  $n = 10 - 105$

15 PEIs constitute a large family of water-soluble polyamines of varying molecular weight, structure, and degree of modification. They may act as weak bases and may exhibit a cationic character depending on the extent of protonation driven by pH.

PEIs are produced by the ring-opening cationic polymerization of ethyleneimine as shown below.



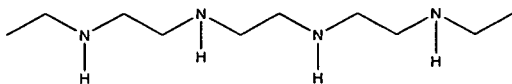
20

PEIs are believed to be highly branched containing primary, secondary, and tertiary amine groups in the ratio of about 1:2:1. PEIs may comprise a primary amine range from about 30% to about 40%, alternatively from about 32% to about 38%, alternatively from about 34% to about 36%. PEIs may comprise a secondary amine range from about 30% to about 40%, alternatively  
25 from about 32% to about 38%, alternatively from about 34% to about 36%. PEIs may comprise

a tertiary amine range from about 25% to about 35%, alternatively from about 27% to about 33%, alternatively from about 29% to about 31%.

Other routes of synthesis may lead to products with a modified branched chain structure or even to linear chain PEIs. Linear PEIs contain amine sites in the main chain while the  
5 branched PEIs contain amines on the main and side chains. Below is an example of a linear PEI

Linear PEI



10 The composition of the present invention may comprise PEIs having a MW of about 800 to about 2,000,000, alternatively about 1,000 to about 2,000,000, alternatively about 1,200 to about 25,000, alternatively about 1,300 to about 25,000, alternatively about 2,000 to about 25,000, alternatively about 10,000 to about 2,000,000, alternatively about 25,000 to about 2,000,000, alternatively about 25,000.

15 In one embodiment, the PEI may have a specific gravity of 1.05 and/or an amine value of 18 (mmol/g, solid). For clarity, such specific gravity and/or amine value of the PEI describes the PEI before it is modified or added as part of an aqueous composition. One skilled in the art will appreciate, for example, the primary and secondary amino groups may react with other components of the composition.

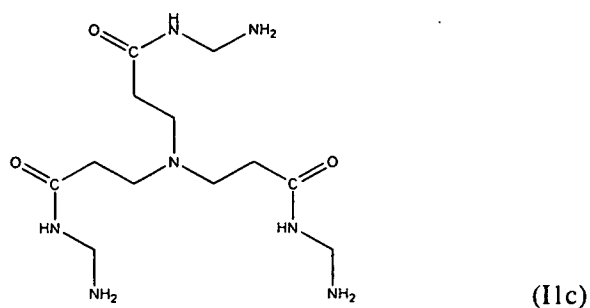
20 Exemplary PEIs include those that are commercially available under the tradename Lupasol® from BASF or the tradename Epomine™ from Nippon Shokubia.

In some embodiments, less than 100% of the active amine sites are substituted with hydrophobic functional groups, alternatively about 0.5% to about 90%, alternatively about 0.5% to about 80%, alternatively about 0.5% to about 70%, alternatively about 0.5% to about 60%,  
25 alternatively about 0.5% to about 50%, alternatively about 0.5% to about 40%, alternatively about 0.5% to about 35%, alternatively about 0.5% to about 30%, alternatively about 1% to about 30%, alternatively about alternatively about 1% to about 25%, alternatively about 1% to about 20%, alternatively about 5% to about 20%, alternatively about 10% to about 30%, alternatively about 20% to about 30%, alternatively about 20% of the active amine sites are substituted with  
30 hydrophobic functional groups. When a PEI has active amine sites that are fully substituted with

hydrophobic functional groups, such hydrophobically modified PEI may have no activity for malodor control.

c. PAMams

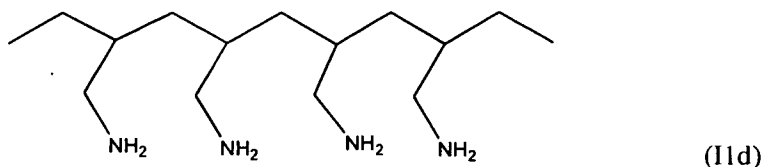
In another embodiment, the HMP includes a PAMam backbone. PAMams are polymers whose backbone chain contains both amino functionalities (NH) and amide functionalities (NH-C(O)). PAMams also contain primary amine groups and/or carboxyl groups at the termini of polymer chain. The general structure of a PAMam is below (I1c):



10

d. PAams

In another embodiment, the HMP includes a PAam backbone. PAams are prepared from polymerization of allyamine— $C_3H_5NH_2$ . Unlike PEIs, they contain only primary amino groups that are linked to the side chains. The general formula for a PAAm is shown below (I1d):



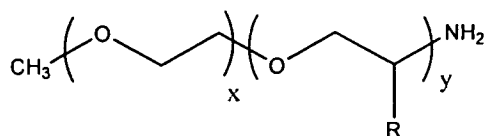
15

e. PEams

In yet another embodiment, the HMP includes a PEam backbone. PEams contain a primary amino groups attached to the end of a polyether backbone. The polyether backbone may be based on propylene oxide (PO), ethylene oxide (EO), or mixed PO/EO. The general formula for a PEam is shown below (I1e):

20

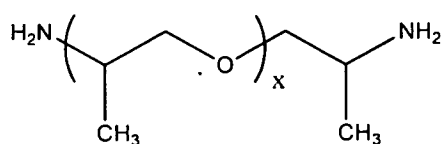




R = H for (EO) or CH3 for (PO)

(11e)

These so-called monoamines, M-series, are commercially available from Hunstman under the tradename Jeffamine<sup>®</sup> monoamines. In another embodiment, the HMP includes a PEam backbone having diamines as shown below (11f):



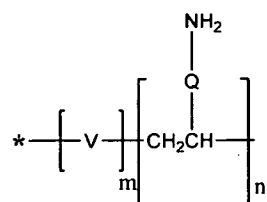
5

(11f)

Diamines are commercially available from Hunstman under the tradename Jeffamine<sup>®</sup> diamines (e.g. D, ED, and EDR series). The HMP may also include a PEam backbone having triamines (e.g. Jeffamine<sup>®</sup> triamine T-series).

2. Other Polymer Units

10 HMPs may include a copolymer of nitrogen-containing polymers having the formula (12):



(12)

where Q is an integer having values between 0-3 and V is a co-monomer.

15 Non-limiting examples of (12) unmodified polymers include vinylamides, vinyl pyrrolidone, vinylimidazole, vinylesters, vinylalcohols, and mixtures thereof.

3. Hydrophobic Group

20 The hydrophobic group of the HMP may be linear, branched, or cyclic alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, alkyl carboxyl, alkyloxide, alkanediyl, amide, or aryl. In some embodiments, the hydrophobic group is a C2 to C26, alternatively a C2 to C12, alternatively a C2 to C10, alternatively a C4 to C10, alternatively a C16 to C26, alternatively a C6. Where cyclodextrin is included in a formulation, it may be desirable to use a HMP that has been modified with a C2 to C10 alkyl group, alternatively a C16-C26 alkyl group, alternatively a C6 alkyl group, since such alkyl groups are cyclodextrin compatible.

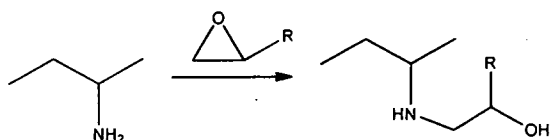
#### 4. Hydrophobic Modification

The polyamine backbones are hydrophobically modified in such a manner that at least one nitrogen, alternatively each nitrogen, of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

5 There are many ways of hydrophobically modifying polyamine polymers. Generally, the modification is one directed to the primary, secondary, and/or tertiary amines of the polymer. By reacting the unmodified polyamine backbone with appropriate reagents, one can render the polyamine polymer hydrophobic, thereby increasing efficacy for malodor removal. The following are non limiting examples of the ways to prepare the HMPs disclosed herein.

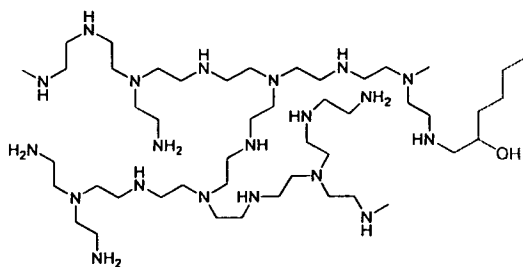
##### 10 a. Alkoxylation

The reaction of polyamine polymer with an epoxide containing hydrocarbons (R) results in substitution of one or more nitrogen moieties on the polymer.



wherein  $R > C_2$ .

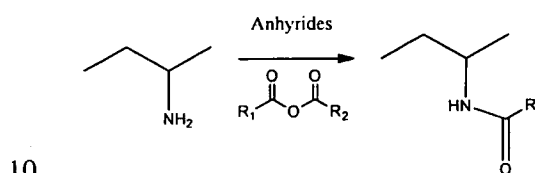
15 Non-limiting example of such hydrocarbons include C2-C26 chain that is substituted or unsubstituted, branched or unbranched. For example, a reaction of dodeceneoxide with PEI polymer results in C6-HMP disclosed herein having a structure shown below.



20 Alternatively, one can modify the base polymer by reacting with EO first and then finish it by alkylation. Additional modifications might also include capping the modified polymer with EO groups if more water solubility is desired. Alternatively, hydroxyl groups can be substituted by further reacting the alkoxyated polymers as described in subparagraph c below.

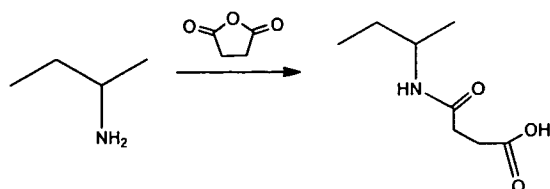
##### b. Amidation

Reaction of polyamine polymers with amide-forming reagents such as anhydrides, lactones, isocyanates, or carboxylic acids results in substitution of one or more nitrogen moieties on the polymer rendering hydrophobic character. Prior to amidation, one can begin with partial substitution of amine sites with EO or PO and then carry out amidation on the remaining amine moieties. Reaction of anhydrides with polyamine polymers leads to the formation of amide units of the polymer by partial substitution of the primary/secondary amine sites. Non-limiting examples include non-cyclic carboxylic anhydrides such as acetic anhydride or cyclic carboxylic anhydrides such as maleic anhydride, succinic anhydride or phthalic anhydride. For example, the reaction of a polyamine with acetic anhydride introduces amide units onto the polymer.

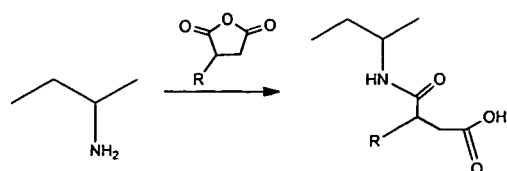


wherein  $R > C_2$ .

On the other hand, the reaction of polyamine polymer with cyclic anhydrides introduces amido acid units onto the polymer.

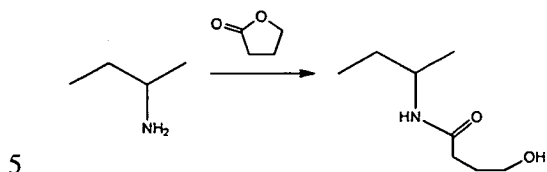


15 More hydrophobically modified derivatives can be prepared by the use of cyclic anhydrides such as alkylene succinic anhydrides, dodecanyl succinic anhydride, or polyisobutane succinic anhydride.

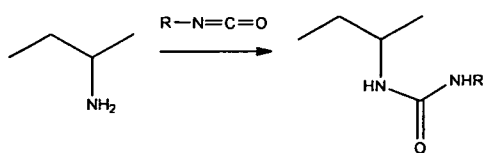


wherein  $R > C_2$ .

Polyamine polymers containing hydroxyl-terminated polyamido units can be prepared by reacting the polymers with lactones. The use of more hydrophobic alkyl substituted lactones may introduce more hydrophobicity. Optionally, hydroxyl-end groups can be further substituted with functional groups as described in the following subparagraph c.



Isocyanate reactions with polyamine polymers result in the formation of urea derivatives as shown below.

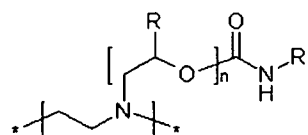


wherein R>C2.

10 c. Alkoxylation followed by substitution of hydroxyl groups

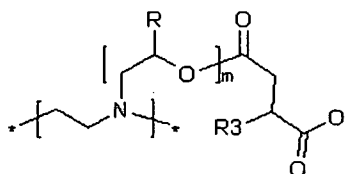
Additional functional groups can be covalently bonded to an OH group on the alkoxyated polyamine polymers (“x” in formula (I)). This can be achieved by further reacting the alkoxyated polymers with bifunctional compounds such as epihalohydrins such as epichlorohydrin, 2-halo acid halides, isocyanates or diisocyanates such as trimethylhexane diisocyanate, or cyclic carboxylic anhydrides such as maleic anhydride or phthalic anhydride.

15 For example, the reaction of alkoxyated PEI with isocyanates yields:



wherein R>C2.

Reaction products of alkoxyated PEI and alk(en)ylsuccinic anhydrides yield



wherein  $R > C_2$ .

All these HMPs disclosed herein can be optionally capped with hydrophilic groups, such as EO, to render water solubility if necessary.

5 In some embodiments, about 0.5% to about 90% of the amine groups on the entire unmodified polyamine polymer may be substituted with a hydrophobic group, alternatively about 0.5% to about 80%, alternatively about 0.5% to about 70%, alternatively about 0.5% to about 60%, alternatively about 0.5% to about 50%, alternatively about 0.5% to about 40%, alternatively about 0.5% to about 35%, alternatively about 0.5% to about 30%, alternatively about 1% to about 30%, alternatively about 1% to about 25%, alternatively about 1% to about 20%, alternatively about 5% to about 20%, alternatively about 10% to about 30%, alternatively about 20% to about 30%, alternatively about 20% of the amine groups on the entire unmodified polyamine polymer may be substituted with a hydrophobic group. The level of substitution of the amine units can be as low as 0.01 mol percent of the theoretical maximum where all primary, secondary, and/or tertiary amine units have been replaced.

HMPs for use herein may have a MW from about 150 to about  $2 \times 10^6$ , alternatively from about 400 to about  $10^6$ , alternatively from about 5000 to about  $10^6$ .

20 Malodor control polymers suitable for use in the present invention are water-soluble or dispersible. In some embodiments, the primary, secondary, and/or tertiary amines of the polyamine chain are partially substituted rendering hydrophobicity while maintaining the desired water solubility. The minimum solubility index of a HMP may be about 2% (i.e. 2g/100ml of water). A suitable HMP for an aqueous fabric refresher formulation may have a water solubility percentage of greater than about 0.5% to 100%, alternatively greater than about 5%, alternatively greater than about 10%, alternatively greater than about 20%.

25 The water solubility index can be determined by the following test.

#### Water Solubility

This test illustrates the benchmarking ambient temperature water solubility of HMPs against beta-cyclodextrin (1.8 g/100 ml) and hydroxypropyl modified beta cyclodextrin (60+

g/100 ml). 1% water solubility is used as a screening criteria for HMPs suitable for use in aqueous fabric refresher formulations.

Room temperature equilibrium water solubility of polymers may be determined by adding weighed quantities of polymers into 100 ml of deionized water and allowing the added polymers to completely dissolve. This process is repeated until the added polymers are no longer soluble. Equilibrium water solubility is then calculated based on how much polymer is dissolved in 100 ml water.

Polymer	Equilibrium Water Solubility (g/100 ml water at 25 oC)
Lupasol G100 (PEI 5,000)	miscible at all levels (70+)
C6 modified PEI 1800 (0.25 C6 / NH)	30+
Dodecene oxide modified PEI5,000 (0.1 dodecene oxide/NH)	~24
Dodecene oxide modified PEI5,000 (0.2 dodecene oxide/NH)	~4
Dodecene oxide modified PEI5,000 (0.5 dodecene oxide/NH)	< 0.1
Dodecene oxide modified PEI25,000 (0.1 dodecene oxide/NH)	~21
Dodecene oxide modified PEI25,000 (0.2 dodecene oxide/NH)	<0.1
Dodecene oxide and EO modified PEI25,000 (0.8 EO and 0.2 dodecene oxide/NH)	~6

When the polymer is not water soluble (e.g. less than 0.05%), capping with a hydrophilic molecule may be desired to assist with water solubility. Suitable hydrophilic molecules include EO or other suitable hydrophilic functional groups.

Suitable levels of HMPS in the present composition are from about 0.01% to about 10%, alternatively from about 0.01% to about 2%, alternatively from about 0.01% to about 1%, alternatively from about 0.01% to about 0.8%, alternatively from about 0.01% to about 0.6%, alternatively from about 0.01% to about 0.1%, alternatively from about 0.01% to about 0.07%,

alternatively about 0.07%, alternatively about 0.5%, by weight of the composition. Compositions with higher amount of HMPs may make fabrics susceptible to soiling and/or leave unacceptable visible stains on fabrics as the composition evaporates off of the fabric.

Suitable HMPs include partially hydrolyzed hydrophobically modified PVams, hydrophobically modified PEIs, hydrophobically modified PAMams, hydrophobically modified PAams, and mixtures thereof.

#### B. Metal Coordinated Complexes

The composition of the present invention may include a malodor control polymer that is a metal coordinated complex or a metallated polymer. The metal coordinated complex comprises a metal and any unmodified polymer disclosed herein (i.e. polyamine polymers), a HMP disclosed herein, or mixtures thereof. Metal coordination may improve the odor neutralization of a malodor control polymer. Metal coordination might also provide reduction of malodor from microbial sources. Suitable metals that coordinate with such polymers include zinc, copper, silver, and mixtures thereof. Suitable metals also include Na, K, Ca, Mg, and non-transition metals, including Sn, Bi, and Al.

Metals that are not coordinated to a polymer may deliver some malodor control using highly ionizable water soluble salts such as zinc chloride or silver nitrate. But, such metals present drawbacks in aqueous formulations. Zinc ions and silver ions have the ability to form insoluble salts with nucleophilic compounds such as valeric acid, skatole, hydrogen sulfide, mercaptan, and like compounds that are typically the cause of environmental malodor. However, zinc chloride aqueous solutions, over time, tend to form insoluble oxychlorides and hydroxides that have low water solubility. As a result, aqueous formulations containing zinc chloride are traditionally kept below pH 4.5 in order to avoid the formation of these insoluble salts that result in cloudy formulations. Just like zinc salts, silver compounds suffer from pH stability, formation of insoluble salts with anions typically present in water. Silver ion, additionally, is very light sensitive and can easily be first reduced to silver metal by photo-reduction process and then oxidized to black silver oxide after lengthy light exposure. For aqueous spray applications, these issues may be considered detriments.

Coordinating zinc ion or silver ion with polyamine polymers may overcome the limitations described above, resulting in water soluble complexes with a wide range pH stability (e.g. > 4.5). Additionally, these complexes may provide synergistic malodor control and prevention efficacy not previously seen with the polymers and metal salts, such as zinc chloride,

alone. For example, by coordinating zinc ions with HMPs, we also discovered efficacy for hydrophobic sulfur odors which traditional zinc salts are not effective against. Because hydrophobic modification might decrease Zn binding capacity as well as water solubility of the polymer, one may wish to control the degree of such modification.

5 Nitrogen containing polymers, such as PEIs, have high binding capacity for metals due to availability of basic nitrogen sites. The strength of the metal-nitrogen ligand interaction is influenced by several factors including the microstructure of polymer, functionality of the binding sites, the density of nitrogen ligands in the polymer, steric constraints, electrostatic interactions, pH, pKa of the polymer, and oxidation state, size, and electronic configuration of  
10 metal. Unlike traditional chelators, such as ethylenediamine (bi-dentate), ethylenediaminetetraacetic acid, or EDTA (hexa-dentate), polymers can be considered poly-dentate due to high density of binding sites. As a result, the chemical formula of metal coordination complex is highly variable.

In some embodiments, the metal coordinated complex is a HMP having at least 5% of its  
15 primary, secondary, and/or tertiary amine sites left unmodified for not only malodor efficacy but also for metal binding capacity.

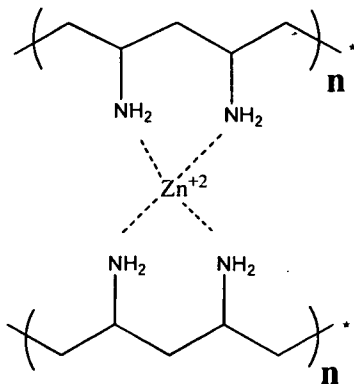
Metal coordinated complexes may have a metal / polymer weight ratio from 0.001 and 50, alternatively from 0.001 to 20, alternatively from 0.001 to 15, alternatively from 0.001 to 10, alternatively from 0.005 to 5.0, alternatively from 0.1 to 1.0, alternatively from 0.1 to 0.5,  
20 alternatively from 0.001 to 0.01.

Metal polymer coordination complexes can be prepared by reacting suitable metal salts with polyamine polymers containing primary or secondary amine sites. The resulting complex can be represented by a general formula,  $M_xP_y$ ; where M is metal, P is an unmodified polyamine polymer or a HMP, and x and y are integers and dependent on coordination number of metal ion,  
25 number of available coordinating sites on the polymer, and pH.

It is believed there is strong competition between the metal ions and protons for the electron pairs on the amine groups of polyamine polymers. This competition is favored for the metal ions at higher pH values, where amine groups are deprotonated and more available for metal binding. It may be assumed that only the non-protonated nitrogen sites of the polymers are  
30 active towards the metal ions; then polyamine polymers will have the highest metal binding capacity at high pH levels. Metal ions can coordinate to four to eight ligands. Zinc ion is known to prefer 4-coordinated tetrahedral sites as shown below, while copper ions tend to form



octahedral coordinations. Examples of possible zinc polymer structures are shown below. For example, zinc ion can bind to 2 nitrogen units on each PVam. Alternatively, a polymer can fold around zinc ion and utilize four nitrogen to form tetrahedral coordination.



5

Protonation and metal binding ability of polyamine polymers are also influenced by polymer microstructure. For instance, branched PEIs have amine sites located in the main and side chains whereas PVams have only primary amino groups linked directly to the main chain. As a result, PVams having ligands only in the side chain are of greater advantage for protonation than the case having in the main chain branched PEIs. Therefore, one might expect different metal binding capacities for PVam and PEI at the same pH levels. Due to its linear structure, PVams show relatively strong interaction in neighboring ammonium groups on the polymer chain in comparison to branched PEIs. This difference is also expected to influence the metal binding capacity of the polymers.

15 In one embodiment, the composition includes a zinc polymer complex having a pH of 7. It is believed that at such pH the competition between protonation and metal coordination of amine sites provides a unique coordination environment for zinc. This unique bonding makes the zinc ions readily available for additional interactions with malodor molecules, while preventing the release of zinc ions from the metal coordinated complex.

### 20 C. Malodor Counteractants

The composition may utilize one or more malodor counteractants. Malodor counteractants may include components which lower the vapor pressure of odorous compounds, solubilize malodor compounds, physically entrap odors (e.g. flocculate or encapsulate), physically bind odors, or physically repel odors from binding to inanimate surfaces.

#### 25 1. Aliphatic aldehydes

In one embodiment, the composition comprises a perfume mixture having one or more fabric-safe, non-yellowing aliphatic aldehydes. Certain types of aldehydes that predominately comprise a straight chain aliphatic backbone will not discolor fabrics, unlike products that utilize types of aldehydes that contain multiple double bonds and benzene rings. The following table illustrates the selection of aldehydes to avoid fabric yellowing.

Aldehyde Solution Tested	Fadometer Test on treated Fabric (0.75 grams of product are pipetted onto a 4 inch X 4 inch (10 cm X 10 cm) swatch which is then subjected to 5 hours of exposure to simulated sunlight using a SUNTEST CPS+ model Fadometer supplied by Atlas, Chicago, Illinois, USA.
Control- untreated fabric swatch	No yellowing
1000 ppm amylic cinnamic aldehyde (aromatic)	Yellowish brown
1000 ppm citronellal (aromatic)	Yellowish brown
1000ppm citral aldehyde (aliphatic)	No yellowing
1000 ppm lauric aldehyde (aliphatic)	No yellowing

Examples of suitable aliphatic aldehydes are R-COH where R is saturated C<sub>7</sub> to C<sub>22</sub> linear and/or branched with no more than two double bonds. Examples of suitable aliphatic aldehydes are bourgeonal, citral, citronellyl oxyacetaldehyde, cymal, decyl aldehyde, helional, hexyl cinnamic aldehyde, lauric aldehyde, ligustral, lyral, melonal, methyl dihydro jasmonate, methyl nonyl acetaldehyde, methyl phenyl carbinyl acetate, nonyl aldehyde, octyl aldehyde, oxane, P. T. buccinal, polysantol, rhubafuran, tripal, or mixtures thereof.

In one embodiment, the composition includes at least one aliphatic aldehyde selected from the group consisting of: bourgeonal, citral, citronellyl oxyacetaldehyde, cymal, decyl

aldehyde, helional, hexyl cinnamic aldehyde, lauric aldehyde, ligustral, lylal, melonal, methyl dihydro jasmonate, methyl nonyl acetaldehyde, methyl phenyl carbonyl acetate, nonyl aldehyde, 2, 6 - nonadien-1-al, octyl aldehyde, oxane, P.T. bucinal, polysantol, rhubafuran, tripal, and mixtures thereof.

5 In another embodiment, the composition includes at least one aliphatic aldehyde selected from the group consisting of: burgeonal, cymal, hexyl cinnamic aldehyde, mmethyl dihydro jasmonate, methyl nonyl acetaldehyde, P.T. bucinal, and mixtures thereof.

The aliphatic aldehydes may be present in an amount from about 0.001% to about 10%, alternatively from about 0.001% to about 5%, alternatively from about 0.01% to about 1%,  
 10 alternatively from about 0.02% to about 1%, alternatively from about 0.02% to about 0.5%, alternatively from about 0.02% to about 0.06%, alternatively about 0.06%, by weight of the composition.

In addition to aliphatic aldehydes, the composition may also include perfume materials for their scent experience including enones, ketones, ionones including ionone alpha, ionone  
 15 beta, ionone gamma methyl, or mixtures thereof. Suitable perfume materials are discussed in US 5,714,137. The composition may contain an effective amount of perfume to provide a freshening fragrance when first sprayed, some lingering fragrance, and some extra fragrance to be released upon fabric rewetting. It may be desirable for the aliphatic aldehydes to have virtually no negative impact on the desired perfume character.

20 Certain malodor counteractants may be odoriferous and negatively impact the overall character of the fragrance. In this case, a perfume/malodor counteractant premix is formed such that the perfume raw materials used are selected to neutralize any odor of the malodor counteractants. This odor neutralized premix can then be added to a parent perfume mixture without affecting the character of the parent fragrance. This permits the malodor counteractants  
 25 to be used broadly with a large variety of fragrance types.

The following are non-limiting examples of perfume formulations that include fabric-safe malodor counteractants.

(1) Pine

Material Name	Amount
Rosemary	10.00
Spike Lavender	10.00

Lavandin Grosso	5.00
Spruce (conf.-manh)	5.00
Camphor Gum	5.00
Melonal	0.30
Eucalyptol	15.00
Iso Menthone	15.00
Iso Bornyl Acetate	21.70
Ionone Beta	8.00
Iso E Super	5.00
	100.00

## (2) Ozonic

Material Name	Amount
Xi Aldehyde	8.00
2 <sup>6</sup> Nonadienol 10% In Dpg	5.00
Helional	13.00
Hydroxycitronellal	11.50
Calone 1951	0.50
2 <sup>6</sup> - Nonadien-1-al/10% In Dpg	5.00
Lyral	20.00
Melonal	1.00
Iso Menthone	10.00
Floralozone	10.00
Bourgeonal	10.00
Delta Muscenone 962191	1.00
Habanolide 100%	5.00
	100.00

## (3) Fruity

Material Name	Amount
Fruitate	5.00
Orange Terpenes	13.00
Ethyl Acetoacetate	3.00
2` 6 Nonadienol 10% In Dpg	1.00
Ethyl Acetate	3.00
Benzaldehyde	2.00
Prenyl Acetate	8.00
Benzyl Acetate	15.00
2` 6 - Nonadien-1-al/10% In Dpg	1.00
Ethyl-2-methyl Butyrate	8.00
Amyl Acetate	3.00
Cis 3 Hexenyl Acetate	3.00
Methyl Dihydro Jasmonate	10.00
Ligustral	5.00
Melonal	1.00
Ethyl 2 Methyl Pentanoate	8.00
Hexyl Acetate	8.00
Habanolide 100%	3.00
	100.00

## 5 (4) Citrus

Material Name	Amount
Orange Terpenes	20.00
Lemon Terpenes X5 Fold	20.00

Lime Oil Cf-8-1285-1 (conf.- berje)	10.00
Grapefruit Phase C- Ref. N*12245	20.00
Italian Orange Phase Oil	22.90
Delta Muscenone 962191	0.50
Oxane	0.30
Iso Menthone	1.00
Rhubafuran	0.30
Habanolide 100%	5.00
	100.00

## (5) Floral

Material Name	Amount
Spike Lavender	5.00
Rosemary	5.00
Helional	10.00
Hydroxycitronellal	10.00
Benzyl Acetate	9.30
Lylal	20.00
Ligustral	2.00
Melonal	0.20
Eucalyptol	2.00
Iso Menthone	8.00
Bourgeonal	20.00
Undecavertol	3.00
Delta Muscenone 962191	0.50
Habanolide 100%	5.00

	100.00
--	--------

In certain cases, fabrics that are laundered will have residual brighteners deposited from detergents with which they are washed. Therefore, it may be desirable for the malodor counteractant to be compatible with brighteners so that the composition will not discolor any  
5 fabrics with which it comes into contact. A number of the examples above are compatible with brighteners.

### 2. Low molecular weight polyols

Low molecular weight polyols with relatively high boiling points, as compared to water, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, and/or glycerine may be utilized as a malodor counteractant for improving odor  
10 neutralization of the freshening composition of the present invention. Some polyols, e.g., dipropylene glycol, are also useful to facilitate the solubilization of some perfume ingredients in the composition of the present invention.

The glycol used in the composition of the present invention may be glycerine, ethylene glycol, propylene glycol, dipropylene glycol, polyethylene glycol, propylene glycol methyl ether, propylene glycol phenyl ether, propylene glycol methyl ether acetate, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, dipropylene glycol n-propyl ether, ethylene glycole phenyl ether, diethylene glycol n-butyl ether, dipropylene glycol n-butyl ether, diethylene glycol mono butyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, tripropylene glycol n-butyl ether, other glycol ethers, or mixtures thereof. In one embodiment, the glycol used  
15 is ethylene glycol, propylene glycol, or mixtures thereof. In another embodiment, the glycol used is diethylene glycol.

Typically, the low molecular weight polyol is added to the composition of the present invention at a level of from about 0.01% to about 5%, by weight of the composition, alternatively  
25 from about 0.05% to about 1%, alternatively from about 0.1% to about 0.5%, by weight of the composition. Compositions with higher concentrations may make fabrics susceptible to soiling and/or leave unacceptable visible stains on fabrics as the solution evaporates off of the fabric. The weight ratio of low molecular weight polyol to the HMP is from about 500:1 to about 4:1, alternatively from about 1:100 to about 25:1, alternatively from about 1:50 to about 4:1,  
30 alternatively about 4:1.

### 3. Cyclodextrin

In some embodiments, the composition may include solubilized, water-soluble, uncomplexed cyclodextrin. As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in a donut-shaped ring. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structure with a hollow interior of a specific volume. The "lining" of the internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms, therefore this surface is fairly hydrophobic. The unique shape and physical-chemical property of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity. Many perfume molecules can fit into the cavity.

Cyclodextrin molecules are described in US 5,714,137, and US 5,942,217. Suitable levels of cyclodextrin are from about 0.1% to about 5%, alternatively from about 0.2% to about 4%, alternatively from about 0.3% to about 3%, alternatively from about 0.4% to about 2%, by weight of the composition. Compositions with higher concentrations can make fabrics susceptible to soiling and/or leave unacceptable visible stains on fabrics as the solution evaporates off of the fabric. The latter is especially a problem on thin, colored, synthetic fabrics. In order to avoid or minimize the occurrence of fabric staining, the fabric may be treated at a level of less than about 5 mg of cyclodextrin per mg of fabric, alternatively less than about 2 mg of cyclodextrin per mg of fabric.

#### D. Buffering agent

The composition of the present invention may include a buffering agent which may be a dibasic acid, carboxylic acid, or a dicarboxylic acid like maleic acid. The acid may be sterically stable, and used in this composition solely for maintaining the desired pH. The composition may have a pH from about 6 to about 8, alternatively from about 6 to about 7, alternatively about 7, alternatively about 6.5

Carboxylic acids such as citric acid may act as metal ion chelants and can form metallic salts with low water solubility. As such, in some embodiments, the freshening composition is essentially free of citric acids. The buffer can be alkaline, acidic or neutral.



Other suitable buffering agents for freshening compositions of this invention include biological buffering agents. Some examples are nitrogen-containing materials, sulfonic acid buffers like 3-(N-morpholino)propanesulfonic acid (MOPS) or N-(2-Acetamido)-2-aminoethanesulfonic acid (ACES), which have a near neutral 6.2 to 7.5 pKa and provide adequate buffering capacity at a neutral pH. Other examples are amino acids such as lysine or lower alcohol amines like mono-, di-, and tri-ethanolamine. Other nitrogen-containing buffering agents are tri(hydroxymethyl)amino methane (HOCH<sub>2</sub>)<sub>3</sub>CNH<sub>3</sub> (TRIS), 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-propanol, 2-amino-2-methyl-1,3-propanol, disodium glutamate, N-methyl diethanolamide, 2-dimethylamino-2-methylpropanol (DMAMP), 1,3-bis(methylamine)-cyclohexane, 1,3-diamino-propanol N,N'-tetra-methyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (bicine) and N-tris (hydroxymethyl)methyl glycine (tricine). Mixtures of any of the above are also acceptable.

The compositions may contain at least about 0%, alternatively at least about 0.001%, alternatively at least about 0.01%, by weight of the composition, of a buffering agent. The composition may also contain no more than about 1%, alternatively no more than about 0.75%, alternatively no more than about 0.5%, by weight of the composition, of a buffering agent.

#### E. Solubilizer

The composition of the present invention may contain a solubilizing aid to solubilize any excess hydrophobic organic materials, particularly any perfume materials, and also optional ingredients (e.g., insect repelling agent, antioxidant, etc.) which can be added to the composition that are not readily soluble in the composition, to form a clear solution. A suitable solubilizing aid is a surfactant, such as a no-foaming or low-foaming surfactant. Suitable surfactants are nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.

In some embodiments, the composition contains nonionic surfactants, cationic surfactants, and mixtures thereof. In one embodiment, the freshening composition contains hydrogenated castor oil. One suitable hydrogenated castor oil that may be used in the present composition is Basophor™, available from BASF.

Compositions containing anionic surfactants and/or detergent surfactants may make fabrics susceptible to soiling and/or leave unacceptable visible stains on fabrics as the solution evaporates off of the fabric. In some embodiments, the freshening composition is free of anionic surfactants and/or detergent surfactants.

When the solubilizing agent is present, it is typically present at a level of from about 0.01% to about 3%, alternatively from about 0.05% to about 1%, alternatively from about 0.01% to about 0.05%, by weight of the freshening composition. Freshening compositions with higher concentrations may make fabrics susceptible to soiling and/or leave unacceptable visible stains on fabrics as the solution evaporates off of the fabric.

F. Antimicrobial Compounds

The composition of the present invention may include an effective amount of a compound for reducing microbes in the air or on inanimate surfaces. Antimicrobial compounds are effective on gram negative and gram positive bacteria and fungi typically found on indoor surfaces that have contacted human skin or pets such as couches, pillows, pet bedding, and carpets. Such microbial species include *Klebsiella pneumoniae*, *Staphylococcus aureus*, *Aspergillus niger*, *Klebsiella pneumoniae*, *Streptococcus pyogenes*, *Salmonella choleraesuis*, *Escherichia coli*, *Trichophyton mentagrophytes*, and *Pseudomonas aeruginosa*. In some embodiments, the antimicrobial compounds are also effective on viruses such as H1-N1, Rhinovirus, Respiratory Syncytial, Poliovirus Type 1, Rotavirus, Influenza A, Herpes simplex types 1 & 2, Hepatitis A, and Human Coronavirus.

Antimicrobial compounds suitable in the composition of the present invention can be any organic material which will not cause damage to fabric appearance (e.g., discoloration, coloration such as yellowing, bleaching). Water-soluble antimicrobial compounds include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary compounds, dehydroacetic acid, phenyl and phenoxy compounds, or mixtures thereof.

In one embodiment, a quaternary compound is used. Examples of commercially available quaternary compounds suitable for use in the composition is Barquat available from Lonza Corporation; and didecyl dimethyl ammonium chloride quat under the trade name Bardac<sup>®</sup> 2250 from Lonza Corporation.

The antimicrobial compound may be present in an amount from about 500 ppm to about 7000 ppm, alternatively about 1000 ppm to about 5000 ppm, alternatively about 1000 ppm to about 3000 ppm, alternatively about 1400 ppm to about 2500 ppm, by weight of the composition.

G. Preservatives

The composition of the present invention may include a preservative. The preservative is included in the present invention in an amount sufficient to prevent spoilage or prevent growth of

inadvertently added microorganisms for a specific period of time, but not sufficient enough to contribute to the odor neutralizing performance of the composition. In other words, the preservative is not being used as the antimicrobial compound to kill microorganisms on the surface onto which the composition is deposited in order to eliminate odors produced by microorganisms. Instead, it is being used to prevent spoilage of the composition in order to increase shelf-life.

The preservative can be any organic preservative material which will not cause damage to fabric appearance, e.g., discoloration, coloration, bleaching. Suitable water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, parabens, propane diaol materials, isothiazolinones, quaternary compounds, benzoates, low molecular weight alcohols, dehydroacetic acid, phenyl and phenoxy compounds, or mixtures thereof.

Non-limiting examples of commercially available water-soluble preservatives for use in the present invention include a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Co.; 5-bromo-5-nitro-1,3-dioxane, available under the tradename Bronidox L® from Henkel; 2-bromo-2-nitropropane-1,3-diol, available under the trade name Bronopol® from Inolex; 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with acetic and digluconic acids; a 95:5 mixture of 1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione and 3-butyl-2-iodopropynyl carbamate, available under the trade name Glydant Plus® from Lonza; N-[1,3-bis(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxy-methyl) urea, commonly known as diazolidinyl urea, available under the trade name Germall® II from Sutton Laboratories, Inc.; N,N''-methylenebis{N'-[1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]urea}, commonly known as imidazolidinyl urea, available, e.g., under the trade name Abiol® from 3V-Sigma, Uicide U-13® from Induchem, Germall 115® from Sutton Laboratories, Inc.; polymethoxy bicyclic oxazolidine, available under the trade name Nuosept® C from Hüls America; formaldehyde; glutaraldehyde; polyaminopropyl biguanide, available under the trade name Cosmocil CQ® from ICI Americas, Inc., or under the trade name Mikrokill® from Brooks, Inc; dehydroacetic acid; and benzisothiazolinone available under the trade name Koralone™ B-119 from Rohm and Hass Corporation.

Suitable levels of preservative are from about 0.0001% to about 0.5%, alternatively from about 0.0002% to about 0.2%, alternatively from about 0.0003% to about 0.1%, by weight of the composition.

#### H. Wetting Agent

5 The composition may include a wetting agent that provides a low surface tension that permits the composition to spread readily and more uniformly on hydrophobic surfaces like polyester and nylon. It has been found that the aqueous solution, without such a wetting agent will not spread satisfactorily. The spreading of the composition also allows it to dry faster, so that the treated material is ready to use sooner. Furthermore, a composition containing a wetting  
 10 agent may penetrate hydrophobic, oily soil better for improved malodor neutralization. A composition containing a wetting agent may also provide improved "in-wear" electrostatic control. For concentrated compositions, the wetting agent facilitates the dispersion of many actives such as antimicrobial actives and perfumes in the concentrated aqueous compositions.

Non-limiting examples of wetting agents include block copolymers of EO and PO.  
 15 Suitable block polyoxyethylene-polyoxypropylene polymeric surfactants include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as the initial reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initial compounds with a single reactive hydrogen atom, such as C<sub>12-18</sub> aliphatic alcohols, are not generally compatible with the cyclodextrin. Certain of the block  
 20 polymer surfactant compounds designated Pluronic<sup>®</sup> and Tetronic<sup>®</sup> by the BASF-Wyandotte Corp., Wyandotte, Michigan, are readily available.

Nonlimiting examples of cyclodextrin-compatible wetting agents of this type are described in US 5,714,137 and include the Silwet<sup>®</sup> surfactants available from Momentive Performance Chemical, Albany, New York. Exemplary Silwet surfactants are as follows:

25	Name	Average MW
	L-7608	600
	L-7607	1,000
	L-77	600
	L-7605	6,000
30	L-7604	4,000
	L-7600	4,000
	L-7657	5,000

L-7602                    3,000;  
and mixtures thereof.

I.     Aqueous carrier

The composition of the present invention may include an aqueous carrier. The aqueous  
5 carrier which is used may be distilled, deionized, or tap water. Water may be present in any  
amount for the composition to be an aqueous solution. In some embodiments, water may be  
present in an amount of about 50% to about 99.5%, alternatively about 85% to about 99.5%,  
alternatively about 90% to about 99.5%, alternatively about 92% to about 99.5%, alternatively  
10 about 95%, by weight of said freshening composition. Water containing a small amount of low  
molecular weight monohydric alcohols, e.g., ethanol, methanol, and isopropanol, or polyols, such  
as ethylene glycol and propylene glycol, can also be useful. However, the volatile low molecular  
weight monohydric alcohols such as ethanol and/or isopropanol should be limited since these  
volatile organic compounds will contribute both to flammability problems and environmental  
15 pollution problems. If small amounts of low molecular weight monohydric alcohols are present  
in the composition of the present invention due to the addition of these alcohols to such things as  
perfumes and as stabilizers for some preservatives, the level of monohydric alcohol may be less  
than about 15%, alternatively less than about 6%, alternatively less than about 3%, alternatively  
less than about 1%, by weight of the composition.

J.     Other Optional ingredients

20 Adjuvants can be optionally added to the composition herein for their known purposes.  
Such adjuvants include, but are not limited to, water soluble metallic salts, antistatic agents,  
insect and moth repelling agents, colorants, antioxidants, and mixtures thereof.

II.    Method of Making

25 The composition can be made in any suitable manner known in the art. All of the  
ingredients can simply be mixed together. In certain embodiments, it may be desirable to make a  
concentrated mixture of ingredients and dilute by adding the same to an aqueous carrier before  
dispersing the composition into the air or on an inanimate surface. In another embodiment, the  
malodor control polymer may be dispersed in one vessel containing deionized water and ethanol,  
30 and low molecular polyols. To this vessel, then, the buffer is added until fully dispersed and  
visually dissolved. In a separate vessel, the solubilizer and perfume are mixed until homogenous.

The solution of solubilizer and perfume are then added to the first mixing vessel, and mixed until homogenous.

### III. Methods of Use

5           The composition of the present invention can be used by dispersing, e.g., by placing an aqueous solution into a dispensing means, such as a spray dispenser and spraying an effective amount into the air or onto the desired surface or article. An effective amount as defined herein means an amount sufficient to neutralize malodor to the point that it is not discernible by the human sense of smell yet not so much as to saturate or create a pool of liquid on an article or  
10 surface and so that, when dry, there is no visual deposit readily discernible. Dispersing can be achieved by using a spray device, a roller, a pad, etc.

          The present invention encompasses the method of dispersing an effective amount of the composition for reducing malodor onto household surfaces. The household surfaces are selected from the group consisting of countertops, cabinets, walls, floors, toilets, bathroom surfaces, and  
15 kitchen surfaces.

          The present invention encompasses the method of dispersing a mist of an effective amount of the composition for reducing malodor onto fabric and/or fabric articles. The fabric and/or fabric articles include, but are not limited to, clothes, curtains, drapes, upholstered furniture, carpeting, bed linens, bath linens, tablecloths, sleeping bags, tents, car interior, e.g., car  
20 carpet, fabric car seats, etc.

          The present invention encompasses the method of dispersing a mist of an effective amount of the composition for reducing malodor impression onto and into shoes wherein the shoes are not sprayed to saturation.

          The present invention encompasses the method of dispersing a mist of an effective  
25 amount of the composition for reducing malodor impression onto shower curtains.

          The present invention relates to the method of dispersing a mist of an effective amount of the composition for reducing malodor impression onto and/or into garbage cans and/or recycling bins.

          The present invention relates to the method of dispersing a mist of an effective amount of  
30 the composition for reducing malodor impression into the air to neutralize malodor.

          The present invention relates to the method of dispersing a mist of an effective amount of the composition for reducing malodor impression into and/or onto major household appliances

including, but not limited to, refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers, etc., to neutralize malodor.

The present invention relates to the method of dispersing a mist of an effective amount of the composition for reducing malodor impression onto cat litter, pet bedding and pet houses to neutralize malodor.

The present invention relates to the method of dispersing a mist of an effective amount of the composition for reducing malodor impression onto household pets to neutralize malodor.

### EXAMPLES

#### 10 Aqueous composition

Table 1 shows non-limiting examples of compositions according to the present invention. A mixture of water, ethanol, and Silwet L-7600 surfactant is prepared by mixing. The final pH is adjusted to 7 using 30% maleic acid and this solution is used as Control 1. Control 2 and Test Solutions I and II are prepared by adding desired ingredients right before adjusting the pH.

15

**Table 1**

Ingredient	Control 1 (Blank)	Control 2 (CD)	Test Solution I (HMP)	Test Solution II (Zn-HMP complex)
Ethanol	3	3	3	3
Surfactant (Silwet L-7600)	0.1	0.1	0.1	0.1
Hydroxypropyl Beta CD	-	0.5	-	-
HMP	-	-	0.5	-
Zn-HMP	-	-	-	0.7
Maleic Acid	As needed	As needed	As needed	As needed
Perfume	-	-	0.05	0.05
Water	Balance	Balance	Balance	Balance
Total	100	100	100	100
Final pH	7	7	7	7

#### Formulation of Metal Polymer Coordination Complexes

This example illustrates the preparation of the present invention containing water soluble zinc-polymer coordination complexes.

A 50 ml mixture of water, ethanol, and Silwet L-7600 surfactant was prepared by mixing. Separately, 50 ml aqueous solution of zinc polymer coordination complexes were prepared by stirring 0.2% ZnCl<sub>2</sub> and 0.5% polymer for 30 minutes in water. Finally the solutions were combined and the solution pH was adjusted to 7 using 30% maleic acid. Two blank solutions (pH 5 and pH 7) were used as representative Controls. Control 3 contained ZnCl<sub>2</sub> at pH 5 since at a higher pH, ZnCl<sub>2</sub> solutions are not stable.

10

**Table 2**

<b>Ingredient</b>	<b>Control 1 (Blank /pH7)</b>	<b>Control 3 (ZnCl<sub>2</sub>)</b>	<b>I (Zn-polymer complexes)</b>
Water	96.85	95.9	96.2
Ethanol	3	3	3
Surfactant (Silwet L-7600)	0.1	0.1	0.1
ZnCl <sub>2</sub>	-	1.0	0.2
Polymer	-	-	0.5
Maleic Acid	as needed	as needed	as needed
Sodium hydroxide	as needed	as needed	-
Total	100	100	100
Final pH	7	5	7

#### Malodor Control Performance

This example illustrates the malodor efficacy of the HMPs of the present invention. Isovaleric acid was chosen as a chemical surrogate for body odor while butylamine was used as a representative for amine-containing odors such as fish, pet urine, etc. Hydrophobic greasy cooking odors were represented by aldehydes such as nonanal.

15



5 ml test solution was placed in a GC-MS vial and spiked with 5 microliters of chemical surrogates shown in Table 3. The solutions are first equilibrated at room temperature for 2 hours, then incubated at 35°C for 30 minutes. The headspace of each vial is finally sampled using a polydimethyl siloxane (PDMS) / Solid-Phase-Micro-Extraction (SPME) fiber and analyzed by GC/MS. The reductions in head space concentrations of odor molecules are measured and the data are normalized to Control.

Results are shown in Table 3. Lower numbers denote high levels of malodor molecules present in the solution that are attributed to high malodor control efficacy of polymers. Table 3 demonstrates that HMPs and metallated polymers have broader malodor removal efficacy over the Controls and unmodified polymers.

Table 3

Technology	Odor Molecules		
	Isovaleric Acid (Body)	Butylamine (Fish)	Nonanal (Grease)
Control 1	1.0	1.0	1.0
Control 2	0.67	1.0	0.48
Hydroxypropyl Beta CD			
Lupasol WF	0.1	0.01	0.78
PEI 25,000 (no hydrophobic modification)			
100% ethyleneoxide/propyleneoxidemodified PEI 600	0.77	1.0	0.87
Lupamin 9000 (PVA) (0% hydrolyzed)	0.93	0.97	0.96
Lupamin 9030 (30% hydrolyzed)	0.61	0.06	0.05
Lupamin 9095 (95% hydrolyzed)	0.37	0.01	0.04
Lupamin 1595 (95% hydrolyzed)	0.26	0.01	0.02

25% C6 modified PEI 1800	0.02	0.01	0.37
ZnCl <sub>2</sub> (pH 5)	1.0	0.0	1.0
Zn-Lupasol WF complex (polymer/ZnCl <sub>2</sub> = 2.5)	0.02	0.11	0.87
Zn-Lupamin 1595 complex (polymer/ZnCl <sub>2</sub> = 2.5)	0.01	0.00	0.03

#### Sulfur odor control performance of zinc polymer complexes

This example illustrates the sulfur odor efficacy of water soluble zinc polymer coordination complexes of the present invention.

5 Butanethiol and dipropyl sulfide were chosen as chemical surrogates for sulfur containing odors such as kitchen (onion/garlic), sewage, etc.. These two molecules also enable the assessment of efficacy of polymer for sulfur molecules having different degrees of hydrophobicity (e.g more hydrophobic dipropylsulfide is usually harder to mitigate with hydrophilic technologies such as cyclodextrin).

10 5 ml test solution was placed in a GC-MS vial and spiked with 3 parts-per-million of butanethiol or dipropylsulfide. The solutions were first equilibrated at room temperature for 2 hours, then incubated at 35 oC for 30 minutes. The headspace of each vial was finally sampled using a PDMS/SPME fiber and analyzed by GC/MS. The reductions in head space concentrations of sulfur molecules were measured and the data were normalized to Control  
15 (Table 4).

**Table 4**

<b>Technology</b>	<b>Butanethiol</b>	<b>Dipropylsulfide</b>
Control	1.0	1.0
Lupasol WF	1.0	1.0
Lupamin 1595 (95% hydrolyzed)	1.0	
ZnCl <sub>2</sub> (pH 5)	0.8	1.0
Zn-Lupasol WF complex (Zn/polymer = 0.2)	0.5	1.0
Zn-Lupamin 1595 complex (Zn/polymer = 0.2)	0.4	-

Zn-Cl2 modified PEI25000 complex (Zn/polymer = 0.2)	0.01	<0.7
--	------	------

Odor prevention performance of zinc polymer complexes

This Example illustrates the odor prevention efficacy of water soluble zinc polymer coordination complexes of the present invention.

5 The Control formulation containing no malodor control polymer or zinc salt, and Formulations containing individual polymers, zinc salts, and zinc-polymer complexes are compared for their effect on odor prevention, through microbe reduction.

Soiled sponge samples were cut into 1x6 cm strips and treated with the solutions (Table 5) for 15 minutes and dried at ambient temperature for 12 hours. The treated 1 cm strips were then cut into 1x1 cm pieces, placed into SOLARIS scintillation vials, and 1 ml of MOPS buffer was added. The open vials were placed into outer SOLARIS vials containing thymolphthalein blue pH indicator and the vials were finally capped. The sealed vials were placed into a SOLARIS machine and incubated for 120 hrs at 37°C. Colorimetric measurements were conducted according to SOLARIS VIV protocol and the detection times of acidic respiratory byproducts were record (Table 5).

**Table 5**

Technology	Respiratory Byproducts Detection Time (hrs)
Control	2.35
ZnCl2	3.38
Lupamin 1595	15.5
Zn-Lupamin 1595 complex (ZnCl2 / polymer = 0.4)	not detected

Throughout this specification, components referred to in the singular are to be understood as referring to both a single or plural of such component.

20 All percentages stated herein are by weight unless otherwise specified.

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 range were all expressly written herein. For example, a stated range of "1 to 10" should be

considered to include any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges beginning with a minimum value of 1 or more and ending with a maximum value of 10 or less, e.g., 1 to 6.1, 3.5 to 7.8, 5.5 to 10, etc.

Further, 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."

Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

## CLAIMS

1. A composition for reducing malodor comprising:
  - (a) an effective amount of a metallated malodor control polymer comprising a water-soluble metal ion and a polymer selected from the group consisting of: partially hydrolyzed PVam, partially hydrolyzed hydrophobically modified PVam, PEI, hydrophobically modified PEI, PAMam, hydrophobically modified PAMam, PAam, hydrophobically modified PAam, PEam, hydrophobically modified PEam, and mixtures thereof;
  - (b) a malodor counteractant comprising a perfume material; and
  - (c) an aqueous carrier;wherein said composition comprises a pH of 5 to 10, preferably a pH of 6 to 8.
2. The composition of Claim 1 wherein said metallated malodor control polymer comprises a metal / polymer weight ratio of 0.001 to 0.01.
3. The composition of Claim 1 wherein said metallated malodor control polymer is selected from the group consisting of: a partially hydrolyzed PVam modified with a C4-C10 alkyl or alkylene; hydrophobically modified, 95% hydrolyzed PVam; a hydrophobically modified PEI; and mixtures thereof.
4. The composition of Claim 1 wherein said metallated malodor control polymer is a C16 to C26 alkyl or alkylene HMP.
5. The composition of Claim 1 wherein said metal ion is Zn.
6. The composition of Claim 1 wherein said malodor control polymer is present in an amount of 0.01% to 10% by weight of said composition.
7. The composition of Claim 1 wherein said perfume mixture comprises at least one aliphatic aldehyde present in the amount of 0.001% to 5% by total weight of said composition, preferably in the amount of 0.001% to 1% by total weight of said composition.

8. The composition of Claim 7 wherein said at least one aliphatic aldehyde selected from the group consisting of bourgeonal, citral, citronellyl oxyacetaldehyde, cymal, decyl aldehyde, helional, hexyl cinnamic aldehyde, lauric aldehyde, ligustral, lyral, melonal, methyl dihydro jasmonate, methyl nonyl acetaldehyde, methyl phenyl carbonyl acetate, nonyl aldehyde, 2` 6 - nonadien-1-al, octyl aldehyde, oxane, P.T. buccinal, polysantol, rhubafuran, tripal, and mixtures thereof.
9. The composition of Claim 1 wherein said composition further comprises a buffering agent selected from the group consisting of carboxylic acid, dicarboxylic acid, N-(2-Acetamido)-2-aminoethanesulfonic acid, and mixtures thereof.
10. The composition of Claim 1 wherein said composition further comprises cyclodextrin.
11. The composition of Claim 1 wherein said composition is free of an ingredient that soils or stains a fabric surface.
12. The composition of Claim 1 wherein said composition comprises no more than 3% surfactant by weight of said composition, preferably no more than 1% surfactant by weight of said composition.
13. The composition of Claim 1 wherein said aqueous carrier is present in an amount of 90% to 99.5%.
14. A method of reducing malodor comprising the steps of:
  - a. providing the composition of Claim 1;
  - b. dispersing an effective amount of said composition on an inanimate surface or in the air.

**INTERNATIONAL SEARCH REPORT**

International application No PCT/US2012/020884
---

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. A61L9/01 A61L101/32 C11D3/00 A61L9/014 C11D3/50  
 A61L15/46  
 ADD. A61L101/20 A61L101/36  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 A61L C11D A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
 EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/084474 A1 (WU BIN [US] ET AL) 21 April 2005 (2005-04-21) abstract; claims; examples; tables paragraphs [0004], [0005], [0016] - [0018], [0022] - [0024], [0029] - [0036], [0046], [0056] - [0058] -----	1-14
Y	US 2003/191034 A1 (WOO RICKY AH-MAN [US] ET AL) 9 October 2003 (2003-10-09) paragraphs [0008], [0011], [0018], [0027], [0028], [0056] - [0067], [0074], [0075], [0094], [0095], [0111], [0112], [0115] - [0123]; examples; tables paragraphs [0300] - [0302], [0308] - [0310]; claims ----- -/--	1-14

Further documents are listed in the continuation of Box C.       See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  11 April 2012	Date of mailing of the international search report  23/04/2012
--	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Nissen, Vagn
--	--

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/020884

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2008/100625 A1 (PROCTER & GAMBLE [US]; SMETS JOHAN [BE]; VANSTEENWINCKEL PASCALE CLAIR) 21 August 2008 (2008-08-21) page 18, lines 17-25; claims; tables page 25, lines 7-31 page 26, lines 10-25 -----	1-14
Y	US 2008/194454 A1 (MORGAN GEORGE KAVIN [US] ET AL) 14 August 2008 (2008-08-14) paragraphs [0063], [0064], [0114]; claims; tables -----	1-14
Y	US 6 103 678 A (MASSCHELEIN AXEL [BE] ET AL) 15 August 2000 (2000-08-15) the whole document -----	1-14
Y	EP 0 841 391 A1 (PROCTER & GAMBLE [US]) 13 May 1998 (1998-05-13) the whole document -----	1-14



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/020884

Patent document cited in search report	Publication date	Publication date	Patent family member(s)	Publication date
US 2005084474	A1	21-04-2005	US 2005084474 A1	21-04-2005
			US 2010275915 A1	04-11-2010
			WO 2005039661 A1	06-05-2005
-----				
US 2003191034	A1	09-10-2003	NONE	
-----				
WO 2008100625	A1	21-08-2008	CA 2675420 A1	21-08-2008
			CA 2675426 A1	21-08-2008
			CN 101611129 A	23-12-2009
			CN 101617036 A	30-12-2009
			EP 2111443 A2	28-10-2009
			EP 2111444 A1	28-10-2009
			JP 2010516862 A	20-05-2010
			JP 2010516863 A	20-05-2010
			US 2008200359 A1	21-08-2008
			US 2008200363 A1	21-08-2008
			US 2009048351 A1	19-02-2009
			US 2010331190 A1	30-12-2010
			WO 2008100601 A2	21-08-2008
			WO 2008100625 A1	21-08-2008
			ZA 200904935 A	28-04-2010
			ZA 200904936 A	28-04-2010
-----				
US 2008194454	A1	14-08-2008	CA 2675259 A1	21-08-2008
			EP 2109661 A1	21-10-2009
			JP 2010518271 A	27-05-2010
			US 2008194454 A1	14-08-2008
			US 2010087357 A1	08-04-2010
			WO 2008100411 A1	21-08-2008
-----				
US 6103678	A	15-08-2000	NONE	
-----				
EP 0841391	A1	13-05-1998	AR 011766 A1	13-09-2000
			BR 9712897 A	21-03-2000
			CA 2270835 A1	14-05-1998
			EP 0841391 A1	13-05-1998
			JP 2001503803 A	21-03-2001
			WO 9820102 A1	14-05-1998
-----				