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(54) Title: ADHESIVE LAVATORY TREATMENT COMPOSITIONS

(57) Abstract: Adhesive lavatory treatment compositions which are essentially anhydrous (comprise less than about 0.01%wt. water, preferably less than about 0.05% water, alternately and/or more preferably, comprise no water as an added constituent to die said compositions) which comprise: about 1 - 50%wt. of an organic solvent constituent; about 5 - 50%wt. of at least one alkanolamide based nonionic surfactant; about 1 - 50 %wt. of at least one nonionic surfactant constituent; and preferably wherein the at least one alkanolamide based nonionic surfactant; and the at least one nonionic surfactant constituent are present in -respective weight ratios of 1 -2 :1 -2; about 0.1 - 10 %wt. of a primary adhesion promoter constituent; optionally, at least one- co-adhesion promoter and further optionally one or more further optional constituents; wherein in use, the said adhesive lavatory treatment compositions may be applied and adhered to a- dry ceramic surface, especially the interior sidewall in a toilet bowl -or other lavatory appliance, and wherein the said adhesive lavatory treatment compositions is retained adhered to the said surface following a plurality of flushes of water impinging upon the adhered adhesive lavatory treatment compositions.



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ADHESIVE LAVATORY TREATMENT COMPOSITIONS

The present invention relates to adhesive lavatory treatment compositions which are adapted to be directly adhered to a part of a lavatory appliance, e.g., the inner sidewall of a toilet bowl.

An adhesive lavatory composition known to the art is that described in US Patent 6667286. Therein is disclosed a sanitary agent for direct application to a sanitary object to be cleaned comprising: an adhesion promoter selected from the group consisting of long and long-chained organic molecules, which are at least partly hydrophilic, and the hydrophilic part of the adhesion promoter interacts at least in part with the water molecules in the presence of water and becomes "sticky" which enables said agent to adhere to said sanitary object even after a large number of rinse actions; water; anionic and/or nonionic and/or amphoteric surfactants ("tensides"); and optional components selected from the group consisting of fragrances, thickeners, colorants, preservatives, and combinations thereof; wherein the viscosity of the agent is at least 15,000 mPas. That document recites that "The agent can be 'sticky' either through a certain water content already in the formulation to be applied or the adhesion can be obtained by a light dampening of the surface – for example, by activating the flush water – and then applying the agent.

Clearly while the compositions disclosed in US Patent 6667286 provide satisfactory performance characteristics, it is also clear that the sanitary agents necessarily require water in order to "become sticky" and thereby provide adhesion between the sanitary agent and a toilet bowl. A further review of this document reveals that the example compositions disclosed therein comprise 3 – 60%wt. of water as a necessary constituent.

Certain adhesive lavatory compositions are disclosed in EP 1978080 A1. The compositions disclosed therein necessarily comprise at least 20%wt., preferably at least 30%wt. of an adhesion promoter constituent.

Thus while the art proposes certain compositions which exhibit satisfactory performance under certain conditions, there remains a real and continued need in the art for further improved lavatory treatment compositions which overcome shortcomings of prior art compositions.

5 The compositions of the adhesive lavatory treatment compositions address and overcome shortcomings of prior art lavatory treatment composition. These and further objects of the present invention will become apparent from a review of the following specification. Further, the compositions of the present invention exhibit excellent surface adhesion to dry surfaces, particularly to dry surfaces of lavatory appliances, e.g.,
10 toilets, bidets, urinals and the like, especially the inner sidewall of a toilet bowl.

Broadly, the present invention provides adhesive lavatory treatment compositions which are essentially anhydrous (comprise less than about 0.01%wt. water, preferably less than about 0.05% water, alternately and/or more preferably, comprise no water as an added constituent to the said compositions) and comprise:

15 about 1 – 50%wt., preferably about 10 – 50%wt. of an organic solvent constituent, further preferably wherein the organic solvent constituent comprises an alkylene glycol;
 about 5 – 50%wt. of at least one alkanolamide based nonionic surfactant;
 about 1 – 50%wt. of at least one nonionic surfactant constituent; and preferably
20 wherein the at least one alkanolamide based nonionic surfactant; and the at least one nonionic surfactant constituent are present in respective weight ratios of 1-2:1-2;
 about 0.1 – 10%wt, of a primary adhesion promoter constituent;
 about 0 – 5%wt. of at least one co-adhesion promoter; and preferably wherein the respective weight ratios of the primary adhesion promoter and co-adhesion promoter is at
25 least about 1.5:1;
 optionally one or more further optional constituents which may impart a further aesthetic or technical benefit to the said adhesive lavatory treatment compositions;
 wherein in use, the said adhesive lavatory treatment compositions may be applied and adhered to a dry ceramic surface, especially the interior sidewall in a toilet bowl or
30 other lavatory appliance, and wherein the said adhesive lavatory treatment compositions

is retained adhered to the said surface following a plurality of flushes of water impinging upon the adhered adhesive lavatory treatment compositions.

In a further aspect the present invention provides methods for the manufacture of the adhesive lavatory treatment compositions disclosed herein, as well as to methods for the use the disclosed adhesive lavatory treatment compositions in the treatment of lavatory appliances, and especially toilet bowls.

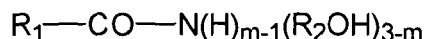
Further features and aspects of the present invention will become more apparent from a further reading of the present specification.

The inventive adhesive lavatory treatment compositions comprise one or more organic solvents as the organic solvent constituent. By way of non-limiting example exemplary useful organic solvents which may be included are those which are at least partially water-miscible such as alcohols (e.g., low molecular weight alcohols, such as, for example, ethanol, propanol, isopropanol, and the like), glycols (such as, for example, ethylene glycol, propylene glycol, hexylene glycol, and the like), water-miscible ethers (e.g. diethylene glycol diethylether, diethylene glycol dimethylether, propylene glycol dimethylether), water-miscible glycol ether (e.g. propylene glycol monomethylether, propylene glycol mono ethylether, propylene glycol monopropylether, propylene glycol monobutylether, ethylene glycol monobutylether, dipropylene glycol monomethylether, diethyleneglycol monobutylether), lower esters of monoalkylethers of ethylene glycol or propylene glycol (e.g. propylene glycol monomethyl ether acetate), and mixtures thereof. Glycol ethers having the general structure R_a-R_b-OH , wherein R_a is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms, and R_b is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Of course, mixtures of two or more organic solvents may be used in the organic solvent constituent.

The organic solvent constituent comprises 1 – 50%wt. of the inventive compositions. Preferably, in order of increasing preference the organic solvent constituent is present in an amount of at least about 1%, 2.5%, 5%, 7%, 9%, 10%, 11%, 12%, 13%, 14%, 15%, 16%, 17%, 18%, 19%, 20% weight of the inventive composition of which they form a part. Preferably, in order of increasing preference the organic solvent constituent comprises not more than about 50%, 48%, 45%, 42.5%, 40%, 38%,

36%, 34%, 32%, 30%, 29%, 28%, 27%, 26%, 25% weight of the inventive composition of which they form a part. Particularly preferred amounts of the organic solvent constituent are recited in one or more of the Examples, with preferred ranges of the organic solvent constituent also disclosed in the Examples.

- 5 The inventive adhesive lavatory treatment compositions also comprise at least one alkanolamide based nonionic surfactant compound; such compound(s) provide additional cleaning and which also functions as a foam booster which improves the overall foaming characteristics of the inventive compositions. Nonlimiting examples of such useful alkanolamides include one or more monoethanol amides, and diethanol amides of fatty acids having an acyl moiety which contains from about 8 to about 18 carbon atoms, and
10 which may be represented in accordance with the formula:



- where R_1 represents a saturated or unsaturated aliphatic hydrocarbon radical of from about 7 to 21 carbon atoms, but preferably from about 11 to 17 carbon atoms; R_2
15 represents a $\text{-CH}_2\text{-}$ or $\text{-CH}_2\text{CH}_2\text{-}$, and m is an integer from 1 to 3, but is preferably 1. Preferably, R_1 is a saturated or unsaturated aliphatic hydrocarbon radical comprising from about 11 to 17 carbon atoms, and m is 1. Specific examples of such compounds include mono-ethanol amine coconut fatty acid amide and diethanol amine dodecyl fatty acid amide. An exemplary useful and particularly preferred fatty acid amides include
20 cocomonethanol amide or cocodiethanolamide, which are presently commercially available as MONAMID CMA or MONAMID MDNA (ex. Mona Industries, Paterson NJ). Further exemplary useful alkanolamides which provide such functions include *inter alia*: cocamide MEA, cocamide DEA, soyamide DEA, lauramide DEA, oleamide MIPA, stearamide MEA, myristamide MEA, lauramide MEA, capramide DEA, ricinoleamide
25 DEA, myristamide DEA, stearamide DEA, oleylamide DEA, tallowamide DEA, lauramide MIPA, tallowamide MEA, isostearamide DEA, isostearamide MEA, and mixtures thereof. Further useful alkanolamide surfactant compounds include alkanolamides, particularly fatty monoalkanolamides and fatty dialkanolamides, including one or more of those marketed under the Ninol® tradename.

- 30 A preferred alkanolamide based nonionic surfactant compound is Ninol® 40-CO (ex. Stepan Co.) which comprises at least 85%wt. of a coco fatty acid alkanolamide

derived from diethanolamide and which also comprises about 8%wt. of 1, 2, 3-propanetriol (glycerine).

The inventive compositions comprise about 5 – 50%wt. of the said at least one alkanolamide based nonionic surfactant. In order of increasing preference, the at least one alkanolamide based nonionic surfactant compound at least about 5%, 7.5%, 10%, 12.5%, 15%, 16%, 17%, 18%, 19%, 20%, 21%, 22%, 23%, 24%, 25%, 26%, 27%, 28%, 29%, 30%, 31%, 32%, 33%, 34%, 35% by weight, based on the total weight of the inventive composition. In order of increasing preference, the at least one alkanolamide based nonionic surfactant compound of not more than about 50%, 49%, 48%, 47%, 46%, 45%, 44%, 43%, 42%, 41%, 40% by weight, based on the total weight of the inventive composition of which the at least one alkanolamide based nonionic surfactant forms a part. Particularly preferred amounts of the at least one alkanolamide based nonionic surfactant are recited in one or more of the Examples.

The present inventive compositions necessarily also include a nonionic surfactant constituent which comprises one or more nonionic surfactants, but exclude the at least one alkanolamide based nonionic surfactant compound which has been recited herein to be another but separate essential surfactant constituent in the inventive compositions taught herein. Virtually all known art nonionic surfactants may be used in the nonionic surfactant constituent of the invention, subject to the foregoing proviso. Non-limiting and illustrative examples of suitable nonionic surfactants include, *inter alia*, condensation products of alkylene oxide groups with an organic hydrophobic compound, such as an aliphatic compound or with an alkyl aromatic compound. Many nonionic synthetic organic detergents generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic detergent. Further, the length of the polyethenoxy hydrophobic and hydrophilic elements may be varied to adjust these properties. Illustrative examples of such nonionic surfactants include the condensation product of one mole of an alkyl phenol having an alkyl group containing from 6 to 12 carbon atoms with from about 5 to 25 moles of an

alkylene oxide. Another example of such a nonionic surfactant is the condensation product of one mole of an aliphatic alcohol which may be a primary, secondary or tertiary alcohol having from 6 to 18 carbon atoms with from 1 to about 10 moles of alkylene oxide. Preferred alkylene oxides are ethylene oxides or propylene oxides which may be present singly, or may be both present.

Illustrative examples of nonionic surfactants include primary and secondary linear and branched alcohol ethoxylates, such as those based on C₆-C₁₈ alcohols which further include an average of from 2 to 80 mols of ethoxylation per mol of alcohol. Examples include the Genapol® series of linear alcohol ethoxylates from Clariant Corp., (Charlotte, NC.) The 26-L series is based on the formula RO(CH₂CH₂O)_nH wherein R is a mixture of linear, even carbon-number hydrocarbon chains ranging from C₁₂H₂₅ to C₁₆H₃₃ and n represents the number of repeating units and is a number of from 1 to about 12. Further examples of useful nonionic surfactants include secondary C₁₂-C₁₅ alcohol ethoxylates, including those which have from about 3 to about 10 moles of ethoxylation. Such are available in the Tergitol® series of nonionic surfactants (ex. Dow Chemical, Midland, MI). Further exemplary nonionic surfactants include linear primary C₁₁-C₁₅ alcohol ethoxylates, including those which have from about 3 to about 10 moles of ethoxylation. Such are available in the Tomadol® series of nonionic surfactants (ex. Tomah Industries.). Still further exemplary nonionic surfactants include C₈-C₁₆ alcohol alkoxylates typically having between about 1-15 moles of ethoxylation, as available in the Tomadol® series of nonionic surfactants (ex. Air Products Inc.) Such include Tomadol® 91-2.5, 91-6, 1-3, 1-7, 23-1, 23-6.5, 25-3, 25-9, 25-12, 45-7 and 45-13 surfactant products. Further useful as the nonionic surfactant constituent are the series of plant derived alcohol based nonionic surfactants commercially available in the Tomadol® L series, e.g., Tomadol® L80, L124, L130 and L144 surfactant products. An exemplary and preferred series of nonionic surfactants include those presently marketed in the Tomadol® 400, 600, 900, 1200 series of surfactants. Such are recited as being environmentally friendly nonionic surfactants particularly well suited as replacements for nonyl phenol ethoxylate based nonionic surfactants. Specific examples include:

	molecular weight	EO content (%wt.)	hydroxyl number (mg. KOH/g)	HLB
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Tomadol® 400	300	44.5	189	8.9
Tomadol® 600	600	53	134	10.6
Tomadol® 900	460	65	122	13.1
Tomadol® 901	445	60	126	12.1
Tomadol® 910	495	59	113	11.8
Tomadol® 1200	590	68	95	13.6

Further examples of useful nonionic surfactants include C₆-C₁₅ straight chain alcohols ethoxylated with about 1 to 13 moles of ethylene oxide, particularly those which include about 4 to about 7 moles of ethylene oxide.

5 Additional examples of suitable nonionic surfactants are alkoxy block copolymers, and in particular, compounds based on ethoxy/propoxy block copolymers. Polymeric alkylene oxide block copolymers include nonionic surfactants in which the major portion of the molecule is made up of block polymeric C₂-C₄ alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting
 10 group, and can have as a starting nucleus almost any active hydrogen containing group including, without limitation, amides, phenols, thiols and secondary alcohols.

Yet further useful nonionic surfactant compounds useful in the nonionic surfactant constituent include one or more amine oxide compounds. Exemplary useful amine oxide surfactant compounds include:

15 alkyl di(C₁-C₇) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples of such compounds include lauryl dimethyl amine oxide, myristyl dimethyl amine oxide, and those in which the alkyl group is a mixture of different amine oxide, dimethyl cocoamine oxide, dimethyl (hydrogenated tallow) amine oxide, and
 20 myristyl/palmityl dimethyl amine oxide;

alkyl di(hydroxy C₁-C₇) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples of such compounds include bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallowamine oxide; and bis(2-hydroxyethyl) stearylamine
 25 oxide;

alkylamidopropyl di(C₁-C₇) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples of such compounds include cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide; and

5 alkylmorpholine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Particularly preferred are alkyl di(C₁-C₂) amine oxides in which the alkyl group has about 10-14, and preferably has 12 carbon atoms, which are preferably saturated. Especially preferred is lauryl dimethyl amine oxide which in preferred embodiments is present to the
10 exclusion of other amine oxides.

One or more nonionic surfactant compounds may be used to comprise the nonionic surfactant constituent. The nonionic surfactant constituent forms about 1 – 50%wt. of the present inventive compositions. Preferably, and in order of increasing preference the nonionic surfactant constituent comprises at least about 1%, 3%, 5%,
15 7.5%, 10%, 12%, 14%, 15%, 16%, 17%, 18%, 19%, 20%, 21%, 22%, 23%, 24%, and 25% by weight of the composition of which it forms a part. Preferably in order of increasing preference the nonionic surfactant constituent comprises not more than about 50%, 48%, 46%, 45%, 44%, 42%, 40%, 38%, 36%, 35%, 34%, 32%, and 30% by weight of the composition of which it forms a part.

20 As in accordance with the present invention both at least one alkanolamide based nonionic surfactant and at least one nonionic surfactant constituent are necessarily present, in preferred embodiments the at least one alkanolamide based nonionic surfactant and the at least one nonionic surfactant constituent are present in respective weight ratios of 1-2:1-2, but more preferably in respective weight ratios of 1.5-1:1.5-1.
25 In particularly preferred embodiments the total amount of the one alkanolamide based nonionic surfactant exceeds the total amount of the at least one nonionic surfactant constituent, and especially preferably the respective weight ratio of the former to the latter constituent(s) is 1.5-1.7:1. Certain particularly preferred and specific respective weight ratios are disclosed with reference to the Examples.

30 In certain preferred embodiments the total amount of the least one alkanolamide based nonionic surfactant and at least one nonionic surfactant constituent comprise from

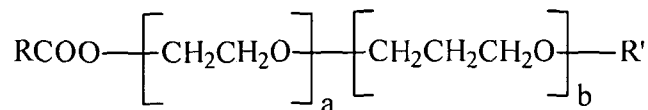
about 40% to about 75%wt. of the adhesive lavatory treatment compositions, with particularly preferred total amounts described with reference to one or more of the Examples.

The compositions of the invention necessarily further comprise about 0.1 –
5 10%wt, of a primary adhesion promoter constituent. According to preferred embodiments the primary adhesion promoter constituent is based on one or more oxyalkylenated compounds. These oxyalkylenated compound(s) typically comprise ethylene oxide groups (“EO”) (oxyethylenated compounds), or propylene oxide groups (“PO”) (oxypropylenated compounds) or both (“EO/PO”) (oxyethylenated/oxypropylenated compounds). Of course, a plurality of oxyalkylenated
10 compound(s) may be used in the primary adhesion promoter constituent of the adhesive lavatory treatment compositions.

Exemplary suitable oxyalkylenated compounds may be selected from:
polyethylene glycols, polyethylene glycol esters and/or polypropylene glycol esters,
15 polyethylene glycol ethers and/or polypropylene glycol ethers, alkoxyated acyl derivatives, ethoxylated acyl polyol derivatives, oxyalkylenated (especially) oxyethylenated triesters of glycerol and of fatty acids, and mixtures thereof.

Non-limiting examples of suitable polyethylene glycols which may be used in the composition of the invention include ethylene oxide polycondensates having a number of
20 ethylene oxide (EO) units of greater than 10, and preferably greater than about 20. The ethylene oxide number preferably range from about 10 to about 50,000 and preferably from about 20 to about 10,000. Non-limiting examples of such polyethylene glycols include polyethylene glycol comprising 7,000 EO (CTFA name: PEG-7M), polyethylene glycol comprising 75 EO (CTFA name: PEG-75), polyethylene glycol comprising 20,000
25 EO (CTFA name: PEG-20M), and polyethylene glycol comprising 150 EO (CTFA name: PEG-150).

Non-limiting examples of suitable polyethylene glycol esters and/or polypropylene glycol esters include condensates of polyethylene glycol and/or polypropylene glycol with one or more fatty acids. These compounds typically have the
30 formula:



wherein:

each of R and R' independently represent: hydrogen or a saturated or unsaturated, linear or branched, hydroxylated or non-hydroxylated alkyl chain containing from 1 to 30

5 carbon atoms, preferably from 12 to 22 carbon atoms, or an aryl chain, with the proviso that R and R' are not simultaneously hydrogen,

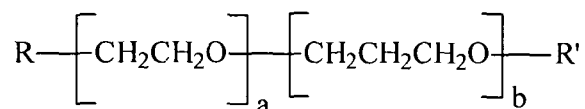
$a = 0 - 300$

$b = 0 - 300$, and preferably $a + b$ is greater than or equal to 10, preferably at least 20, still more preferably at least 30.

10 Non-limiting examples of polyethylene glycol acid esters and/or polypropylene glycol acid esters include polyethylene glycol distearate (150 EO), PEG-150 dibehenate, polyethylene glycol palmitostearate (120 EO), the copolymer of polyethylene glycol (30 EO) and of 12-hydroxystearic acid, and polyethylene glycol stearate (40 EO). Examples of compounds according to the foregoing formula wherein R and R' are both hydrogen,

15 such compound may be polyoxyethylene polyoxypropylene copolymers.

Non-limiting examples of polyethylene glycol ethers and/or polypropylene glycol ethers include condensates of polyethylene glycol and/or polypropylene glycol with one or more fatty alcohols. These compounds typically conform to the formula:



20 wherein:

each of R and R' represent, independently of each other, hydrogen or a saturated or unsaturated, linear or branched, hydroxylated or non-hydroxylated alkyl chain containing from 1 to 30 carbon atoms, preferably from 12 to 22 carbon atoms, or an aryl chain, with the proviso that R and R' are not simultaneously hydrogen.

25 $a = 0 - 300$

$b = 0 - 300$, and preferably $a + b$ is greater than or equal to 10, preferably at least 20, still more preferably at least 30.

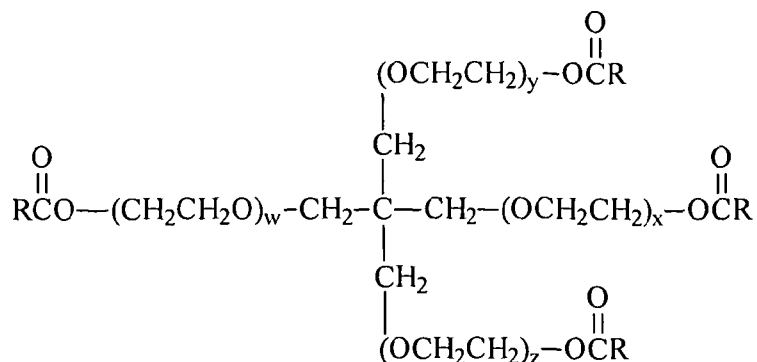
Non-limiting examples of such polyethylene glycol ethers include oxyethylenated (30 EO) cetyl alcohol, oxyethylenated (15 EO) oleyl alcohol, oxyethylenated (50 EO) oleyl alcohol, oxyethylenated (10 EO) behenyl alcohol, oxyethylenated (30 EO) behenyl alcohol, oxyethylenated (12 EO) lauryl alcohol, oxyethylenated (23 EO) lauryl alcohol, oxyethylenated (20 EO) 2-octyldodecyl alcohol, oxyethylenated (20 EO) isocetyl alcohol, oxyethylenated (10 EO) oleyl alcohol, oxyethylenated (20 EO) oleyl alcohol, oxyethylenated (100 EO) stearyl alcohol, and oxyethylenated (21 EO) stearyl alcohol.

Non-limiting examples of polyethylene glycol/polypropylene glycol ethers in particular, include oxyethylenated (5 EO) oxypropylenated (5 PO) lauryl alcohol, oxypropylenated (3 PO) myristyl alcohol, oxyethylenated (20 EO) oxypropylenated (5 PO) cetyl alcohol, oxyethylenated (26 EO) oxypropylenated (26 PO) butyl alcohol, oxyethylenated (26 EO) oxypropylenated (26 PO) butyl alcohol, oxyethylenated (30 EO) oxypropylenated (6 PO) decyltetradecanol, and oxyethylenated (25 EO) oxypropylenated (25 PO) lauryl alcohol.

Non-limiting examples of ethoxylated alkyl or aryl derivatives of polyol include oxyethylenated derivatives of fatty acid esters or of fatty alcohol ethers and of a polyol such as glycerol, sorbitol, glucose or pentaerythritol. Suitable derivatives of this type include, for example, oxyethylenated (78 EO) glyceryl cocoate, oxyethylenated (120 EO) methylglucose dioleate, oxyethylenated (40 EO) sorbitan septaoleate, oxyethylenated (10 EO) polyglyceryl (2 mol of glycerol) laurate, oxyethylenated (60 EO) glyceryl isostearate, oxyethylenated (20 EO) glyceryl monostearate, oxyethylenated (200 EO) glyceryl stearate, and oxyethylenated (150 EO) pentaerythrityl tetrastearate, such as the product sold under the name Crothix.(TM) (ex. Croda, Inc.)

Non-limiting examples of suitable oxyalkylenated glyceryl triesters of fatty acids include, for example, oxyethylenated (6 EO) caprylic/capric acid glycerides, and oxyethylenated (50 EO) olive oil.

Particularly preferred for use in the primary adhesion promoter constituent compounds according to the structure:



wherein,

R is a fatty acid moiety, preferably a stearic fatty acid moiety, and

the sum of $w + x + y + z$ is in the range of 50 – 1500, preferably in the range of 70 – 500,

5 more preferably in the range of about 100 – 350 and especially preferably about 150.

A particularly preferred primary adhesion promoter constituent is a material presently commercially available under the tradename Crothix OG-CS (ex. Croda, Inc.).

As noted, the primary adhesion promoter constituent comprises from 0.1 – 10%wt. of the adhesive lavatory treatment compositions taught herein. Advantageously,

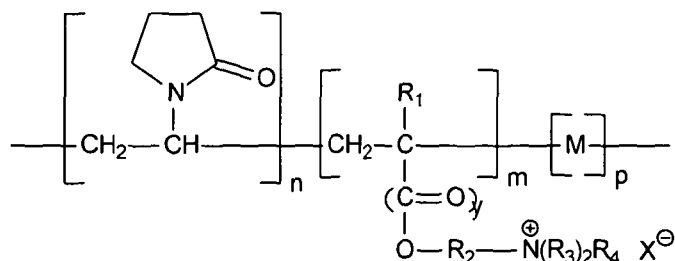
10 and in order of increasing preference the primary adhesion promoter constituent comprises at least 0.5%wt., 1%wt., 1.5%wt., 2%wt., 2.5%wt., 3%wt., 3.5%wt., 4%wt., 4.5%wt., 5%wt., 5.5%wt., 6%wt., 6.5%wt., 7%wt. and 7.5%wt. of the inventive composition. Concurrently the primary adhesion promoter constituent comprises not more than 10%wt, and in order of increasing preference, not more than 9.5%wt., 9%wt.,

15 8.5%wt., 8%wt., 7.5%wt., 7%wt., 6.5%wt., 6%wt., 5.5%wt., and 5%wt., based on the total weight of the inventive composition of which it forms a part.

The compositions of the invention may further comprise about 0 – 5%wt. of a co-adhesion promoter constituent, which while being an optional constituent and not necessary in all embodiments of the invention, is nonetheless preferably present.

20 Preferred co-adhesion promoters are based on water soluble or water dispersible materials, and are preferably based on water soluble or water dispersible film-forming polymers. Non-limiting examples of such polymers include:

1) a polymer having the formula



in which n represents from 20 to 99 and preferably from 40 to 90 mol %, m represents from 1 to 80 and preferably from 5 to 40 mol %; p represents 0 to 50 mol, (n+m+p=100); R₁ represents H or CH₃; y represents 0 or 1; R₂ represents --CH₂--CHOH--CH₂-- or C_xH_{2x} in which x is 2 to 18; R₃ represents CH₃, C₂H₅ or t-butyl; R₄ represents CH₃, C₂H₅ or benzyl; X represents Cl, Br, I, 1/2SO₄, HSO₄ and CH₃SO₃; and M is a vinyl or vinylidene monomer copolymerisable with vinyl pyrrolidone other than the monomer identified in []_m;

- 2) water soluble or water dispersible polyethylene oxide ("PEG");
- 3) polyvinylpyrrolidone;
- 4) high molecular weight polyethylene glycol;
- 5) polyvinylcaprolactam;
- 6) vinylpyrrolidone/vinyl acetate copolymer;
- 7) vinylpyrrolidone/vinyl caprolactam/ammonium derivative terpolymer,
- especially where the ammonium derivative is selected from diallylamino alkyl methacrylamides, dialkyl dialkenyl ammonium halides, and a dialkylamino alkyl methacrylate or acrylate;
- 8) polyvinylalcohol;
- 9) cationic cellulose polymer;
- 10) film-forming fatty quaternary ammonium compounds;
- 11) polyol ester;
- 12) polyacrylate homopolymers and copolymers comprising polyacrylate moieties;

one or more of which may be present in the co-adhesion promoter.

- Each of the foregoing water soluble or water dispersible film-forming polymers exhibit a weight average molecular weight of at least 500, preferably of at least 1000 with

water soluble or water dispersible film-forming polymers having weight avg. molecular weights of at least 5000 being particularly preferred.

In embodiments of the invention, wherein both a primary adhesion promoter and a co-adhesion promoter are concurrently present, preferably the weight ratio of the former to the latter is at least about 1.25:1, and especially preferably at least about 1.5:1.

The inventor has found that the inclusion of one or more of the foregoing polymers as an co-adhesion promoter constituent typically advantageously increases the adhesivity of the adhesive lavatory treatment compositions to surface.

The adhesive lavatory treatment compositions are essentially anhydrous, that is to say that the said compositions comprise less than about 0.01%wt. water, preferably less than about 0.05%wt. water, as water is not added as a constituent to the compositions and the selection of constituents are based on the absence of water present either as free water or as "bound water" such as may be present in certain inorganic compounds. Alternately the adhesive lavatory treatment compositions, comprise no water as an added constituent to the said compositions. Prior to being contacted with flush water in a lavatory appliance, e.g., water present as a film or laminar of water on a surface of the lavatory appliance or flush water contacting a mass or dose of the adhesive lavatory treatment composition subsequent to being applied to a surface of a lavatory appliance, the sole amount of water which may be present may be that absorbed from the ambient atmosphere, which typically is less than about 0.01%wt. water, preferably less than about 0.05%wt. water, and yet more preferably is less than about 0.025%wt. water.

The present inventor has surprisingly found that the adhesive lavatory treatment compositions exhibit good adhesivity to sloped or inclined hard surfaces, and may be very satisfactorily applied to dry hard surfaces, particularly to dry glazed or unglazed ceramic surfaces are may be found in many lavatory appliances, particularly toilet bowl interior surfaces, and in particular the interior inner sidewalls of toilet bowls. The adhesive lavatory treatment compositions may also be applied to such surfaces when they are wet or wetted with water, but wetted surfaces or the presence of any added water to the adhesive lavatory treatment compositions is not required in order to establish adhesion to such surfaces. The adhered adhesive lavatory treatment compositions of the invention also retain good adhesivity through many flush cycles of the lavatory appliance

to which they have been applied, and slowly erode over a series of flush cycles wherein one or more constituents of the adhesive lavatory treatment compositions are eluted to the flush water to form a lavatory treatment composition which is used to treat the lavatory appliance. The adhesive lavatory treatment compositions advantageously also release a
5 visible foam which may be seen by a consumer who typically equates the presence of foam in the toilet bowl with a cleaning benefit.

Further surprisingly the present inventor has found that notwithstanding the relatively high amounts of surfactant present in the adhesive lavatory treatment compositions, contrary to expectation the adhesive lavatory treatment compositions are
10 not overly quickly eroded and thus the adhesive lavatory treatment compositions when used to treat a lavatory appliance have a very satisfactory surface life.

As noted, the adhesive lavatory treatment compositions may further comprise one or more further optional constituents which may impart a further aesthetic or technical benefit to the said adhesive lavatory treatment compositions. When present, such further
15 optional constituents are generally present in a cumulative amount of less than about 25%wt. based on the total weight of the adhesive lavatory treatment compositions wherein one or more such further optional constituents may be present. By way of non-limiting example such further optional constituents include one or more of: coloring agents, fragrances and fragrance solubilizers, viscosity modifying agents, thickeners,
20 bleaches, bleach releasing compounds, oxidizing agents, germicidal agents, further surfactants in addition to those previously described as being essential to the adhesive lavatory treatment compositions, pH adjusting agents and pH buffers including organic and inorganic salts as well as organic and inorganic acids, builders, chelating agents, opacifying agents, titanium dioxide, inert inorganic or organic fillers, visually discernible
25 additive materials, hydrotropes, enzymes as well as other biologically active constituents, anti-oxidants, preservatives, and anti-corrosion agents, as well as other optional constituents known to the skilled artisan.. When one or more of the optional constituents is added, i.e., fragrance and/or coloring agents, the esthetic and consumer appeal of the product is often favorably improved. The use and selection of these optional constituents
30 should be based on imparting a desired additional aesthetic or technical benefit, as well as to ensure compatibility with the further constituents present in the inventive adhesive

lavatory treatment compositions, especially such that the desirable adhesive properties of the adhesive lavatory treatment compositions are not deleteriously diminished.

One class of optional constituents are further surfactants in addition to those previously described as being essential to the adhesive lavatory treatment compositions.

- 5 These include anionic, cationic, nonionic, amphoteric or zwitterionic surfactant compounds.

Exemplary useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their
10 molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the
15 alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain. Exemplary useful are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14.

Other exemplary useful anionic surfactants herein are the water soluble salts of:
20 paraffin sulfonates containing from about 8 to about 24 (preferably about 12 to 18) carbon atoms; alkyl glyceryl ether sulfonates, especially those ethers of C₈₋₁₈ alcohols (e.g., those derived from tallow and coconut oil); alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group; and alkyl ethylene oxide ether
25 sulfates containing about 1 to about 4 units of ethylene oxide per molecule and from about 10 to about 20 carbon atoms in the alkyl group.

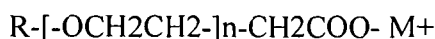
Other useful anionic surfactants herein include the water soluble salts of esters of α -sulfonated fatty acids containing from about 0 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water soluble salts of 2-
30 acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble

salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and β -alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Further exemplary useful as anionic surfactants are carboxylates such as alkyl
5 carboxylates which include those which may be represented by the general formula:

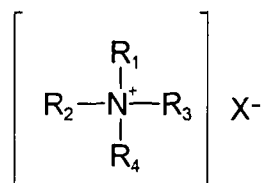


wherein R is a straight or branched hydrocarbon chain containing from about 9 to 21 carbon atoms, and M is a metal or ammonium ion; polyalkoxycarboxylates, representative of which are polyethoxycarboxylates which may be represented by the
10 general formula:



wherein R is a straight chained or branched hydrocarbon chain which may include an aryl moiety, but is desirably a straight chained or branched hydrocarbon chain; and n is an integer value of from 1 – 24.

15 Exemplary useful cationic surfactants include quaternary ammonium compounds and salts thereof which may include quaternary ammonium germicides characterized by the general structural formula:

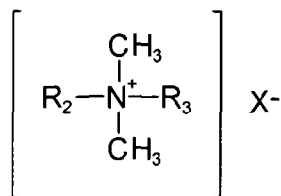


where at least one of R₁, R₂, R₃ and R₄ is a alkyl, aryl or alkylaryl substituent of from 6 to
20 26 carbon atoms, and desirably the entire cation portion of the molecule has a molecular weight of at least 165. The alkyl substituents may be long-chain alkyl, long-chain alkoxyaryl, long-chain alkylaryl, halogen-substituted long-chain alkylaryl, long-chain alkylphenoxyalkyl, arylalkyl, etc. The remaining substituents on the nitrogen atoms other than the abovementioned alkyl substituents are hydrocarbons usually containing no more
25 than 12 carbon atoms. The substituents R₁, R₂, R₃ and R₄ may be straight-chained or may be branched, but are preferably straight-chained, and may include one or more amide, ether or ester linkages. The counterion X may be any salt-forming anion which permits

water solubility of the quaternary ammonium complex. Exemplary counterions include halides, for example chloride, bromide or iodide, or methosulfate.

Exemplary quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide, ether or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Particularly preferred quaternary ammonium compounds which act as germicides and which are be found useful in the practice of the present invention include those which have the structural formula:



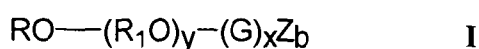
wherein R₂ and R₃ are the same or different C₈-C₁₂alkyl, or R₂ is C₁₂-C₁₆alkyl, C₈-C₁₈alkylethoxy, C₈-C₁₈alkylphenoethoxy and R₃ is benzyl, and X is a halide, for example chloride, bromide or iodide, or methosulfate. The alkyl groups recited in R₂ and R₃ may be straight-chained or branched, but are preferably substantially linear. The counterion X is as described previously.

Exemplary useful albeit optional nonionic surfactants, include known art nonionic surfactant compounds. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene

glycol, to form a water soluble nonionic surfactant compound. Further, the length of the polyethylenoxy hydrophobic and hydrophilic elements may vary. Exemplary nonionic compounds include the polyoxyethylene ethers of alkyl aromatic hydroxy compounds, e.g., alkylated polyoxyethylene phenols, polyoxyethylene ethers of long chain aliphatic alcohols, the polyoxyethylene ethers of hydrophobic propylene oxide polymers, and the higher alkyl amine oxides. Alkoxylated alkyl phenols including those commercially available under the tradename Triton® X series (Union Carbide Chem. Co., Danbury CT) may be advantageously added.

Further nonionic surfactants which may be optionally present in the inventive composition are alkyl polyglycoside. Suitable alkyl polyglycosides are known nonionic surfactants which are alkaline and electrolyte stable. Alkyl mono and polyglycosides are prepared generally by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide with an alcohol such as a fatty alcohol in an acid medium. Various glycoside and polyglycoside compounds including alkoxylated glycosides and processes for making them are disclosed in U.S. Patent No. 2,974,134; U.S. Patent No. 3,219,656; U.S. Patent No. 3,598,865; U.S. Patent No. 3,640,998; U.S. Patent No. 3,707,535; U.S. Patent No. 3,772,269; U.S. Patent No. 3,839,318; U.S. Patent No. 3,974,138; U.S. Patent No. 4,223,129; and U.S. Patent No. 4,528,106.

A preferred group of alkyl glycoside surfactants suitable for use in the practice of this invention may be represented by formula I below:

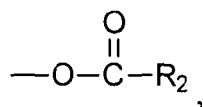


wherein:

- R is a monovalent organic radical containing from about 6 to about 30, preferably from about 8 to about 18 carbon atoms;
- R₁ is a divalent hydrocarbon radical containing from about 2 to about 4 carbon atoms;
- O is an oxygen atom;
- y is a number which has an average value from about 0 to about 1 and is preferably 0;
- G is a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; and

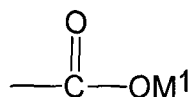
x is a number having an average value from about 1 to 5 (preferably from 1.1 to 2);

Z is O_2M^1 ,



5 $\text{O}(\text{CH}_2)$, CO_2M^1 , OSO_3M^1 , or $\text{O}(\text{CH}_2)\text{SO}_3\text{M}^1$; R_2 is $(\text{CH}_2)\text{CO}_2\text{M}^1$ or $\text{CH}=\text{CHCO}_2\text{M}^1$; (with the proviso that Z can be O_2M^1 only if Z is in place of a primary hydroxyl group in which the primary hydroxyl-bearing carbon atom,

$\text{—CH}_2\text{OH}$, is oxidized to form a



10

group);

b is a number of from 0 to $3x+1$ preferably an average of from 0.5 to 2 per glycosal group;

p is 1 to 10,

15 M^1 is H^+ or an organic or inorganic cation, such as, for example, an alkali metal, ammonium, monoethanolamine, or calcium.

As defined in Formula I above, R is generally the residue of a fatty alcohol having from about 8 to 30 and preferably 8 to 18 carbon atoms. Examples of such alkylglycosides as described above include, for example, APG™ 325 CS GLYCOSIDE
20 which is described as being a 50% $\text{C}_9\text{—C}_{11}$ alkyl polyglycoside, also commonly referred to as D-glucopyranoside, (commercially available from Henkel Corp, Ambler PA) and GLUCOPON™ 625 CS which is described as being a 50% $\text{C}_{10}\text{—C}_{16}$ alkyl polyglycoside, also commonly referred to as a D-glucopyranoside.

A further class of optionally included nonionic surfactants include nonionic
25 surfactant compounds which are based on a polymeric alkylene oxide block copolymer. Polymeric alkylene oxide block copolymers include nonionic surfactants in which the major portion of the molecule is made up of block polymeric $\text{C}_2\text{—C}_4$ alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting

group, and can have as a starting nucleus almost any active hydrogen containing group including, without limitation, amides, phenols, thiols and secondary alcohols. One preferred class of such nonionic surfactants containing the characteristic alkylene oxide blocks are those which may be generally represented by the formula (A):



5

where EO represents ethylene oxide,

PO represents propylene oxide,

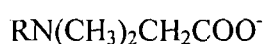
y equals at least 15,

$(\text{EO})_{x+z}$ equals 20 to 50% of the total weight of said compounds, and,

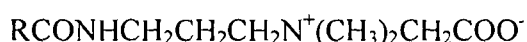
10 the total molecular weight is preferably in the range of about 2000 to 15,000.

Examples of particularly useful nonionic surfactant compounds which include as a major portion of the molecule a block polymeric alkylene oxide block are those materials presently commercially available under the tradename "Pluronic®", and in particular the Pluronic®F series, Pluronic®L series, Pluronic®P series, as well as in the
15 Pluronic®R series, each of which are generally described to be block copolymers of propylene oxide and ethylene oxide, and are presently commercially available from BASF AG (Ludwigshafen, Germany) as well as from BASF Corp. (Mt. Olive Township, New Jersey).

Exemplary useful albeit optional amphoteric surfactants include alkylbetaines,
20 particularly those which may be represented by the following structural formula:

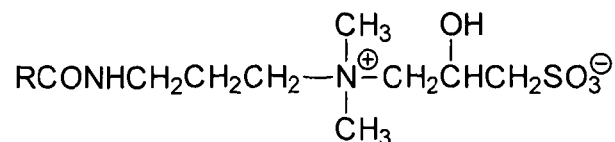


wherein R is a straight or branched hydrocarbon chain which may include an aryl moiety, but is preferably a straight hydrocarbon chain containing from about 6 to 30 carbon atoms. Further exemplary useful amphoteric surfactants include amidoalkylbetaines,
25 such as amidopropylbetaines which may be represented by the following structural formula:



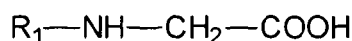
wherein R is a straight or branched hydrocarbon chain which may include an aryl moiety, but is preferably a straight hydrocarbon chain containing from about 6 to 30 carbon

atoms. Further useful amphoteric surfactants include sultaines, including compounds which may be represented by the following formula:



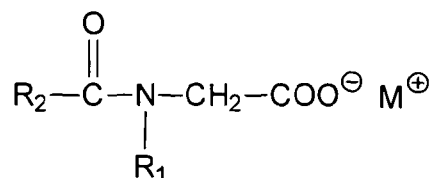
- 5 In the above formulae, R represents a C₈ to C₂₄ alkyl group, and is preferably a C₁₀ to C₁₆ alkyl group.

Further exemplary useful optional surfactants include sarcosinate surfactants which are alkali metal salts of N-alkyl-N-acyl amino acids. These are salts derived from
10 the reaction of (1) N-alkyl substituted amino acids of the formula:

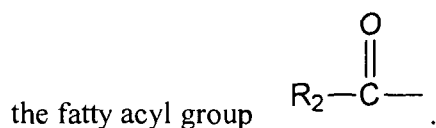


- where R₁ is a linear or branched chain lower alkyl of from 1 to 4 carbon atoms, especially a methyl, for example, aminoacetic acids such as N-methylaminoacetic acid (i.e. N-methyl glycine or sarcosine), N-ethyl-aminoacetic acid, N-butylaminoacetic acid, etc.,
15 with (2) saturated natural or synthetic fatty acids having from 8 to 18 carbon atoms, especially from 10 to 14 carbon atoms, e.g. lauric acid, and the like.

The resultant reaction products are salts which may have the formula:



- where M is an alkali metal ion such as sodium, potassium or lithium; R₁ is as
20 defined above; and wherein R₂ represents a hydrocarbon chain, preferably a saturated hydrocarbon chain, having from 7 to 17 carbon atoms, especially 9 to 13 carbon atoms of



Exemplary useful sarcosinate surfactants include cocoyl sarcosinate, lauroyl sarcosinate, myristoyl sarcosinate, palmitoyl sarcosinate, stearoyl sarcosinate and oleoyl

sarcosinate, and tallow sarcosinate. Such materials are also referred to as N-acyl sarcosinates.

Optionally the inventive compositions may comprise a germicide constituent (other than the cationic germicidally active quaternary ammonium halide surfactants noted above) which has germicidal or antimicrobial efficacy against at least one of gram-positive or gram-negative pathogens, e.g., bacteria or other microorganisms. Such may be based, for example, on one or more non-cationic antimicrobial compounds or constituents, e.g., halophenols such 3-trifluoromethyl-4,4'-dichlorocarbaniide, 3,3',4-trichlorocarbaniide, as well as 2,4-dichloro-3,5-m-xyleneol ("DCMX"). The phenol based non-cationic antimicrobials are preferred, of which parachlorometacresol ("PCMC") and especially parachlorometaxyleneol ("PCMX").

Alternately such may be based, for example, on one or more phenol derivatives such as those based on 2-hydroxydiphenyl compounds, including Triclosan® (ex. Ciba), those based on 2,2'-hydroxy-5,5'-dibromo-diphenyl ethers, such as one or more of chlorophenols (o-, m-, p-), 2,4-dichlorophenol, p-nitrophenol, picric acid, xyleneol, p-chloro-m-xyleneol, cresols (o-, m-, p-), p-chloro-m-cresol, pyrocatechol, resorcinol, 4-n-hexylresorcinol, pyrogallol, phloroglucin, carvacrol, thymol, p-chlorothymol, o-phenylphenol, o-benzylphenol, p-chloro-o-benzylphenol, phenol, 4-ethylphenol, and 4-phenolsulfonic acid, as well as further diphenol compounds such as hexachlorophene, tetrachlorophene, dichlorophene, 2,3-dihydroxy-5,5'-dichlorodiphenyl sulfide, 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenyl sulfide, 2,2'-dihydroxy-3,5',5,5', 6,6'-hexachlorodiphenyl sulfide, and 3,3'-dibromo-5,5'-dichloro-2,2'-dihydroxydiphenylamine, and especially "Triclocarban", 3,4,4'-trichlorocarbaniide as well as derivatives therero

The optional germicide constituent may also be based on one or more acids, including organic acids such as salicylic and citric acid, and/or inorganic acid such as hydrochloric acid when present in effective amounts in order to sufficiently acidify the treatment composition formed from the inventive compositions.

Optionally the inventive compositions may comprise bleaches and/or bleach releasing compounds. Examples of such bleaches and/or bleach releasing compounds include those selected from the group of the alkali metal and alkaline earth salts of

hypohalite, haloamines, haloimines, haloimides and haloamides. All of these are believed to produce hypohalous bleaching species in situ. Hypochlorite and compounds producing hypochlorite in aqueous solution are preferred, although hypobromite is also suitable.

Representative hypochlorite-producing compounds include sodium, potassium, lithium and calcium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium and sodium dichloroisocyanurate and trichlorocyanuric acid. Organic bleach sources suitable for use include heterocyclic N-bromo and N-chloro imides such as trichlorocyanuric and tribromocyanuric acid, dibromo- and dichlorocyanuric acid, and potassium and sodium salts thereof, N-brominated and N-chlorinated succinimide, malonimide, phthalimide and naphthalimide. Also suitable are hydantoins, such as dibromo- and dichloro dimethylhydantoin, chlorobromodimethyl hydantoin, N-chlorosulfamide (haloamide) and chloramine (haloamine). Particularly preferred is sodium hypochlorite having the chemical formula NaOCl

Optionally an oxidizing constituent or agent may be present in the inventive compositions. Examples of such an oxidizing agent include peroxyhydrates or other agent which releases hydrogen peroxide in aqueous solution. Such materials are per se, known to the art. Peroxyhydrates are to be understood as including hydrogen peroxide as well as any material or compound which in an aqueous composition yields hydrogen peroxide. Non-limiting examples of such materials and compounds include: alkali metal peroxides including sodium peroxide and potassium peroxide, alkali perborate monohydrates, alkali metal perborate tetrahydrates, alkali metal persulfate, alkali metal percarbonates, alkali metal peroxyhydrate, alkali metal peroxydihydrates, and alkali metal carbonates especially where such alkali metals are sodium or potassium. Further useful are various peroxydihydrate, and organic peroxyhydrates such as urea peroxide. Desirably, when present, the oxidizing agent is hydrogen peroxide.

When an oxidizing agent is present, minor amounts ($< 1\%$ wt.) of one or more known art hydrogen peroxide stabilizers such as one or more organic phosphonates, stannates, pyrophosphates, as well as citric acid, may also be present.

Optionally the inventive composition may include visibly discernible materials which may, for example, be particles or particulates which are visibly discernible to a consumer, particularly by a consumer having normal "20/20" vision, visually inspecting a

mass or dose of the adhesive lavatory treatment compositions applied to a hard surface.

Non-limiting examples of such visibly discernible materials include materials which provide a visual effect of suspended inclusions within the mass of an adhesive lavatory treatment compositions which may be advantageous from a consumer standpoint. Such

5 visibly discernible materials may for example be particulates of mica, colored beads such as glass beads or beads, comminuted particles or spheres formed from uncolored or colored synthetic polymers, visible light reflective particles (commonly referred to as “glitter”) which are typically formed of comminuted metallized or reflective polymer particles, alginate beads such as those described in PCT/US95/08313, US Patent
10 7196046, US Patent 7291586 B2, as well as other visibly discernible materials known to the art which would provide a similar function. Preferably such visibly discernible materials have a maximum dimension in the the range of from about 100 to about 1000 μm .

Optionally the inventive compositions may include one or more inert inorganic or
15 inert organic fillers compounds or materials which are preferably insoluble in water or in organic solvents. Non-limiting examples of such inert fillers include powders such as silicates, chalk, talc, kaolin, chemically modified magnesium aluminum silicate, hydrated aluminum silicate, fumed silica, and mixtures thereof

Optionally the inventive compositions may include one or more constituents
20 which function as viscosity modifying agents or thickeners. Non-limiting examples of such materials include polysaccharide polymers especially those selected from cellulose, alkyl celluloses, alkoxy celluloses, hydroxy alkyl celluloses, alkyl hydroxy alkyl celluloses, carboxy alkyl celluloses, carboxy alkyl hydroxy alkyl celluloses, naturally occurring polysaccharide polymers such as xanthan gum, guar gum, locust bean gum,
25 tragacanth gum, or derivatives thereof Further constituents which function as viscosity modifying agents or thickeners include polycarboxylate polymers, polyacrylamides, clays, and mixtures thereof.

Non-limiting examples of useful cellulose derivatives include methyl cellulose
ethyl cellulose, hydroxymethyl cellulose hydroxy ethyl cellulose, hydroxy propyl
30 cellulose, carboxy methyl cellulose, carboxy methyl hydroxyethyl cellulose,

hydroxypropyl cellulose, hydroxy propyl methyl cellulose, ethylhydroxymethyl cellulose and ethyl hydroxy ethyl cellulose.

Non-limiting examples of useful polycarboxylate polymers are those have a molecular weight from about 500,000 to about 4,000,000, preferably from about
5 1,000,000 to about 4,000,000, with, preferably, from about 0.5% to about 4% crosslinking. Preferred polycarboxylate polymers include polyacrylate polymers including those sold under trade names Carbopol®, Acrysol® ICS-1 and Sokalan®. The preferred polymers are polyacrylates. Other monomers besides acrylic acid can be used to form these polymers including such monomers as ethylene and propylene which act as
10 diluents, and maleic anhydride which acts as a source of additional carboxylic groups.

Non-limiting examples of further useful polycarboxylic acid polymer compositions which can be employed include, for example, crosslinked copolymers of acrylates, (meth)acrylic acid, maleic anhydride, and various combinations thereof.

Non-limiting examples of useful clay thickeners include colloid-forming clays,
15 for example, such as smectite and/or attapulgite types. The clay materials can be described as expandable layered clays, i.e., aluminosilicates and magnesium silicates. The term "expandable" as used to describe the instant clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The expandable clays used herein are those materials classified geologically as smectites (or
20 montmorillonite) and attapulgites (or polygorskites). Commercially available clays include, for example, montmorillonite, bentonite, volchonskoite, nontronite, beidellite, hectorite, saponite, sauconite and vermiculite. The clays herein are available under various trade names such as Gelwhite GP, Gelwhite H, Mineral Colloid BP, and Laponite from Southern Clay Products, Inc., Texas; and Van Gel O from R. T. Vanderbilt.

25 The compositions of the invention may be formed by first gently heating the organic solvent constituent to about 100 - 120°C and thereafter under stirring conditions adding thereto the primary adhesion promoter constituent. Mixing is continued for approximately 30 minutes to ensure the formation of a homogenous mixture, and thereafter the heat sources is removed or turned off, and the temperature of the mixture is
30 monitored. Thereafter, under constant mixing conditions, after the temperature of the mixture has been reduced to approximately 80°C, are thereafter added the surfactants, and

mixing continues until the mixture is homogenous. Subsequently the co-adhesion promoter is added and mixing continues. Thereafter, when the temperature of the mixture has been reduced to about 40°C, under high speed mixing are next added the co-adhesion promoters (when present), and then the remaining constituents, and mixing continues
5 under high speed until the mixture is homogenous, after which mixing ceases and the composition is allowed to reduce its temperature to room temperature (approx. 20 - 22°C). Thereafter the composition may be removed from the mixing vessel and used.

Preferred adhesive lavatory treatment compositions of the invention are viscous or pasty, and may be characterized in having a viscosity in the range of from about 150,000
10 cP to about 7,000,000 cP, but preferably from about 200,000 to about 5,000,000. The viscosity may be determined utilizing conventional analytical instruments.

The compositions of the invention may be applied directly to hard surfaces, which may be vertical, or sloped, and may be applied to and retained thereupon even on dry surfaces. As previously noted, especially preferred hard surfaces include non-wetted or
15 dry surfaces of lavatory appliances, particularly the interior surface of a toilet bowl. Once applied, the compositions may be flushed away after a plurality of flushing operations, preferably following a relatively large number of flushing operations. While it is naturally understood that the operating parameters of lavatory devices, e.g., toilets, vary considerably and that the range of compositions which are taught herein are also
20 variable, preferably, once applied a mass (preferably between about 2 and about 10 grams, more preferably from about 3 to about 7 grams, and covering a surface area of approximately about 1 to about 10 cm²) of the inventive composition are retained in the hard surface for at least 5, and in order of increasing preference, at least 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80 flushes, or until the mass of the of the
25 adhesive lavatory treatment compositions is eroded by the flushing water of the lavatory device.

The compositions of the invention may be applied either directly by a consumer, but are more conveniently applied utilizing a dispensing means which contains a quantity of an the adhesive lavatory treatment composition as taught herein. For example, a larger
30 quantity of an the adhesive lavatory treatment compositions may be provided in a dispenser such as compressible tube, or bottle, compressible piston and syringe type

dispenser, compressible bag or blister-type formed package which is compressed by a consumer to expel and dispense a quantity of the adhesive lavatory treatment composition onto a hard surface. The amount dispensed per dispensing operation may be variable, or may be predetermined so that an approximately uniform mass/quantity of the adhesive lavatory treatment composition may be applied as a dose to a hard surface. The adhesive lavatory treatment compositions may be supplied in a suitable dispenser which dispenses a single dose of the compositions during an application step or application operation. Such dispensing means may be, for example, prefilled cartridges such as blisters, dispensing devices such as may comprise a plurality of cartridges each of which contains a single unit dose, which is expelled from the device, piston containing cylindrical dispensers which may include means to limit the travel of the piston through the bore of the cylindrical dispenser so that upon displacement of the piston, a dose of the adhesive lavatory treatment composition is expelled. Also suitable dispensing means are a pouch which contains in its interior a mass of the adhesive lavatory treatment composition; in application the pouch may be opened at one end thereof and the adhesive lavatory treatment composition squeezed out onto a hard surface, or one part of the pouch may be peeled away, e.g., a film, and thereafter the exposed adhesive lavatory treatment composition may be applied to a hard surface by a consumer, and thereafter the remaining part of the pouch may be withdrawn and discarded by a consumer. Certain particularly preferred dispensing means include those disclosed in copending patent applications GB patent application 1007066.2, or GB patent application 1007064.7, filed 28.Apr.2010, the contents of which are herein incorporated by reference, or may be supplied in a suitable dispenser which dispenses a plurality of single doses. Other dispensing means which provide a similar function as described above and herein may also be used and are considered suitable as dispensing means for the adhesive lavatory treatment compositions taught herein.

Each form of dispensing means provides specific advantages. Dispensers such as compressible tubes, or compressible bottles and flasks may permit for the dispensing of variable amounts of the adhesive lavatory treatment compositions which may be desired from a consumer standpoint, so that the amounts delivered on each application are not limited to a specific dose. However dispensers which supply an approximately uniform

mass and/or quantity of the adhesive lavatory treatment composition on each dispensing operation may be advantageous as providing a consistent amount which may be preferred in certain applications or by consumers.

5 Compositions of adhesive lavatory treatment compositions according to the invention are particularly well adapted for use with a lavatory appliance in order to provide a cleaning and/or fragrancing and/or sanitizing and/or other technical benefit thereto. In use, a quantity of an adhesive lavatory treatment composition is applied directly to a part of a lavatory appliance, advantageously in a part thereof wherein the adhered adhesive lavatory treatment composition is in the path of flowing water, e.g.,
10 flush water, which impinges upon the adhered adhesive lavatory treatment compositions and slowly erodes the same, and thereby forming a lavatory treatment liquid which comprises the water which entrains one or more of the constituents of the adhesive lavatory treatment compositions which has been released by the water. Depending upon the specific constituents used to form the adhesive lavatory treatment compositions,
15 various technical benefits may be provided by the thus formed lavatory treatment liquid. Thus, an aspect of the invention provides a method of for treating a lavatory appliance comprising the steps of: applying an adhesive lavatory treatment composition directly to a part of a lavatory appliance wherein the adhered adhesive lavatory treatment composition is in the path of flowing water, e.g., flush water, which impinges upon the
20 adhered adhesive lavatory treatment compositions and slowly erodes the same, and, operating the lavatory appliance to dispense a flow of water which impinges on the adhesive lavatory treatment composition is in the path of flowing water thereby forming a lavatory treatment liquid which treats the lavatory appliance.

25 Examples:

Compositions of adhesive lavatory treatment compositions according to the invention were produced, and are identified on Table 1. These example compositions were formed generally in accordance with the following steps.

30 To a mixing vessel equipped with a motorized stirrer and with a hotplate or suitable heating mantle was first added the organic solvent constituent, to which was added the primary adhesion promoter constituent. Next, the motorized stirrer was

activated, and the contents of the mixing vessel was stirred throughout the balance of the process, and the contents of the vessel was heated to approximately 120°C. The mixture of within the vessel were stirred until the primary adhesion promoter was fully melted, and the contents of the vessel were homogenous. Thereafter, the heat was disengaged, and mixing was continued until the composition was homogenous. The heat was removed, and under stirring the contents and the mixing vessel was allowed to cool under ambient room temperature (20 - 22°C) conditions, until the temperature of the vessel contents was about 80°C. Thereafter under stirring conditions were added the surfactants, and these were mixed in until the composition was again homogenous. Then the speed of the agitator of the mixer was increased to a high speed, and then were added the co-adhesion promoters, and mixing continued until the composition was again homogenous, and the temperature was allowed to further decrease. When the temperature of the mixing composition was about 40 - 45°C, the remaining constituents were added to the mixing vessel, and mixing continued until the composition was again homogenous, after which the motorized stirrer was removed from the mixing vessel and the composition was allowed to cool under ambient room temperature conditions to room temperature, after which the composition was withdrawn and used.

Table 1

	E1	E2	E3	E4	E5	E6	E7	E8
Crothix OG-CS	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
propylene glycol	42.0	42.6	42.4	42.0	34.1	28.8	23.8	17.8
Ninol CO 40	27.0	27.0	27.0	20.0	35.0	40.0	40.0	40.0
Biosoft 91-2.5	20.0	20.0	20.0	--	--	--	--	--
Tomadol 600	--	--	--	27.0	20.0	20.0	25.0	30.0
Luvitec K90	1.0	0.4	0.6	--	0.9	1.2	1.2	1.2
Luvitek VA 64	--	--	--	--	--	--	--	--
Priolube 3986	--	--	--	1.0	--	--	--	--
fragrance	3.0	3.0	3.0	3.0	3.0	3.0	3.0	4.0
TOTAL	100	100	100	100	100	100	100	100

Table 1

	E9	E10	E11	E12	E13	E14	E15
Crothix OG-CS	6.0	6.0	6.0	6.0	6.0	5.0	4.0
propylene glycol	23.8	23.3	22.0	22.4	22.2	23.0	24.0
Ninol CO 40	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Biosoft 91-2.5	--	--	--	--	--	--	--
Tomadol 600	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Luvitec K90	1.2	1.2	1.0	0.8	0.9	1.0	1.0
Luvitek VA 64	--	0.5	2.0	1.8	1.9	2.0	2.0
Priolube 3986	--	--	--	--	--	--	--
fragrance	4.0	4.0	4.0	4.0	4.0	4.0	4.0
TOTAL	100	100	100	100	100	100	100

The identity of the constituents of Table 1 are disclosed on the following Table 2.

Table 2	
Crothix OG-CS	polymer resin, 90-100%wt. actives (ex. Croda)
propylene glycol	propylene glycol, 100%wt. actives (technical grade)
Ninol CO 40	coconut diethanolamide, nonionic surfactant / Ninol CO 40 / 100%wt. actives
Biosoft 91-2.5	nonionic surfactant, C ₉ -C ₁₁ alcohol ethoxylate (2.5 EO), 100%wt. actives (ex. Stepan)
Tomadol 600	C ₁₀ -C ₁₆ alcohol ethoxylate used "as-supplied", recited by its supplier to have a molecular weight of 400, have an EO content of 53%wt, and an HLB of 10.6, and having 95-100%wt. actives (ex. Air Products and Chemicals, Inc.)
Luvitek K90	vinylpyrrolidone polymer (powder), 95 - 100%wt. actives (ex. BASF)
Luvitek VA 64	polyvinylpyrrolidone and vinylacetate copolymer (60%/40% monomer ratio) (powder), 95 - 100%wt. actives (ex. BASF)
Priolube 3986	ester-saturated polyol ester, 95 - 100%wt. actives (ex. Croda)
fragrance	proprietary composition

Samples of the compositions of the invention were very viscous or pasty and are self-supporting, viz., and did not sag or run under their own weight.

The viscosities of the Example compositions of Table 1 were measured utilizing an AR2000 ex device (ex. TA Instruments), using a sample of each composition located between parallel, 20 mm stainless steel plates at a testing shear rate of 0.1 – 0.5 reciprocal seconds (1/sec.) having a gap of 1000 micrometers between the two plates and the test temperature of the sample was 30°C. The viscosity of certain of these compositions is reported on Table 3 as follows:

Table 3		
Composition	Shear rate (1/sec)	Viscosity (cP)
E1	0.223	3867000
E2	0.223	4916000
E3	0.223	7543000
E4	0.223	6602000
E5	0.222	4776000
E6	0.223	5669000
E7	0.222	4431000
E8	0.223	7700000
E9	0.223	5244000

E10	0.223	3832000
E11	0.223	5672000
E12	0.224	4503000
E13	0.222	7354000
E14	0.224	3424000
E15	0.224	1858000

5

Adhesion Testing:

Samples of compositions according to Example compositions E1, E4, E8, E12 and E15 were tested for their adhesivity and expected useful service life. Sample aliquots averaging approximately 3 grams and having a surface coverage area of about 35 mm by about 22 mm and having a thickness of about 4 mm, were applied to the inner sidewall of toilet bowl which had been carefully dried prior to application of the sample, either allowed to air dry in the ambient environment, or had been dried using a heated air blow drier. The aliquots were applied by means of a suitable applicator (e.g., a dispensing means as disclosed in one of copending patent applications GB patent application 1007066.2, filed 28.Apr.2010, and GB patent application 1007064.7, filed 28.Apr.2010, by first locating the applicator containing the aliquot of a sample composition, and thereafter manually operating (compressing) the applicator to deliver the sample therefrom such that the sample was contacted with, and adhered to the sidewall of the toilet bowl. The location of the applied sample composition was at position between about 2 and 15 cm below the rim of the toilet bowl. Three sample aliquots of each formulation were tested at different positions within each toilet bowl, with one sample aliquot placed on the inner sidewall of the toilet bowl at its front, viz., the part opposite to that of the tank or cistern of the toilet bowl. The second and third aliquots were adhered on the inner sidewall of the toilet bowl at points midway between the front of the toilet bowl, and the back of the toilet bowl, viz., the part proximate to the tank or cistern of the toilet, the second aliquot on the "right" side of the toilet bowl, and the third aliquot on the "left" side of the toilet bowl. The toilet bowls were model "Brive" toilet bowls, (ex., Jacob Delafon (France)) and were automatically flushed at flush intervals of 15 minutes between flushes, which automatic flushing operation continued for 36 hours. The average water temperature of the flush water was about 17°C, and the average room

temperature was about 20°C. The foregoing is a harsh testing regimen, as it is an accelerated testing protocol.

During the testing, the appearance and displacement (if any) of the applied sample aliquots were observed and noted every hour. The results of this test are reported in the

5 following Table 4:

Table 4		
	position/# of flushes	observations:
E1	right/4	slid downwardly approx. 2 cm
	middle/5	slid downwardly approx. 2.5 cm
	left/5	fell off sidewall
E4	right/12	slid downwardly approx. 0.7 cm
	middle/7	fell off sidewall
	left/6	fell off sidewall
E8	right/16	slight rotation
	middle/45	slid downwardly approx. 0.7 cm
	left1/6	slid downwardly approx. 0.7 cm
E12	right/36	fell off sidewall
	middle/45	slid downwardly approx. 1.2 cm
	left1/36	slight rotation
E15	right/36	fell off sidewall
	middle/17	fell off sidewall
	left/19	slight rotation

As is evident from the above, preferred example compositions exhibited adhesivity and a satisfactory service life even under the hard conditions to which the
 10 sample aliquots were exposed.

While the invention is susceptible of various modifications and alternative forms, it is to be understood that specific embodiments thereof have been shown by way of example in the drawings which are not intended to limit the invention to the particular forms disclosed; on the contrary the intention is to cover all modifications, equivalents
 15 and alternatives falling within the scope and spirit of the invention as expressed in the appended claims.

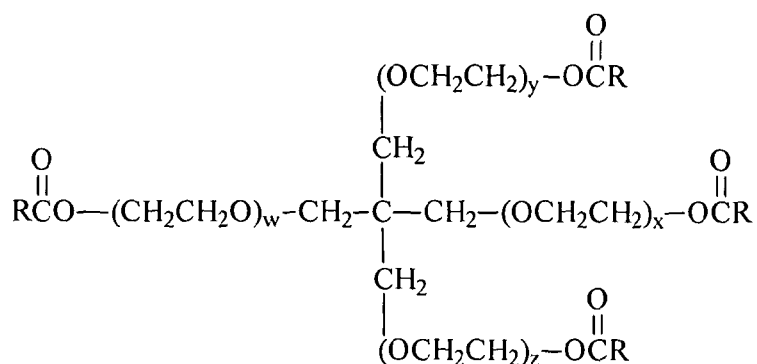
Claims:

1. Adhesive lavatory treatment compositions which are essentially anhydrous which
comprise:
- 5 1 – 50%wt. of an organic solvent constituent;
 5 – 50%wt. of at least one alkanolamide based nonionic surfactant;
 1 – 50%wt. of at least one nonionic surfactant constituent; and preferably
 wherein the at least one alkanolamide based nonionic surfactant; and the at least
 one nonionic surfactant constituent are present in respective weight ratios of 1-
10 2:1-2;
 0.1 – 10%wt, of a primary adhesion promoter constituent;
 optionally, at least one co-adhesion promoter; and.
 further optionally one or more further optional constituents; wherein in
 use, the said adhesive lavatory treatment compositions may be applied and
15 adhered to a dry ceramic surface, preferably the interior sidewall in a toilet bowl
 or other lavatory appliance, and wherein the said adhesive lavatory treatment
 compositions is retained adhered to the said surface following a plurality of
 flushes of water impinging upon the adhered adhesive lavatory treatment
 compositions.
- 20 2. An adhesive lavatory treatment composition according to claim 1, wherein:
 the at least one alkanolamide based nonionic surfactant is selected from
 fatty monoalkanolamides and fatty dialkanolamides.
- 25 3. An adhesive lavatory treatment composition according to claim 1, wherein:
 the nonionic surfactant constituent comprises a nonionic ethoxylated
 alcohol surfactant having a molecular weight of at least about 300.
- 30 4. An adhesive lavatory treatment composition according to any preceding claim,
 wherein:

the total amount of the least one alkanolamide based nonionic surfactant and at least one nonionic surfactant constituent comprise from about 40% to about 75%wt. of the adhesive lavatory treatment compositions.

- 5 5. An adhesive lavatory treatment composition according to any preceding claim, wherein:

the primary adhesion promoter constituent compounds according to the structure:



10 wherein,

R is a fatty acid moiety, preferably a stearic fatty acid moiety, and the sum of $w + x + y + z$ is in the range of 50 – 1500, preferably in the range of 70 – 500, more preferably in the range of about 100 – 350 and especially preferably about 150.

15

6. An adhesive lavatory treatment composition according to any preceding claim, which further comprises a co-adhesion promoter constituent.

7. A method treating a lavatory appliance comprising the steps of:

20 applying an adhesive lavatory treatment composition directly to a part of a lavatory appliance wherein the adhered adhesive lavatory treatment composition is in the path of flowing water, e.g., flush water, which impinges upon the adhered adhesive lavatory treatment compositions and slowly erodes the same, and, operating the lavatory appliance to dispense a flow of water which
25 impinges on the adhesive lavatory treatment composition is in the path of flowing

water thereby forming a lavatory treatment liquid which treats the lavatory appliance.

8. The method according to claim 7 wherein the lavatory appliance is a toilet.

5

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/051119

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D1/825 C11D3/20 C11D3/37 C11D17/00
ADD.

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)
C11D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 573 908 A (NKRO CHEMICALS LTD) 28 August 1980 (1980-08-28) column 1, lines 23-49; claims 1-39; examples 1-6	1-3,6
X	DE 10 2008 051173 A1 (BUCK CHEM TECH WERKE [DE]) 15 April 2010 (2010-04-15) paragraphs [0001], [0010] - [0014], [0019], [0045], [0047], [0062] - [0065], [0076], [0082], [0084], [0085]; claims 1,22-24; tables 1,2	7,8
X	EP 1 978 080 A1 (BOLTON MANITOBA SPA [IT]) 8 October 2008 (2008-10-08) paragraphs [0001] - [0005], [0010] - [0014], [0018], [0056]; claims 1-22; example 1	7,8
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2011/051119

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 088 612 A1 (BRIDGEMACE LIMITED [GB]) 14 September 1983 (1983-09-14) page 1, lines 8-19; claims 1,2,6-12,16,19-21; examples 1-8 page 6, lines 1-12 page 7, lines 9-15 -----	1-4,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2011/051119

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1573908	A	28-08-1980	NONE
DE 102008051173	A1	15-04-2010	NONE
EP 1978080	A1	08-10-2008	NONE
EP 0088612	A1	14-09-1983	DE 3369157 D1 19-02-1987 GB 2116994 A 05-10-1983