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COMPOSITIONS WITH SUBSTANTIVE
FOAMING BENEFITS AND IMPROVED
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(2), (4) Date: **Aug. 16, 2010**(30) **Foreign Application Priority Data**(75) Inventor: **Robert Zhong Lu, Guangzhou
(CN)**

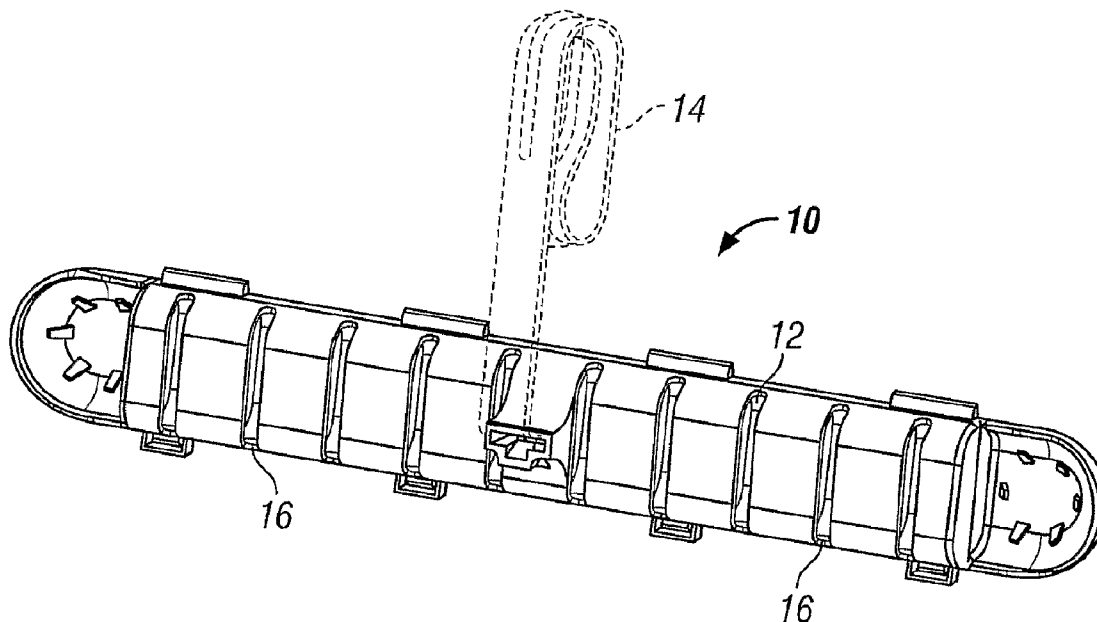
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Correspondence Address:

**PARFOMAK, ANDREW N.
NORRIS MCLAUGHLIN & MARCUS PA
875 THIRD AVE, 8TH FLOOR
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Lavatory treatment blocks which provide improved foaming benefit and improved foam substantivity are provided. The lavatory treatment blocks may be used with or without a lavatory treatment device, such as an in the bowl type, or in the cistern type device. Preferred embodiments of the lavatory treatment blocks provide a cleaning and/or sanitizing and/or disinfecting benefit to a sanitary appliance being treated using the lavatory treatment blocks.

(73) Assignee: **RECKITT BENCKISER, INC.,
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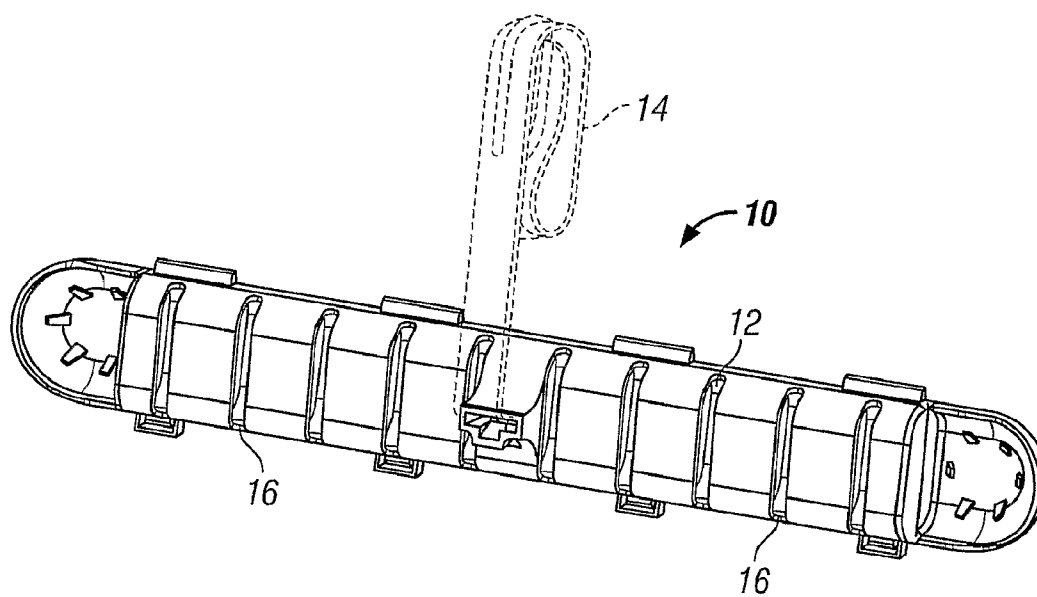


FIG. 1

**LAVATORY TREATMENT BLOCK
COMPOSITIONS WITH SUBSTANTIVE
FOAMING BENEFITS AND IMPROVED
LIFESPAN**

[0001] The present invention relates to improved solid treatment block compositions useful for providing an active treatment composition to a sanitary appliance, e.g., a toilet or urinal.

[0002] Solid treatment blocks have found widespread use in the cleaning and/or disinfecting treatment of sanitary appliances as, once installed they require little or no user intervention during their effective service life. Such solid treatment block compositions are considered to operate in an automatic fashion and their effective functioning is dependent in great part upon their composition, their dissolution characteristics when contacted with water and their placement within the sanitary appliance which they are used to treat. Typically such solid treatment block compositions are used in either one of two modes, either as an "ITC" or "in the cistern" mode, or as an "ITB" or "in the bowl" mode. In the former the solid treatment block composition is placed in water supply tank, also known as the cistern or toilet tank wherein it is expected to dissolve over a period of time and thus deliver active cleaning and/or disinfecting constituents to the water present in the cistern which is periodically used to flush the toilet bowl or other sanitary appliance, e.g., a urinal. Such a solid treatment block composition may be supplied to the interior of the cistern as a tablet or other self supporting shape, or alternately the solid treatment block composition may be provided in a container or cage, or as part of a dispensing device, from which the active cleaning and/or disinfecting constituents are delivered to the water present in the cistern. In the latter, the solid treatment block composition is placed within the bowl, typically supported by a device, cage, or even a simple bent wire such that the active cleaning and/or disinfecting constituents are contacted with water flushed into the sanitary appliance, especially the bowl of a toilet, or the interior of a urinal. In such an installation it is expected that a part of the solid treatment block composition is dissolved with each flush of water passing through the device such that an amount of active cleaning and/or disinfecting constituents are dispensed to the toilet bowl, urinal, etc.

[0003] The art is replete with many forms of solid treatment block compositions which find use either as ITB or ITC type compositions. Examples of such solid treatment block compositions include those described in the following: U.S. Pat. No. 4,246,129; U.S. Pat. No. 4,269,723; U.S. Pat. No. 4,043,931; U.S. Pat. No. 4,460,490; U.S. Pat. No. 4,722,802; U.S. Pat. No. 4,820,449; U.S. Pat. No. 5,342,550; U.S. Pat. No. 5,562,850; U.S. Pat. No. 5,711,920; U.S. Pat. No. 5,759,974; U.S. Pat. No. 5,939,372; U.S. Pat. No. 6,001,789 as well as U.S. Pat. No. 6,294,510. Each of these patents disclosed solid treatment block compositions which provide specific technical benefits, or overcome specific technical shortcomings which were hitherto known to the art until the time of the respective invention. For example, various processing shortcomings are known from the manufacture of such blocks, or from the dissolution characteristics of such blocks as are described in these patents or which are otherwise known to the relevant art.

[0004] A primary shortcoming resides in the fact that the foam formation characteristics of such devices including con-

ventional lavatory treatment blocks are poor. Frequently little or no foam is retained in the sanitary appliance, e.g., a toilet bowl at the conclusion of a flush cycle for any appreciable period of time. Such foam, if formed, rarely covers the surface of the water present in the bottom of a toilet bowl for any satisfactory length of time, and such foam frequently rather quickly breaks down or dissipates. When such foam is formed it generally not particularly voluminous and/or particularly substantive and may appear thin, and also frequently rather quickly breaks down or dissipates. Thus, prior art compositions suffer these and other technical shortcomings which the present invention addresses.

[0005] The present invention, in its various aspects, provides lavatory treatment blocks which are used to deliver a treatment composition to a sanitary appliance, particularly to a toilet, which treatment composition contains one or more chemical constituents e.g., coloring agents, cleaning agents, disinfecting agents, anti-lime scale agents which blocks are used to provide a cleaning composition and/or a sanitizing composition and/or disinfecting composition to a sanitary appliance, e.g. a toilet bowl. The lavatory treatment blocks can be used either as an ITC type device, or an ITB type device for a sanitary appliance such as a urinal, toilet tank or toilet bowl, or can be used independently in the form of a block, tablet or cake and not necessarily as a part of an ITC or ITB device. In certain preferred embodiments the device according to the invention is used as an ITB type device. In certain alternate preferred embodiments the device according to the invention is used as an ITC type device. In particularly preferred embodiments the lavatory treatment blocks provide improved foaming benefits, which may be manifested by improved foaming and/or improved substantivity of foam formed with the use of the improved lavatory treatment blocks taught herein.

[0006] According to a first aspect of the invention there are provided lavatory treatment blocks with improved foaming benefits wherein the said blocks contain a foam improving amount of glycerine.

[0007] According to a second aspect of the invention there are provided lavatory treatment blocks with improved foaming benefits wherein the said blocks contain a foam improving amount of a surfactant constituent which comprises glycerine.

[0008] According to a third aspect of the invention there are provided lavatory treatment blocks with improved foaming benefits wherein the said blocks contain a foam improving amount of a surfactant constituent which comprises, in combination, a fatty amide, such as cocoamide diethanolamide with glycerine.

[0009] According to a fourth aspect of the invention there is provided a lavatory dispensing device, preferably which may be an ITB device or an ITC device, comprising one or more lavatory treatment blocks according to the first, second or third aspects of the invention which are adapted for use with a sanitary appliance, preferably a toilet.

[0010] According to a fifth aspect of the invention there is provided a lavatory dispensing device comprising one or more lavatory treatment blocks according to the first, second or third aspects of the invention which are adapted for use with a sanitary appliance, preferably a toilet, wherein the said blocks provide an improved foaming benefit.

[0011] According to a sixth aspect of the invention there is provided a process for delivering a treatment composition to a sanitary appliance, especially preferably, to the interior of a

toilet bowl, which process comprises: providing one or more lavatory treatment blocks according to the first, second or third aspects recited above, and, periodically flushing water about the exterior of the said blocks to elute at least one chemical constituent to form a treatment composition with said water which treatment composition is used to treat a part of the sanitary appliance.

[0012] According to a seventh aspect of the invention there is provided a process for delivering a treatment composition to a toilet bowl which process comprises: providing one or more lavatory treatment blocks according to the first, second or third aspects recited above, and, periodically flushing water about the exterior of the said blocks to elute at least one chemical constituent to form a treatment composition with said water which treatment composition is used to treat a part of the sanitary appliance.

[0013] According to an eighth aspect of the invention there is provided a process for delivering a treatment composition to a sanitary appliance, especially preferably, to the interior of a toilet cistern or toilet tank, which process comprises: providing one or more lavatory treatment blocks according to the first, second or third aspects recited above within the said cistern or tank, and, continuously immersing or periodically immersing at least a part of the blocks in the water within the cistern or tank so to elute at least one chemical constituent from each of the lavatory treatment blocks to form a treatment composition with the water which is used to treat a part of the sanitary appliance.

[0014] According to a ninth aspect of the invention there is provided a process for delivering a treatment composition to a to the interior of a toilet bowl, which process comprises: providing one or more lavatory treatment blocks according to the first, second or third aspects recited above, preferably via use of an ITB device, suspending said block from a part of the toilet bowl, preferably from a part of the rim thereof, such that at least one chemical constituent of the block is used to form a treatment composition therefrom which is used to treat the interior of the toilet bowl when the treatment composition formed is used to flush the toilet bowl.

[0015] In accordance with a tenth aspect of the invention there is provided as a vendible article, one or more lavatory treatment blocks according to the first, second or third aspects recited above for use with a sanitary appliance, particularly a toilet.

[0016] In accordance with an eleventh aspect of the invention there is provided as a vendible article, a lavatory dispensing device comprising one or more lavatory treatment blocks according to the first, second or third aspects recited above for use with a sanitary appliance, particularly a toilet.

[0017] These and other aspects of the invention will be more evident from a reading of the following specification.

[0018] The lavatory treatment blocks of the invention, in particularly preferred embodiments, provide an improved foaming benefit. Such may be provided, for example by including glycerine as an essential constituent in order to improve the foaming characteristics of the blocks. Glycerine may be provided as a separate or discrete constituent which used to form a block composition, or it may be provided as part of a surfactant constituent or composition which comprises glycerine, such as a commercially available surfactant preparation which in addition to at least one surfactant such as a fatty amide, such as cocoamide diethanolamide, also includes glycerine.

[0019] The lavatory treatment blocks may additionally include one or more further chemical constituents such that when the block is immersed, rinsed or washed with water, said chemical constituents are eluted or dissolved into said water and forms a treatment composition which is useful in treating a sanitary appliance, and particularly a toilet tank or cistern or a toilet bowl. Such a treatment composition formed from the blocks may provide a cleaning and/or sanitizing and/or disinfecting benefit to the toilet or other sanitary appliance being treated with the blocks of the invention.

[0020] As further chemical constituents the lavatory treatment blocks may include any known art cleaning agents or cleaning constituents known to those of ordinary skill in the relevant art, and without limitation include one or more deter- sive surfactants selected from anionic, cationic, nonionic as well as amphoteric or zwitterionic surfactants. Certain deter- sive surfactants may also provide a dual role in providing detergency as well as a disinfecting effect, viz, certain cationic surfactants, which are described hereinafter as a disin- fecting agent. These one or more cleaning agents or cleaning constituents may be used with or without other constituents being present in the lavatory treatment blocks of the inven- tion.

[0021] The lavatory treatment blocks of the invention desir- ably comprises a surfactant constituent which may be one or more deter- sive surfactants. Exemplary useful surfactants include anionic, nonionic, cationic, amphoteric, and zwitte- rionic surfactants, particularly those whose melting points are sufficiently high, above about 110° F., preferably above 125° F., to permit processing according to known art techniques. However, small amounts of low melting point surfactants and even liquid surfactants may be used in providing the surfac- tant constituent.

[0022] Exemplary useful anionic surfactants which may be used in the treatment block compositions of the invention can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric acid reaction prod- ucts having in their molecular structure an alkyl or alkaryl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the anionic surfactants which can be employed in practic- ing the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); paraffin sulfonate sur- factants having the general formula RSO₃ M, wherein R is a primary or secondary alkyl group containing from about 8 to about 22 carbon atoms (preferably 10 to 18 carbon atoms) and M is an alkali metal, e.g., sodium, lithium or potassium; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from about 8 to about 12 carbon atoms; the reaction

products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium β -acetoxo- or β -acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

[0023] A preferred class of anionic surfactants are linear alkyl benzene sulfonate surfactant wherein the alkyl portion contains 8 to 16 carbon atoms, and most preferably about 11 to 13 carbon atoms. According to particularly preferred embodiments of the invention, the solid block compositions necessarily include an anionic surfactant.

[0024] A further preferred class of anionic surfactants are alpha olefin sulfonates, as well as salts thereof, e.g., alkali metal salts. Preferred are C_8 through C_{22} alpha olefin sulfonates, particularly C_{12} through C_{18} , and especially C_{14} , and C_{16} alpha olefin sulfonates as well as blends of two or more thereof. According to particularly preferred embodiments of the invention, the solid block compositions necessarily include an alpha olefin sulfonate anionic surfactant.

[0025] A yet further preferred class of anionic surfactants are linear alkyl benzene sulfonate surfactant wherein the alkyl portion contains 8 to 16 carbon atoms, and most preferably about 11 to 13 carbon atoms. According to particularly preferred embodiments of the invention, the solid block compositions necessarily include an anionic surfactant, especially linear alkyl benzene sulfonates containing 11, 12 or 13 carbon atoms, as well as salt forms thereof. The most preferred anionic surfactants are sodium alkylaryl sulfonates sold commercially by Albright & Wilson Warley, England under the trademarks NANSA, and UFARYL sold by Unger Fabrikker, Fredstad, Norway, either individually or in combination.

[0026] The deterative surfactant constituent of the solid block compositions of the invention may include one or more nonionic surfactants. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with an alkylene oxide, especially ethylene oxide or with the polyhydration product thereof, a polyalkylene glycol, especially polyethylene glycol, to form a water soluble or water dispersible nonionic surfactant compound. Further, the length of the polyethenoxy 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.

[0027] One class of useful nonionic surfactants include polyalkylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with an alkylene oxide, especially an ethylene oxide, the ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of

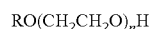
phenol and diisooctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol.

[0028] A further class of useful nonionic surfactants include the condensation products of aliphatic alcohols with from about 1 to about 60 moles of an alkylene oxide, especially an ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from about 10 to 14 carbon atoms). Other examples are those C_6 - C_{11} straight-chain alcohols which are ethoxylated with from about 3 to about 6 moles of ethylene oxide. Their derivation is well known in the art. Examples include Alfonic® 810-4.5, which is described in product literature from Sasol as a C_8 - C_{10} straight-chain alcohol having an average molecular weight of 356, an ethylene oxide content of about 4.85 moles (about 60 wt. %), and an HLB of about 12; Alfonic® 810-2, which is described in product literature as a C_8 - C_{10} straight-chain alcohols having an average molecular weight of 242, an ethylene oxide content of about 2.1 moles (about 40 wt. %), and an HLB of about 12; and Alfonic® 610-3.5, which is described in product literature as having an average molecular weight of 276, an ethylene oxide content of about 3.1 moles (about 50 wt. %), and an HLB of 10. Other examples of alcohol ethoxylates are C_{10} oxo-alcohol ethoxylates available from BASF under the Lutensol® ON tradename. They are available in grades containing from about 3 to about 11 moles of ethylene oxide (available under the names Lutensol® ON 30; Lutensol® ON 50; Lutensol® ON 60; Lutensol® ON 65; Lutensol® ON 66; Lutensol® ON 70; Lutensol® ON 80; and Lutensol® ON 110). Other examples of ethoxylated alcohols include the Neodol® 91 series non-ionic surfactants available from Shell Chemical Company which are described as C_9 - C_{11} ethoxylated alcohols. The Neodol® 91 series non-ionic surfactants of interest include Neodol® 91-2.5, Neodol® 91-6, and Neodol® 91-8. Neodol® 91-2.5 has been described as having about 2.5 ethoxy groups per molecule; Neodol 91-6 has been described as having about 6 ethoxy groups per molecule; and Neodol 91-8 has been described as having about 8 ethoxy groups per molecule. Further examples of ethoxylated alcohols include the Rhodasurf® DA series non-ionic surfactants available from Rhodia which are described to be branched isodecyl alcohol ethoxylates. Rhodasurf® DA-530 has been described as having 4 moles of ethoxylation and an HLB of 10.5; Rhodasurf® DA-630 has been described as having 6 moles of ethoxylation with an HLB of 12.5; and Rhodasurf® DA-639 is a 90% solution of DA-630. Further examples of ethoxylated alcohols include those from Tomah Products (Milton, Wis.) under the Tomadol® tradename with the formula $RO(CH_2CH_2O)_nH$ where R is the primary linear alcohol and n is the total number of moles of ethylene oxide. The ethoxylated alcohol series from Tomah include 91-2.5; 91-6; 91-8—where R is linear $C_9/C_{10}/C_{11}$ and n is 2.5, 6, or 8; 1-3; 1-5; 1-7; 1-73B; 1-9; where R is linear C_{11} and n is 3, 5, 7 or 9; 23-1; 23-3; 23-5; 23-6.5—where R is linear C_{12}/C_{13} and n is 1, 3, 5, or 6.5; 25-3; 25-7; 25-9; 25-12—where R is linear $C_{12}/C_{13}/C_{14}/C_{15}$ and n is 3, 7, 9, or 12; and 45-7; 45-13—where R is linear C_{14}/C_{15} and n is 7 or 13.

[0029] A further class of useful 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 moles of ethoxylation per mol of alcohol. These examples include the Genapol® UD (ex. Clariant, Muttenz, Switzerland) described under the tradenames Genapol® UD 030, C₁₁-oxo-alcohol polyglycol ether with 3 EO; Genapol® UD, 050 C₁₁-oxo-alcohol polyglycol ether with 5 EO; Genapol® UD 070, C₁₁-oxo-alcohol polyglycol ether with 7 EO; Genapol® UD 080, C₁₁-oxo-alcohol polyglycol ether with 8 EO; Genapol® UD 088, C₁₁-oxo-alcohol polyglycol ether with 8 EO; and Genapol® UD 110, C₁₁-oxo-alcohol polyglycol ether with 11 EO.

[0030] Exemplary useful nonionic surfactants include the condensation products of a secondary aliphatic alcohols containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are those presently commercially available under the trade name of Tergitol® such as Tergitol 15-S-12 which is described as being C₁₁-C₁₅ secondary alkanol condensed with 9 ethylene oxide units, or Tergitol 15-S-9 which is described as being C₁₁-C₁₅ secondary alkanol condensed with 12 ethylene oxide units per molecule.

[0031] A further class of useful nonionic surfactants include those surfactants having a formula:



wherein;

R is a mixture of linear, even carbon-number hydrocarbon chains ranging from C₁₂H₂₅ to C₁₆H₃₃ and n represents the number of ethoxy repeating units and is a number of from about 1 to about 12.

[0032] Surfactants of this formula are presently marketed under the Genapol® tradename (ex. Clariant), which surfactants include the "26-L" series of the general 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, such as 26-L-1, 26-L-1.6, 26-L-2, 26-L-3, 26-L-5, 26-L-45, 26-L-50, 26-L-60, 26-L-60N, 26-L-75, 26-L-80, 26-L-98N, and the 24-L series, derived from synthetic sources and typically contain about 55% C₁₂ and 45% C₁₄ alcohols, such as 24-L-3, 24-L-45, 24-L-50, 24-L-60, 24-L-60N, 24-L-75, 24-L-92, and 24-L-98N, all sold under the Genapol® tradename.

[0033] Further useful non-ionic surfactants which may be used in the inventive compositions include those presently marketed under the trade name Plurionics® (ex. BASF). The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is of the order of 950 to 4,000 and preferably 200 to 2,500. The addition of polyoxyethylene radicals of the hydrophobic portion tends to increase the solubility of the molecule as a whole so as to make the surfactant water-soluble. The molecular weight of the block polymers varies from 1,000 to 15,000 and the polyethylene oxide content may comprise 20% to 80% by weight. Preferably, these surfactants are in liquid form and particularly satisfactory surfactants are available as those marketed as Plurionics® L62 and Plurionics® L64.

[0034] Further nonionic surfactants which may be included in the inventive compositions include alkoxyated alkanolamides, preferably C₈-C₂₄ alkyl di(C₂-C₃ alkanol amides), as represented by the following formula:



wherein R₅ is a branched or straight chain C₈-C₂₄ alkyl radical, preferably a C₁₀-C₁₆ alkyl radical and more preferably a C₁₂-C₁₄ alkyl radical, and R₆ is a C₁-C₄ alkyl radical, preferably an ethyl radical.

[0035] According to certain particularly preferred embodiments the deterative surfactant constituent necessarily comprises a nonionic surfactant based on a linear primary alcohol ethoxylate particularly wherein the alkyl portion is a C₈ to C₁₆, but particularly a C₉ to C₁₁ alkyl group, and having an average of between about 6 to about 8 moles of ethoxylation.

[0036] One further useful class of nonionic surfactants include those in which the major portion of the molecule is made up of block polymeric C₂-C₄ alkylene oxides, with alkylene oxide blocks containing C₃ to C₄ alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting group, can have as a starting nucleus almost any active hydrogen containing group including, without limitation, amides, phenols, and secondary alcohols.

[0037] One group of nonionic surfactants containing the characteristic alkylene oxide blocks are those which may be generally represented by the formula (A):



where

[0038] EO represents ethylene oxide,

[0039] PO represents propylene oxide,

[0040] y equals at least 15,

[0041] (EO)_{x+z} equals 20 to 50% of the total weight of said compounds, and,

[0042] the total molecular weight is preferably in the range of about 2000 to 15,000.

[0043] Another group of nonionic surfactants appropriate for use in the new compositions can be represented by the formula (B):



wherein R is an alkyl, aryl or aralkyl group,

[0044] the alkoxy group contains 1 to 20 carbon atoms, the weight percent of EO is within the range of 0 to 45% in one of the blocks a, b, and within the range of 60 to 100% in the other of the blocks a, b, and the total number of moles of combined EO and PO is in the range of 6 to 125 moles, with 1 to 50 moles in the PO rich block and 5 to 100 moles in the EO rich block.

[0045] Further nonionic surfactants which in general are encompassed by Formula B include butoxy derivatives of propylene oxide/ethylene oxide block polymers having molecular weights within the range of about 2000-5000.

[0046] Still further useful nonionic surfactants containing polymeric butoxy (BO) groups can be represented by formula (C) as follows:



wherein R is an alkyl group containing 1 to 20 carbon atoms,

[0047] n is about 15 and x is about 15.

[0048] Also useful as the nonionic block copolymer surfactants which also include polymeric butoxy groups are those which may be represented by the following formula (D):



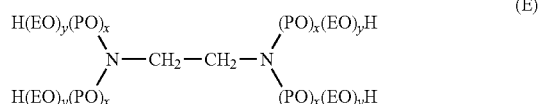
wherein

[0049] n is about 15,

[0050] x is about 15 and

[0051] y is about 15.

[0052] Still further useful nonionic block copolymer surfactants include ethoxylated derivatives of propoxylated ethylene diamine, which may be represented by the following formula:



where (EO) represents ethoxy,

[0053] (PO) represents propoxy,

[0054] the amount of (PO)_x is such as to provide a molecular weight prior to ethoxylation of about 300 to 7500, and the amount of (EO)_y is such as to provide about 20% to 90% of the total weight of said compound.

Further useful nonionic surfactants include nonionic amine oxide constituent. Exemplary amine oxides include:

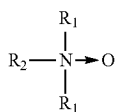
[0055] A) Alkyl di (lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. The lower alkyl groups include between 1 and 7 carbon atoms. Examples include lauryl dimethyl amine oxide, myristyl 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 myristyl/palmityl dimethyl amine oxide;

[0056] B) Alkyl di (hydroxy lower alkyl) 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 are bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallowamine oxide; and bis(2-hydroxyethyl) stearylamine oxide;

[0057] C) Alkylamidopropyl di(lower alkyl) 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 are cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide; and

[0058] D) 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.

[0059] Preferably the amine oxide constituent is an alkyl di (lower alkyl) amine oxide as denoted above and which may be represented by the following structure:



wherein each:

[0060] R₁ is a straight chained C₁-C₄ alkyl group, preferably both R₁ are methyl groups; and,

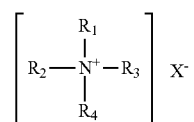
[0061] R₂ is a straight chained C₈-C₁₈ alkyl group, preferably is C₁₀-C₁₄ alkyl group, most preferably is a C₁₂ alkyl group.

[0062] Each of the alkyl groups may be linear or branched, but most preferably are linear. Most preferably the amine oxide constituent is lauryl dimethyl amine oxide. Technical grade mixtures of two or more amine oxides may be used, wherein amine oxides of varying chains of the R₂ group are present. Preferably, the amine oxides used in the present invention include R₂ groups which comprise at least 50% wt., preferably at least 60% wt. of C₁₂ alkyl groups and at least 25% wt. of C₁₄ alkyl groups, with not more than 15% wt. of C₁₆, C₁₈ or higher alkyl groups as the R₂ group.

[0063] Still further exemplary useful nonionic surfactants which may be used include certain alkanolamides including monoethanolamides and diethanolamides, particularly fatty monoalkanolamides and fatty dialkanolamides.

[0064] A cationic surfactant may be incorporated as a germicide or as a deterative surfactant in the solid block composition of the present invention, particularly wherein a bleach constituent is absent from the solid block composition. Cationic surfactants are per se, well known, and exemplary useful cationic surfactants may be one or more of those described for example in *McCutcheon's Functional Materials*, Vol. 2, 1998; *Kirk-Othmer, Encyclopedia of Chemical Technology*, 4th Ed., Vol. 23, pp. 481-541 (1997), the contents of which are herein incorporated by reference. These are also described in the respective product specifications and literature available from the suppliers of these cationic surfactants.

[0065] Examples of preferred cationic surfactant compositions useful in the practice of the instant invention are those which provide a germicidal effect to the concentrate compositions, and especially preferred are quaternary ammonium compounds and salts thereof, which may be characterized by the general structural formula:

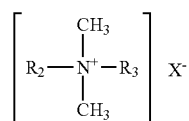


where at least one of R₁, R₂, R₃ and R₄ is a alkyl, aryl or alkaryl substituent of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The alkyl substituents may be long-chain alkyl, long-chain alkoxyaryl, long-chain alkylaryl, halogen-substituted long-chain alkylaryl, long-chain alkylphenoxy-alkyl, arylalkyl, etc. The remaining substituents on the nitrogen atoms other than the abovementioned alkyl substituents are hydrocarbons usually containing no more 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.

[0066] 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.

[0067] Preferred quaternary ammonium compounds which act as germicides and which are 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 C₁₂₋₁₆alkyl, C₈₋₁₈alkylethoxy, C₈₋₁₈alkylphenoethoxy and R₃ is benzyl, and X is a halide, for example chloride, bromide or iodide, or is a methosulfate anion. The alkyl groups recited in R₂ and R₃ may be straight-chained or branched, but are preferably substantially linear.

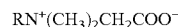
[0068] Particularly useful quaternary germicides include compositions which include a single quaternary compound, as well as mixtures of two or more different quaternary compounds. Such useful quaternary compounds are available under the BARDAC®, BARQUAT®, HYAMINE®, LONZABAC®, and ONYXIDE® trademarks, which are more fully described in, for example, *McCutcheon's Functional Materials* (Vol. 2), North American Edition, 1998, as well as the respective product literature from the suppliers identified below. For example, BARDAC® 205M is described to be a liquid containing alkyl dimethyl benzyl ammonium chloride, octyl decyl dimethyl ammonium chloride; didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (also available as 80% active (BARDAC® 208M)); described generally in McCutcheon's as a combination of alkyl dimethyl benzyl ammonium chloride and dialkyl dimethyl ammonium chloride; BARDAC® 2050 is described to be a combination of octyl decyl dimethyl ammonium chloride/didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (also available as 80% active (BARDAC® 2080)); BARDAC® 2250 is described to be didecyl dimethyl ammonium chloride (50% active); BARDAC® LF (or BARDAC® LF-80), described as being based on dioctyl dimethyl ammonium chloride (BARQUAT® MB-50, MX-50, OJ-50 (each 50% liquid) and MB-80 or MX-80 (each 80% liquid) are each described as an alkyl dimethyl benzyl ammonium chloride; BARDAC® 4250 and BARQUAT® 4250Z (each 50% active) or BARQUAT® 4280 and BARQUAT® 4280Z (each 80% active) are each described as alkyl dimethyl benzyl ammonium chloride/alkyl dimethyl ethyl benzyl ammonium chloride. Also, HYAMINE® 1622, described as diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride (50% solution); HYAMINE® 3500 (50% actives), described as alkyl dimethyl benzyl ammonium chloride (also available as 80% active (HYAMINE® 3500-80)); and HYMAINE®

2389 described as being based on methyldodecylbenzyl ammonium chloride and/or methyldodecylxylene-bis-trimethyl ammonium chloride. (BARDAC®, BARQUAT® and HYAMINE® are presently commercially available from Lonza, Inc., Fairlawn, N.J.). BTC® 50 NF (or BTC® 65 NF) is described to be alkyl dimethyl benzyl ammonium chloride (50% active); BTC® 99 is described as didecyl dimethyl ammonium chloride (50% active); BTC® 776 is described to be myrisalkonium chloride (50% active); BTC® 818 is described as being octyl decyl dimethyl ammonium chloride, didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (available also as 80% active (BTC® 818-80%)); BTC® 824 and BTC® 835 are each described as being of alkyl dimethyl benzyl ammonium chloride (each 50% active); BTC® 885 is described as a combination of BTC® 835 and BTC® 818 (50% active) (available also as 80% active (BTC® 888)); BTC® 1010 is described as didecyl dimethyl ammonium chloride (50% active) (also available as 80% active (BTC® 1010-80)); BTC® 2125 (or BTC® 2125 M) is described as alkyl dimethyl benzyl ammonium chloride and alkyl dimethyl ethylbenzyl ammonium chloride (each 50% active) (also available as 80% active (BTC® 2125 80 or BTC® 2125 M)); BTC® 2565 is described as alkyl dimethyl benzyl ammonium chlorides (50% active) (also available as 80% active (BTC® 2568)); BTC® 8248 (or BTC® 8358) is described as alkyl dimethyl benzyl ammonium chloride (80% active) (also available as 90% active (BTC® 8249)); ONYXIDE® 3300 is described as n-alkyl dimethyl benzyl ammonium saccharinate (95% active). (BTC® and ONYXIDE® are presently commercially available from Stepan Company, Northfield, Ill.) Polymeric quaternary ammonium salts based on these monomeric structures are also considered desirable for the present invention. One example is POLYQUAT®, described as being a 2-butenyldimethyl ammonium chloride polymer.

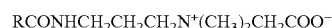
[0069] Preferred quaternary germicides used in the solid block compositions are those which are supplied in a solid or powdered form, as such greatly facilitates the manufacture of the solid block compositions.

[0070] When present in a solid block composition, it is preferred that the germicidal cationic surfactant(s) are present in amounts so to dispense at least about 200 parts per million (ppm) in the water flushed into the sanitary appliance, e.g., toilet bowl, or into the water retained in the sanitary appliance at the conclusion of the flush cycle.

[0071] Further deterative surfactants which may be included are amphoteric and zwitterionic surfactants which provide a deterative effect. Exemplary useful amphoteric surfactants include alkylbetaines, 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 amidalkylbetaines, 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.

[0072] As noted above, preferred deterative surfactants are those which exhibit a melting points above about 110° F.,

preferably above 125° F., in order to permit convenient processing according to known art techniques. Nonetheless small amounts of low melting point surfactants, i.e., those exhibiting melting points below about 110° F. and even liquid surfactants may be used in providing the surfactant constituent of the solid block composition.

[0073] As the performance requirements of the lavatory treatment blocks may differ according to their use as either in a ITB or in a ITC application, the amounts of the constituents present in a particular solid block of the device may vary as well depending upon the final intended use of the treatment block.

[0074] When intended for use as in an ITB application or device, the deterative surfactant constituent may be present in any effective amount and generally comprises up to about 90% wt. of the total weight of a solid block composition, and the resultant treatment block formed therefrom. Preferably the deterative surfactant constituent comprises about 20-90% wt., more preferably 35-80% wt. of a solid block composition, and when used as an ITB block the deterative surfactant constituent most preferably comprises about 50-75% wt. Of a solid block composition, and the resultant treatment block formed therefrom. When intended for use in an ITC application, the deterative surfactant constituent may be present in any effective amount and generally comprises up to about 60% wt. of the total weight of a solid block composition, and the resultant treatment block formed therefrom. Preferably the deterative surfactant constituent comprises about 10-55% wt., more preferably 20-50% wt. of a solid block composition, and the resultant treatment block formed therefrom.

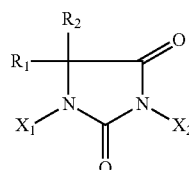
[0075] In particularly preferred embodiments the lavatory treatment blocks of the invention necessarily comprise at least one surfactant, preferably at least one anionic surfactant.

[0076] Further exemplary chemical constituents may be one or more sanitizing agents or germicides which may be present with our without other constituents being present in the lavatory treatment blocks of the present invention.

[0077] The sanitizing agent can be any sanitizing composition known to those of ordinary skill in the relevant art, and without limitation exemplary sanitizing compositions include materials containing alkyl halohydantoin, alkali metal haloisocyanurates, bleach, essential oils, non-quaternary ammonium based germicidal compounds as well as quaternary ammonium germicidal compounds.

[0078] The blocks may also include a bleach constituent. The bleach constituent is relatively inert in the dry state but, which on contact with water, releases oxygen, hypochlorite or a halogen especially chlorine. Representative examples of typical oxygen-release bleaching agents, suitable for incorporation in the solid block composition include the alkali metal perborates, e.g., sodium perborate, and alkali metal monopersulfates, e.g., sodium monopersulfates, potassium monopersulfate, alkali metal monoperphosphates, e.g., disodium monoperphosphate and dipotassium monoperphosphate, as well as other conventional bleaching agents capable of liberating hypochlorite, e.g., hypochlorite and/or hypobromite, include heterocyclic N-bromo- and N-chloro-cyanurates such as trichloroisocyanuric and tribromoisocyanuric acid, dibromocyanuric acid, dichlorocyanuric acid, N-mono-bromo-N-mono-chlorocyanuric acid and N-monobromo-N, N-dichlorocyanuric acid, as well as the salts thereof with water solubilizing cations such as potassium and sodium, e.g., sodium N-monobromo-N-monochlorocyanurate, potassium dichlorocyanurate, sodium dichlorocyanurate, as well

as other N-bromo and N-chloro-imides, such as N-brominated and N-chlorinated succinimide, malonimide, phthalimide and naphthalimide. Also useful in the solid block composition as hypochlorite-releasing bleaches are halohydantoin which may be used include those which may be represented by the general structure:



wherein:

[0079] X₁ and X₂ are independently hydrogen, chlorine or bromine; and,

[0080] R₁ and R₂ are independently alkyl groups having from 1 to 6 carbon atoms.

[0081] Examples of halohydantoin include, for example, N,N'-dichloro-dimethyl-hydantoin, N-bromo-N-chloro-dimethyl-hydantoin, N,N'-dibromo-dimethyl-hydantoin, 1,4-dichloro, 5,5-dialkyl substituted hydantoin, wherein each alkyl group independently has 1 to 6 carbon atoms, N-mono-halogenated hydantoin such as chlorodimethylhydantoin (MCDMH) and N-bromo-dimethylhydantoin (MBDMH); dihalogenated hydantoin such as dichlorodimethylhydantoin (DCDMH), dibromodimethylhydantoin (DBDMH), and 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH); and halogenated methylethylhydantoin such as chloromethylethylhydantoin (MCMEH), dichloromethylethylhydantoin (DCMEH), bromomethylethylhydantoin (MBMEH), dibromomethylethylhydantoin (DBMEH), and bromochloromethylethylhydantoin (BCMEH), and mixtures thereof. Other suitable organic hypochlorite liberating bleaching agents include halogenated melamines such as tribromomelamine and trichloromelamine. Suitable inorganic hypochlorite-releasing bleaching agents include lithium and calcium hypochlorites and hypobromites. The various chlorine, bromine or hypochlorite liberating agents may, if desired, be provided in the form of stable, solid complexes or hydrates, such as sodium p-toluene sulfobromamine trihydrate; sodium benzene sulfochloramine dihydrate; calcium hypobromite tetrahydrate; and calcium hypochlorite tetrahydrate. Brominated and chlorinated trisodium phosphates formed by the reaction of the corresponding sodium hypochlorite solution with trisodium orthophosphate (and water, as necessary) likewise comprise useful inorganic bleaching agents for incorporation into the solid lavatory treatment blocks formed therefrom.

[0082] When present, preferably the bleach constituent is a hypochlorite liberating compound and more preferably is a hypochlorite liberating compound in the form of a solid complex or hydrate thereof. Particularly preferred are chloroisocyanuric acids and alkali metal salts thereof, preferably potassium, and especially sodium salts thereof. Examples of such compounds include trichloroisocyanuric acid, dichloroisocyanuric acid, sodium dichloroisocyanurate, potassium dichloroisocyanurate, and trichloro-potassium dichloroisocyanurate complex. The most preferred chlorine bleach material is sodium dichloroisocyanurate; the dihydrate of this material being particularly preferred.

[0083] When present, the bleach constituent may be present in any effective amount and may comprise up to about 90% wt., preferably at least about 0.1-60% wt of the solid block composition. More preferably, when present, the bleach constituent comprises about 0.5-50% wt., more preferably at least 1-40% wt. of the solid block composition.

[0084] Other germicidally effective agents useful as sanitizing agents include sodium dichloroisocyanurate (DCCNa) and sodium dibromoisocyanurate. Further examples of non-quaternary ammonium based sanitizing agents include pyrrhionones, dimethyldimethylol hydantoin, methylchloroisothiazolinone/methylisothiazolinone sodium sulfite, sodium bisulfite, imidazolidinyl urea, diazolidinyl urea, benzyl alcohol, 2-bromo-2-nitropropane-1,3-diol, formalin (formaldehyde), iodopropenyl butylcarbamate, chloroacetamide, methanamine, methyldibromonitrile glutaronitrile, glutaraldehyde, 5-bromo-5-nitro-1,3-dioxane, phenethyl alcohol, o-phenylphenol/sodium o-phenylphenol, sodium hydroxymethylglycinate, polymethoxy bicyclic oxazolidine, dimethoxane, thimersal dichlorobenzyl alcohol, captan, chlorophenenesin, dichlorophene, chlorbutanol, glyceryl laurate, halogenated diphenyl ethers, phenolic compounds, mono- and poly-alkyl and aromatic halophenols, resorcinol and its derivatives, bisphenolic compounds, benzoic esters (parabens), halogenated carbanilides, 3-trifluoromethyl-4,4'-dichlorocarbanilide, and 3,3',4-trichlorocarbanilide. More preferably, the non-cationic antimicrobial agent is a mono- and poly-alkyl and aromatic halophenol selected from the group p-chlorophenol, methyl p-chlorophenol, ethyl p-chlorophenol, n-propyl p-chlorophenol, n-butyl p-chlorophenol, n-amyl p-chlorophenol, sec-amyl p-chlorophenol, n-hexyl p-chlorophenol, cyclohexyl p-chlorophenol, n-heptyl p-chlorophenol, n-octyl p-chlorophenol, o-chlorophenol, methyl o-chlorophenol, ethyl o-chlorophenol, n-propyl o-chlorophenol, n-butyl o-chlorophenol, n-amyl o-chlorophenol, tert-amyl o-chlorophenol, n-hexyl o-chlorophenol, n-heptyl o-chlorophenol, o-benzyl p-chlorophenol, o-benzyl-m-methyl p-chlorophenol, o-benzyl-m, m-dimethyl p-chlorophenol, o-phenylethyl p-chlorophenol, o-phenylethyl-m-methyl p-chlorophenol, 3-methyl p-chlorophenol, 3,5-dimethyl p-chlorophenol, 6-ethyl-3-methyl p-chlorophenol, 6-n-propyl-3-methyl p-chlorophenol, 6-iso-propyl-3-methyl p-chlorophenol, 2-ethyl-3,5-dimethyl p-chlorophenol, 6-sec-butyl-3-methyl p-chlorophenol, 2-iso-propyl-3,5-dimethyl p-chlorophenol, 6-diethylmethyl-3-methyl p-chlorophenol, 6-iso-propyl-2-ethyl-3-methyl p-chlorophenol, 2-sec-amyl-3,5-dimethyl p-chlorophenol 2-diethylmethyl-3,5-dimethyl p-chlorophenol, 6-sec-octyl-3-methyl p-chlorophenol, p-chloro-m-cresol, p-bromophenol, methyl p-bromophenol, ethyl p-bromophenol, n-propyl p-bromophenol, n-butyl p-bromophenol, n-amyl p-bromophenol, sec-amyl p-bromophenol, n-hexyl p-bromophenol, cyclohexyl p-bromophenol, o-bromophenol, tert-amyl o-bromophenol, n-hexyl o-bromophenol, n-propyl-m,m-dimethyl o-bromophenol, 2-phenyl phenol, 4-chloro-2-methyl phenol, 4-chloro-3-methyl phenol, 4-chloro-3,5-dimethyl phenol, 2,4-dichloro-3,5-dimethylphenol, 3,4,5,6-tetrabromo-2-methylphenol, 5-methyl-2-pentylphenol, 4-isopropyl-3-methylphenol, para-chloro-meta-xylene, dichloro meta xylene, chlorothymol, and 5-chloro-2-hydroxydiphenylmethane.

[0085] Quaternary ammonium based sanitizing agents include any cationic surfactant which is known or may be

found to provide a broad antibacterial or sanitizing function; these have been described above with reference to deterative surfactants.

[0086] As a further chemical constituent, the solid block compositions of the invention may also comprise a coloring agent which imparts either a color to the lavatory treatment blocks, to the water in which it comes into contact, but especially which imparts color to the water contained within the sanitary appliance. Where the sanitary appliance is a toilet, desirably the coloring agent imparts a color to the water contained within the cistern, or within the toilet bowl particularly following the flush cycle of a toilet, or may impart a color in both locations. Such coloring agents have great consumer appeal, and indeed any known art coloring agent may be provided in any effective amount in order to impart a coloring effect. Colorants, especially dyes, are preferred when formulated as dry powders to enable direct incorporation into lavatory treatment blocks of the invention, however, liquid colorants may be employed in conjunction with suitable carriers. Useful colorants include any materials which may provide a desired coloring effect. Exemplarily useful coloring agents include dyes, e.g., Alizarine Light Blue B (C.I. 63010), Carta Blue VP (C.I. 24401), Acid Green 2G (C.I. 42085), Astragon Green D (C.I. 42040) Supranol Cyanine 7B (C.I. 42675), Maxilon Blue 3RL (C.I. Basic Blue 80), acid yellow 23, acid violet 17, a direct violet dye (Direct violet 51), Drimarine Blue Z-RL (C.I. Reactive Blue 18), Alizarine Light Blue H-RL (C.I. Acid Blue 182), FD&C Blue No. 1, FD&C Green No. 3 and Acid Blue No. 9. When a bleach constituent is included in the solid block composition, the colorant, e.g., dye, should be selected so to ensure the compatibility of the colorant with the bleach constituent, or so that its color persists despite the presence in the toilet bowl of a concentration of hypochlorite which is effective to maintain sanitary conditions. Frequently however, a solid block composition which includes a bleach constituent do not comprise any colorants. Desirably the colorants, when present, do not exceed 15% wt. of the solid block composition, although generally lesser amounts are usually effective. When present, colorants are desirably present in an amount from about 0.1 to 15 percent of the total weight of the chemical composition.

[0087] The solid block compositions may include a fragrance or other air treatment constituent. The fragrance may be any composition which is known to the art to provide a perceptible fragrancing benefit, any may be based on naturally occurring materials such as one or more essential oils, or may be based on synthetically produced compounds as well. Examples of essential oils include pine oil, Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Perui), Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB, Bonneol Flakes (China), Camphor oil, White, Camphor powder synthetic technical, Canaga oil (Java), Cardamom oil, Cassia oil (China), Cedarwood oil (China) BP, Cinnamon bark oil, Cinnamon leaf oil, Citronella oil, Clove bud oil, Clove leaf, Coriander (Russia), Coumarin 69° C. (China), Cyclamen Aldehyde, Diphenyl oxide, Ethyl vanillin, Eucalyptol, Eucalyptus oil, Eucalyptus citriodora, Fennel oil, Geranium oil, Ginger oil, Ginger oleoresin (India), White grapefruit oil, Guaiacwood oil, Gurjun balsam, Heliotropin, Isobornyl acetate, Isolongifolene, Juniper berry oil, L-methyl acetate, Lavender oil, Lemon oil, Lemongrass oil, Lime oil distilled, Litsea Cubeba oil, Longifolene, Menthol crystals, Methyl cedryl ketone, Methyl chavicol, Methyl salicylate, Musk

ambrette, Musk ketone, Musk xylol, Nutmeg oil, Orange oil, Patchouli oil, Peppermint oil, Phenyl ethyl alcohol, Pimento berry oil, Pimento leaf oil, Rosalin, Sandalwood oil, Sandenol, Sage oil, Clary sage, Sassafras oil, Spearmint oil, Spike lavender, Tagetes, Tea tree oil, Vanilin, Vetyver oil (Java), and Wintergreen oil.

[0088] Many of these essential function as a fragrance agent, which fragrance agent which may be a substance or mixture of various substances including those which are naturally derived (i.e., obtained by extraction of flower, herb, blossom or plant), those which are artificially derived or produced (i.e., mixture of natural oils and/or oil constituents), and those which are synthetically produced substances (odiferous substances). Generally fragrance agents are complex mixtures or blends various organic compounds including, but not limited to, certain alcohols, aldehydes, ethers, alomatic compounds and varying amounts of essential oils such as from about 0 to about 25% by weight, usually from about 0.05 to about 12% by weight, the essential oils themselves being volatile odiferous compounds and also functioning to aid in the dissolution of the other components of the fragrance agent. In the present invention, the precise composition of the fragrance agent desirably emanates a pleasing fragrance, but the nature of the fragrance agent is not critical to the success of the invention.

[0089] As noted above, in conjunction with or in the absence of a fragrance constituent, the solid block compositions may comprise an air treatment constituent. Such may be any other material which is useful in providing treatment of ambient air, such as a sanitizing agents. e.g., one or more glycols or alcohols, or materials which are intended to counteract, neutralize, or mask odors in the absence of, or in conjunction with, the fragrance composition of the present invention. Alternatively, the air treatment constituent may be one or more materials which provide and effective insecticide repelling or insecticidal benefit; such would be particularly useful in climates or environments where insects present a nuisance or health hazard.

[0090] As further chemical constituents, the solid block compositions of the invention may comprise an anti-limescale agent, which can be generally classified as a cleaning agent in that it provides a cleaning effect to treated lavatory device surfaces. The anti-limescale agent can virtually any known anti-limescale agent compositions known to those of ordinary skill in the relevant art. For example, compositions containing anionic and/or nonionic surfactants together with typical anti-limescale agents, for example, amidosulfonic acid, bisulfate salts, organic acids, organic phosphoric salts, alkali metal polyphosphates, and the like. Examples of anti-limescale agent compositions can be found in, for example, U.S. Pat. Nos. 5,759,974; 4,460,490; and 4,578,207, the contents of which are herein incorporated by reference. Further examples of anti-limescale agents include organic acids (for example, citric acid, lactic acid, adipic acid, oxalic acid and the like), organic phosphoric salts, alkali metal polyphosphates, sulfonic, and sulfamic acids and their salts, bisulfate salts, EDTA, phosphonates, and the like.

[0091] The solid block compositions may comprise stain inhibiting materials. The solid block composition of the invention may, for example, include an effective amount of a manganese stain inhibiting agent which is advantageously included wherein the sanitary appliance is supplied by a water source having an appreciable or high amount of manganese. Such water containing a high manganese content are known

to frequently deposit unsightly stains on surfaces of sanitary appliances, especially when the solid block composition also contains a bleach source which provides a hypochlorite. To counteract such an effect the solid block composition of the present invention may comprise a manganese stain inhibiting agent, such as a partially hydrolyzed polyacrylamide having a molecular weight of about 2000 to about 10,000, a polyacrylate with a molecular weight of about 2000 to about 10,000, and/or copolymers of ethylene and maleic acid anhydride with a molecular weight of from about 20,000 to about 100,000. When present the stain inhibiting materials may comprise to about 10% wt. of the weight of the solid block composition.

[0092] The solid block compositions of the invention may include one or more preservatives. Such preservatives are primarily included to reduce the growth of undesired microorganisms within the lavatory treatment blocks formed from the solid block composition during storage prior to use or while used, although it is expected that the such a preservative may impart a beneficial antimicrobial effect to the water in the sanitary appliance to which the treatment block is provided. Exemplary useful preservatives include compositions which include parabens, including methyl parabens and ethyl parabens, glutaraldehyde, formaldehyde, 2-bromo-2-nitropropane-1,3-diol, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazoline-3-one, and mixtures thereof. One exemplary composition is a combination 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one where the amount of either component may be present in the mixture anywhere from 0.001 to 99.99 weight percent, based on the total amount of the preservative. For reasons of availability, the most preferred preservative are those commercially available preservative comprising a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one marketed under the trademark KATHON® CG/ICP as a preservative composition presently commercially available from Rohm and Haas (Philadelphia, Pa.). Further useful preservative compositions include KATHON® CG/ICP II, a further preservative composition presently commercially available from Rohm and Haas (Philadelphia, Pa.), PROXEL® which is presently commercially available from Zeneca Biocides (Wilmington, Del.), SUTTOCID® A which is presently commercially available from Sutton Laboratories (Chatam, N.J.) as well as TEXTAMER® 38AD which is presently commercially available from Calgon Corp. (Pittsburgh, Pa.). When present, the optional preservative constituent should not exceed about 5% wt. of the solid block composition, although generally lesser amounts are usually effective.

[0093] The inventive solid block compositions may include a binder constituent. The binder may function in part controlling the rate of dissolution of the tablet. The binder constituent may be a clay, but preferably is a water-soluble or water-dispersible gel-forming organic polymer. The term "gel-forming" as applied to this polymer is intended to indicate that on dissolution or dispersion in water it first forms a gel which, upon dilution with further water, is dissolved or dispersed to form a free-flowing liquid. The organic polymer serves essentially as binder for the tablets produced in accordance with the invention although, as will be appreciated, certain of the polymers envisaged for use in accordance with the invention also have surface active properties and thereby serve not only as binders but also enhance the cleansing ability of the tablets of the invention. Further certain organic

polymers, such as substituted celluloses, also serve as soil antiredeposition agents. A wide variety of water-soluble organic polymers are suitable for use in the solid block composition of the present invention. Such polymers may be wholly synthetic or may be semi-synthetic organic polymers derived from natural materials. Thus, for example, on class of organic polymers for use in accordance with the invention are chemically modified celluloses such as ethyl cellulose, methyl cellulose, sodium carboxymethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, ethyl hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, and hydroxyethyl cellulose. Another class of organic polymers which may be used include naturally derived or manufactured (fermented) polymeric materials such as alginates and carageenan. Also, water-soluble starches and gelatin may be used as the optional binder constituent. The cellulose based binders are a preferred class of binders for use in the solid block composition and may possess the property of inverse solubility that is their solubility decreases with increasing temperature, thereby rendering the tablets of the invention suitable for use in locations having a relatively high ambient temperature.

[0094] The optional binder constituent may also be one or more synthetic polymers e.g. polyvinyl alcohols; water-soluble partially hydrolyzed polyvinyl acetates; polyacrylonitriles; polyvinyl pyrrolidones; water-soluble polymers of ethylenically unsaturated carboxylic acids, such as acrylic acid and methacrylic acid, and salts thereof; base-hydrolysed starch-polyacrylonitrile copolymers; polyacrylamides; ethylene oxide polymers and copolymers; as well as carboxypoly-methylenes.

[0095] In the case of the organic polymeric binders it may be noted that, in general, the higher the molecular weight of the polymer the greater the in-use life of the treatment block of the invention. When present, the total binder content may comprise up to 75% wt. of the solid block composition, but preferably is from 0.5 to 70% by weight, preferably from 1 to 65% by weight, more preferably from 5 to 60% by weight.

[0096] The solid block composition may optionally include one or more dissolution control agents. Such dissolution control agent are materials which provide a degree of hydrophobicity to the treatment block formed from the solid block composition whose presence in the treatment block contributes to the slow uniform dissolution of the treatment block when contacted with water, and simultaneously the controlled release of the active constituents of the solid block composition. Preferred for use as the dissolution control agents are mono- or di-alkanol amides derived from C_8 - C_{16} fatty acids, especially C_{12} - C_{14} fatty acids having a C_2 - C_6 monoamine or diamine moiety. When included the dissolution control agent may be included in any effective amount, but desirably the dissolution control agent is present in an amount not to exceed about 600% wt. of the solid block composition, although generally lesser amounts are usually effective. Generally wherein the treatment block is to be used in an ITB application the dissolution control agent is present to about 12% wt., more preferably is present from 0.1-10% wt. and most preferably is present from about 3-8% wt. of the solid block compositions, as well as in the lavatory treatment blocks formed therefrom. Generally wherein the treatment block is to be used in an ITC application the dissolution control agent is present to about 50% wt., more preferably is present from 1-50% wt. and most preferably is present from

about 10-40% wt. of the solid block compositions, as well as in the lavatory treatment blocks formed therefrom.

[0097] The solid block compositions may optionally include one or more water-softening agents or one or more chelating agents, for example inorganic water-softening agents such as sodium hexametaphosphate or other alkali metal polyphosphates or organic water-softening agents such as ethylenediaminetetraacetic acid and nitrilotriacetic acid and alkali metal salts thereof. When present, such water-softening agents or chelating agents should not exceed about 20% wt. of the solid block composition, although generally lesser amounts are usually effective.

[0098] The solid block composition may optionally include one or more solid water-soluble acids or acid-release agents such as sulphamic acid, citric acid or sodium hydrogen sulphate. When present, such solid water-soluble acids or acid-release agents should not exceed about 20% wt. of the solid block composition, although generally lesser amounts are usually effective.

[0099] The solid block compositions may include diluent materials may be included to provide additional bulk of the product solid block composition and may enhance leaching out of the surfactant constituent when the solid block composition is placed in water. Exemplary diluent materials include any soluble inorganic alkali, alkaline earth metal salt or hydrate thereof, for example, chlorides such as sodium chloride, magnesium chloride and the like, carbonates and bicarbonates such as sodium carbonate, sodium bicarbonate and the like, sulfates such as magnesium sulfate, copper sulfate, sodium sulfate, zinc sulfate and the like, borax, borates such as sodium borate and the like, as well as others known to the art but not particularly recited herein. Exemplary organic diluents include, inter alia, urea, as well as water soluble high molecular weight polyethylene glycol and polypropylene glycol. When present, such diluent materials should not exceed about 80% wt. of the solid block composition, although generally lesser amounts are usually effective.

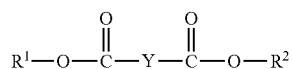
[0100] The solid block composition and lavatory treatment blocks formed therefrom may include one or more fillers. Such fillers are typically particulate solid water-insoluble materials which may be based on inorganic materials such as talc or silica, particulate organic polymeric materials such as finely comminuted water insoluble synthetic polymers. When present, such fillers should not exceed about 30% wt. of the solid block composition, although generally lesser amounts are usually effective.

[0101] Preferably the solid block of the invention includes silica. Silica has been observed to aid in the controlling the rate of dissolution of the lavatory treatment blocks of the invention.

[0102] The solid block composition and lavatory treatment blocks formed therefrom may include one or more further processing aids. For example, the solid block composition may also include other binding and/or plasticizing ingredients serving to assist in the manufacture thereof, for example, polypropylene glycol having a molecular weight from about 300 to about 10,000 in an amount up to about 20% by weight, preferably about 4% to about 15% by weight of the mixture may be used. The polypropylene glycol reduces the melt viscosity, acts as a demolding agent and also acts to plasticize the block when the composition is prepared by a casting process. Other suitable plasticizers such as pine oil fractions, d-limonene, dipentene and the ethylene oxide-propylene oxide block copolymers may be utilized. Other useful pro-

cessing aids include tableting lubricants such as metallic stearates, stearic acid, paraffin oils or waxes or sodium borate which facilitate in the formation of the lavatory treatment blocks in a tableting press or die.

[0103] One advantageously utilized processing aid is a diester constituent which may be represented by the following structure:



wherein:

R^1 and R^2 can independently be C_1 - C_6 alkyl which may optionally substituted,

Y is $(CH_2)_x$, wherein x is 0-10, but is preferably 1-8, and while Y may be a linear alkyl or phenyl moiety, desirably Y includes one or more oxygen atoms and/or is a branched moiety.

[0104] Exemplary diester constituents include the following diester compounds according to the foregoing structure: dimethyl oxalate, diethyl oxalate, diethyl oxalate, dipropyl oxalate, dibutyl oxalate, diisobutyl oxalate, dimethyl succinate, diethyl succinate, diethylhexyl succinate, dimethyl glutarate, diisostearyl glutarate, dimethyl adipate, diethyl adipate, diisopropyl adipate, dipropyl adipate, dibutyl adipate, diisobutyl adipate, dihexyladipate, di- C_{12-15} -alkyl adipate, dicapryl adipate, dicetyl adipate, diisodecyl adipate, diisocetyl adipate, diisononyl adipate, diheptylundecyl adipate, dtridecyl adipate, diisostearyl adipate, diethyl sebacate, diisopropyl sebacate, dibutyl sebacate, diethylhexylsebacate, diisocetyl dodecanedioate, dimethyl brassylate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate.

[0105] Preferred diester constituents include those wherein Y is $-(CH_2)_x-$ wherein x has a value of from 0-6, preferably a value of 0-5, more preferably a value of from 1-4, while R^1 and R^2 are C_1 - C_6 alkyl groups which may be straight chained alkyl but preferably are branched, e.g. iso- and tert-moieties. Particularly preferred diester compounds are those in which the compounds terminate in ester groups.

[0106] A further advantageously utilized processing aid is a hydrocarbon solvent constituent. The hydrocarbon solvents are immiscible in water, may be linear or branched, saturated or unsaturated hydrocarbons having from about 6 to about 24 carbon atoms, preferably comprising from about 12 to about 16 carbon atoms. Saturated hydrocarbons are preferred, as are branched hydrocarbons. Such hydrocarbon solvents are typically available as technical grade mixtures of two or more specific solvent compounds, and are often petroleum distillates. Nonlimiting examples of some suitable linear hydrocarbons include decane, dodecane, decene, tridecene, and combinations thereof. Mineral oil is one particularly preferred form of a useful hydrocarbon solvent. Further preferred hydrocarbon solvents include paraffinic hydrocarbons including both linear and branched paraffinic hydrocarbons. The former are commercially available as NORPAR solvents (ex. ExxonMobil Corp.) while the latter are available as ISOPAR solvents (ex. ExxonMobil Corp.) Mixtures of branched hydrocarbons especially as isoparaffins form a further particularly preferred form of a useful hydrocarbon solvent of the invention. Particularly useful technical grade mixtures of isoparaffins include mixtures of isoparaffinic organic solvents having a relatively narrow boiling range. Examples of these commercially available isoparaffinic organic solvents include

ISOPAR C described to be primarily a mixture of C_7 - C_8 isoparaffins, ISOPAR E described to be primarily a mixture of C_8 - C_9 isoparaffins, ISOPAR G described to be primarily a mixture of C_{10} - C_{11} isoparaffins, ISOPAR H described to be primarily a mixture of C_{11} - C_{12} isoparaffins, ISOPAR J, ISOPAR K described to be primarily a mixture of C_{11} - C_{12} isoparaffins, ISOPAR L described to be primarily a mixture of C_{11} - C_{13} isoparaffins, ISOPAR M described to be primarily a mixture of C_{13} - C_{14} isoparaffins, ISOPAR P and ISOPAR V described to be primarily a mixture of C_{12} - C_{20} isoparaffins.

[0107] When present such further processing aids are typically included in amounts of up to about 30% by weight, preferably to 20% wt. of the solid block composition, although generally lesser amounts are usually effective.

[0108] Optionally but in some cases, preferably one or more of the foregoing constituents may be provided as an encapsulated, particularly a microencapsulated material. That is to say, quantities of one or more constituents are provided covered or encapsulated in an encapsulating material. Methods suitable for such an encapsulation include the customary methods and also the encapsulation of the granules by a melt consisting e.g. of a water-soluble wax, coacervation, complex coacervation and surface polymerization. Non-limiting examples of useful encapsulating materials include e.g. water-soluble, water-dispersible or water-emulsifiable polymers and waxes. Advantageously, reactive chemical constituents, particularly the fragrance composition when present, may be provided in an encapsulated form so to ensure that they do not prematurely degrade during processing of the constituents used to form the solid block composition and that they are retained with minimal degradation in the solid block composition prior to their use. The use of water soluble encapsulating material is preferred as such will release the one or more chemical constituents when the solid block composition is contacted with water supplied either in the cistern or in the toilet bowl.

[0109] Ideally the lavatory treatment blocks exhibit a density greater than that of water which ensures that they will sink when suspended in a body of water, e.g., the water present within a cistern. Preferably the lavatory treatment blocks formed from the solid block composition exhibit a density in excess of about 1 g/cc of water, preferably a density in excess of about 1.5 g/cc of water and most preferably a density of at least about 2 g/cc of water.

[0110] While the mass of the lavatory treatment blocks may vary, and amount of up to an including 500 grams may be practiced, generally the mass of the solid block compositions do not exceed about 150 grams. Advantageously the mass of the lavatory treatment blocks is between about 20 and 100 grams. It is appreciated that lavatory treatment blocks having great mass should provide a longer useful service life of the lavatory treatment blocks, with the converse being equally true.

[0111] The lavatory treatment blocks according to the present invention may also be provided with a coating of a water-soluble film, such as polyvinyl acetate following the formation of the lavatory treatment blocks from the recited solid block composition. Such may be desired for improved handling, however such is often unnecessary as preferred embodiments of the blocks exhibit a lower likelihood of sticking to one another following manufacture than many prior art treatment block compositions.

[0112] It will be appreciated by those of ordinary skill in the art that several of the components which are directed to provide a chemical composition can be blended into one chemical composition with the additional appreciation that potential blending of incompatible components will be avoided. For example, those of ordinary skill in the art will appreciate that certain anionic surfactants may have to be avoided as some may be incompatible with certain sanitizing agents and/or certain anti-lime scale agents mentioned herein. Those of ordinary skill in the art will appreciate that the compatibility of the anionic surfactant and the various sanitizing and anti-limescale agents can be easily determined and thus incompatibility can be avoided in the situations.

[0113] The lavatory treatment blocks may be formed of a single chemical composition, or may be formed of two (or more) different chemical compositions which may be provided as separate regions of a solid block, such as a first layer of a solid block consisting of a first chemical composition, alongside a second layer of a solid block consisting of a second chemical composition which is different than the first chemical composition. The block may also be formed of two or more separate blocks which are simply layered or otherwise assembled, without or without the use of an adhesive. Further layers of still further different chemical compositions may also be present. Such solid blocks formed having two or more discrete layers or regions of, respectively, two or more different chemical compositions may be referred to as composite blocks.

[0114] Any form of the lavatory treatment blocks may also be provided with a coating film or coating layer, such as a water soluble film which is used to overwrap the chemical composition provided in the device which film provides a vapor barrier when dry, but which dissolves when contacted with water. Alternately the lavatory treatment blocks may be oversprayed or dipped into a bath of a water soluble film forming constituent, and thereafter removed and thus allowing the water soluble film forming constituent to dry and form a coating layer on the solid block.

[0115] Exemplary materials which may be used to provide such a coating on some or all of the surfaces of the solid block compositions include one or more of the following: Rhodasurf TB-970 described by its supplier to be a tridecyl alcohol having a degree of ethoxylation of approximately 100 having an HLB of 19, and exhibiting a melting point in the range of 52-55° C.; Antarox F-108 which is described to be an EO-PO block copolymer having a degree of ethoxylation of approximately 80% and having a melting point in the range of 54-60° C.; further materials including those identified as Pluriol Z8000, and Pluriol E8000 which are believed to be optionally substituted, high molecular weight polyethylene glycols ("PEG") having a sufficiently high molecular weight such that they have a melting point of at least 25° C., preferably a melting point of at least about 30° C. may also be used. Other water soluble materials, desirably those which have a melting point in the range of about 30-70° C., and which may be used to provide a water soluble or water dispersible coating on the lavatory treatment blocks are also contemplated to be useful, especially synthetic or naturally occurring waxy materials, and high molecular weight polyalkylene glycols, especially polyethylene glycols. Certain of these coating materials may be surfactants. Generally such materials may be provided as a

dispersion in water, an organic solvent or in an aqueous/organic solvent, but preferably are used as supplied from their respective supplier and are heated to at least their melting points in order to form a liquid bath. Conveniently, the lavatory treatment blocks affixed to the plate of a hanger are then conveniently dipped into the said bath, thereby providing a coating layer to the lavatory treatment blocks. Alternately, the coating materials may be sprayed, brushed on or padded onto at least part of the surfaces of the previously formed lavatory treatment blocks.

[0116] The application of a water soluble film or coating is preferred in certain embodiments of the invention as the surface film may facilitate the handling of the blocks during packaging and storage prior to use of the lavatory treatment blocks. Further, the application of a water soluble film or coating is preferred as certain water soluble film former compositions may impart a desirable surface gloss to the lavatory blocks.

[0117] The present inventor has surprisingly found that improved foaming benefits are attained when lavatory treatment blocks comprise glycerine in even minor amounts. Advantageously, glycerine forms from 0.001% wt. to about 5% wt., preferably from 0.005% wt. of the total mass of a lavatory treatment block composition. While not wishing to be bound by the following theory, the inclusion of glycerine is believed to impart improved substantivity to the foam formed from the lavatory treatment blocks when contacted with water, which often provides for a more dense foam, and frequently also provides for a greater initial volume of foam formed with each flush of the lavatory appliance as compared with like compositions wherein the glycerine is however omitted. Such foam formed from a lavatory treatment block containing glycerine has also been observed to have a longer lifespan prior to breakdown. Such benefits of increased foam production and/or increased foam volume and/or improved foam lifespan are particularly advantageous from a technical viewpoint as well as from a consumer viewpoint, as providing for improved cleaning of sanitary appliance surfaces above the water line present in the sanitary appliance.

[0118] Further surprisingly, the present inventors have also unexpectedly discovered that the inclusion of glycerine in the lavatory block compositions provides improved foaming benefits, but at the same time reduces the rate of erosion of the lavatory treatment blocks, hence improving their lifespan and useful service life. Such a result is counterintuitive and unexpected in the relevant art, as normally improved foaming benefits would dictate a greater rate of delivery of foaming surfactants to the interior of a lavatory appliance which would require greater rates of treatment block erosion. According to preferred embodiments of lavatory block compositions taught herein, the converse has been discovered to be true.

[0119] Glycerine as an essential constituent of the lavatory treatment blocks of the invention. As used in this specification the term glycerine is to be understood to encompass glycerol, and is to be understood to encompass C₃-C₈ alkanols (preferably C₃-C₆ alkanols) comprising a plurality of hydroxyl groups within the molecule, preferably including a hydroxyl group on each carbon atom present in the molecule. Of these, glycerine, which may also be referred to as 1,2,3-propanetriol is particularly preferred. The glycerine may be provided as a

separate or discrete constituent which used to form a treatment block composition, or it may be provided as part of a surfactant constituent or composition which comprises glycerine, such as a commercially available surfactant preparation. The glycerine may be present in any effective amount, but in order of increasing preference is present in amounts of: 0.001, 0.01, 0.025, 0.05, 0.075, 0.1, 0.2, 0.25, 0.5, 0.75, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.2, 2.4, 2.5, 3, 3.5, 4, 4.5 to about 5% wt., based of the total mass of a lavatory treatment block composition of which the glycerine forms a part.

[0120] The glycerine may be provided as a part of or a component of a commercially preparation, such as a commercially available surfactant preparation. One such exemplary and preferred commercially available surfactant preparation is one which includes a fatty acid alkanolamides that are derived from alkanol amines, such as the diethanolamide of coconut fatty acids (cocamide diethanolamide) and mixtures thereof which also include glycerine. One such commercially available material 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).

[0121] Preferably the lavatory treatment blocks are those which comprise at least one surfactant, preferably at least one anionic or nonionic surfactant.

[0122] Exemplary compositions which can be used to form the lavatory treatment blocks of the present invention are shown in the following table below; the amounts indicates are in % wt. of the "as supplied" constituent used to form an example block compositions, labeled A through F.

Component	A	B	C	E	F
dodecyl Benzene Sulfonate Na ¹	20-25	5-10	35-40	30-35	30-35
Alfa Olefin Sulfonate Na ²	25	10	5	32	32
lauryl monoethanolamide ³	10	8	5	2	5
sodium Lauryl Ether Sulfate ⁴	10	—	—	4.5	5
Pluronic 68 ⁵	10	—	—	3	—
Na Sulfate	20	—	—	21.5	21
Pluronic 87 or 88 ⁶	—	70	50	—	—
alcohol ethoxylate C ₉ -C ₁₁ 6EO ⁷	—	2	—	—	—
silica	—	—	—	2	2
glycerine	0.001-5	0.001-5	0.001-5	0.001-5	0.001-5

¹Dodecyl Benzene Sulfonate Sodium (80-90% active) -- anionic

²Alpha Olefin Sulfonate Sodium -- anionic

³Lauryl Monoethanolamide -- non-ionic

⁴Sodium Lauryl Ether Sulfate (70% active) -- anionic

⁵Polyoxyethylene (160) polyoxypropylene (30) glycol -- non-ionic

⁶Pluronic 87 E₆₁ P_{41.5} E₆₁ -- Molecular Weight 7700 -- HLB 24 -- non-ionic

Pluronic 88 E₉₈ P_{41.5} E₉₈ -- Molecular Weight 10800 -- HLB 28 -- non-ionic

⁷Alcohol ethoxylate C₉-C₁₁ 6EO -- non-ionic

[0123] Further exemplary bleach containing compositions which can be used to form the lavatory treatment blocks of the present invention include compositions indicated on the next table having the general ranges as follows:

	% w/% w
alpha olefin sulfonate	0-35
sodium lauryl ether sulfate	3.0-6.0
bleaching agent (e.g., DCCNa or Hydantoin)	0.5-25
lauryl monoethanolamide	2.0-5.0
dodecyl benzene sulfonate Na	50-70
Na sulfate anhydrous	15-25
silica	1.0-2.0
glycerine	0.001-5

[0124] Further exemplary preferred embodiments of blocks which are useful as lavatory treatment blocks of the present invention include those which comprise:

[0125] 10-35% wt., preferably 15-30% wt. of an alpha olefin sulfonate anionic surfactant;

[0126] 10-35% wt., preferably 15-30% wt. of a linear monoethanolamide;

[0127] 5-50% wt., preferably 15-35% wt. of a linear dodecylbenzene sulfonate anionic surfactant;

[0128] 5-50% wt., preferably 20-35% wt. of sodium sulfate

[0129] 0.1-15% wt., preferably 0.5-5% wt. of silica

[0130] 0.1-25% wt., preferably 1-10% wt. sodium lauryl ether sulfate,

[0131] 0.001-5% wt. glycerine.

[0132] optionally to 40% wt. further additive constituents, including but not limited to further surfactants, fillers, binders, fragrances, processing aids such as lubricants and tabletting aids, bleaches, sanitizing compositions and the like.

[0133] Yet further exemplary compositions which include a bleach constituent which find use as lavatory treatment blocks of the present invention include those recited on the following tables, and labeled as G through N:

	G	H	I	J	K	L
dodecylbenzene sulfonate, sodium salt (80%)	22-27.0	22.0-27	27-32.0	30-35.00	32-37.8	27-32.0
sodium C14/C16 olefin sulfonates (80%)	15.0	20.0	15.0	22.0	23.62	20.0
silica	2.0	2.0	2.0	2.0	1.89	2.0
lauramide monoethanol amide (98%)	30.0	30.0	25.0	15.00	12.28	20.0
sodium sulfate	20.5	20.5	20.5	20.50	18.90	20.5
dichlorocyanurate dihydrate, sodium salt (56% bleach)	2.5	2.5	2.5	2.4	2.41	2.5
paraffinic hydrocarbons	3.0	3.0	3.0	3.1	3.09	3.0
glycerine	0.001-5	0.001-5	0.001-5	0.001-5	0.001-5	0.001-5

-continued

	M	N	O
dodecylbenzene sulfonate, sodium salt (80%)	30-35.0	30-37.0	27-32.0
sodium C14/C16 olefin sulfonates (80%)	22.0	25.0	20.0
silica	2.0	2.0	2.0
lauramide monoethanol amide (98%)	15.0	10.0	20.0
sodium sulfate	20.5	20.5	18.5
dichlorocyanurate dihydrate, sodium salt (56% bleach)	2.5	2.5	2.5
paraffinic hydrocarbons	3	3	5
glycerine	0.001-5	0.001-5	0.001-5

[0134] The identity of the constituents used to form the foregoing lavatory treatment blocks G-O are identified more specifically on the following table.

dodecylbenzene sulfonate, sodium salt (80%)	anionic surfactant, dodecylbenzene sulfonate, 80% wt. actives
sodium C14/C16 olefin	anionic surfactant,

sulfonates (80%)	sodium C14/C16 olefin sulfonates, 80% wt. actives
silica	filler anhydrous silica, 100% wt. actives.
lauramide monoethanol amide (98%)	solubility control agent, lauramide monoethanol amide, 98% wt. actives
sodium sulfate	diluent, sodium sulfate, 100% wt. actives
dichlorocyanurate dihydrate, sodium salt (56%)	bleach constituent, dichlorocyanurate dihydrate, sodium salt, 56% wt. bleach actives
Isopar M	hydrocarbon solvent, isoparaffinic organic solvents, 100% wt. actives
mineral oil	Hydrocarbon solvent, mineral oil, 100% wt. actives
paraffinic hydrocarbons	Hydrocarbon solvent, white paraffin oil, 100% wt. actives
glycerine	1,2,3-propanetriol

[0135] Still further exemplary compositions which include diisopropyl adipates which find use as lavatory treatment blocks of the present invention include those recited on the following tables, and labeled as P through W:

	P	Q	R	S
dodecylbenzene sulfonate, sodium salt (80%)	50-55.85	53-58.85	57-62.51	57-62.51
silica	2.41	2.41	2.56	2.56
lauramide monoethanolamide (98%)	6.01	6.01	6.38	6.38
sodium sulfate	12	12	12.75	12.75
dichlorocyanurate dihydrate, sodium salt (56%)	14.63	14.63	9.32	9.32
diisopropyl adipate	6.1	6.1	6.48	6.48
glycerine	0.001-5	0.001-5	0.001-5	0.001-5

	T	U	V	W
dodecylbenzene sulfonate, sodium salt (80%)	53-58.61	62-67.27	64-69.25	65-70.83
silica	2.40	1.91	1.96	2.01
lauramide monoethanolamide (98%)	5.98	4.74	4.88	4.99
sodium sulfate	11.95	17.37	17.88	18.29
dichlorocyanurate dihydrate, sodium salt (56%)	14.6	4.98	2.41	0.55
diisopropyl adipate	6.46	3.73	3.61	3.33
Glycerine	0.001-5	0.001-5	0.001-5	0.001-5

[0136] The identity of the constituents used to form the foregoing lavatory treatment blocks labeled P through W are identified more specifically on the following table:

dodecylbenzene sulfonate, sodium salt (80%)	anionic surfactant, dodecylbenzene sulfonate, 80% wt. actives
silica	anhydrous silica, 100% wt. actives.
lauramide	solubility control agent, lauramide
monoethanolamide (98%)	monoethanolamide, 98% wt. actives
sodium sulfate	diluent, sodium sulfate, 100% wt. actives
dichlorocyanurate dihydrate, sodium salt (56%)	bleach constituent, dichlorocyanurate dihydrate, sodium salt, 56% wt. bleach actives
diisopropyl adipate	diester constituent, diisopropyl adipate, 100% wt. actives
glycerine	1,2,3-propanetriol

[0137] Yet further exemplary compositions which include paraffinic hydrocarbon solvents or mineral oil which find use as lavatory treatment blocks of the present invention include those recited on the following tables, and labeled as AA through AK:

	AA	AB	AC	AD	AE
dodecylbenzene sulfonate, sodium salt (80%)	60-65.8	60-65.8	60-65	60-64.17	60-69.25
silica	2.69	2.69	2.66	2.63	1.96
lauramide	6.72	6.72	6.64	6.55	4.88
monoethanolamine (98%)					
sodium sulfate	13.42	13.42	13.26	13.09	17.88
dichlorocyanurate dihydrate, sodium salt (56% bleach)	8.89	8.89	8.78	9.57	2.41
Isopar M	2.47	2.47	—	—	—
mineral oil	—	—	3.66	3.99	3.61
glycerine	0.001-5	0.001-5	0.001-5	0.001-5	0.001-5

	AF	AG	AH	AI	AJ	AK
dodecylbenzene sulfonate, sodium salt (80%)	65-70.83	64-69.25	64-69.25	64-69.25	65-70.83	63-68.31
silica	2.01	1.96	1.96	1.96	2.01	2.90
lauramide	4.99	4.88	4.88	4.88	4.99	4.88
monoethanolamine (98%)						
sodium sulfate	16-18.29	15-17.88	15-17.88	15-17.88	15-18.29	15-17.88
dichlorocyanurate dihydrate, sodium salt (56% bleach)	0.55	2.41	2.41	2.41	0.55	2.41
Isopar M	3.33	3.61	3.61	—	—	3.61
mineral oil	—	—	—	3.61	3.33	—
glycerine	0.001-5	0.001-5	0.001-5	0.001-5	0.001-5	0.001-5

[0138] The identity of the constituents used to form the foregoing blocks AA through AK are identified more specifically on the following table:

dodecylbenzene sulfonate, sodium salt (80%)	anionic surfactant, dodecylbenzene sulfonate, 80% wt. actives
silica	filler anhydrous silica, 100% wt. actives.
lauramide	solubility control agent, lauramide
monoethanolamide (98%)	monoethanolamide, 98% wt. actives
sodium sulfate	diluent, sodium sulfate, 100% wt. actives

-continued

dichlorocyanurate dihydrate, sodium salt (56%)	bleach constituent, dichlorocyanurate dihydrate, sodium salt, 56% wt. bleach actives
Isopar M	hydrocarbon solvent, isoparaffinic organic solvents, 100% wt. actives
mineral oil	Hydrocarbon solvent, mineral oil, 100% wt. actives
glycerine	1,2,3-propanetriol

[0139] Yet further and particularly preferred embodiments of lavatory treatment blocks and their compositions include those which are recited on Table 1.

[0140] The manufacture of the lavatory treatment blocks of the invention contemplates mixing the constituents of the block composition into a generally homogenous mass such as by noodling, as well as by plodding, but preferably by extruding, and thereafter forming a “preform” from a measured quantity of the homogenous mass. Usually all of the solid ingredients are mixed in any suitable blending equipment followed by the addition of liquid ingredients under blending

conditions. In an extrusion process a mixture of the chemical constituents used to ultimately form the solid block composition is made, followed by extrusion of this mixture into a rod or bar form which is then cut into appropriately sized pieces or blocks which are to be used in and of themselves, or which may be used with an ITB device and/or an ITC device including virtually any ITB and/or ITC device which is known to the art. By way of non-limiting examples such ITB and ITC devices include those described in one or more of: PCT/GB2005/002831, published as WO2006/013321; U.S. Pat. No. D541,902, US 20050014668 A1; U.S. Pat. No. D514,661; U.S. Pat. No. D501,532; U.S. Pat. No. D508,106;

EP1797251 the contents of which are incorporated herein by reference. The lavatory treatment blocks may also be useful in so called “cageless” lavatory dispensing devices, such as disclosed in U.S. Pat. No. D548,304, U.S. Pat. No. D547,418 and in one or more of WO2007/107769, WO2007/107750, WO2007/107755, EP1797251 the contents of which are incorporated herein by reference. In further embodiments, the lavatory treatment blocks may be used as formed or shaped, and thus wholly independently from any device, hanger, cage or holder.

[0141] In preferred embodiments the service life of the lavatory treatment blocks of the devices of the invention should be from about 5 to about 30 days, based on 6 flushes per day. Preferably the service life of the lavatory treatment blocks is measured when the devices of the invention are installed on the rim of a toilet bowl such that the said block is positioned adjacent to the sloping interior sidewall of the toilet bowl and is subjected to between 6-12 flushes per day. Preferably the temperature of the water which is flushed is in the range of 16-24° C. The length of life of the plurality of lavatory treatment blocks will of course depend on a variety of factors including their individual formulation, their relative position to the sidewall of the lavatory appliance, their geometries, the water temperature, tank size, the number of flushes over the period of use and the volume of the water which contacts the lavatory treatment blocks.

EXAMPLES

[0142] Several embodiments of lavatory treatment blocks were formed in order to evaluate their performance characteristics, including foaming characteristics and block lifespan characteristics against a similar comparative lavatory treatment block which excluded the surfactant preparation which comprised 8% wt. of glycerine. Samples of lavatory block compositions having the compositions according to Table 1 which were formed by mixing the specified constituents, thereafter providing them to an extruder and extruding the compositions into an extruded column which was cut into blocks having a size of 35 g and a mass of between about 45 g.

TABLE 1

	E1	E2	(comparative example) C1
C ₁₀ -C ₁₄ benzene sulfonate, sodium salt (80%)	23	23	23
C14/C16 olefin sulfonate, sodium salt (80%)	26.4	26.4	26.4
coco fatty acid alkanolamide	1.84	5.52	—
silica	2	2	2
sodium sulfate	40.6	37.1	41.6
citric acid	1	1	1
glycerine	0.16	0.48	—
fragrance	4.5	4.5	4.5
mineral oil	0.5	—	1.5

[0143] The identity of the constituents used to form the lavatory treatment blocks are identified more specifically on the following Table 2. The individual constituents were used “as supplied” from their respective suppliers and may constitute less than 100% wt, or 100% wt. of the named compound, as indicated in Tables 1 and 2.

TABLE 2

C ₁₀ -C ₁₄ benzene sulfonate, sodium salt (80%)	anionic surfactant, dodecylbenzene sulfonate, 80% wt. actives, supplied as NANSAs HS 80/PF
C14/C16 olefin sulfonate, sodium salt (80%)	C14/C16 olefin sulfonate, sodium salt (80% wt. actives), supplied as NANSAs LSS 480/H, or other equivalent material
coco fatty acid alkanolamide	coco fatty acid alkanolamide, 100% wt. actives, supplied as component of Ninol® CO-40
silica	filler anhydrous silica, 100% wt. actives, supplied as MICROFIL ED, or other equivalent material
sodium sulfate	anhydrous sodium sulfate, 100% wt. actives
citric acid	anhydrous citric acid, 100% wt. actives
glycerine	1,2,3-propanetriol, 100% wt. actives, supplied as component of Ninol® CO-40
fragrance	proprietary fragrance composition, 100% wt. actives (presumed)
mineral oil	mineral oil, 100% wt. actives

[0144] In accordance with the test samples in the form of rectangular solid lavatory treatment blocks were supplied to the interior of a ITB cage of a lavatory dispensing devices as disclosed on FIG. 1. With respect to FIG. 1, therein is depicted an embodiment of an ITB device 10, including a body 12 which includes an integral cage adapted to receive and retain in its interior a treatment block composition according to the invention. The body 12 containing a treatment block composition may be suspended via a hook 14, from the rim of a toilet bowl such that the body 12 is positioned beneath the rim and within the path of flush water released by a sanitary appliance, e.g., a toilet bowl. Flush water enters and exits into the interior of the body 12 via one or more passages 16 wherein it contacts the treatment block and forms a treatment composition by dissolving a part thereof. The initial masses of the individual solid lavatory treatment blocks, and their weights during various time intervals during the test are reported on the following Tables 3A, 3B and 3C below. Samples of each solid treatment block compositions indicated on Table 1 in such a lavatory dispensing device were separately supplied to one or more of three toilets, a “Remo” model toilet bowl, (ex. Shires Co., Ireland), and/or an “Alto” model toilet bowl (ex. Ideal Standard Co, UK), and/or a “Jacob Delafon” toilet bowl (ex. Delafon, France). The placement of the ITB device varied but once positioned prior to the test was not moved until the test was concluded. The test was performed over a number of successive days, and all testing was performed at approximately room temperature (19-22° C.). Each of the toilets was periodically and automatically flushed by a machine-controlled device which operated the toilets to flush 24 times daily at intervals of approximately 30 minutes between flushes. This flushing protocol was considered to be particularly harsh, and simulated exceptionally heavy usage far in excess of what is normally expected in a domestic household environment. The loss of the mass of the solid treatment block compositions were evaluated at regular intervals. The results of the test are indicated on the following Tables 3A, 3B and 3C.

TABLE 3A

E1 lavatory treatment block compositions					
Total flushes	0	94	169	258	306
Remo toilet; block mass (grams)					
Ex. B1E1	40.94	38.72	32.22	21.18	17.95
Ex. B2E1	40.71	40.34	23.32	9.72	5.76
Jacob Delafon toilet; block mass (grams)					
Ex. B3E1	40.90	38.18	27.70	8.58	1.90
Ex. B4E1	40.77	36.76	31.09	19.24	12.83
Ex. B5E1	40.37	27.08	10.28	0.74	0.00
Ex. B6E1	40.85	33.29	29.28	19.78	14.76
Ex. B7E1	40.95	38.46	30.08	16.33	9.19
Ex. B8E1	40.48	32.98	18.91	2.79	0.62

TABLE 3B

E2 lavatory treatment block compositions					
Total flushes	0	94	169	258	306
Remo toilet; block mass (grams)					
Ex. B1E2	42.4	37.19	20.91	4.56	3.01
Ex. B2E2	41.1	31.58	22.71	7.79	5.05
Ex. B3E2	40.9	35.80	21.91	11.04	5.23
Ex. B4E2	41.15	36.38	27.20	14.08	8.67
Ideal Standard Alto toilet; block mass (grams)					
Ex. B5E2	41.08	44.55	42.45	40.37	38.41
Ex. B6E2	41.17	46.16	43.58	39.60	36.46
Ex. B7E2	41.17	36.50	23.77	11.72	7.09
Jacob Delafon toilet; block mass (grams)					
Ex. B8E2	40.85	37.54	29.92	19.57	12.52
Ex. B9E2	41.05	40.55	35.72	28.19	24.97
Ex. B10E2	40.32	33.47	19.94	3.13	1.03
Ex. B11E2	40.97	38.92	33.31	22.73	16.29
Ex. B12E2	40.82	40.14	36.54	27.18	22.57
Ex. B13E2	40.23	31.52	17.08	3.44	1.51

TABLE 3C

C1 lavatory treatment block compositions (comparative examples)					
Total flushes	0	94	169	258	306
Remo toilet; block mass (grams)					
Ex. B1C1	40.62	30.15	20.91	12.09	6.17
Ex. B2C1	41.06	38.39	24.33	2.43	0.00
Ex. B3C1	40.59	30.04	6.97	0.00	0.00
Ex. B4C1	41.08	25.64	21.72	16.40	10.67
Ideal Standard Alto toilet; block mass (grams)					
Ex. B5C1	40.65	42.38	33.94	28.79	20.98
Ex. B6C1	40.36	41.35	36.91	29.71	24.70
Ex. B7C1	40.94	25.75	7.47	2.12	0.00
Jacob Delafon toilet; block mass (grams)					
Ex. B8C1	40.97	25.96	21.41	10.43	6.66
Ex. B9C1	40.89	24.94	17.40	7.61	3.18
Ex. B10C1	40.43	19.98	8.87	1.33	0.00
Ex. B11C1	41.11	40.67	33.32	25.58	19.40
Ex. B12C1	40.90	33.94	28.15	17.11	9.54
Ex. B13C1	40.81	19.47	8.76	2.33	0.00

[0145] As can be seen from the foregoing the block compositions according to the examples (E1, E2) described on

Table 1 exhibited a good service life and furthermore, while not disclosed in the table, provided superior foaming as compared to the solid block composition according to the comparative example (C1). This was particularly surprising as the improved foaming benefit was provided by block composition which apparently underwent less dissolution per flush of the toilet bowl. It is further generally surprising that the blocks according to the invention, viz. according to E1 and E2 exhibited a good service life notwithstanding the frequency of daily flushings, which provided at most about 30 minutes of time for the solid block composition to dry before being contacted with water from the next flush cycle. The variance in the rate of dissolution of the solid block compositions was influenced with the respective positioning of the ITB containing the solid block composition within a toilet bowl, as certain regions of the rim of a particular toilet bowl released a greater or lesser amount of flush water during each flush cycle. Hence, tested ITBs containing a block composition may have undergone greater dissolution of a solid block composition primarily caused by a greater volume of water exiting the rim of a toilet bowl at a specific location thereof.

[0146] 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 and alternatives falling within the scope and spirit of the invention as expressed in the appended claims.

1. Lavatory treatment blocks with improved foaming benefits wherein the said blocks contain a foam improving amount of glycerine.

2. Lavatory treatment blocks with improved foaming benefits wherein the said blocks contain a foam improving amount of a surfactant constituent which comprises glycerine.

3. Lavatory treatment blocks with improved foaming benefits wherein the said blocks contain a foam improving amount of a surfactant constituent which comprises, in combination, a fatty amide, such as cocoamide diethanolamide with glycerine.

4. A lavatory dispensing device adapted for use with a sanitary appliance, preferably an ITB device or an ITC device, comprising one or more lavatory treatment blocks according to any of claim 1, 2 or 3.

5. A process for delivering a treatment composition to a sanitary appliance, especially preferably, to the interior of a toilet bowl, which process comprises: providing one or more lavatory treatment blocks according to claim 1, 2 or 3, and, periodically flushing water about the exterior of the said blocks to elute at least one chemical constituent to form a treatment composition with said water which treatment composition is used to treat a part of the sanitary appliance.

6. A process for delivering a treatment composition to a sanitary appliance according to claim 5 which process comprises: providing one or more lavatory treatment blocks according to claim 1, 2 or 3, and, periodically flushing water about the exterior of the said blocks to elute at least one chemical constituent to form a treatment composition with said water which treatment composition is used to treat a part of the sanitary appliance.

7. A process for delivering a treatment composition to a sanitary appliance according to claim 5 which process comprises: providing one or more lavatory treatment blocks according to claim 1, 2 or 3 within a cistern or tank of the

sanitary appliance, and, continuously immersing or periodically immersing at least a part of the blocks in the water within the cistern or tank so to elute at least one chemical constituent from each of the lavatory treatment blocks to form a treatment composition with the water which is used to treat a part of the sanitary appliance.

8. A process for delivering a treatment composition to a sanitary appliance according to claim **5** which process comprises: providing one or more lavatory treatment blocks

according to claim **1**, **2** or **3** via use of an ITB device, suspending said block from a part of the toilet bowl, preferably from a part of the rim thereof, such that at least one chemical constituent of the block is used to form a treatment composition therefrom which is used to treat the interior of the toilet bowl when the treatment composition formed is used to flush the toilet bowl.

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