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(54) Title: CLEANING COMPOSITIONS

(57) Abstract: Aqueous, dilutable hard surface cleaning compositions which comprise one or more anionic and/or nonionic surfactants, a thickener and an opacifying constituent particularly wherein the opacifying constituent also provides a pearlescent effect to the compositions are disclosed.

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CLEANING COMPOSITIONS

Cleaning compositions are commercially important products and enjoy a wide field of utility in assisting in the removal of dirt and grime from surfaces, especially those characterized as useful with “hard surfaces”. Hard surfaces are those which are frequently encountered in lavatories such as lavatory fixtures such as toilets, shower stalls, bathtubs, bidets, sinks, etc., as well as countertops, walls, floors, etc. Such cleaning compositions are typically provided for use “as-is” wherein they are intended to be used as supplied from a manufacturer, or in “concentrate” form wherein they are intended to be diluted in a larger volume of water prior to use in the cleaning treatment of hard surfaces.

While the art is replete with various hard surface cleaning formulations which provide some cleaning benefit there is nonetheless a real and continuing need in the art for further improved hard surface cleaning compositions.

In one aspect the present invention relates to aqueous, dilutable hard surface cleaning compositions which comprise (preferably consists of, more preferably consisting essentially of):

one or more detersive surfactants, preferably containing one or more anionic surfactants including anionic soaps optionally but preferably in conjunction with one or more nonionic surfactants;

one or more thickener constituents;

one or more opacifying constituents;

optionally but desirably one or more organic solvents;

optionally one or more constituents for improving the aesthetic or functional features of the inventive compositions;

and, water.

The hard surface cleaning compositions of the present invention provide slightly viscous compositions which feature a desirable opacified appearance which is highly sought by consumers.

Further aspects of the invention are directed to processes for the manufacture of aqueous, dilutable hard surface cleaning compositions as well as processes for the treatment of hard surfaces utilizing the aforesaid aqueous, dilutable hard surface cleaning compositions.

The inventive compositions necessarily comprise one or more detersive surfactants, preferably containing one or more anionic surfactants including anionic soaps optionally but preferably in conjunction with one or more nonionic surfactants

The detersive surfactant constituent necessarily includes at least one anionic surfactant. Exemplary useful anionic surfactants such as alkali metal salts, ammonium salts, amine salts, aminoalcohol salts or the magnesium salts of one or more of the following compounds: alkyl sulfates, alkyl ether sulfates, alkylamidoether sulfates, alkylaryl polyether sulfates, alkylaryl sulfates, alkylaryl sulfonates, monoglyceride sulfates, alkylsulfonates, alkylamide sulfonates, alkylarylsulfonates, olefinsulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfosuccinamate, alkyl sulfoacetates, alkyl phosphates, alkyl ether phosphates, acyl sarconsinates, acyl isethionates, and N-acyl taurates. Generally, the alkyl or acyl radical in these various compounds comprise a carbon chain containing 12 to 20 carbon atoms. Of these anionic surfactants, the alkylaryl sulfonates are preferred, of which sodium dodecylbenzene sulfonate is particularly preferred. Such preferred alkylaryl sulfonates may be supplied as a constituent, or may be formed *in situ* by the reaction of appropriate molar amounts of sulfonic acid with a sodium comprising base material such as NaOH.

Anionic soap surfactants may also be present in the detersive surfactant constituent either in place of the anionic surfactant or in conjunction with the anionic surfactant described above. Exemplary useful anionic soap surfactants include includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkanol-ammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural sources such as, for instance, plant or animal esters (*e.g.*, palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease, lard, and mixtures thereof). The fatty acids also can be synthetically prepared (*e.g.*, by the oxidation of petroleum, or by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Naphthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful is the sodium or potassium salt of the mixtures of fatty acids derived from castor oil, i.e., sodium or potassium castor oil soap. Of the anionic soap surfactants contemplated herein, the alkyl metal soaps, such as sodium soaps of naturally derived fatty acids, are preferred.

Optionally but in many instances desirably, the detersive surfactant constituent includes 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. By way of non-limiting example, particularly examples of suitable nonionic surfactants which may be used in the present invention include the following:

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.

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, WI) 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.

A further class of useful nonionic surfactants include primary and secondary linear and branched alcohol ethoxylates, such as those based on C_6-C_{18} 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, C_{11}-oxo-alcohol polyglycol ether with 3 EO; Genapol® UD, 050 C_{11}-oxo-alcohol polyglycol ether with 5 EO; Genapol® UD 070, C_{11}-oxo-alcohol polyglycol ether with 7 EO; Genapol® UD 080, C_{11}-oxo-alcohol polyglycol ether with 8 EO; Genapol® UD 088, C_{11}-oxo-alcohol polyglycol ether with 8 EO; and Genapol® UD 110, C_{11}-oxo-alcohol polyglycol ether with 11 EO.

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 C_{11}- C_{15} secondary alkanol condensed with 9 ethylene oxide units, or Tergitol 15-S-9 which is described as being C_{11} -C_{15} secondary alkanol condensed with 12 ethylene oxide units per molecule.

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

$$RO(CH_2CH_2O)_nH$$

wherein;

R is a mixture of linear, even carbon-number hydrocarbon chains ranging from $C_{12}H_{25}$ to $C_{16}H_{33}$ and n represents the number of ethoxy repeating units and is a number of from about 1 to about 12.

Surfactants of this formula are presently marketed under the Genapol® tradename (ex. Clariant), which surfactants include the "26-L" series of the general formula $RO(CH_2CH_2O)_nH$ wherein R is a mixture of linear, even carbon-number hydrocarbon chains ranging from $C_{12}H_{25}$ to $C_{16}H_{33}$ 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% C_{12} and 45% C_{14} 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.

A further class of useful nonionic surfactants include alkoxy block copolymers, and in particular, compounds based on ethoxy/propoxy block copolymers. Polymeric alkylene oxide block copolymers include nonionic surfactants in which the major portion of the molecule is made up of block polymeric C_2-C_4 alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting group, and can have as a starting nucleus almost any active hydrogen containing group including, without limitation, amides, phenols, thiols and secondary alcohols.

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

$$HO\text{-}(EO)_x(PO)_y(EO)_z\text{-}H \qquad (A)$$

where EO represents ethylene oxide,
PO represents propylene oxide,
y equals at least 15,
$(EO)_{x+y}$ equals 20 to 50% of the total weight of said compounds, and, the total molecular weight is preferably in the range of about 2000 to 15,000. These surfactants are available under the PLURONIC (ex. BASF) or Emulgen (ex. Kao.)

A further group of such useful nonionic surfactants containing the characteristic alkylene oxide blocks are those can be represented by the formula (B):

$$R\text{-}(EO,PO)_a(EO,PO)_b\text{-}H \qquad (B)$$

wherein R is an alkyl, aryl or aralkyl group, where the R 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. Specific 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.

Still further examples of useful nonionic surfactants include those which can be represented by formula (C) as follows:

$$RO\text{-}(BO)_n(EO)_x\text{-}H \qquad (C)$$

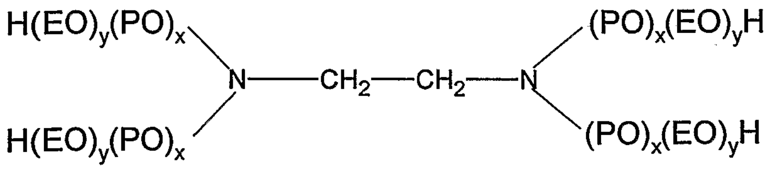
wherein EO represents ethylene oxide,
BO represents butylene oxide,
R is an alkyl group containing I to 20 carbon atoms,
n is about 5-15 and x is about 5-15.

Yet further useful nonionic surfactants include those which may be represented by the following formula (D):

$$HO\text{-}(EO)_x(BO)_n(EO)_y\text{-}H \qquad (D)$$

wherein EO represents ethylene oxide,
BO represents butylene oxide,
n is about 5-15, preferably about 15,
x is about 5-15, preferably about 15, and
y is about 5-15, preferably about 15.

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



(E)

where (EO) represents ethoxy,

(PO) represents propoxy,

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 non-ionic surfactants which may be used in the inventive compositions include those presently marketed under the trade name Pluronics® (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 Pluronics® L62 and Pluronics® L64.

Alkylmonoglycosides and alkylpolyglycosides which find use in the present inventive compositions include known nonionic surfactants which are alkaline and electrolyte stable. Alkylmonoglycosides and alkylpolyglycosides are prepared generally by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide with an alcohol such as a fatty alcohol in an acid medium. Various glycoside and polyglycoside compounds including alkoxylated glycosides and processes for making them are disclosed in U.S. Pat. Nos. 2,974,134; 3,219,656; 3,598,865; 3,640,998; 3,707,535, 3,772,269; 3,839,318; 3,974,138; 4,223,129 and 4,528,106 the contents of which are incorporated by reference.

One exemplary group of such useful alkylpolyglycosides include those according to the formula:

$$R_2O\text{-}(C_nH_{2n}O)_r\text{-}(Z)_x$$

wherein:

R_2 is a hydrophobic group selected from alkyl groups, alkylphenyl groups, hydroxyalkylphenyl groups as well as mixtures thereof, wherein the alkyl groups may be straight chained or branched, and which contain from about 8 to about 18 carbon atoms,

n has a value of 2 – 8, especially a value of 2 or 3;

r is an integer from 0 to 10, but is preferably 0,

Z is derived from glucose; and,

x is a value from about 1 to 8, preferably from about 1.5 to 5.

Preferably the alkylpolyglycosides are nonionic fatty alkylpolyglucosides which contain a straight chain or branched chain C_8 -C_{15} alkyl group, and have an average of from about 1 to 5 glucose units per fatty alkylpolyglucoside molecule. More preferably, the nonionic fatty alkylpolyglucosides which contain straight chain or branched C_8 -C_{15} alkyl group, and have an average of from about 1 to about 2 glucose units per fatty alkylpolyglucoside molecule.

A further exemplary group of alkyl glycoside surfactants suitable for use in the practice of this invention may be presented by the following formula (A):

$$RO\text{-}(R_1O)_y\text{-}(G)_x\, Z_b \qquad \text{(A)}$$

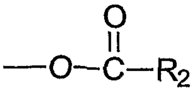
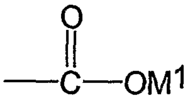
wherein:

R is a monovalent organic radical containing from about 6 to about 30, preferably from about 8 to 18 carbon atoms,

R_1 is a divalent hydrocarbon radical containing from about 2 to about 4 carbon atoms,

y is a number which has an average value from about 0 to about 1 and is preferably 0,

G is a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; and, x is a number having an average value from about 1 to 5 (preferably from 1.1 to 2);

Z is O_2M^1,  $-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2$, $O(CH_2)$, CO_2M^1, OSO_3M^1, or $O(CH_2)SO_3M^1$; R_2 is $(CH_2)CO_2\,M^1$ or $CH{=}CHCO_2M^1$; (with the proviso that Z can be O_2M^1 only if Z is in place of a primary hydroxyl group in which the primary hydroxyl-bearing carbon atom, --CH_2OH, is oxidized to form a  $-\overset{\overset{\displaystyle O}{\|}}{C}-OM1$ group

b is a number of from 0 to 3x+1 preferably an average of from 0.5 to 2 per glycosal group; p is 1 to 10, M^1 is H^+ or an organic or inorganic counterion, particularly cations such as, for example, an alkali metal cation, ammonium cation, monoethanolamine cation or calcium cation. As defined in Formula (A) above, R is generally the residue of a fatty alcohol having from about 8 to 30 and preferably 8 to 18 carbon atoms. Examples of such alkylglycosides as described above include, for example APG 325 CS Glycoside® which is described as being a 50% C_9 -C_{11} alkyl polyglycoside, also commonly referred to as D-glucopyranoside, (commercially available from Henkel KGaA) and Glucopon® 625 CS which is described as being a 50% C_{10} -C_{16} alkyl polyglycoside, also commonly referred to as a D-glucopyranoside, (ex. Henkel), well as Glucopon® 225DK, a further alkylpolyglycoside which is more specifically described as being 68 – 72%wt. of alkyl μ(+b) mono- and oligo- C_8 -C_{10} glucopyranosides (ex. Henkel) which is derived from glucose derivatives of maize, and fatty alcohols derived from coconut and palm kern oils. Further commercially available examples of suitable alkyl polyglycosides having differing carbon chain lengths include those currently marketed under the tradename Glucopon 220, Glucopon 225, Glucopon 425, Glucopon 600, and Glucopon 625, all available from Henkel Corporation

Further nonionic surfactants which may be included in the inventive compositions include alkoxylated alkanolamides, preferably C_8-C_{24} alkyl di(C_2-C_3 alkanol amides), as represented by the following formula:

$$R_5\text{-}CO\text{-}NH\text{-}R_6\text{-}OH$$

wherein R_5 is a branched or straight chain C_8-C_{24} alkyl radical, preferably a C_{10}-C_{16} alkyl radical and more preferably a C_{12}-C_{14} alkyl radical, and R_6 is a C_1-C_4 alkyl radical, preferably an ethyl radical.

According to certain particularly preferred embodiments the detersive surfactant constituent necessarily comprises a nonionic surfactant based on a linear primary alcohol ethoxylate particularly wherein the alkyl portion is a C_8 to C_{16}, but particularly a C_9 to C_{11} alkyl group, and having an average of between about 6 to about 8 moles of ethoxylation.

The detersive surfactant constituent according to the invention desirably includes at least one anionic surfactant and/or anionic soap surfactant in conjunction with at least one nonionic surfactant, particularly a nonionic surfactant derived from alcohol alkoxylates.

The detersive surfactant constituent of the present invention comprises from about 0.1 to about 30 wt%, preferably from about 1 to about 20 wt%, and more preferably from about 2 to about 10 wt% of the dilutable hard surface cleaning composition of which they form a part.

The dilutable hard surface cleaning compositions of the invention necessarily include at least one thickener constituent. Thickeners useful in the present invention to achieve this viscosity are selected from the group consisting of polysaccharide polymers selected from cellulose, alkyl celluloses, alkoxy celluloses, hydroxy alkyl celluloses, alkyl hydroxy alkyl celluloses, carboxy alkyl celluloses, carboxy alkyl hydroxy alkyl celluloses, naturally occurring polysaccharide polymers such as xanthan gum, guar gum, locust bean gum, tragacanth gum, or derivatives thereof, polycarboxylate polymers, polyacrylamides, clays, and mixtures thereof.

Examples of the cellulose derivatives include methyl cellulose ethyl cellulose, hydroxymethyl cellulose hydroxy ethyl cellulose, hydroxy propyl cellulose, carboxy methyl cellulose, carboxy methyl hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxy propyl methyl cellulose, ethylhydroxymethyl cellulose and ethyl hydroxy ethyl cellulose.

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

The polycarboxylate polymer can be a non-associative thickener or stabilizer, such as a homopolymer or a copolymer of an olefinically unsaturated carboxylic acid or anhydride monomers containing at least one activated carbon to carbon olefinic double bond and at least one carboxyl group or an alkali soluble acrylic emulsion, or an associative thickener or stabilizer, such as a hydrophobically modified alkali soluble acrylic emulsion or a hydrophobically modified nonionic polyol polymer, i.e., a hydrophobically modified urethane polymer, or combinations thereof. The copolymers are preferably of a polycarboxylic acid monomer and a hydrophobic monomer. The preferred carboxylic acid is acrylic acid. The homopolymers and copolymers preferably are crosslinked.

Homopolymers of polyacrylic acid are described, for example, in U.S. Pat. No. 2,798,053. Examples of homopolymers which are useful include Carbopol® 934, 940, 941, Ultrez 10, ETD 2050, and 974P polymers, which are available from Noveon. Such polymers are homopolymers of unsaturated, polymerizable carboxylic monomers such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, maleic anhydride, and the like.

Hydrophobically modified polyacrylic acid polymers are described, for example, in U.S. Pat. Nos. 3,915,921, 4,421,902, 4,509,949, 4,923,940, 4,996,274, 5,004,598, and 5,349,030. These polymers have a large water-loving hydrophilic portion (the polyacrylic acid portion) and a smaller oil-loving hydrophobic portion (which can be derived from a long carbon chain acrylate ester). Representative higher alkyl acrylic esters are decycl acrylate, lauryl acrylate, stearyl acrylate, behenyl acrylate and melissyl acrylate, and the corresponding methacrylates. It should be understood that more than one carboxylic monomer and more than one acrylate ester or vinyl ester or ether or styrenic can be used in the monomer charge. The polymers can be dispersed in water and neutralized with base to thicken the aqueous composition, form a gel, or emulsify or suspend a deliverable. Useful polymers are sold as Carbopol® 1342 and 1382 and Pemulen® TR-1, TR-2, 1621, and 1622, all available from Noveon. The carboxyl containing polymers are prepared from monomers containing at least one activated vinyl group and a carboxyl group, and would include copolymers of polymerizable carboxylic monomers with acrylate esters, acrylamides, alkylated acrylamides, olefins, vinyl esters, vinyl ethers, or styrenics. The carboxyl containing polymers have molecular weights greater than about 500 to as high as several billion, or more, usually greater than about 10,000 to 900,000 or more.

Also useful are interpolymers of hydrophobically modified monomers and steric stabilizing polymeric surface active agents having at least one hydrophilic moiety and at least one hydrophobic moiety or a linear block or random comb configuration or mixtures thereof. Examples of steric stabilizers which can be used are Hypermer®, which is a poly(12-hydroxystearic acid) polymer, available from Imperial Chemical Industries Inc. and Pecosil®, which is a methyl-3-polyethoxypropyl siloxane-ω-phosphate polymer, available from Phoenix Chemical, Somerville, N.J. These are taught by U.S. Pat. Nos. 4,203,877 and 5,349,030, the disclosures of which are incorporated herein by reference.

The polymers can be crosslinked in a manner known in the art by including, in the monomer charge, a suitable crosslinker in amount of about 0.1 to 4%, preferably 0.2 to 1% by weight based on the combined weight of the carboxylic monomer and the comonomer(s). The crosslinker is selected from polymerizable monomers which contain a polymerizable vinyl group and at least one other polymerizable group. Polymerization of the carboxyl-containing monomers is usually carried out in a catalyzed, free radical polymerization process, usually in inert diluents, as is known in the art.

Other polycarboxylic acid polymer compositions which can be employed include, for example, crosslinked copolymers of acrylates, (meth)acrylic acid, maleic anhydride, and various combinations thereof. Commercial polymers are available from Rheox Inc., Highstown, N.J. (such as Rheolate® 5000 polymer), 3 V Sigma, Bergamo, Italy (such as Stabelyn® 30 polymer, which is an acrylic acid/vinyl ester copolymer, or Polygel® and Synthalen® polymers, which are crosslinked acrylic acid polymers and copolymers), Noveon (such as Carbopol 674 (lightly crosslinked polyacrylate polymer), Carbopol 676 (highly crosslinked polyacrylate polymer), Carbopol EP-1 thickener, which is a acrylic emulsion thickener), or Rohm and Haas (such as Acrysol® ICS-1 and Aculyn® 22 thickeners, which are hydrophobically modified alkali-soluble acrylic polymer emulsions and Aculyn® 44 thickener, which is a hydrophobically modified nonionic polyol). Preferred are the Carbopol® and Pemulen® polymers, generally. The choice of the specific polymer to be employed will depend upon the desired rheology of the composition, and the identity of other compositional ingredients.

Clay thickeners comprise, for example, colloid-forming clays, for example, such as smectite and/or attapulgite types. The clay materials can be described as expandable layered clays, i.e., aluminosilicates and magnesium silicates. The term "expandable" as used to describe the instant clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The expandable clays used herein are those materials classified geologically as smectites (or montmorillonite) and attapulgites (or polygorskites).

Smectites are three-layered clays. There are two distinct classes of smectite-type clays. In the first, aluminum oxide is present in the silicate crystal lattice; in the second class of smectites, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectites are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)(OH)_2$, for the aluminum and magnesium oxide type clays, respectively. It is to be recognized that the range of the water of hydration in the above formulas may vary with the processing to which the clay has been subjected.

Commercially available clays include, for example, montmorillonite, bentonite, volchonskoite, nontronite, beidellite, hectorite, saponite, sauconite and vermiculite. The clays herein are available under various trade names such as Gelwhite GP, Gelwhite H, Mineral Colloid BP, and Laponite from Southern Clay Products, Inc., Texas; and Van Gel O from R. T. Vanderbilt. Gelwhite H-NF has a typical chemical analysis of SiO_2 66.5%; Al_2O_3 14.7%; MgO 3.2%; Fe_2O_3 0.8%; CaO 2.2%; Na_2O 3.3%; K_2O 0.1%; TiO_2 0.2%. Gelwhite L-NF has a typical chemical analysis of SiO_2 66.5%; Al_2O_3 14.7%; MgO .3.2%; Fe_2O_3 0.8%; CaO 2.2%; Na_2O 3.3%; K_2O 0.1%; TiO_2 0.2%. Gelwhite GP has a typical chemical analysis of SiO_2 66.5%; Al_2O_3 14.7%; MgO 3.2%; Fe_2O_3 0.8%; CaO 2.2%; Na_2O 3.3%; K_2O 0.1%; TiO_2 0.2%. Mineral Colloid BP has a typical chemical analysis of SiO_2 62.9%; Al_2O3 17.1%; MgO 2.4%; Fe_2O_3 4.8%; CaO 0.7%; Na_2O 2.1%; K_2O 0.2%; TiO_2 0.1%.

A second type of expandable clay material useful in the instant invention is classified geologically as attapulgite (polygorskite). Attapulgites are magnesium-rich clays having principles of superposition of tetrahedral and octahedral unit cell elements different from the smectites. A typical attapulgite analyses yields 55.02% SiO_2; 10.24% Al_2O_3; 3.53% Fe_2O_3; 10.45% MgO; 0.47% K_2O; 9.73% H_2O removed at 150°C.; 10.13% H_2O removed at higher temperatures. Like the smectites, attapulgite clays are commercially available. For example, such clays are marketed under the tradename Attagel, i.e. Attagel 40, Attagel 50 and Attagel 150 from Engelhard Minerals & Chemicals Corporation.

The preferred clay thickeners comprise the inorganic, colloid forming clays of smectite and/or attapulgite types. Preferred clays include products from Vanderbilt Chemical Company such as VanGel O.

The amount of thickener used in the present invention can range from about 0.1 to 10 wt%. The ultimate viscosity of the inventive compositions is largely due to the selection of the thickening constituent. The inventive compositions exhibit a viscosity greater than that of water, and desirably exhibit a viscosity of at least about 50 cps. More preferably the inventive compositions exhibit a viscosity of from about 50 cps to about 2000 cps, but most preferably exhibit a viscosity of between about 300 cps and 700 cps, and most particularly of about 500 cps. The inventors have found that the inventive compositions need be maintained in a thickened state in order to provide sufficient suspension of the at least one opacifying agent present.

The dilutable hard surface cleaning compositions of the invention necessarily include at least one opacifying constituent. Such materials are typically either polymers, oleochemical fatty dispersions or minerals such as mica. Exemplary useful and preferred materials include alkylene glycol mono- and di-stearates particularly C_1-C_6 glycol mono- and di-stearates, especially ethylene glycol monostearate, ethylene glycol distearate and propylene glycol monostearate, presently commercially available as Sipoest® materials, glycerol mono- and di-stearate. Further useful materials which may be used to impart an opacifying and pearlescent appearance to the inventive compositions are those presently commercially available as Euperlan® materials. Such include Euperlan® PK 771 and Euperlan® PK 810 both described to be a mixture of sodium laureth sulfate, glycol distearate, cocoamine monoethanolamine and laureth-10; Euperlan® PK 900 described to be a mixture of PEG-3 distearate and sodium laureth sulfate; Euperlan® PK 1200 described to be a mixture of coco-glucoside, glycol distearate and glycerin; Euperlan® PK 3000 and Euperlan® PK 4000 both described to be a mixture of glycol distearate, laureth-4 and cocoamidopropyl betaine. These Euperlan® materials are preferred as they provide not only an opacifying effect but also provide for a pearlescent appearance to the final product which is highly desirable. The specific opacifying constituent should be selected to be compatible with the detersive surfactant constituent. Typically the amount of the opacifying constituent used in the present invention can range from about 0.1 to 10 wt%.

While optional, in preferred embodiments the present inventive compositions comprise one or more water soluble or water dispersible organic solvents. Exemplarly useful water soluble organic solvents include short chain C_1-C_6 alcohols, glycol ethers, and mixtures thereof. Such water soluble organic solvents provide effective solubilization of many types of greases and fats which may be encountered in soils on hard surfaces. Of course two or more organic solvents may be used as the organic solvent constituent according to the invention. Examples of short chain alcohols include ethanol, propanol, and isopropanol. Examples of such useful glycol ethers include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol n-propyl ether, diethylene glycol methyl ether, ethylene glycol butyl ether, diethylene glycol methyl ether, and mixtures thereof. The glycol ethers are preferred, and particularly preferred are compositions wherein the organic solvent constituent is solely one or more glycol ethers. The water soluble organic solvent constituent may be present in the inventive compositions in amounts of from about 0.1 to about 20 wt%, preferably in amounts of from about 0.5 to about 10 wt%.

The compositions of the present invention can also optionally comprise one or more further constituents which are directed to improving the aesthetic or functional features of the inventive compositions. By way of non-limiting example such further constituents include one or more coloring agents, fragrances and fragrance solubilizers, other surfactants, pH adjusting agents and pH buffers including organic and inorganic salts, optical brighteners, hydrotropes, antifoaming agents, anti-oxidants, AND preservatives. When one or more of the optional constituents is added, i.e., fragrance and/or coloring agents, the esthetic and consumer appeal of the product is often favorably improved. The use and selection of these optional constituents is well known to those of ordinary skill in the art. When present, the one or more optional constituents present in the inventive compositions do not exceed about 10%wt., preferably do not exceed 5%wt.

The compositions according to the invention optionally but desirably include an amount of a pH adjusting agent or pH buffer composition. Such compositions include many which are known to the art and which are conventionally used. By way of non-limiting example pH adjusting agents include phosphorus containing compounds, monovalent and polyvalent salts such as of silicates, carbonates, and borates, certain acids and bases, tartrates and certain acetates. Further exemplary pH adjusting agents include mineral acids, basic compositions, and organic acids, which are typically required in only minor amounts. By way of further non-limiting example pH buffering compositions include the alkali metal phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, bicarbonates, polycarbonateshydroxides, and mixtures of the same. Certain salts, such as the alkaline earth phosphates, carbonates, hydroxides, can also function as buffers. It may also be suitable to use as buffers such materials as aluminosilicates (zeolites), borates, aluminates and certain organic materials such as gluconates, succinates, maleates, and their alkali metal salts. Desirably the compositions according to the invention include an effective amount of an organic acid and/or an inorganic salt form thereof which may be used to adjust and maintain the pH of the compositions of the invention to the desired pH range. Particularly useful is are carbonates and bicarbonates and particularly and metal salts thereof such as sodium carbonate, sodium bicarbonate which are widely available and which are effective in providing pH adjustment and buffering effects.

Preferably the pH of the inventive compositions are alkaline, desirably in excess of 7, more desirably the pH of the compositions are 8 or greater, still more preferably are about 9 or greater.

Further optional, but advantageously included constituents are one or more coloring agents which find use in modifying the appearance of the compositions and enhance their appearance from the perspective of a consumer or other end user. Known coloring agents may be incorporated in the compositions in any effective amount to improve or impart to compositions a desired appearance or color. Such a coloring agent or coloring agents may be added in a conventional fashion, i.e., admixing to a composition or blending with other constituents used to form a composition. Such coloring agent may be based on naturally occurring coloring agents, or may be based on one or more synthetically produced materials including synthetic dyes and pigments particularly those recited in the Color Index.

Further optional, but desirable constituent include fragrances, natural or synthetically produced. Such fragrances may be added in any conventional manner, admixing to a composition or blending with other constituents used to form a composition, in amounts which are found to be useful to enhance or impart the desired scent characteristic to the composition, and/or to cleaning compositions formed therefrom. Exemplary useful fragrances include those based on digeranyl succinate, dineryl succinate, geranyl neryl succinate, geranyl phenylacetate, neryl phenylacetate, geranyl laurate, neryl laurate, di(b-citronellyl) maleate, dinonadol maleate, diphenoxyanol maleate, di(3,7-dimethyl-1-octanyl) succinate, di(cyclohexylethyl) maleate, diflralyl succinate, di(phenylethyl) adipate, 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene, ionone methyl, ionone gamma methyl, methyl cedrylone, methyl dihydrojasmonate, methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone, 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin, 4-acetyl-6-tert-butyl-1- ,1-dimethyl indane, para-hydroxy-phenyl-butanone, benzophenone, methyl beta-naphthyl ketone, 6-acetyl-1,1,2,3,3,5hexamethyl indane, 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane, 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde, 7-hydroxy-3,7-dimethyl ocatanal, 10-undecen-1-al, isohexenyl cyclohexyl carboxaldehyde, formyl tricyclodecane, condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol, 2-methyl-3-(para-tert-butylphenyl)-propionaldehyd- e, ethyl vanillin, heliotropin, hexyl cinnamic aldehyde, amyl cinnamic aldehyde, 2-methyl-2-

(para-iso-propylphenyl)propionaldehyde, coumarin, decalactone gamma, cyclopentadecanolide, 16-hydroxy-9-hexadecenoic acid lactone, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-b- enzopyrane, beta-naphthol methyl ether, ambroxane, dodecahydro-3a,6,6,9a-t- etramethyinaphtho[2,1b]furan, cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-- 3-methylpentan-2-ol, 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-bute- n-1-ol, caryophyllene alcohol, tricyclodecenyl propionate, tricyclodecenyl acetate, benzyl salicylate, cedryl acetate, para-(tert-butyl) cyclohexyl acetate, essential oils, resinoids, and resins from a variety of sources including but not limited to orange oil, lemon oil, patchouli, Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander, lavandin, and lavender, phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)cyclohexanol acetate, benzyl acetate, orange terpenes, eugenol, diethylphthalate, and combinations thereof. The fragrance constituent may also be based on one or more essential oils including one or more selected from the group consisting of: Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Peru), Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB, Borneol 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 vanilin, 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-methhyl 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), Wintergreen. Other fragrance compounds not particularly eludicated here but which are found useful in providing a desirable fragrancing effect may also be included in the inventive compositions. When present, the fragrance constituent may be included in any effective amount, and of course mixtures of two or more fragrance compounds may be used to provide the fragrance constituent. Desirably the fragrance constituent in present in an amount not exceeding 5%wt. of the inventive composition of which it forms a part, and more preferably is present in an amount not exceeding 1%wt.

In compositions which include a fragrance, it is frequently desirable to include a fragrance solubilizer which assists in the dispersion, solution or mixing of the fragrance constituent in an aqueous base. These include known art compounds, including condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri-C_{10}-C_{20} alkanoic acid known to be useful as nonionic surfactants. Further examples of such suitable surfactants include water soluble nonionic surfactants of which many are commercially known and by way of non-limiting example include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates on primary alkanols, and condensates of ethylene oxide with sorbitan fatty acid esters.. This fragrance solubilizer component is added in minor amounts, particularly amount which are found effective in aiding in the solubilization of the fragrance component, but not in any significantly greater proportion, such that it would be considered as a surfactant constituent. Such minor amounts of fragrance solubilizer recited herein is generally up to about 0.2% by weight of the fragrance constituent in the inventive compositions but is more generally an amount of about 0.1% by weight and less, and preferably is present in amounts of about 0.05% by weight and less.

The inventive compositions optionally but desirably comprise a preservative constituent. Since a significant portion of the inventive compositions comprise water, it is preferably that the preservative be water soluble. Desirably, the selected water soluble preservatives are those which exhibit stability and efficacy in the aqueous compositions according to the invention at neutral, but preferably at alkaline pH's especially in the preferred pH ranges noted above. Such water soluble preservatives include compositions which include parabens, including methyl parabens and ethyl parabens, glutaraldehyde, formaldehyde, 2-bromo-2-nitropropoane-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, DE), SUTTOCIDE® A which is presently commercially available from Sutton Laboratories (Chatam, NJ) as well as TEXTAMER® 38AD which is presently commercially available from Calgon Corp. (Pittsburgh, PA). Particularly preferred for use in the inventive composition is a preparation containing 1,3-dihydroxymethyl-5,5-dimethylhydantoin and 3-iodo-2-propynyl butyl carbamate which is presently commercially available as Dantogard® Plus Liquid from Lonza Corp. (Fairlawn, NJ.)

When included, the preservative constituent is present in the dilutable hard surface cleaning compositions of the present invention in any amount which is effective in retarding or eliminating the growth of undesired microorganisms in the inventive compositions particularly upon standing. The preservative constituent need be present in only minor amounts, and is advantageously present in amounts for from about 0.001%wt. to about 0.5%wt., more preferably is present in an amount of from about 0.01 – 0.1%wt. In preferred embodiments of the invention the preservative constituent is necessarily present.

As the concentrate compositions are aqueous, water forms a major constituent. Water is added in order to provide 100 wt% of the concentrate composition. The water may be tap water, but is preferably distilled and/or deionized water. If the water is tap water, it is preferably appropriately filtered in order to remove any undesirable impurities such as organics or inorganics, especially mineral salts which are present in hard water which may thus interfere with the operation of the other constituents of the invention, as well as any other optional components of the liquid concentrates according to the invention.

The compositions according to the invention are useful in the cleaning of surfaces, especially hard surfaces in need of such treatment. In accordance with the present inventive process, cleaning of such surfaces comprises the step of applying a stain releasing effective amount of a composition as taught herein to such a stained surface. Afterwards, the compositions are optionally but desirably wiped, scrubbed or otherwise physically contacted with the hard surface, and further optionally, may be subsequently rinsed from such a cleaned hard surface.

While the inventive compositions described herein may be provided as a ready to use product which may be directly applied to a hard surface, it is desirably provided in a concentrated form intended to be diluted in water to form a cleaning composition therefrom. What is to be understood by the term "concentrate" and "concentrate composition" in this specification and claims is the pre-consumer dilution and composition of the cleaning composition which is the essentially the form of the product prepared for sale to the consumer or other end user with required product shelf life. Such a consumer or other end user would then normally be expected to dilute the same with water to form a cleaning composition. It is to be understood however that nothing in this invention would bar its use as cleaning composition without any further dilution and it may be used in the concentrations in which it was prepared for sale. Similarly, what is to be understood by the term "cleaning compositions" are the water diluted compositions which are expected to be prepared by the consumer or other end user by mixing a measured amount of the "concentrate" with water in order to form an appropriately diluted cleaning composition which is suitable for use in cleaning applications, especially in the cleaning of hard surfaces.

It is also to be understood, that proportions of one or more constituents have been and generally are referred to as percent by weight or as parts by weight based on a measure of 100% by weight, unless otherwise indicated.

As generally denoted above, the formulations according to the invention include both cleaning compositions and concentrates as outlined above which differ only in the relative proportion of water to that of the other constituents forming such formulations.

While the concentrated form of the cleaning compositions find use in their original form, they are more frequently used in the formation of a cleaning composition therefrom. Such may be easily prepared by diluting measured amounts of the concentrate compositions in water by the consumer or other end user in certain weight ratios of concentrate:water, and optionally, agitating the same to ensure even distribution of the concentrate in the water. As noted, the concentrate may be used without dilution, i.e., in concentrate:water concentrations of 1:0, to extremely dilute dilutions such as 1:200. Desirably, the concentrate is diluted in the range of 1:0.1-1:100, preferably in the range of 1:10-1:50. The actual dilution selected is in part determinable by the degree and amount of dirt and grime to be removed from a surface(s), the amount of mechanical force imparted to remove the same, as well as the observed efficacy of a particular dilution. Generally better results and faster removal is to be expected at lower relative dilutions of the concentrate in water.

The following examples illustrate an exemplary formulation of the invention and particular preferred embodiments of the inventive compositions. The terms "parts by weight" or "percentage weight" as well as "%wt." are used interchangeably in the specification and in the following Examples wherein the weight percentages of each of the individual constituents are indicated in weight percent based on the total weight of the composition, unless indicated otherwise.

Example

Preparation of Example Formulations:

Exemplary formulations illustrating certain preferred embodiments of the inventive compositions and described in more detail in Table 1 below were formulated generally in accordance with the following protocol. These constituents were used "as is" from their respective supplier.

Into a suitably sized vessel, a measured amount of water was provided after which the constituents were added in no specific or uniform sequence, which indicated that the order of addition of the constituents was not critical. All of the constituents were supplied at room temperature, and any remaining amount of water was added thereafter. Mixing of the constituents was achieved by the use of a mechanical stirrer with a small diameter propeller at the end of its rotating shaft. Mixing, which generally lasted from 5 minutes to 120 minutes was maintained until the particular exemplary formulation appeared to be homogeneous. The exemplary compositions were readily pourable, and retained well mixed characteristics (i.e., stable mixtures) upon standing for extend periods. The compositions of the example formulations are listed on Table 1.

Table 1	Ex.1
Unitol L80 (100%)	0.58
sulfonic acid (96%)	3.171
Surflex LSC 401 (40%)	0.50
Dowanol DB (95%+)	1.23
sodium carbonate (100%)	0.127
sodium bicarbonate (100%)	0.50
sodium hydroxide (50%)	0.90
Cellosize QP 100 MH (100%)	0.50
Euperlan PK 810	0.27
Coryna 116 XC	0.09
Solantine Turquoise G Powder	0.001
Tartrazine	0.00017
fragrance	0.350
water	q.s., to 100

As is indicated, to all of the formulations of Table 1 was added sufficient deionized water in "quantum sufficient" to provide 100 parts by weight of a particular formulation.

The identity of the constituents of Table 1 above are described in more detail on Table 2, below, including the "actives" percentage of each were a constituent was not provided by its supplier as 100%wt. "actives".

Table 2	
Unitol L80 (100%)	lauryl alcohol ethoxylate, avg. 8 ethoxy groups (100%wt.)
sulfonic acid (96%)	sulfonic acid (96%wt.)
Surflex LSC 401 (40%)	anionic soap based on coconut oil (40%wt.)
Dowanol DB (95%+)	diethylene glycol monobutyl ether (95+%wt.)
sodium carbonate (100%)	sodium carbonate, anhydrous (100%wt)
sodium bicarbonate (100%)	sodium bicarbonate, anhydrous (100%wt.)
sodium hydroxide (50%)	sodium hydroxide, aqueous dilution (50%wt.)
Cellosize QP 100 MH (100%)	hydroxyethyl cellulose (100%wt.)
Euperlan PK 810	mixture of glycol distearate, sodium laureth sulfate, cocamide monoethanolamine and laureth-10
Coryna 116 XC	preservative constituent
Solantine Turquoise G Powder	Color Index 74180
Tartrazine	Color Index 19140
fragrance	proprietary composition
water	soft water

The composition according to Example 1 provided good cleaning of hard surfaces when used without further dilution, as well as when diluted in further ratios of composition:water of 1:20 and 1:50 .

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.

Claims:

1. Aqueous, dilutable hard surface cleaning compositions which comprise:
one or more detersive surfactants, preferably containing one or more anionic surfactants including anionic soaps optionally but preferably in conjunction with one or more nonionic surfactants;
one or more thickener constituents;
one or more opacifying constituents;
optionally but desirably one or more organic solvents;
optionally one or more constituents for improving the aesthetic or functional features of the inventive compositions;
and, water.

2. The composition according to claim 1 which comprises an anionic soap.

3. The composition according to claim 1 which comprises an nonionic surfactant.

4. The composition according to claim 4 which comprises a linear alcohol ethoxylated surfactant.

5. The composition according to any preceding claim which comprises a sulfonate based anionic surfactant.

6. The composition according to any preceding claim which comprises an opacifiving constituent selected from one or more of: mixtures of sodium laureth sulfate, glycol distearate, cocoamine monoethanolamine and laureth-10; mixtures of PEG-3 distearate and sodium laureth sulfate; mixtures of coco-glucoside, glycol distearate and glycerin; and, mixtures of glycol distearate, laureth-4 and cocoamidopropyl betaine.

7. The composition according to any preceding claim wherein the composition exhibits a viscosity of at least about 50 cps.

8. The composition according to claim 7 wherein the composition exhibits a viscosity from about 50 cps to about 2000 cps.

9. A composition of claim 1 substantially as described with reference to the Example.

INTERNATIONAL SEARCH REPORT

In nal Application No
PCT/GB2004/004798

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D10/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 246 613 A (GILBERT ET AL) 21 September 1993 (1993-09-21) column 2, line 65 - column 3, line 38; claims 1,8; examples III,IV,VI	1-5,7-9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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