

GERMICIDAL DISHWASHING DETERGENT COMPOSITIONS

5 The present invention relates to detergent compositions, particularly liquid or gel dishwashing detergent compositions which provide good deterative and physical characteristics, and further provide germicidal activity.

Background of the Invention

10 The present invention relates to foaming, germicidal liquid or gel dishwashing detergent compositions of the type which are a general usage in many commercial and domestic environments. Such compositions are particularly suitable for use in hand washing of soiled dishes, cooking utensils, as well as in certain general duty cleaning applications; and their use is also known as hard surface cleaners, glass cleaners and in the hand washing of textiles and garments. While many dishwashing detergent formulations are presently commercially available, these generally include a large proportion of one or more anionic detergent agents which are recognized as providing good deterative action, and which also provide good foaming characteristics. Such foaming characteristics are highly desirable as consumer perceptions frequently associate superior deterative action with compositions which build and retain foam during a cleaning operation.

20 Also generally known to the art are cleaning compositions and compounds which feature germicidal activity, and thus provide a disinfecting or sanitizing effect. These include cationic quaternary ammonium compounds. However, being cationic in such compounds would be expected to be incompatible in formulations where an anionic surfactant is present as these compounds would be expected to form a complex which would either detract from the foaming characteristic imparted by the anionic surfactant, or destroy the germicidal activity of the cationic quaternary ammonium compound, but most likely both of these effects. Due to this characteristic, the use of such quaternary ammonium compounds, is generally limited to cleaning compositions in applications other than dishwashing detergent compositions, viz., where good foam buildup and retention are not highly desirable properties for such a cleaning composition. Certain compositions to certain detergent compositions including a cationic quaternary ammonium compound and anionic surfactants are known, such as in U.S. 4,576,729 to Paszek, U.S. 5,378,409 to Ofusu-Asante et al., and U.S. 4,264,457 to Beeks. Nonetheless, there remains a continuing need in the art for improvements to dishwashing detergent compositions which provide good deterative and foaming characteristics, and an efficacious germicidal effect.

30 Therefore, it is among the objects of the invention to provide improved dishwashing detergent compositions in both concentrated and diluted (aqueous) form wherein said dishwashing detergent is characterized by good foaming, satisfactory deterative properties, and germicidal

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activity. Such compositions are particularly useful in hard surface cleaning applications such as in the cleaning of soiled dishes, utensils, hard surfaces, and the like. The compositions according to the invention also find use in certain textile and garment cleaning applications.

Summary of the Invention

5 The present invention provides a germicidal light-duty aqueous dishwashing detergent composition in either a gel, liquid, or semi-liquid form, which comprise, but desirably consist essentially of, in parts by weight of the following constituents:

- A) 0.5 - 10 parts quarternary ammonium germicidal compound;
B) 0.5 - 40 parts anionic alkyl ether carboxylate surfactant of formula:



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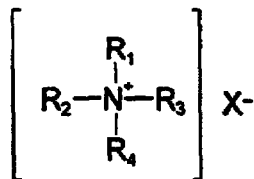
where x is 4 to 11, R is a C₉₋₁₁ alkyl, M is counterion,

- C) 10 - 40 parts nonionic surfactant;
D) 0.01-30 parts of a suds stabilizing or suds boosting agent;
E) water.

15 The compositions may further include 0-40 parts by weight of one or more conventionally known and used additives, including but not limited to further surfactants particularly those which are effective to add further deterative effects and/or further suds boosting characteristics to the composition, viscosity modifying agents, foam stabilizing agents, sequestering agents, coloring agents, pH modifying agent (buffers), fragrances, fillers, optical brighteners, as well as one or more
20 solubilizing/compatibilizing agents;

The aqueous dishwashing detergent compositions of the invention feature a pH in the range of 5 - 10, more preferably a pH in the range of 6-8, and most preferably a pH of about 7.

Component A Useful germicidal agents in the compositions of the present invention include certain quarternary ammonium compounds and their salts which are also known as cationic
25 surfactants. Examples of preferred cationic surfactant compositions useful in the practice of the instant invention include quarternary ammonium compounds and salts thereof may be characterized by the general structural formula:



30 where at least one R₁, R₂, R₃ and R₄ is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular



weight of at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substitued long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, aryl alkyl, etc. The remaining radicals on the nitrogen atoms other than the hydrophobic radicals are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon atoms.

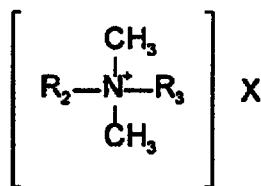
5 The radicals R₁, R₂, R₃ and R₄ may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ether linkages. The radical X may be any salt-forming anionic radical.

Exemplary quarternary 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 quarternary ammonium salts include those in which the molecule contains either amide or ether linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quarternary ammonium compounds which are useful as

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15 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.

20 Preferred quarternary ammonium compounds which act as germicides and which are be found useful in the practice of the present invention include those which have the structural formula:



25 wherein R₂ and R₃ are the same or different C₈-C₁₂alkyl groups, or R₂ is C₁₂-₁₆alkyl, C₈-₁₈alkylethoxy, C₈-₁₈alkylphenoethoxy group and R₃ is a benzyl group, and X may be any salt-forming anionic radical, but is preferably a halide, such as a chloride, bromide or iodide, or is a methosulfate radical. The alkyl groups recited in R₂ and R₃ may be straight chained or branched, but are preferably substantially linear.

30 Various such useful quarternary germicides are commercially available under the tradenames BARDAC, BARQUAT and HYAMINE from Lonza, Inc., Fairlawn, NJ (USA) as well as the tradename BTC from the Stepan Chemical Co., Chicago, IL (USA).

The quarternary ammonium germicidal compounds are desirably present in amounts of from 0.5 to 10 parts by weight, more desirably are present in amounts of from 1 to 8 parts by weight. In an aqueous cleaning composition formed by the addition of measured amounts of the detergent composition described above to a larger volume of water, the cationic surfactant is preferably present in a sufficient to provide at least 50 parts per million ("ppm") in such an aqueous cleaning composition.

Constituent B The anionic alkyl ether carboxylates useful in the practice of the instant invention include those having the general structural formula:



wherein R is a straight or branched, long chain, alkyl group containing from 8 to 18 carbon atoms, n is an integer from 2 to 4, m is an integer from 1 to 100, R₁ is CH₂, CH₂CH₂, or CH₂CH₂CH₂, and M is a counterion such as an organic or inorganic cation including singly valent cations as well as polyvalent cations. Exemplary cations include cations of an alkali metal including sodium or lithium, or organic cations such as ammonium, diethylammonium, or triethylammonium cations, as well as other cations not particularly recited here. Such anionic alkyl ether carboxylates are known to be useful as surfactant compositions. In the compositions according to the instant invention, preferably n is 2, m is 4 - 11, R is C₉-C₁₆, R₁ is CH₂ and M is the cation of an alkali metal, preferably sodium. Such surfactants are presently commercially available under the trade name Sandopan® (Clariant Chemical Corp., Charlotte NC), Neodox®25-6 and Neodox®23-4 (Shell Chemical Co., Houston, TX), as well as Surfina® WLG (Finetex Inc., Elmwood Park, NJ).

While the anionic alkyl ether carboxylate surfactant may be provided in its free acid form, it is most preferable to provide this surfactant in its salt form as it has been observed that the surfactant in its non-salt form features poor foaming action at reduced pH's. When in free acid form, the anionic alkyl ether carboxylate surfactant is preferably neutralized for example by adding NaOH, KOH, or other base to the composition of the invention.

These anionic alkyl ether carboxylates are present in amount of from 0.5 to 40 parts by weight, but are preferably present in an amount of 2 to 10 parts by weight. It is further to be understood that mixtures of two or more different anionic alkyl ether carboxylates may also be used as Constituent B.

In particular preferred embodiments, the anionic alkyl ether carboxylate component is present in particular proportions relative to the cationic surfactant composition according to Constituent A. Such proportions are in the range of cationic surfactant composition: alkyl ether carboxylate component of 1:1-4 preferably 1:1.5-3.5. It has been found that with such weight

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ratios, it has been observed that good foaming is observed while maintaining satisfactory antimicrobial activity. Values outside of these recited proportions may be used, however it has been observed by the inventor that ratios lower than those described above exhibit poorer foaming, while ratios higher than those described above have good foaming, but generally also have a reduced antimicrobial activity.

Constituent C Suitable nonionic surfactants which can be used in the instant invention include water soluble nonionic surfactants, many which are well known and conventionally used in the art. Nonlimiting examples of nonionic surfactants which may be employed in the composition include those which are water soluble or water miscible and include one or more of the following: amine oxides, block copolymers, alkoxylated alkanolamides, ethoxylated alcohols, and ethoxylated alkyl phenols, and the like, with a more complete listing of commercially available nonionic surfactants found under these class listings in the "Chemical Classification" section of McCutcheon's *Emulsifier & Detergents North American Edition*, 1991.

Useful water soluble nonionic surfactants in the compositions according to the present invention include commercially well known surfactant compositions, including the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates of primary alkanols. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with a hydrophilic group containing an ethylene oxide and/or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic surfactant.

A preferred group of the foregoing nonionic surfactants are certain ethoxylates presently commercially available under the trade name NEODOL (Shell Chemical Co., Houston, TX(USA)), which are ethoxylated higher aliphatic, primary alcohols. Such ethoxylates have an HLB (hydrophobic to lipophilic balance) value of about 8 to 15 and give good oil/water emulsification, whereas ethoxylates with HLB values below 8 contain less than 5 ethylene oxide groups and tend to be poor emulsifiers and poor detergents. Additional satisfactory nonionic surfactant compositions 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 (Union Carbide Co., Danbury, CT(USA)). Other suitable nonionic surfactant compositions include the polyethylene oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms in a straight-

or branched chain alkyl group with about 5 to 30 moles of ethylene oxide, including those which are presently commercially available under the trade name of IGEPAL (Rhône-Poulenc, Princeton NJ(USA)). Further useful nonionic surfactants include the water-soluble condensation products of a C₈-C₂₀ alkanol with a mixture of ethylene oxide and propylene oxide wherein the weight ratio of ethylene oxide to propylene oxide is from 2.5:1 to 4:1, preferably 2.89:1 to 3.3:1, with the total of the ethylene oxide; and propylene oxide (including the terminal ethanol or propanol group) being from 60-85%, preferably 70 to 80%, by weight. Such include those commercially available under the trade name of PLURAFAC (BASF Corp., Hackettstown, NJ (USA)). Still further useful water-soluble nonionic surfactants include condensation products of a C₈-C₂₀ alkanols with a mixture of ethylene oxide and/or propylene oxide. Such are commercially available under the tradename POLYTERGENT (Olin Chemical Co., Stamford CT(USA)). Further suitable water-soluble nonionic surfactants which are somewhat less preferred but which are nonetheless useful are those which are marketed under the trade name PLURONICS (BASF Corp., Hackettstown, NJ (USA)). These are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Further useful nonionic surfactants include Alkylmonoglycosides and alkylpolyglycosides which are alkaline and electrolyte stable. Such 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 alkoxyated glycosides may be used. An exemplary useful polyglycoside is one according to the formula:



where Z is derived from glucose, R 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, which contain from about 8 to about 18 carbon atoms, n is 2 or 3, r is an integer from 0 to 10, but is preferably 0, 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 C₈-C₁₅ alkyl group, and have an average of from about 1 to about 5 glucose units per fatty alkylpolyglucoside molecule. More preferably, the nonionic fatty alkylpolyglucosides which contain straight chain or branched C₈-C₁₅ alkyl group, and have an average of from about 1 to about 2 glucose units per fatty alkylpolyglucoside molecule.

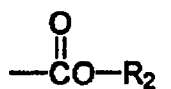
A further exemplary group of alkyl glycoside surfactants suitable for use in the practice of this invention may be represented by formula I below:

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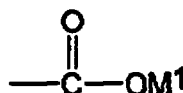


wherein: R is a monovalent organic radical containing from about 6 to about 30, preferably from about 8 to about 18 carbon atoms; R₁ is a divalent hydrocarbon radical containing from about 2 to about 4 carbon atoms; O is an oxygen atom;

- 5 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 O₂M¹,



- 10 O(CH₂), CO₂M¹, OSO₃M¹, or O(CH₂)SO₃M¹; R₂ is (CH₂)CO₂M¹ or CH=CHCO₂M¹; (with the proviso that Z can be O₂M¹ only if Z is in place of a primary hydroxyl group in which the primary hydroxyl-bearing carbon atom, —CH₂OH, is oxidized to form a



- 15 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, M¹ 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.

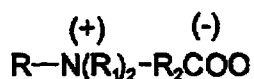
- 20 As defined in Formula I above, R is generally the residue of a fatty alcohol having from about 8 to 30 and preferably 8 to 18 carbon atoms. Examples of such alkylglycosides as described above include, for example, APGTM 325 CS Glycoside® which is described as being a 50% C₉-C₁₁ alkyl polyglycoside, also commonly referred to as D-glucopyranoside, (commercially available from Henkel Corp, Ambler PA) and GlucoponTM 625 CS which is described as being a 50% C₁₀-C₁₆ alkyl polyglycoside, also commonly referred to as a D-glucopyranoside, (available from
- 25 Henkel Corp., Ambler PA).

The nonionic surfactant can be present either singly, or a mixture of two or more nonionic surfactant compounds as defined above. The nonionic surfactant in the present inventive compositions may be present in amount of up to about 40 parts by weight, and more preferably is present in amounts of about 10 to 30 parts by weight, most preferably the nonionic surfactant is

present in amounts of 10 to 25 parts by weight. Desirably, at least 10% of the dishwashing detergent composition of the invention is an ethoxylated nonionic surfactant.

Constituent D The compositions of the invention include one or more agents which are useful in stabilizing and or boosting the suds formed by the compositions. These agents include known art surfactant compositions, including betaines, ethylene oxide condensates, fatty acid amides, and amine oxide semi-polar nonionic surfactants.

Of known art betaine surfactants, particularly useful betaine surfactants include those according to the general formula:



wherein R is a hydrophobic group selected from the group consisting of alkyl groups containing from about 10 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms, alkyl aryl and aryl alkyl groups containing a similar number of carbon atoms with a benzene ring being treated as equivalent to about 2 carbon atoms, and similar structures interrupted by amido or ether linkages; each R₁ is an alkyl group containing from 1 to about 3 carbon atoms; and R₂ is an alkylene group containing from 1 to about 6 carbon atoms.

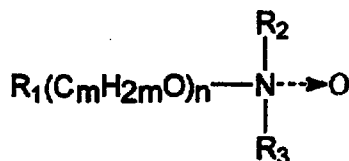
Examples of preferred betaines are dodecyl dimethyl betaine, cetyl dimethyl betaine, dodecyl amidopropyldimethyl betaine, tetradecyldimethyl betaine, tetradecylamidopropyldimethyl betaine, and dodecyldimethylammonium hexanoate.

Useful fatty acid amides which exhibit suds stabilizing effects include those which are known to the art. Particular exemplary fatty acid amide surfactants include ammonia, monoethanol, and diethanol amides of fatty acids having an acyl moiety which contains from about 8 to about 18 carbon atoms, and which may be represented in accordance with the formula:



where R₁ represents a saturated or unsaturated aliphatic hydrocarbon radical of from about 7 to 21 carbon atoms, but preferably from about 11 to 17 carbon atoms; R₂ represents a -CH₂- or -CH₂CH₂-, and m is an integer from 1 to 3, but is preferably 1. Preferably, R₁ is a saturated or unsaturated aliphatic hydrocarbon radical comprising from about 11 to 17 carbon atoms, and m is 1. Further examples of such compounds include mono-ethanol amine coconut fatty acid amide and diethanol amine dodecyl fatty acid amide. An exemplary useful fatty acid amide includes cocomonethanol amide or cocodiethanolamide, which are presently commercially available as MONAMID CMA or MONAMID MDNA (both from Mona Industries, Paterson NJ (USA)).

Known art amine oxide semi-polar nonionic surfactants which are useful as suds stabilizing agents may be included in the present inventive compositions. Non-limiting examples of useful amine oxide semi-polar nonionic surfactants include those according to the formula:



- 5 wherein R_1 is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical where the alkyl and alkoxy parts contain from about 8 to about 18 carbon atoms, R_2 and R_3 are independently selected from methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl, m is an integer from 2 to 4, and n is an integer from 0 to about 10. Preferably, the amine oxide semi-polar nonionic surfactants are those according to the formula immediately
- 10 preceeding wherein R_1 is an alkyl radical of from 12 to 16 carbon atoms, R_2 and R_3 are independently selected from methyl or ethyl, m is 2, and n is 0.

Examples of such useful amine oxide semi-polar nonionic surfactants include cetyl-, myristil- or lauryl- dimethyl amine oxide or mixtures thereof.

- 15 These compositions useful as suds stabilizers may be used individually, or in mixtures, and also, it is to be understood that certain non-ionic surfactants may also exhibit desirable suds stabilizing characteristics and may be used in the place of, or in addition to one or more of the suds stabilizers recited above. One example of such a non-ionic surfactant which exhibit suds stabilizing effects include ethoxylates of higher aliphatic, primary alcohols particularly alcohols containing about 9-15 carbon atoms.

- 20 The compositions which comprise Constituent D may be present in amounts of up to about 30 parts by weight, more preferably comprise from about 5 to about 25 parts by weight, and most desirably comprise from 10 to 20 parts by weight.

- Constituent E: The compositions according to the invention further include water which is added to the balance of the constituents present so to provide 100% by weight of the concentrate composition. The water may be tap water, but is preferably distilled and/or deionized water.
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- Optional Constituent (Constituent F): The compositions according to the invention may comprise one or more further optional constituents which may desirably included in certain formulations including, but not limited to; one or more further surface active agents, rheology modifying agents, neutralizing agents, chelating agents, sequestrants, coloring agents, solvents including alcohols such as ethanol and propylene glycol, hydrotropes such as sodium and potassium sulfonates, pH
- 30 modifying agents (buffers), fragrances, fillers, optical brighteners, as well as one or more

solubilizing/compatibilizing agents which may be desirable or necessary to improve the solubility/miscibility of one or more of the aforementioned constituents. Many of these are known to the art, and include those which are described in *McCutcheon's Functional Materials*, Vol.2, North American Edition, (1991).

5 Exemplary pH stabilizing agents, interchangeably referred to as pH buffers, include the alkali metal phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, hydroxides, and mixtures of the same. Certain salts, such as the alkaline earth phosphates, carbonates and hydroxides can also function as buffers. Also useful buffers include gluconates, succinates, maleates, and their alkali metal salts. Citric acid is
10 both useful and preferred as it is effective and is widely available at a low cost. The compositions of the instant invention exhibit a pH in the range of 5-10, more preferably a pH in the range 6-8, and and as noted above, most preferably a pH of about 7. The incorporation of an effective amount of such a pH stabilizing agent ensures the stability of the compositions, and when added to water will tend to adjust the pH of a cleaning composition to a more neutral pH.

15 The inventive compositions may include a detergency builder component, which may be of the organic or inorganic type. These may be used alone, in admixture with other water soluble inorganic builders, as well as with one or more organic alkaline sequestrant builder salt. Exemplary detergency builders include alkali metal carbonates, phosphates, polyphosphates and silicates. More specific examples include sodium tripolyphosphate, sodium carbonate, potassium carbonate,
20 sodium polyphosphate, potassium pyrophosphate, potassium tripolyphosphate, and sodium hexametaphosphate.

Exemplary organic alkaline sequestrant builder salts include alkali metal polycarboxylates including water-soluble citrates such as calcium, sodium and potassium citrate, calcium, sodium and potassium tartarate, calcium, sodium and potassium ethylenediaminetetraacetate, calcium,
25 sodium and potassium N-(2-hydroxyethyl)-ethylene diamine triacetates, calcium, sodium and potassium nitrilo triacetates, as well as calcium, sodium and potassium tartrate mono- and di-succinates. These salts may be used individually, in combination of two or more organic builder salts, as well as with one or more detergency builders. Especially preferred as the builder salt is ethylenediaminetetraacetic acid, and hydroxyethylethylenediaminetriacetic acid particularly the calcium and sodium salts thereof. Sodium gluconate, gluconic acid and salts thereof and sorbitol
30 may also be used as the sequestrant builder salt.

A further optional constituent includes one or more neutralizing agents, such as a base, i.e., KOH, NaOH, which may be added to the compositions according to the invention, especially where the anionic alkyl ether carboxylate is provided in a free acid form.

Further optional constituents which may be included include fragrances, which may be derived from natural sources or which may be synthetically produced, as well as a fragrance solubilizer constituent. One or more coloring agents may be used to provide a desired appearance.

5 The compositions according to the invention may be used in their concentrated form, *i.e.*, in the form which it is intended to be marketed and sold to a consumer or the end user, but are usually expected to be diluted with a further excess of water in order to form a cleaning composition therefrom. The term "composition" in this specification is the composition of the cleaning composition which is essentially the form of the product prepared for sale to the consumer or other end user. What is to be understood by the term "cleaning compositions" as used in this
10 specification 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 "composition" with water in order to form an appropriately diluted cleaning composition which is suitable for use in cleaning applications, especially in dishwashing. Nothing in this specification, however, would bar an end user or consumer from using the composition without further dilution in water to form a cleaning
15 composition therewith. The germicidal light-duty aqueous dishwashing detergent compositions described herein may be useful in other applications, such as a hard surface cleaner, or liquid soap for use in a laundry application, spot cleaning of textiles or garments, or as a personal care product, including a liquid hand soap for providing both a cleaning and a sanitizing effect.

Cleaning compositions may be easily prepared by diluting measured amounts of the
20 inventive compositions in water by the consumer in certain weight ratios of composition:water. Particularly useful temperatures are those conventionally known in the art, *i.e.*, 20°C to 40°C. As noted, the composition may be used without dilution, *i.e.*, in composition:water concentrations of 1:0, to extremely dilute dilutions such as 1:10,000, but are desirably in the range of 1:100 - 1:10,000, preferably from 1:1 - 1:1000, most preferably from 1:100 - 1:600, with a dilution in the
25 ratio of about 1:256 being typical. To obtain a satisfactory sanitizing effect, the cationic surfactant is preferably present in aqueous cleaning compositions in an amount of at least 50 parts per million ("ppm"), where it will normally provide an effective germicidal effect.

As may be seen from the foregoing, the present invention provides a shelf stable light duty aqueous dishwashing detergent composition which is readily dispersible in a further amount of
30 water to form an aqueous cleaning composition therefrom, which has performance characteristics which are favorably comparable to known commercially available dishwashing detergent. These germicidal dishwashing liquid compositions provide good deterative activity as the various classes of nonionic surfactants included in the composition provide varying chain lengths and degrees of ethoxylation/propoxylation which allows for the formulation of compositions which are effective

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over a broad range of food stains and residues, including fatty food soils and oily food soils, have acceptable foaming and further provide a useful germicidal effect.

5 In the preceeding specification, as well as in the examples below, unless otherwise specified, references to "part" and "parts by weight" are used interchangeably and weight percentages or weight proportions, are to be understood as parts by weight of the constituent being referred to based on 100 parts by weight of a composition.

Certain preferred examples of the inventive compositions are described below.

Examples:

Formulations:

Various exemplary formulations were prepared by mixing measured amounts of the constituents into a glass vessel containing a volume of water in a conventional manner to form the compositions noted on Table 1.

Table I - Example Formulations

ID#	Constituent	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7
1	Neodol® 23-6.5 ¹	10.00	---	---	---	---	---	---
2	Neodol® 91-8 ²	---	10.00	10.00	10.00	10.00	15.00	10.00
3	Neodox® 23-4 ³ (78%wt. active)	7.69	7.69	---	7.69	7.69	---	5.13
4	Neodox 25-6 ⁴ (78% wt. active)	---	---	4.67	---	---	---	---
5	Mackam® DZ ⁵ (30% wt. active)	16.67	16.67	16.16	16.67	16.67	16.67	16.16
6	Monamid® CMA ⁶	2.00	2.00	2.00	2.00	2.00	2.00	2.00
7	Ninol® 49-CE ⁷	4.00	4.00	4.00	---	---	3.00	---
8	BTC 8358 ⁸ (80% wt. active)	2.50	2.50	2.50	2.50	---	2.50	2.50
9	BTC 818 ⁹ (50% wt. active)	---	---	---	4.00	---	---	---
10	Hyamine® 1622 ¹⁰ (50% wt. active)	---	---	---	---	8.00	---	---
11	Versene Na2 ¹¹	---	---	---	---	---	---	1.00
12	Surfine® WLG ¹² (51% wt. active)	---	---	---	---	---	5.88	---
13	Surfox® MCO ¹³ (30% wt. active)	---	---	---	---	---	---	---
14	distilled water	57.14	57.14	60.70	57.14	53.10	54.95	62.70

¹ alcohol ethoxylate; described as having an average of 6.5 ethoxy units per molecule (Shell Chem. Co., Houston TX)² alcohol ethoxylate; described as having an average of 8 ethoxy units per molecule (Shell Chem. Co., Houston TX)³ sodium alkyl ether carboxylate; described as having an average of 4 ethoxy units per molecule, neutralized with 50% NaOH aqueous solution (Shell Chem. Co., Houston TX)⁴ sodium alkyl ether carboxylate; described as having an average of 6 ethoxy units per molecule, neutralized with 50% NaOH aqueous solution (Shell Chem. Co., Houston TX)⁵ cocoamidopropylbetaine; (MacIntyre Group Ltd., University Park IL)⁶ cocomonooethanol amide; (Mona Industries Inc., Paterson NJ)⁷ cocodiethanol amide; (Stepan Chem. Co., Chicago IL)⁸ alkyl benzyl dimethyl ammonium chloride; (Stepan Chem. Co., Chicago IL)⁹ dialkyl dimethyl ammonium chloride; (Stepan Chem. Co., Chicago IL)¹⁰ octyl phenoxy ethoxyethyl dimethyl ammonium chloride; (Lonza Co., Fairlawn NJ)¹¹ disodium ethylene diamine tetraacetic acid; (Dow Chemical Co., Midland MI)¹² sodium alkyl ether carboxylate; described as having an average of 7 ethoxy units per molecule (Finetex, Elmwood Park NJ)¹³ cetyl myristic amine oxide; (Surfactants Inc., South Plainfield NJ)

Table I - Example Formulations (continued)

ID#	Constituent	Ex.8	Ex.9
1	Neodol® 23-6.5 ¹	---	---
2	Neodol® 91-8 ²	10.00	25.00
3	Neodox® 23-4 ³ (78%wt. active)	---	---
4	Neodox 25-6 ⁴ (78% wt. active)	7.01	12.50
5	Mackam® DZ ⁵ (30% wt. active)	8.08	41.25
6	Monamid® CMA ⁶	4.00	---
7	Ninol® 49-CE ⁷	4.00	15.00
8	BTC 8358 ⁸ (80% wt. active)	2.50	6.25
9	BTC 818 ⁹ (50% wt. active)	---	---
10	Hyamine® 1622 ¹⁰ (50% wt. active)	---	---
11	Versene Na2 ¹¹	---	---
12	Surfine® WLG ¹² (51% wt. active)	---	---
13	Surfox® MCO ¹³ (30% wt. active)	6.67	---
14	distilled water	57.74	---

¹ alcohol ethoxylate; described as having an average of 6.5 ethoxy units per molecule (Shell Chem. Co., Houston TX)

² alcohol ethoxylate; described as having an average of 8 ethoxy units per molecule (Shell Chem. Co., Houston TX)

³ sodium alkyl ether carboxylate; described as having an average of 4 ethoxy units per molecule, neutralized with 50% NaOH aqueous solution (Shell Chem. Co., Houston TX)

⁴ sodium alkyl ether carboxylate; described as having an average of 6 ethoxy units per molecule, neutralized with 50% NaOH aqueous solution (Shell Chem. Co., Houston TX)

⁵ cocoamidopropylbetaine; (MacIntyre Group Ltd., University Park IL)

⁶ cocomonooethanol amide; (Mona Industries Inc., Paterson NJ)

⁷ cocodiethanol amide; (Stepan Chem. Co., Chicago IL)

⁸ alkyl benzyl dimethyl ammonium chloride; (Stepan Chem. Co., Chicago IL)

⁹ dialkyl dimethyl ammonium chloride; (Stepan Chem. Co., Chicago IL)

¹⁰ octyl phenoxy ethoxyethyl dimethyl ammonium chloride; (Lonza Co., Fairlawn NJ)

¹¹ disodium ethylene diamine tetraacetic acid; (Dow Chemical Co., Midland MI)

¹² sodium alkyl ether carboxylate; described as having an average of 7 ethoxy units per molecule (Finetex, Elmwood Park NJ)

¹³ cetyl myristic amine oxide; (Surfactants Inc., South Plainfield NJ)

A minor amount of an aqueous 10% sodium hydroxide solution was added to the formulations of Ex. 4, Ex. 5 and Ex. 7 to adjust the formulations to a pH of 7. Similarly, an aqueous 10% hydrochloric acid solution was added to the formulation of Ex. 3 to adjust it to pH of 7.

The functional categorization of each of the constituents noted in Table 1 above is described in Table 2, below. The constituent identification numbers "ID#" for Table 1 and Table 2 are in direct correlation, and the Constituent Class, noted as "Const. Class" on Table 2 provides a correlation of the specific constituent and its function with respect to the defined invention in the specification, above.

Table 2

ID#	Constituent	Const. Class	Function
1	alcohol ethoxylate	C	nonionic surfactant
2	alcohol ethoxylate	C	nonionic surfactant
3	sodium alkyl ether carboxylate	B	anionic surfactant
4	sodium alkyl ether carboxylate	B	anionic surfactant
5	cocoamidopropylbetaine	D	suds stabilizer
6	cocomonoethanol amide	D	suds stabilizer
7	cocodiethanol amide	D	suds stabilizer
8	alkyl benzyl dimethyl ammonium chloride	A	quarternary ammonium germicidal agent
9	dialkyl dimethyl ammonium chloride	A	quarternary ammonium germicidal agent
10	octyl phenoxy ethoxyethyl dimethyl ammonium chloride	A	quarternary ammonium germicidal agent
11	disodium ethylene diamine tetraacetic acid	Optional	sequestrant
12	sodium alkyl ether carboxylate	B	anionic surfactant
13	cetyl myristic amine oxide	D	suds stabilizer
14	distilled water	--	water

10 Evaluation of Foaming

Evaluation of the foam heights of various of the Examples was performed by following generally, the protocol outlined in ASTM D1173-53 (Reapproved 1986) titled "Standard Test Method for Foaming Properties of Surface-Active Agents". The method was modified by using a 500 ml graduated cylinder as the foam receiver as well as by using a 1:1000 dilution of the tested composition. Foam heights in the foam receiver were taken immediately. The results from the foam height evaluation are reported on Table 3 below.

Table 3 - Foam Heights

Example No:	Foam Height (cm)
Ex. 1	7.5
Ex. 2	12
Ex. 3	7
Ex. 4	6.5
Ex. 5	12
Ex. 6	6
Ex. 7	7
Ex. 8	8
Ex. 9	13
Comp. 1*	13

* Dial Dishwashing Detergent (commercially available)

As can be seen, the formulations according to the Examples featured favorable foaming characteristics when compared to a commercially available dishwashing detergent formulation based on anionic surfactants which class of surfactants are known to exhibit excellent foaming.

Antibacterial Efficacy - Log₁₀ Reduction Test

The antibacterial efficacy of certain formulations from the Examples of Table 1 were tested for antimicrobial activity against *Staphylococcus aureus* and *Salmonella choleraesuis* by a quantitative suspension test. The test was carried out for each of the Example formulations at dilution of one part of a respective Example's formulation to 256 parts of deionized water at 40°C for a 10 minute contact time. The test protocol followed for each test was generally as follows.

1. Inoculation of the Samples:

- A. Inoculate 1.0 ml of the 24 hour test culture into each 9.0 ml sample tube; and test in duplicate.
- B. Subculture 1.0 ml of the sample after 10 minutes contact time with the respective diluted Example formulation.
- C. Subculture the sample into 9.0 ml of DIFCO AOAC Letheen Broth to form a "10⁻¹ Sample" dilution.

2. Sample Dilutions and Plating

- A. Plate the 10⁻¹, 10⁻³, and 10⁻⁵ dilutions for each sample/organism/contact time combination by the following general protocol:
 1. From the 10⁻¹ "Sample" dilution, plate 1.0 ml to form a 10⁻¹ "Sample" plate.

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2. Pipet and transfer 0.1 ml of the 10^{-1} Sample dilution into 9.9 ml of DIFCO AOAC Letheen Broth to form a " 10^{-3} Sample" dilution and form a 10^{-3} plate.
3. Pipet and transfer 0.1 ml of 10^{-3} Sample dilution to 9.9 ml DIFCO AOAC Letheen Broth to form a " 10^{-5} Sample" dilution and form a 10^{-5} plate.
- B. Pour each of the 10^{-1} plates, 10^{-3} plate, and 10^{-5} plate with Tryptic Soy Agar containing polysorbate 80 and lecithin (either DIFCO or BBL).
- C. Incubate the plates for 48 hours at 35C.
3. Control Counts: Dilutions and Plating
 - A. Inoculate 1.0 ml of 24 hour test culture into 9.0 ml DIFCO AOAC Letheen Broth to form a "Control" dilution.
 - B. Subculture 1.0 ml of the Control dilution into 9.0 ml DIFCO AOAC Letheen Broth at 10 minutes exposure; these are the " 10^{-1} Control" dilution tubes for the 10 minutes contact time controls.
 - C. Plate 10^{-4} and 10^{-5} dilutions of the 10^{-1} Control dilution for each contact time by the following protocol:
 1. Pipet 0.1 ml of the 10^{-1} Control dilution into 9.9 ml DIFCO AOAC Letheen Broth to form a " 10^{-3} Control" dilution.
 2. Plate 1.0 ml of the 10^{-3} Control dilution into 9.0 ml DIFCO AOAC Letheen Broth to form a " 10^{-4} Control" dilution and form a " 10^{-4} Control" plate.
 3. Pipet 0.1 ml of the 10^{-3} Control dilution into 9.9 ml of ml DIFCO AOAC Letheen Broth to form a " 10^{-5} Control" dilution, and to form a " 10^{-5} Control" plate.
 4. Pour the 10^{-4} and 10^{-5} Control plates with Tryptic Soy Agar containing polysorbate 80 and lecithin, and incubate at 35°C for 48hr.
4. Calculation of Log₁₀ Reduction:
 - A. Determine the number of bacteria survivors at each contact time for both the controls and test samples of each of the plates produced in accordance with the protocols outlined for steps 1 - 3 denoted above.
 1. Count the number of colonies on the petri dish. The plate is acceptable for counting with a colony count between 25 and 250.

2. Multiply the number of colonies by the plate dilution factor = the number of surviving bacteria/ml.

B. Determine the Log Reduction in bacteria for each sample/organism/contact time combination in accordance with the following equation:

$$\text{Log}_{10} (\text{Control Count}) - \text{Log}_{10} (\text{Survivor Count}) = \# \text{ Logs of bacteria reduced by the sample.}$$

The results from this antibacterial efficacy evaluation are reported on Table 4 below.

Table 4 - Antibacterial Efficacy		
Example:	Log₁₀ Reduction of <i>Staphylococcus aureus</i>	Log₁₀ Reduction of <i>Salmonella choleraesuis</i>
Ex.1	3.36	0.21
Ex.4	6.22	6.21
Ex.6	5.04	6.21
Ex.7	6.22	6.21
Ex.8	6.22	1.31
Ex.9	6.22	4.02

The reported results of Table 4 are illustrated on Figure 1. Any Log₁₀ reduction value greater than a "2" indicates that at least 99% of the tested organisms have been destroyed; similarly any value greater than a "3" indicates that at least 99.9% of the tested organisms have been destroyed; higher Log₁₀ reduction values of "4" indicate at least 99.99% of the tested organisms have been destroyed, a yet higher Log₁₀ reduction value of "5" indicates at least 99.999% of the tested organisms have been destroyed, with higher Log₁₀ reduction values indicating still higher rates of germicidal efficacy.

Antibacterial Efficacy - AOAC Test

The antibacterial efficacy of certain formulations from the Examples of Table 1 was evaluated against two representative bacterial species, *Salmonella choleraesuis* and *Staphylococcus aureus*. As is known in the art, each of these bacterial species is commonly found in kitchen environments and foodstuffs, and is desirably removed or destroyed during a cleaning procedure.

Antimicrobial efficacy of the prepared dilutions according to examples were evaluated generally in accordance with the standardized AOAC Use-Dilution test method based on AOAC Official Methods of Analysis Procedures 955.14 "Testing disinfectants against *Salmonella Choleraesuis*," and Procedure 955.15 "Testing disinfectants against *Staphylococcus Aureus*" (15th Edition, 1990, pages 135-137, Use Dilution Methods). The results reported on Table 4

indicate the proportion of the number of sample test tubes within which the organism remained alive after 10 minutes of exposure at 40°C over the total number of test tube samples used in testing the exemplary formulations of Table 1 for their germicidal activity, wherein the tested compositions were tested in a dilution of 1 part composition:256 parts water.

- 5 A comparative sample of a commercially available product was also evaluated using a commercially available product, Dial® Dishwashing Liquid, against *S.aureus* at a dilution of 1 part composition:256 parts water, and against *S.choleraesuis* at "full strength", directly as packaged and without further dilution in water. The results from the antibacterial efficacy evaluation are reported on Table 5 below.

Table 5 - Antimicrobial Efficacy

<u>Example No:</u>	<i>Staphylococcus aureus</i>	<i>Salmonella choleraesuis</i>
Ex. 3	0/20	0/20
Ex. 5	0/20	0/20
Comp. 1	30/30 [†]	28/30 [*]

10

[†] Dial® Dishwashing Detergent in a 1:256 dilution with water.

^{*} Dial® Dishwashing Detergent used directly as provided and used at full strength, i.e., not further diluted with water.

15

As can be seen from the results reported in Table 5, the exemplary formulations featured excellent germicidal efficacy compared to a commercially available dishwashing detergent formulation used without dilution in water, which commercially available dishwashing detergent showed no or poor germicidal efficacy under the test conditions.

Foam Height and Ratio of Quaternary Ammonium: Alkyl Ether Carboxylate

20

Further compositions according to the invention were produced, and are listed on Table 6 below, wherein the amounts indicate % weight (%wt.), based on a composition of 100%wt. In each, sufficient deionized water was added in *quantum sufficient* (q.s.)

TABLE 6					
	Ex.10	Ex.11	Ex.12	Ex.13	Comp.2
Neodox 23-4 (78% active)	10.23	7.96	10.23	7.69	--
BTC 8358 (80% active)	2.50	2.50	5.00	5.00	2.50
Neodol 91-8	10.00	10.00	10.00	10.00	--
Mackam DZ (31% active)	16.67	16.67	16.67	16.67	16.89
Monamid CMA	2.00	2.00	2.00	2.00	2.00
Neodol 23-6.5	--	--	--	--	13.00
Neodol 25-12	--	--	--	--	3.0
DI water	q.s.	q.s.	q.s.	q.s.	q.s.

The identify of the specific constituents in these compositions are indicated on Table 7 below. The formulations of Ex.10 - 13 illustrate the invention, are illustrative of the invention, while Comp.2 which contains no anionic, alkyl ether carboxylate constituent is provided by way of comparison.

TABLE 7	
Neodox 23-4 (78% active)	anionic, alkyl ether carboxylate, 78%wt. actives
BTC 8358 (80% active)	alkyl benzyl dimethyl ammonium chloride, 80%wt. actives
Neodol 91-8	C ₁₂ -C ₁₃ linear primary alcohol condensed with 8 mols of ethylene oxide, 100%wt. active
Mackam DZ (31% active)	cocoamidopropylbetaine, 31 %wt. active
Monamid CMA	cocomonoethanol fatty acid amide
Neodol 23-6.5	C ₁₂ -C ₁₃ linear primary alcohol condensed with 6.5 mols of ethylene oxide, 100%wt. active
Neodol 25-12	C ₁₂ -C ₁₅ linear primary alcohol condensed with 12 mols of ethylene oxide, 100%wt. active
DI water	deionized water

The compositions of Table 6 were evaluated as to their foaming characteristics in the manner described above under "Foam Heights". The results as well as the weight ratios of the anionic alkyl ether carboxylate constituent : cationic quaternary ammonium compound is reported below on Table 8.

TABLE 8					
	Ex.10	Ex.11	Ex.12	Ex.13	Comp.2
weight ratios of the anionic alkyl ether carboxylate constituent : cationic quaternary ammonium compound	4:1	3:1	2:1	1.5:1	----
Foam Height (cm)	14.5	12.0	9.5	6.0	6.0

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As may be seen, compositions according to the preferred ratios of anionic alkyl ether carboxylate constituent : cationic quaternary ammonium compound invention featured surprisingly good foaming characteristics.

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Claims:

1. Germicidal light-duty dishwashing detergent composition in either a gel, liquid, or semi-liquid form, which comprises:

- 5 A) 0.5 - 10 parts by weight of quarternary ammonium germicidal compound;
 B) 0.5 - 40 parts by weight of an anionic alkyl ether carboxylate surfactant of formula:

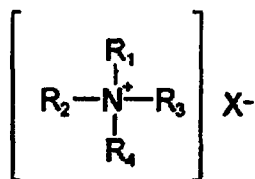


where x is 4 to 11, R is a C₉₋₁₁ alkyl, M is counterion;

- 10 C) 10 - 40 parts by weight of a nonionic surfactant;
 D) 0.01-30 parts by weight of an of a suds stabilizing or suds boosting agent;
 E) water;
 F) 0 - 40 parts by weight of one or more additives,
 wherein the ratio of the quarternary ammonium germicidal agent to the anionic alkyl ether carboxylate surfactant is 1:1-4, and,
 15 the compositions exhibit a pH in the range of 5 - 10.

2. The composition according to claim 1 wherein the ratio of the quarternary ammonium germicidal compound to the anionic alkyl ether carboxylate surfactant is 1:1.5-3.5.

20 3. The composition according to claim 1 or 2 wherein the quarternary ammonium germicidal compound is compound according to the formula:



wherein:

25 at least one R₁, R₂, R₃ and R₄ is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165.

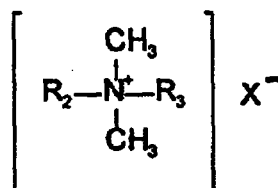
4. The composition according to Claim 3 wherein at least one R₁, R₂, R₃ and R₄ is a hydrophobic radical selected from long-chain alkyl, long-chain alkoxy aryl, long-chain



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alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, or aryl alkyl radicals, and,
 remaining R₁, R₂, R₃ and R₄ radicals on the nitrogen are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon which may optionally include one or more amide or ether linkages.

- 5
5. The composition according to claim 1 wherein the quarternary ammonium germicidal compound is compound according to the formula:



10 wherein:

R₂ and R₃ are the same or different C₈-C₁₂alkyl groups,

or, R₂ is an C₁₂-16alkyl, C₈-18alkylethoxy, or C₈-18alkylphenoethoxy group and R₃ is benzyl; and,

15 X is a salt forming anionic radical.

6. The composition according to claim 1 to 6 wherein the nonionic surfactant is a condensation product of an organic aliphatic or alkyl aromatic hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to a nitrogen atom with hydrophilic group containing ethylene oxide and/or polyethylene glycol.
- 20
7. An aqueous cleaning composition comprising in parts by weight:
 one part of the composition according to claim 1 per about 256 parts water, wherein the aqueous cleaning composition exhibits at least a "2" log reduction against *Staphylococcus aureus* and *Salmonella choleraesuis* by a quantitative suspension test.
- 25
8. An aqueous cleaning composition according to claim 7 wherein the aqueous cleaning composition exhibits at least a "3" log reduction against *Staphylococcus aureus* and *Salmonella choleraesuis* by a quantitative suspension test.
- 30



9. A process for washing of soiled dishes or cooking utensils to provide both disinfecting and cleaning benefits thereto, which comprises the step of:
washing said soiled dishes or cooking utensils in an aqueous composition which
5 comprises the composition according to claim 1.

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