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Remarks:
•Claims 17-45 are deemed to be abandoned due to non-payment of the claims fees (Rule 45(3) EPC).
•Amended claims in accordance with Rule 137(2) EPC.

(54) Use of oxidized humic acid its salts and derivatives in dishwashing compositions

(57) The present invention relates to the field of dishwashing compositions. In particular this invention relates to the use of oxidized humic acid compounds, its salts and derivatives or its mixtures in dishwashing compositions. Such cleaning compositions have improved foaming capacities due to excellent builder properties of oxidized humic acid, its salts and derivatives. This effective builder is useful for enhancement of cleaning capacity. Dishwashing compositions of the present invention are prepared by using oxidized humic acid, its salts and derivatives or mixtures thereof and used for cleaning purposes of glass, metal, porcellain and plastic dishes.

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Description

FIELD OF THE INVENTION

[0001] This application relates to dishwashing compositions.

[0002] Particularly this application relates to the use of oxidized humic acid, its salts, its derivatives and mixtures thereof in dishwashing compositions.

[0003] This application relates to the dishwashing compositions whereas oxidized humic acid, its salts, its derivatives and mixtures thereof is added to the composition in situ after synthesis or after separation of oxidized humic acid from reaction mixture.

[0004] This application relates to the synthesis of oxidized humic acid which is compatible for the use in dishwashing compositions.

BACKGROUND OF THE INVENTION

[0005] Hereinafter in the text the synonym "oxidized humic acid" will be standing for "oxidized humic acid, its salts, its derivatives and mixtures thereof".

[0006] Detergents are surfactants with cleaning properties in dilute solutions. Detergents are ions or molecules that contain both polar and nonpolar components. The polar end allows the detergent to dissolve in the water, whereas the nonpolar end solubilizes hydrophobic materials which are main target of the cleaning process.

[0007] Surfactant is the most important part of any cleaning composition. In general they are chemicals that, when dissolved in water or another solvent they orient themselves at the boundary between the liquid and a solid. Long nonpolar chain part of the surfactant molecule is attracted to oil, grease and dirt which are hydrophobic nature and another part of the molecule is attracted to water. The surfactant surround dirt until it is dislodged from the boundary.

[0008] However surfactants are precipitated or removed from washing medium in presence of earth metal cations like Ca and Mg and loose their cleaning capabilities. Therefore earth alkaline metal cations must be removed from washing water to reveal full surfactant capability.

[0009] Removal of earth alkaline metal cations are accomplished to date by complexation agents. The multivalent metal ions are surrounded from negative functionality ends of complexating agent. Thus ,chelated metal ions remain tied up in solution where they will not use up the surfactants.

[0010] Common chelating agents used in cleaning compositions are phosphates, Ethylene diamine tetra acetic acid (EDTA) its alkaline metal salts, citrate salts and zeolit. Among them phosphates are about to be banned due to environmental concerns. Zeolit and citrate are not strong enough complexating agent and are to be used in excess amounts. EDTA have been developed as phosphate substitue. However its high price and limitation due to health concern raise question of their replacement. Builders are often a good alternative to said complexation agents.

[0011] Builders are added to a cleaning composition to enhance efficiency of surfactants. They have a number of functions including softening, buffering, emulsifying and removal of multivalent cations from water. Builders provide a desirable level of alkalinity which aids in cleaning. Builders help emulsify oily or greasy soil by breaking them up to tiny globules and keep it from settling back on the cleaned surface.

[0012] One of the most used builder is sodium triphosphate, which is used on very large scale for this purpose. The heavy use of sodium triphosphate and its discharge into natural waters led to the problems of algae growth in excess of phosphorous, which cause oxygen depletion, consequently fish and plant death in stream and lakes. European Union introduced regulations to require biodegradability in all detergents and intend to ban phosphates in domestic products from 2013.

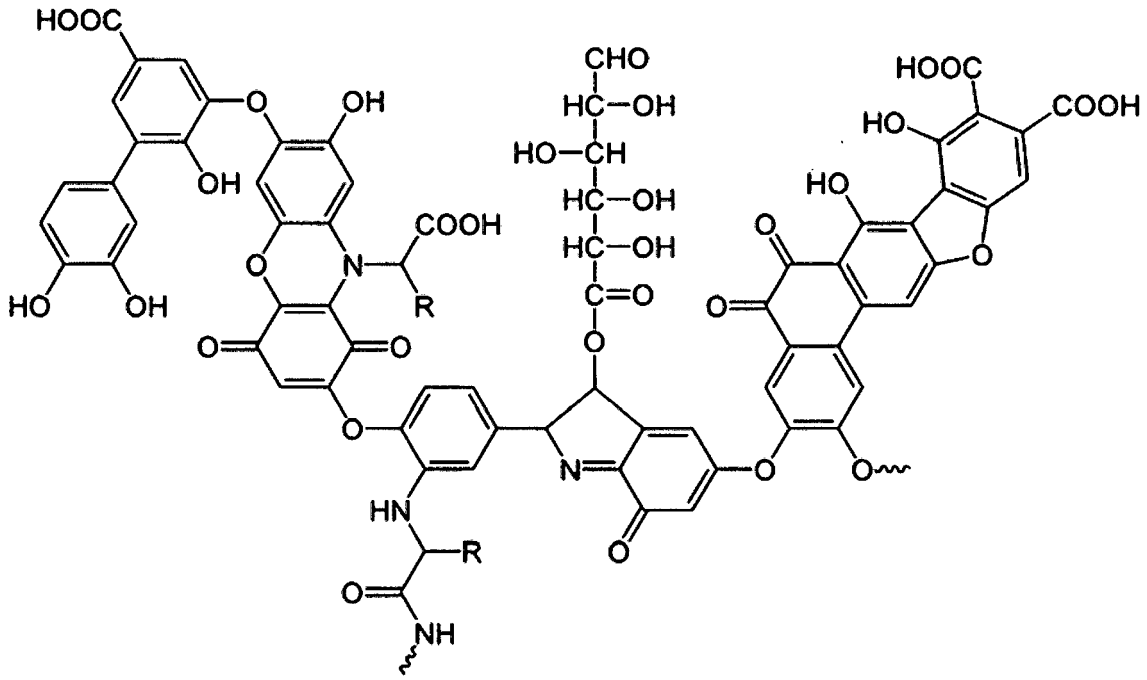
[0013] Existing alternatives to polyphosphatesare of polyacrylate nature which are again suspect of being hazardous due to their synthetic nature and remaining monomer residues.

[0014] There still exist a need to have builder with high binding capacity, less environmental concern and prefferably of organic origin to eliminate actuel and future concerns.

[0015] Humic acid is a principal component of humic substances, which are the major organic constituents of soil, peat and coal. It is produced by biodegradation of dead organic matter. It is not a single acid; rather, it is a complex mixture of many different acids containing carboxyl and phenolate groups, so that the mixture behaves dibasic or tribasic functionally.

[0016] A typical humic substance is a mixture of many molecules having aromatic, phenolic, carboxylic substituents linked together.

[0017] Below is a typical structure of unmodified humic acid having a variety of components including phenol, quinone, catechol and sugar moieties.



[0018] Oxidized humic acid which is the subject matter of the present invention has differencies as some bonds are disrupted and some functionalities are oxidized. Oxidized humic acid has generally smaller molecular weight and increased number of hydroxy and carboxyl groups.

[0019] Oxidized humid acid compounds are used in the technic as fertilizer, regeneration of polluted grounds, animal breeding and water regeneration mainly.

[0020] US5451244 R. Trowbridge teaches us use of humic acid in preparation of fertilizer compositions. Such humic acid containing compositions stimulates plant growth especially by humic acids water holding capacity

[0021] US5201930 W. Campbell teaches us use of oxidized humic acid compositions in fertilizer. Such oxidized humic acid containing compositions serve as plant growth stimulant WO2010094985 to Lomoskiy et al teaches us preparation method of oxidized humic acid and its use for recultivation of heavy metal polluted land.

[0022] DE19624982 Pfueller et al teaches us use of humic acid and its oxidized forms for purification of sewage water. Such treated water can be used as drinking water.

[0023] There exist to date no usage of oxidized humic acid in cleaning compositions, especially in detergent compositions more particularly dishwashing compositions.

[0024] It is therefore an object of the present invention to provide alternative detergent builder for dishwashing compositions that has no drawback of the marketed ones and superior to them.

DESCRIPTION OF DISCLOSURE

[0025] The present invention relates to a new use of oxidized humic acid.

[0026] By the search of an acceptable builder for use in cleaning compositions the present inventor surprisingly come to the finding that humic acid in oxidized form is an appropriate builder compound.

[0027] The present inventor has discovered that by adding oxidized humic acid to the dishwashing compositions foaming and cleaning capacity has increased.

[0028] Oxidized humic acid is not used in dishwashing compositions to date. There exist no commercially available dishwashing composition product containing oxidized humic acid on the market.

[0029] Due to the complex mixture character of humic acid and consequently complex mixture character of oxidized humic acid, in the text the synonym "oxidized humic acid" will be standing for "oxidized humic acid , its salts, its derivatives and mixtures thereof". Further the same synonym will be standing for compounds of oxidized humic acid and its salts and mixtures which is derivatized afterwards; and derivatized humic acid, which is oxidized afterwards and its salts and mixtures thereof.

[0030] In the present invention used oxidized humic acid may be in form of its salts. Due to the presence of carboxylic acids in the structure salts may be cationic character of any type.

[0031] The presence of carboxylate and phenolate groups give humic acid the ability to form complexes with ions such as Mg^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}. This capability is enhanced by oxidation of humic acid.

[0032] In the past no complex binding capacity of oxidized humic acid is measured. The present inventor additionally measured metal ion binding capacity and found that oxidized humic acid is an excellent builder with high earth alkaline metal cation capturing capability. By the search and measurements and further investigations the present inventor found that oxidized humic acids is by far superior to classic builder such as polyphosphate and even superior to the new generation builders which are of acrylic acid copolymer nature. Oxidized humic acid with 1350 mg Ca ion binding capacity per gram has stronger complexation capability than any other commercially available builder currently as shown herewith below.

Comparison of Ca2+ Complex Binding Capacities of Builders

[0033]

Sodium tripolyphosphate	198 mg Ca/g
Citric acid	270 mg Ca/g
Acrylic copolymer	400 mg Ca/g
Sulphonated acrylic copolymer	1150 mg Ca/g
Oxidized humic acid	1350 mg Ca/g

[0034] Calcium ion binding capacity in mg with respect to per gram builder used in aqueous solutions is measured titrimetrically.

[0035] Classical builder compounds have their drawbacks such as polyphosphate, which is overfertilizing water sources. Polyacrylate are strong builders but due to their chemical origin some ecological reservations are existing. Considering its builder strength, relatively small amounts of oxidized humic acid is needed which is both economically and environmentally advantageous.

[0036] The ideal builder should have strong earth alkaline metal cation capturing capacity, should be of organic origin and ecologically acceptable. The present inventor unexpectedly found that humic acid in oxidized form is an excellent builder with high earth alkaline metal cation capturing capability. Furthermore oxidized humic acid has not ecologically nature originated drawbacks since it is of organic origin and decompose naturally in the natural environment.

[0037] Oxidized humic acid serve due to its complex organic structure as emulsifying agent, as a base for buffering purposes and furthermore as complexation agent. All these properties summed establish oxidized humic acid as a good builder.

[0038] The compositions disclosed in the present invention have improved foaming thus cleaning properties due to high builder capabilities of oxidized humic acid used. Builders in detergent industry are compounds capable of capturing earth alkaline metal cations which are responsable for the hardness of water. Surfactants which are the main component of cleaners cannot reveal their full cleaning capabilities in presence of those cations. Oxidized humic acid is more prone to capture Mg2+ and Ca2+ cations then commercially already used builders. It is a good working,organic, with less ecological concern builder compound thus superior to already existing builders.

[0039] Humic acid is originated from wood decomposition products. It is a renewable source and existing in large scale. Considering additionally its organic nature humic acid is an ideal compound as builder from economical and environmental aspect both.

[0040] The presence of carboxylate and phenolate groups give humic acid the ability to form complexes with ions such as Mg2+, Ca2+, Fe2+, Fe3+.

[0041] This capability is enhanced by oxidation of humic acid. Therefore oxidized humic acid is superior to the humic acid as builder. The present inventor assume that additional oxidized phenol and carboxylate groups formed during oxidation procedure enhance the complexation capability. Measurements of the present inventor reveal that humic acid in oxidized form has higher earth alkaline metal cation complexation capability hence is a better builder. In comparative washing tests achieved results support this fact as well. With oxidized humic acid replaced cleaning compositions are at least as good as classic builder containing dishwashing compositions regarding cleaning capabilities. We assume that oxidized humic acid has relatively more phenolate, carboxylate groups which are participating by complexation process.

[0042] Humic acid is a deep black colored substance due to high content of pigments which makes it non desirable to use in cleaning compositions. This fact may be the reason for not using humic acid and staying away from its derivatives in field of cleaning compositions. Applying excess amount of oxidizing agent by synthesis of oxidized humic acid convert much of the pigments to noncolored substances. Oxidized humic acid obtained as such is light colored enough to be able to used for cleaning purposes. This color issue is an additional reason beside having higher complexation capacity for giving preference to oxidized humic acid and not to humic acid in the present invention.

[0043] Builders are compounds having the capability to capture the multivalent metal cations from water and remove

them from the cleaning or washing medium. In the absence of these cations ,surfactants, which are the main active washing agents, are not captured from these cations and can reveal their full washing strength.

[0044] Builders have multiple anionic functional groups which are capable to bind by complexation earth alkaline metal cations. First commercially used builders were polyphosphates which are stil in use. They were able to capture multivalent metal cations and remove it from the medium by precipitating, since phosphate salts of these metal cations are less soluble in water. But due to environmental concerns related to overfertilizing water with phosphate and consuming of oxygen by water plants ,which affect the life in water, polyphosphate builder are needed to be replaced with alternative builders. Existing alternatives are of polyacrylate nature which are again suspect of being hazardous due to their synthetic nature. Especially unreacted monomer residues remaining in polymers are main concern .

[0045] There still exist a need to have builder with high binding capacity, less environmental concern and prefferably of organic origin to eliminate actuel and future concerns.

[0046] According to the present invention there is provided dishwashing compositions comprising oxidized humic acid, its salts and derivatives and their mixtures.

[0047] Oxidized humic acid used in dishwashing compositions in the present invention are stable in nature. They maintain their builder properties in ambient conditions for a long time and at considerable harsh conditions for reasonable time period in comparison to the existing commercially available cleaning products. Oxidized humic acid containing dishwashing compositions have same performance, durability, foaming capacity, cleaning capacity and stability compared to the equivalents in the marketed products. The oxidized humic acid containing compositions of the present invention are equal or superior to the commercially available dishwashing composition products.

[0048] In present invention used oxidized humic acid amounts by weight are by far less than the existing commercially available composition products due to superior builder capacity. This makes its use more economical and with less environmental concern. Due to its stable nature oxidized humic acid can be used in liquid dishwashing compositions of the present invention as well and last without degradation or negative effects for adequate time period.

[0049] According to present invention oxidized humic acid is used in compositions for cleaning glass, metal, porcellain, plastic dishes of every art.

[0050] Oxidized humic acid of the present invention is used in dishwashing compositions in liquid, solid and semisolid state as well. The application forms are including cream, gel, lotion, solution, colloid, suspension, powder, granul, tablet, pouch and capsul among others. Pouch and tablet forms may include multicompartments comprising liquid, solid or gel forms.

[0051] Oxidized humic acid of the present invention may be prepared from humic acid or humic acid containing mixtures like lignite, peat, coal and the like by addition of oxidizing agent.

[0052] Particularly oxidized humic acid of the present invention is prepared starting from humic acid or humic acid source in a solvent in the presence of hydrogen peroxide.

[0053] Oxidized humic acid FTIR spectrums reveal in comparison to humic acid increased number of aliphatic hydrogen, phenolic groups and carbonyl moieties at respective wavelengths. This is indicating the cleavage and oxidation of bonds of humic acid and increase in carboxylic acid groups content.

[0054] In the present invention, oxidized humic acid is typically used in the form of aqueous solutions. As such it can be added to the liquid compositions directly from synthesis mixture without any treatment. As such oxidized humic acid containing reaction mixtures can be added directly to solid compositions for granulating purposes to achieve again solid compositions.

[0055] Alternatively said oxidized humic acid is used in solid form such as powder or granule. As such solid oxidized humic acid can be prepared from synthesis reaction mixture by removing the solvent without any other separation of the reaction byproducts and reactants. Solid oxidized humic acid obtained that manner are used in solid dishwashing compositions, or in liquid dishwashing compositions by dissolving in it.

[0056] Oxidized humic acid of the present invention can be used in dishwashing compositions after separation from the synthesis reaction mixture.

[0057] Oxidized humic acid of the present invention added to the dishwashing compositions as reaction mixture in situ after the synthesis reaction are of the same or very similar performance with regard to complex binding capacity compared to separated oxidized humic acid.

[0058] Such compositions has no drawbacks with potential hydrogen peroxide residues. It is assumed that during the oxidation reaction all hydrogen peroxide is consumed and converted to percarboxylic acid residues of the oxidized humic acid compounds .Remaining hydrogen peroxide is decomposed. As such this way of introduction of oxidized humic acid is convenient, feasable and economically advantageous. Both in application in liquid form dishwashing compositions and solid form dishwashing compositions. Application to the liquid composition is very convenient due to being same physical state. Application to the solid composition is advantageously as being granulation solvent as well.

[0059] Application of solid nonseparated oxidized humic acid to the solid composition is of convenient being the same physical state. Solid form oxidized humic acid may be advantageous with respect of storage and handling. Separated form oxidized humic acid may be advantageous with respect of especially storage potential.

[0060] Typically, dishwashing compositions of the present invention are prepared by combining the ingredients with water to provide liquid solutions. Alternatively the components may be mixed in dry form.

[0061] The amounts of oxidized humic acid used in the dishwashing compositions according to the present invention may be varied depending on the use purpose and desired concentrations.

[0062] Oxidized humic acid used in the present invention compositions found to be effective starting from the concentration of 0.01 % of weight. Beyond 15 % of weight no additional effectiveness is to be observed as builder.

[0063] The amounts of oxidized humic acid used in the dishwashing compositions according to the present invention may be within the range of 0.01% to 15%, prefferably %0.02 to % 10, most prefferably %0.05 to % 5 of weight.

[0064] Dishwashing is the process of cleaning cooking utensils, dishes and cutlery. This is achieved either by hand or using dishwasher.

[0065] Hand dishwasher detergents are usually liquid or in gel form. Dishwasher machine detergents may be in powder, tablet, gel or liquid form. Hand dishwashing liquids are usually highly foaming mixture of surfactants with low skin irritation.

[0066] Dishwashing machine used detergents contain mainly non bubbling surfactants which may be nonionic character beside water hardness remover which are builder. Too much suds will be causing the dishwasher machine to overflow and smother the water action necessary for cleaning.

[0067] Surfactants lower surface tension of water which has a wetting effect and helps remove soil. Nonionic surfactants are preffered ones because of their low sudsing character. Builder combines with water hardness causing minerals and holds them in solution so that no insoluble spots or films remains on dishes which are not desired by the consumers.

[0068] The dishwashing compositions of the present invention surfactants and builder as oxidized humic acid as the main ingredient .Suitable surfactants for such use may be of anionic, nonionic and amphotheric nature.

[0069] Hand dishwashing compositions are mainly comprised of surfactants, stability agents, preservatives, foaming agents, foam boosting agents, skin compatibility agents.

[0070] Surfactants are primary ingredients in a liquid hand dishwashing detergent. Often a combination of surfactants is used to produce good grease cutting capability, soil suspension and stable sud levels.

[0071] Stability and dispensing aids are added to keep the product homogeneous under varying storage conditions. Hydrotropes and salts are often used. Preservatives are added if needed in small amounts to help prevent any microbiological growth in the product.

[0072] **Hand dishwashing** composition of the present invention comprise as ingredients beside the present invention builder oxidized humic acid, surfactants, builder, hydrotropes, solvents, preservatives, antimicrobials, buffering agents, salts, fragrances, perfume, foam booster, enzymes and skin compatibility agents.

[0073] Surfactants are primary ingredients in a liquid hand dishwashing detergent. Often a combination of surfactants is used.

[0074] **Surfactant** lowers surface tension of water, act as wetness agent which makes the soil removing possible. Suitable surfactants for such use may be of anionic, cationic, nonionic and amphotheric nature. Surfactants are used in the present invention in the range of %1 to %50 varying with respect of concentration or purpose of the commpositions **Anionic surfactants** used in the dishwashing compositions of the present invention comprise sulfate surfactants, linear alkylbenzene sulfonic acid, sodium lauryl ether sulfate, alpha olefin sulfonate, phosphate esters, sulfosuccinate surfactants, sodium dioctyl sulphosuccinate, sulfonate surfactants , alkyl benzene sulfonate, allylsulfate, sodium alkyl glyceryl ether sulfonate, alpha olefin sulfonate, linear alkyl benzene sulfonate, alcohol ether sulfate, dodecyl benzene sulfate, alkyl ethoxy sulfonate, alkylethoxy phosphate, and mixtures thereof. Alkyl ethoxy sulfonate surfactants of the present invention used have average ethoxylation degree from 0.01 to 10, preferably from 0.02 to 4 and more preferably from 0.03 to 3.

[0075] **Cationic surfactants** used in the present invention help removing oily stain. Long chain quaternary ammonium compounds, cocoalkyl trimethyl ammonium methosulfate, lauryl amido propyl trimethyl ammonium methosulfate, polyglycolether, cocoammonium methosulfate, cetyl trimethyl ammonium chloride and betaines are the compounds of choice.

[0076] **Nonionic surfactants** used in the present invention are ethoxylated alcohols like linear alcohol ethoxylates,alkyl phenol ethoxylate octyl phenol ethoxylates, nonyl phenol ethoxylates, alkyl amine ethoxylate, alkyl polyglycoside like sodium gluconate, fatty alkanolamide, amine polyglycol ether, fatty amine oxide.

[0077] **Amphoteric surfactants** used in the liquid hand dishwashing compositions of the present invention comprise alkyl dimethyl betaine, alkyl amidopropylbetaine and alkyl amine oxide. Specifically N,N-dimethylacetic acid betaine, alkylamidepropyl-N,Ndimethyl-2-hydroxypropylsulfobetaine, alkylamidepropyl N, N-dimethylpropylsulfobetaine, lauramidepropyl-N,N-dimethylacetic acid betaine, myristamidepropyl-N, N-dimethylacetic acid betaine, alkylcarbobetaine, alkylsulfobetaine, alkylhydroxysulfobetaine, alkylamideamine -type betaine and alkylimidazoline-type betaine. Cocamidepropyl-N,N-dimethylacetic acid betaine and the like are particularly preferable in terms of detergency, foam producing ability and rinsing property.

[0078] In the present invention, the above-mentioned amidobetaine-type amphoteric surfactants can be used singly or in combination of two or more. They are incorporated in amounts of 0.1-30% by weight. When the amount of amidobetaine type amphoteric surfactant is less than 0.1%, sufficient detergency cannot be obtained. On the other hand,

amounts exceeding 30% are not economical, because the effects of the amphoteric surfactant (a) are saturated and cannot be enhanced any more.

[0079] **Foam boosting** compounds used in hand wash laundry of the present invention are amides examplary lauryl myristyl monoethanolamide, betaines, examplary cocoamido propyl betaine, sulfobetaine and amine oxides such as alkyl- or alkenyl- amine oxides having a linear or branched alkyl or alkenyl group having 1 to 24 carbon atoms, examplary, lauryl amido propyl amine oxide , myristal amido propyl amine oxide, lauryl dimethyl amine oxide, alkyl dimethyl amine oxides, cocodimethyl amine oxide, alkyl dihydroxyethyl amine oxide, coconut allyl dimethyl amine oxide, Cocoamido-propyl amine oxide and cocoamide diethanolamide, prefferably cocodimethyl amine oxide. These compounds add foam enhancement and stability, emulsification and viscosity building properties to the compositions of the present invention. Foam boosting agents are used in the present invention in the range of 0.1% to 20% by weight.

[0080] **Hydrotropes** are solubilizers maintaining the pouring characteristic by preventing separation of the composition into layers. Hydrotrope compounds of the present invention are xylene sulfonate, cumen sulfonate, glycol ether sulfate and the like. Hydrotropes are used in the present invention in the range of 1% to 20% by weight, varying with respect of concentration or purpose of the commpositions.

[0081] **Solvents** are needed for preventing phasing out the composition and to dissolve some ingredients. Organic solvents are the main solvents used for this purpose and comprise for the present invention, ethanol, propanol, isopropanol, butoxy propoxy propanol, butoxy propanol, butoxy ethanol, , butyl diglycoether, benzyl alcohol, propoxy propoxy propanol, polypropylene glycol, ethers and diethers, alkoxylated glycols, C6-C16 glycol ethers, aliphatic branched alcohols, alkoxylated aliphatic alcohols, alkoxylated linear C1-C5 alcohols, linear C1-C5 alcohols and mixtures thereof. Used solvent amounts in the present invention may vary.

[0082] Surfactants interact with skin by binding to skin protein and causing swelling. An example is sodium lauryl sulfate which is limiting its use by hand wash detergents. A solution to this problem constitute use of mild surfactants, use of ethoxylated alcohols and skin compatibility agents.

[0083] **Skin compatibility agents** of the present invention may comprise methyl ester sulfonate, coco fatty acid methyl ester sulfonate, betaine compounds, prefferably cocamidepropyl-N,N-dimethylacetic acid.

[0084] **Preservatives** which can be optionally used in the present invention compositions at a concentration of 0 wt. % to 3 wt. % comprise benzalkonium chloride, benzethonium chloride, sodium benzoate, 5-bromo-5-nitro-1,3 dioxane, 2-bromo-2-nitropropane-1,3-diol , alkyl trimethyl ammonium bromide; N- (hydroxymethyl)-N-(1,3-dihydroxy methyl-2, 5-dioxo-4-imidaxolidinyl-N'-(hydroxy methyl) urea; 1-3-dimethyol- 5, 5-dimethyl hydantoin; formaldehyde; iodopropynl butyl carbamate, butyl paraben; ethyl paraben; methyl paraben; propyl paraben, mixture of methyl isothiazolinone/methyl-chloroisothiazoline; mixture of phenoxythanol/butyl paraben/methyl paraben/propylparaben; 2-phenoxyethanol ; tris-hydroxyethyl-hexahydrotriazine ; methylisothiazolinone; 5-chloro-2-methyl-4-isothiazol- 3-one; 2-methyl-4-isothiazol- 3-one; 1,2-dibromo-2,4-dicyanobutane; 1- (3-chloroalkyl)-3, 5,7-triaza- azoniaadamantane and mixtures thereof.

[0085] PH adjusting agents of basic nature such as sodium hydroxide, potassium hydroxide, alkali metal hydroxide, alkali metal carbonate, bicarbonate may be added to the present invention compositions.

[0086] PH adjusting agents of of acidic nature, organic acids such as citric acid, fumaric acid, inorganic acids such as hydrochloric acid and sulfuric acid may be added to the present invention compositions.

[0087] Furthermore salts may be added to the compositions of the present invention. Said salts may be organic or inorganic nature such as sodium chloride, magnesium sulfate, calcium chloride, sodium citrate, sodium sulfate among others.

[0088] Dishwashing machine compositions of the present invention may be in form of powder, liquid, gel, tablet and unit dose pouches.

[0089] **Dishwashing machine** composition of the present invention comprise as ingredients beside the present invention builder oxidized humic acid, surfactants, corrosion inhibitor, chlorine compounds, additional alkali, perfume and processing aids. Surfactants constitute less than 5% by weight of dishwashing machine compositions. Builders make up the bulk of the compositions.

[0090] Builders combines with water hardness minerals and holds them in solution so that the minerals cannot combine with food soils. Consequently minerals cannot combine with food soils and leave insoluble spots or films on dishes. Minerals themselves may leave spots on dishes after washing, hence they are removed by builders as well. In the present invention used builder is oxidized humic acid which is the subject matter of the present invention. Oxidized humic acid may be used alone wherever possible and can be used in mixture of builders. Being a strong builder oxidized humic acid may help reducing bulk builder amount.

[0091] Surfactant lowers surface tension of water, act as wetness agent which makes the soil removing possible. Nonionic surfactants are used in dishwasher machine compositions because they have lowest sudsing effect.

[0092] In the present invention used surfactants are nonionic surfactants comprising ethoxylated alcohols, alkyl polyglycosides, fatty alkanolamides, amine polyglycol ethers, imidazolines, amine oxides among others.

[0093] Corrosion inhibitor helps protect machine parts and prevent corrosion of metals. In the present invention used corrosion inhibitors are sodium silicate, zinc salts and bismuth salts.

[0094] Chlorine compounds aid in sanitizing, make protein soils like egg and milk soluble, remove caffee or tea stains and lessens spotting of glassware. In the present invention used chlorine compounds are sodium chlorite, sodium hypochlorite among others.

[0095] Additional alkalis may be used in handling greasy food soils. In the present invention used alkali compounds are alkali metal carbonate, bicarbonate and hydroxide like sodium carbonate, caustic soda among others.

[0096] Special additives may be used to inhibit overglaze and pattern removal from the porcellain. In the present invention used additive compounds may be sodium aluminate, boric oxide, aluminium phosphate among others.

[0097] Additionally perfumes, thickening agents like polyacrylate and xanthan gum and processing aids may be added.

[0098] A dishwashing composition according to the present invention is prepared by mixing oxidized humic acid and surfactants and other desirable ingredients necessary mixed in water to obtain liquid dishwashing composition of the present invention.

[0099] Alternatively a dishwashing composition of the present invention is prepared by mixing oxidized humic acid and surfactants and other desirable ingredients necessary in solid state to obtain solid dishwashing composition of the present invention.

[0100] The following examples are given by way of illustration and therefore should not be construed to limit the scope of the present invention.

EXAMPLES

EXAMPLE A: Preparation of Oxidized Humic Acid

[0101] 2 grams of sodium salt of humic acid is dissolved in 45ml water. 5 ml of 30% aqueous solution of hydrogen peroxide is added and pH of the reaction solution is adjusted to 12 with sodium hydroxide. Reaction mixture is stirred at 70 C for 3 hours. After ceasing gas evolution reaction is considered to be completed. FTIR spectrum indicates increase of aliphatic hydrogen, phenolic groups and carbonyl moieties compared to humic acid FTIR spectrum.

[0102] Obtained rection mixture in solution is used directly in dish washing compositions. Alternatively reaction mixture solvent is removed and remaining solid mixture is used in dish washing compositions.

[0103] By a separate preparation, oxidized humic acid reaction mixture solution is removed by spray drying technic to obtain a powder, which is used in the compositions of the present inventions as solide reaction mixture.

[0104] Another alternative is purification of oxidized humic acid from unreacted humic acid , reactant and reaction byproducts. This is achieved by separation of unreacted reactants and reaction byproducts and removing solvent or precipitating oxidized humic acid before or after removal of reaction byproducts and unreacted reactants.

[0105] By a separate preparation, oxidized humic acid formed is separated from reaction mixture by removal of reaction solvent and subsequent ethanol addition as precipitation. Obtained powder which is called separated oxidized humic acid is used in the compositions of the present invention

EXAMPLE 1: Preparation of Oxidized Humic Acid Containing Liquid Hand Dishwashing Composition

[0106]

Linear alkyl benzene sulfonic acid Sodium salt	14.6 %
Caustic soda	3.81 %
Sodium lauryl ether sulphate	8.5 %
*Parmetol A 28 S	0.1 %
Oxidized humic acid	0.2 %
Water	72 % (as required to complete to 100%)

*Parmetol A 28 S : mixture of 5-Chloro-2-Methyl-2H-isothiazol-3-one and 2-Methyl-2H-isothiazol-3-one

[0107] Ingredients are mixed in water, from example A obtained oxidized humic acid reaction mixture solution is added directly after completion of oxidation reaction. Remaining water is added to obtain a solution and to complete %100.

Comparative Example 1: Preparation of EDTA Containing Liquid Hand Dishwashing Composition

[0108] Oxidized humic acid is replaced with % 0.1 commonly used complexation agent ethylene diamine tetra acetic acid tetrasodium salt Na4EDTA. Remaining ingredients are exactly the same with same ranges and methode of preparation.

Comparative Washing Tests

[0109] To measure the effectiveness of oxidized humic acid containing dishwashing compositions in comparison to substituted comparative dishwashing compositions foaming capacity tests are conducted. Foaming height and duration is a good indication of washing strength of dishwashing compositions and conducted routinely in the industry.

[0110] **No oil tests :** are conducted with water containing 0.5g of example 1 and comparative example 1 solution each in 2L water.

[0111] **Oil tests :** with 4, 8 and 12 drops of oil each are conducted with 1g of example 1 and comparative example 1 solution each in 2L water.

[0112] In tests used water is containing 450 ppm calcium ion Ca2+ and test temperature is 25C.

[0113] Test sample is prepared by adding 1g cleaning composition in 2 Liter of water, adding oil drops and taking 200 ml from this mixture in a glass cylinder having 4 cm inner diameter and 70 cm of height. Glass cylinder is stoppered and revolved with 40 revolution per minute for 3 minutes. After stopping 10 seconds waited and height of foam is measured.

[0114] Measured foam heights are in proportional relationship to the cleaning capacity of respective dishwasher compositions.

Comparative Dish Washing Test Results

[0115]

Soil	Example 1 (foam height in cm)	Comparative Example 1 (foam heigth in cm)
No oil	26	21
4 drops of oil	26	19
8 drops of oil	22	9
12 drops of oil	9	5

[0116] As can be seen from tests, compositions containing oxidized humic acid are superior with respect to foaming capacity to nonoxidized humic acid containing corresponding compositions, which is an indication of washing strength in dish washing composition.

EXAMPLE 2 : Preparation of Oxidized Humic Acid Containing Powder Dishwashing Machine Composition

[0117]

*SMET MC 16	12%
Tetra acetyl ethylene diamine	%0.3
*Dehypon LS 54	1%
Sodium percarbonate	4.5%
Enzyme (Genencor twin power)	1.1%
Oxidized humic acid	0.5%
Sodium carbonate	38%
Sodium sulfate	42.6%

*SMET MC 16: Polysilicate, carbonate mixture

*DEHYPON LS 54: Fatty alcohol C12-14 with 5 moles of ethylene oxide and 4 moles of propylene oxide

[0118] Ingredients are mixed together. Oxidized humic acid powder, prepared by reaction solvent removal by spray drying technic is added to the composition.

Comparative Example 2 : Preparation of Polyacrylic Acid Builder Containing Powder Dishwashing Machine Composition

[0119] Oxidized humic acid of example 2 is replaced with %5 ACUSOL 497 NG which is an acrylic maleic acid copolymer used as builder in cleaning compositions. Remaining ingredients are exactly the same with same ranges and same methode of preparation.

[0120] Comparative dishwashing tests same as in Example 1 are performed with Example 2 and comparative example

2 revealing that oxidized humic acid containing composition is performing at least as good as comparative dishwashing composition, regarding cleaning capability.

EXAMPLE 3: Preparation of Oxidized Humic Acid Containing Gel Dishwashing Machine Composition

[0121]

Borax	%1
Monopropylene glycol	%9
*DEHYPON LS 54	2%
Potassium silicate	4%
Oxidized humic acid	0.5%
Trisodium citrate	5%
Citric acid	6.5%
Enzyme mixture	4.5%
Xanthan gum	0.5%
Caustic soda (%30 aqueous solution)	9,5
Water	57.5%

*DEHYPON LS 54: Fatty alcohol C12-14 with 5 moles of ethylene oxide and 4 moles of propylene oxide

[0122] Ingredients are mixed in water. From example A obtained oxidized humic acid is separated from reaction mixture by removal of reaction solvent and in ethanol precipitated and added to the composition. Remaining water is added to obtain a solution and to complete %100.

Comparative Example 3 : Preparation of Polyacrylic Acid Sodium Builder Containing Gel Dishwashing Machine Composition

[0123] Oxidized humic acid of example 2 is replaced with 6% by weight of SOKALAN PA 30 CL which is polyacrylic acid of low molecular weight, used as builder in cleaning compositions. Remaining ingredients are exactly the same with same ranges and same methode of preparation.

[0124] Comparative dishwashing tests same as in Example 1 are performed with Example 3 and comparative example 3 revealing that oxidized humic acid containing composition is performing at least as good as comparative dishwashing composition, regarding cleaning capability.

Claims

1. Use of oxidized humic acid, its salts and derivatives or mixtures thereof in dishwashing compositions.

2. A dishwashing composition according to claim 1, wherein dishwashing composition is in liquid or gel form.

3. A dishwashing composition according to claim 1, wherein dishwashing composition is in solid or semisolid form.

4. A dishwashing composition according to claim 1, comprising from 0.01 % to 15% weight percent of oxidized humic acid , its salts and derivatives , prefferably from 0.02 % to 10 % weight percent of oxidized humic acid , its salts and derivatives, most prefferably from 0.05 to 5% weight percent of oxidized humic acid , its salts and derivatives.

5. A dishwashing composition according to preceding claims, comprising addition of oxidized humic acid to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without any separation.

6. A dishwashing composition according to claims 1 to 4, comprising addition of oxidized humic acid to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

7. A dishwashing composition according to claims 1 to 4, comprising addition of separated oxidized humic acid to the dishwashing composition.

8. A dishwashing composition according to preceding claims, which further comprises a surfactant or surfactants.

9. A dishwashing composition according to preceding claims, which further comprises bleaching agents, hydrotropes, solvents, preservatives, antimicrobials, buffering agents, basic agents, salts, fragrances, perfume, softening agents, foaming agent, foam reducing agent, opacifying agent, dye transfer inhibitor, redeposition inhibitor and enzymes.

10. A liquid dishwashing composition according to claim 1, claim2 and claims 4 to 9, comprising

a) from 1% to 35 % by weight of surfactant or surfactants
b) from 0.01% to 15% by weight of oxidized humic acid, its salts and derivatives
c)water

11. A liquid dishwashing composition according to claim 10, comprising

a) from 2% to 30 % by weight of surfactant or surfactants
b) from 0.02% to 10 % by weight of oxidized humic acid, its salts and derivatives
c)water

12. A liquid dishwashing composition according to claim 1, claim2 and claims 4 to 9, comprising

a)from 1% to 30% by weight of anionic surfactant
b) from 0.0 1% to 4 % by weight of disinfectant
c)from 0.5% to 10% by weight of basic agent
d) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
e) water

13. A liquid dishwashing composition according to claim 12, comprising

a) from 10% to 25% by weight of sodium lauryl ether sulfate
b) from 3% to 15% by weight of linear alkyl benzene sulfonic acid sodium salt
c) from 0.01% to 4 % by weight of disinfectant based on isothiazolone compounds
d) from 0.5% to 10% by weight of caustic soda
e) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
f) water

14. A liquid dishwashing composition according to claim 10, comprising

a) from 1% to 35 % by weight of surfactant or surfactants
b) from 0.01% to 15% by weight of oxidized humic acid, its salts and derivatives
c)water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.

15. A liquid dishwashing composition according to claim 12, comprising

a)from 1% to 30% by weight of anionic surfactant
b) from 0.0 1% to 4 % by weight of disinfectant
c)from 0.5% to 10% by weight of basic agent
d) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
e) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.

16. A liquid dishwashing composition according to claim 13, comprising

a) from 10% to 25% by weight of sodium lauryl ether sulfate

b) from 3% to 15% by weight of linear alkyl benzene sulfonic acid sodium salt
c) from 0.01% to 4 % by weight of disinfectant based on isothiazolone compounds
d)from 0.5% to 10% by weight of caustic soda
e) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
f) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.

17. A liquid dishwashing composition according to claim 10, comprising

a) from 1% to 35 % by weight of surfactant or surfactants
b) from 0.01% to 15% by weight of oxidized humic acid, its salts and derivatives
c)water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

18. A liquid dishwashing composition according to claim 12, comprising

a)from 1% to 30% by weight of anionic surfactant
b) from 0.01% to 4 % by weight of disinfectant
c)from 0.5% to 10% by weight of basic agent
d) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
e) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

19. A liquid dishwashing composition according to claim 13, comprising

a) from 10% to 25% by weight of sodium lauryl ether sulfate
b) from 3% to 15% by weight of linear alkyl benzene sulfonic acid sodium salt
c) from 0.01% to 4 % by weight of disinfectant based on isothiazolone compounds
d)from 0.5% to 10% by weight of caustic soda
e) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
f) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

20. A liquid dishwashing composition according to claim 10, comprising

a) from 1% to 35 % by weight of surfactant or surfactants
b) from 0.01% to 15% by weight of oxidized humic acid, its salts and derivatives
c)water

wherein, separated oxidized humic acid is added to the dishwashing composition.

21. A liquid dishwashing composition according to claim 12, comprising

a)from 1% to 30% by weight of anionic surfactant
b) from 0.0 1% to 4 % by weight of disinfectant
c)from 0.5% to 10% by weight of basic agent
d) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
e) water

wherein, separated oxidized humic acid is added to the dishwashing composition.

22. A liquid dishwashing composition according to claim 13, comprising

a) from 10% to 25% by weight of sodium lauryl ether sulfate
b) from 3% to 15% by weight of linear alkyl benzene sulfonic acid sodium salt
c) from 0.01% to 4 % by weight of disinfectant based on isothiazolone compounds
d)from 0.5% to 10% by weight of caustic soda
e) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
f) water

wherein, separated oxidized humic acid is added to the dishwashing composition.

23. A gel dishwashing composition according to claim 1, claim 2 and claim 4 to 9, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% basic agent
e) from 1 %to 25% by weight of organic solvent
f) from 0.2% to 15% by weight of gelling agent
g) water

24. A gel dishwashing composition according to claim 23, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% caustic soda
e) from 1 %to 25% by weight of monopropylene glycol
f) from 0.2% to 10% by weight of xanthan gum
g) water

25. A gel dishwashing composition according to claim 23, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% basic agent
e) from 1 %to 25% by weight of organic solvent
f) from 0.2% to 15% by weight of gelling agent
g) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.

26. A gel dishwashing composition according to claim 24, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% caustic soda
e) from 1 %to 25% by weight of monopropylene glycol
f) from 0.2% to 10% by weight of xanthan gum
g) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.

27. A gel dishwashing composition according to claim 23, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% basic agent
e) from 1 %to 25% by weight of organic solvent
f) from 0.2% to 15% by weight of gelling agent
g) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

28. A gel dishwashing composition according to claim 24, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% caustic soda
e) from 1 %to 25% by weight of monopropylene glycol
f) from 0.2% to 10% by weight of xanthan gum
g) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

29. A gel dishwashing composition according to claim 23, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% basic agent
e) from 1 %to 25% by weight of organic solvent
f) from 0.2% to 15% by weight of gelling agent
g) water

wherein, separated oxidized humic acid is added to the dishwashing composition.

30. A gel dishwashing composition according to claim 24, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d)from 1% to 25% caustic soda
e) from 1 %to 25% by weight of monopropylene glycol
f) from 0.2% to 10% by weight of xanthan gum
g) water

wherein, separated oxidized humic acid is added to the dishwashing composition.

31. A solid dishwashing composition according to claim 1 and claims 3 to 9, whereas said solid composition may be in powder, granul, capsulated or tabletted form.

32. A solid dishwashing composition according to claim 1 and claims 3 to 9, comprising

a) from 1% to 20 % by weight of surfactant or surfactants
b) from 0.01% to 15% by weight of oxidized humic acid, its salts and derivatives

33. A solid dishwashing composition according to claim 1 and claims 3 to 9, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1 % to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 70% by weight of basic agent
e)from 1% to 20% by weight of bleaching agent
f)from 1% to 25% by weight of silicate

34. A solid dishwashing composition according to claim 33, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 60% by weight of sodium carbonate
e)from 1% to 20% by weight of sodium percarbonate
f)from 1% to 25% by weight of polimerized silicate
g)from 0.01% to 3% by weight of bleaching agent activating agent

35. A solid dishwashing composition according to claim 33, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 70% by weight of basic agent
e)from 1% to 20% by weight of bleaching agent
f)from 1% to 25% by weight of silicate

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.

36. A solid dishwashing composition according to claim 34, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 60% by weight of sodium carbonate
e)from 1% to 20% by weight of sodium percarbonate
f)from 1% to 25% by weight of polimerized silicate
g)from 0.01% to 3% by weight of bleaching agent activating agent

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.

37. A solid dishwashing composition according to claim 33, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1 % to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 70% by weight of basic agent
e)from 1% to 20% by weight of bleaching agent
f)from 1% to 25% by weight of silicate

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

38. A solid dishwashing composition according to claim 34, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme

c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 60% by weight of sodium carbonate
e)from 1% to 20% by weight of sodium percarbonate
f)from 1% to 25% by weight of polimerized silicate
g)from 0.01% to 3% by weight of bleaching agent activating agent

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.

39. A solid dishwashing composition according to claim 33, comprising

a)from 1% to 20% by weight of nonionic surfactant
b) from 0.1 % to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 70% by weight of basic agent
e)from 1% to 20% by weight of bleaching agent
f)from 1% to 25% by weight of silicate

wherein, separated oxidized humic acid is added to the dishwashing composition.

40. A solid dishwashing composition according to claim 34, comprising

a)from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid, its salts and derivatives
d) from 3% to 60% by weight of sodium carbonate
e)from 1% to 20% by weight of sodium percarbonate
f)from 1% to 25% by weight of polimerized silicate
g)from 0.01% to 3% by weight of bleaching agent activating agent

wherein, separated oxidized humic acid is added to the dishwashing composition.

41. A tabletted dishwashing composition according to preceding claims.

42. A multicompartmental tabletted dishwashing composition according to preceding claims, wherein tabletted form is comprising at least two solid, liquid or gel form compartments.

43. A dishwashing composition according to preceding claims, wherein said composition is in pouch form.

44. A multicompartmental pouch dishwashing composition according to preceding claims, wherein pouch form is comprising at least two solid, liquid or gel form compartments.

45. A cleaning composition as claimed in any preceding claims, having application prefferably on glass, metal, porcellain and plastic dishes.

Amended claims in accordance with Rule 137(2) EPC.

1. Use of oxidized humic acid, or its salts as a builder in dishwashing compositions
"Derivatives" term was removed to avoid humic acid involvement from whole of the claim set. By agreeing with the examiner, the term "as builder" was added in order to underline that oxidized humic acids functionality is being builder.

2. A dishwashing composition according to claim 1, wherein dishwashing composition is in liquid, gel, solid or semisolid form.
Claim 2 and 3 of previous claim set was united. This claim indicates the forms that oxidized humic acid comprising dishwashing compositions can take, as *stated in description part page 8.*

3. A dishwashing composition according to claim 1, comprising from 0.02% to 10% weight percent of oxidized humic

acid or its salts, preferably from 0.05% to 5% weight percent of oxidized humic acid or it salts.
The section "0.01% to 15%"weight percent of oxidized humic acid" in previous claim 4 *was removed to specify that oxidized humic acid can be used* as *efficient builder in amounts 10% or less by weight of the total composition.*

4. A dishwashing composition according to preceding claims, comprising addition of oxidized humic acid or its salts to dishwashing composition as reaction mixture after completion of oxidation of humic acid without any separation.
Claim 4 is Claim 5 of previous claim set. In present invention the product obtained from the oxidation reaction can be directly applied in dishwashing compositions without any further isolation/purification/separation. Hence, a more naturaly ready biodegradable, biological builder that needs lesser processing prior to use in dishwashing composition is provided. Claim 4 denotes that oxidized humic acid or its salts are advantegous in terms of uncomplicated and economical obtainability.

5. A dishwashing composition according to claims 1 to 3, comprising addition of oxidized humic acid or its salts to dishwashing composition as reaction mixture after completion of oxidation of humic acid and removal of reaction solvent.
Claim 5 is Claim 6 of previous claim set. Claim 5 indicates that oxidized humic acid may also be used in dishwashing compositions after removing the reaction solvent from the oxidation reaction mixture. Solvent removed oxidized humic acid is especially useful for the solid form dishwashing compositions, and feasible in comparison to separated oxidized humic acid.

6. A dishwashing composition according to preceding claims, which further comprises a surfactant or surfactants, bleaching agents, hydrotropes, solvents, preservatives, antimicrobials, buffering agents, basic agents, salts, fragrances, perfume, softening agents, foaming agent, foam reducing agent, opacifying agent, dye transfer inhibitor, redeposition inhibitor and enzymes.
Claim 8 and Claim 9 of previous claim set was united. Claim 6 underlines that oxidized humic acid or its salts are applicable and compatable with the common dishwashing ingredients.

7. A dishwashing composition according to preceding claims, comprising

a) from 1 % to 35% by weight of surfactant or surfactants
b) from 0.02% to 10% by weight of oxidized humic acid or its salts.

Claim 7 is reorganized form of claim 10 in previous claim set. Claim 7 indicates the necessity of surfactant existence in dishwashing compositions of the present invention since oxidized humic acid was not intented to perform as surfactant.
Humic acid also cannot be used in large amounts as *typical for surfactants due to slight coloring effects. Therefore oxidized humic acid cannot replace surfactants in wide use range, and surfactants should be included to dishwashing compositions. "liquid" and "water" terms were removed from previous claim 10 to indicate not only liquid form but every form of dishwashing composition needs a co-existence* of a *surfactant or surfactants.*

8. A liquid dishwashing composition according to claim 7, comprising

a) from 10% to 25% by weight of sodium lauryl ether sulfate
b) from 3% to 15% by weight of linear alkyl benzene sulfonic acid sodium salt
c) from 0.01% to 4% by weight of disinfectant based on isothiazolone compounds
d) from 0.5% to 10% by weight of caustic soda
e) from 0.02% to 10% by weight of oxidized humic acid or its salts
f) water

Claim 8 is Claim 13 of previous claim set. Claim indicates that oxidized humic acid is compatible with specific surfactants such as sodium lauryl ether sulfate and linear alkyl benzene sulfonic acid sodium salt, and other ingredients such as isothiazolone compounds and caustic soda.

9. A liquid dishwashing composition according to claim 7, comprising

a) from 1% to 30% by weight of anionic surfactant
b) from 0.01 % to 4% by weight of disinfectant
c) from 0.5% to 10% by weight of basic agent

d) from 0.02% to 10% by weight of oxidized humic acid or its salts
e) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid or its salts without removing reaction solvent.
Claim 9 is Claim 15 of *previous claim set. This claim is about liquid dishwashing composition whereby oxidized humic acid is added to the composition without any separation step with reaction solvent. Thus, the composition is economically advantegous and favoured by its simplicity.*

10. A gel dishwashing composition according to claim 7, comprising

a) from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid or its salts
d) from 1% to 25% by weight of caustic soda
e) from 1% to 25% by weight of monopropylene glycol
f) from 0.2% to 15% by weight of xanthan gum
g) water

This claim is about gel dishwashing composition whereby oxidized humic acid demonstrates compliance as builder with specific type igredients of dishwashing compositions such as *medium ethoxylated fatty alcohol, enzyme, caustic soda, monopropylene glycol and xanthan gum. This type of dishwashing formulation was indicated by Example 3 in description part (page 19).*

11. A gel dishwashing composition according to claim 7, comprising

a) from 1% to 20% by weight of nonionic surfactant
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid or its salts
d) from 1 % to 25% by weight of basic agent
e) from 1 % to 25% by weight of organic solvent
f) from 0.2% to 15% by weight of gelling agent
g) water

wherein, oxidized humic acid is added to the dishwashing composition as reaction mixture after completion of oxidation of humic acid without removing reaction solvent.
This claim is about gel dishwashing composition whereby oxidized humic acid is added to the composition without any separation step with reaction solvent. Thus, the composition is economically advantegous and favoured by its simplicity. This type of dishwashing formulation was indicated by Example 3 in description part (page 19).

12. A solid dishwashing composition according to claim 1 to claim 7, wherein said solid composition may be in powder, granul, capsulated or tabletted form.
This claim indicates that the oxidized humic acid can be present in solid form dishwashing compositions such as *powder, granul, capsules or tablet as indicated in description part page 8 and page 9.*

13. A solid dishwashing composition according to claim 12, comprising

a) from 1% to 20% by weight of medium ethoxylated fatty alcohol
b) from 0.1% to 5% by weight of enzyme
c) from 0.02% to 10% by weight of oxidized humic acid or its salts
d) from 3% to 60% by weight of sodium carbonate
e) from 1% to 20% by weight of sodium percarbonate
f) from 1% to 25% by weight of polimerized silicate
g) from 0.01% to 3% by weight of bleaching agent activating agent

This claim is about solid dishwashing composition whereby oxidized humic acid demonstrates compliance as builder with specific type igredients of dishwashing compositions such as *medium ethoxylated fatty alcohol, enzyme, sodium carbonate, sodium percarbonate, polimerized silicate and bleaching agent activating agent. This type of dishwashing*

formulation was indicated by Example 2 in description part (page 18).

14. A dishwashing composition according to preceding claims, wherein the dishwashing composition is in multicompartmental unit dose form such as tablet or pouch, and comprises at least two solid, liquid or gel form compartments.
Claim 14 shows that oxidized humic acid may be comprised by the multicompartmented tablet or multicompartmented water soluble pouches as *indicated in description part page 8 and page 14.*

15. A dishwashing composition as claimed in any preceding claims, having application prefferably on glass, metal, porcellain and plastic dishes.
Claim 15 indicates that compositions of present invention can be prefferably used on glass, metal, porcellain and plastic dishes as indicated in description part page 8. "A cleaning composition" term here was changed with "A dishwashing composition" in order to maintain uniformity of new claim set.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 00 1599

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	ALLARD ET AL: "Oxidation of humic acids from an agricultural soil and a lignite deposit: Analysis of lipophilic and hydrophilic products", ORGANIC GEOCHEMISTRY, PERGAMON, AMSTERDAM, NL, vol. 38, no. 12, 14 November 2007 (2007-11-14), pages 2036-2057, XP022344502, ISSN: 0146-6380, DOI: 10.1016/J.ORGGEOCHEM.2007.08.005 * page 2046; table 1 *	1-16	INV. C11D1/04 C11D1/36 C11D3/20
X	WO 2008/075084 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; FREY STEFAN) 26 June 2008 (2008-06-26) * examples * * the bridging paragraph; page 7 - page 8 * * page 8, line 19 - line 32 *	1-16	
A	SILVIA SALATI ET AL: "Perspective on the use of humic acids from biomass as natural surfactants for industrial applications", BIOTECHNOLOGY ADVANCES, ELSEVIER PUBLISHING, BARKING, GB, vol. 29, no. 6, 21 July 2011 (2011-07-21), pages 913-922, XP028306425, ISSN: 0734-9750, DOI: 10.1016/J.BIOTECHADV.2011.07.012 [retrieved on 2011-07-29] * the whole document *	1-16	TECHNICAL FIELDS SEARCHED (IPC) C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	12 February 2015	Culmann, J

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EPO FORM 1503 03.82 (P04C01)

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Application Number
EP 14 00 1599

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

[X] Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

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LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008075084 A1	26-06-2008	EP 2126022 A1	02-12-2009
		US 2010132741 A1	03-06-2010
		WO 2008075084 A1	26-06-2008

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Patent documents cited in the description

- US 5451244 A, R. Trowbridge **[0020]**
- US 5201930 A, W. Campbell **[0021]**
- WO 2010094985 A, Lomoskiy **[0021]**
- DE 19624982, Pfueller **[0022]**