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

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

(57) The present invention relates to the field of cleaners. In particular this invention relates to the use of oxidized humic acid compounds, its salts and derivatives or its mixtures, in cleaning 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. Cleaning compositions prepared by using oxidized humic acid, its salts and derivatives or mixtures thereof, are used as dishwasher, laundry and hard surface cleaning purposes among other capabilities.

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Description

FIELD OF THE INVENTION

[0001] This application relates to cleaning compositions.

[0002] Particularly this application relates to a new field of use of oxidized humic acid, its salts its derivatives and mixtures thereof.

[0003] More particularly this application relates to the use of alternative builder in cleaning compositions.

[0004] The field of present invention is the new use of oxidized humic acid compounds in detergent compositions.

[0005] To the present invention related cleaning compositions can be used in laundry, dishwashing, surface cleaning, cleaning of carpets, metal and ceramic surfaces and the like.

[0006] Hereinafter in the text the synonym "oxidized humic acid" will be standing for "oxidized humic acid , its salts, its derivatives and mixtures thereof" .

BACKGROUND OF THE INVENTION

[0007] 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.

[0008] 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. Surfactant surround dirt until it is dislodged from the boundary.

[0009] A surfactant can be a soap or a synthetic detergent. Soaps are made from animal fat and lye. They are alkali metal salts of long chain carboxylic acids. Soaps are precipitated with earth metal cations like Ca and Mg and loose their cleaning capabilities. Therefore its use is limited to personal hygiene due to their mildness.

[0010] Synthetic surfactants are of choice nowadays due to their relatively less sensitiveness to multivalent cations. However earth alkaline metal cations must be removed from washing water for synthetic surfactants as well to reveal their full surfactant capability.

[0011] Removal of earth alkaline metal cations are accomplished 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.

[0012] 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 agents and are 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.

[0013] 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 are accomplishing this by sequestration ; holding metal ions in solution or removing them from solution as insoluble material as precipitate. Builders provide a desirable level of alkalinity which aids in cleaning. They help emulsify oily or greasy soil by breaking them up to tiny globules and keep it from settling back on the cleaned surface.

[0014] Most commonly used builders ; phosphates and sodium citrate are common sequestering builders, sodium carbonate is precipitating builder and zeolite is ion exchange builder. Builders remove calcium ions present in the water by complexation or precipitation. Typical builders are sodium carbonate, complexation agents, soap and zeolites. One of the most common builder is sodium triphosphate , which is used on very large scale for this purpose.

[0015] 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.

[0016] Builders initially used in cleaner industry are polyphosphates which are stil in use. But due to environmental concerns related to overfertilizing of water and consuming oxygen in it 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 and remaining monomer residues.

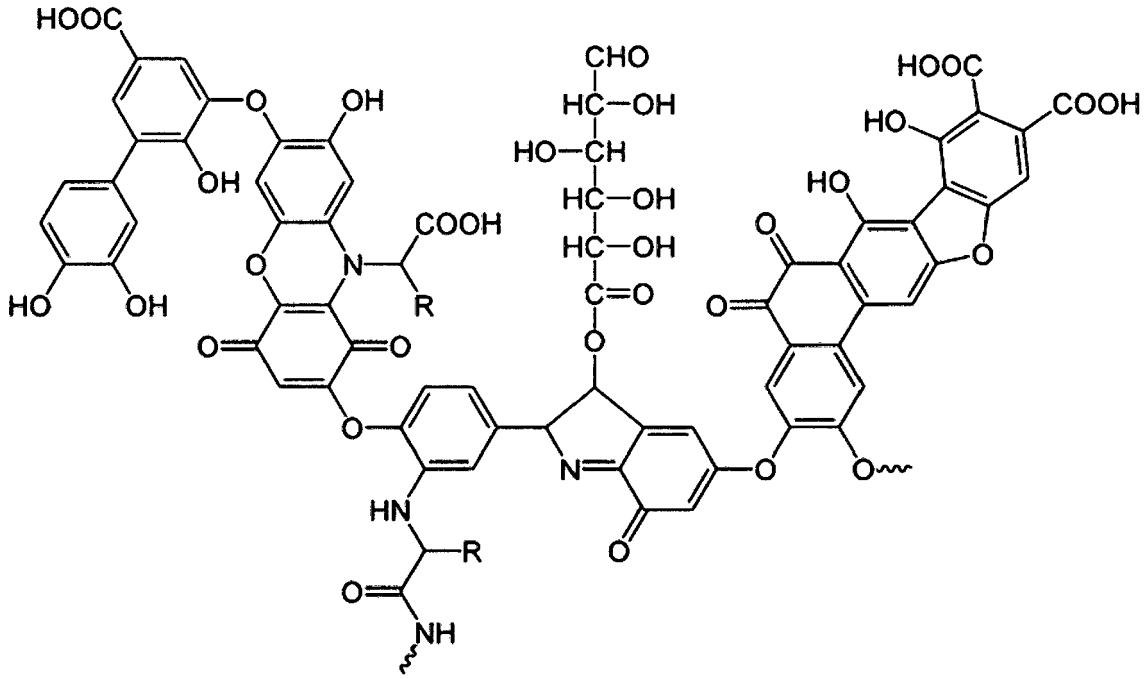
[0017] There still exist a need to have builder with high binding capacity, less environmental concern and prefferably of organic origin to eliminate actuel and future concerns.

[0018] 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 .

[0019] A typical humic substance is a mixture of many molecules having aromatic, phenolic, carboxylic substituents linked together .

[0020] Below is a typical structure of unmodified humic acid having a variety of components including phenol, quinone, catechol and sugar moieties.



[0021] 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.

[0022] Humic acid is commonly used as a soil supplement in agriculture, and less commonly as a human nutritional supplement.

[0023] Oxidized humid acid compounds are used in the technic as fertilizer, regeneration of polluted grounds, animal breeding and water regeneration mainly.

[0024] 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

[0025] 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.

[0026] 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.

[0027] There exist to date no usage of oxidized humic acid in cleaning compositions especially in detergent compositions more particularly in dishwasher, laundry and surface cleaner.

[0028] It is therefore an object of the present invention to provide alternative detergent builder that has no drawback of the marketed ones and superior to them.

DESCRIPTION OF DISCLOSURE

[0029] The present invention relates to a new use of oxidized humic acid.

[0030] 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.

[0031] The present inventor has discovered that by adding oxidized humic acid compounds to the cleaning compositions foaming and cleaning capacity has increased.

[0032] To the best of our knowledge oxidized humic acid is not used in cleaning compositions. There exist no commercially available cleaning composition product containing oxidized humic acid on the market.

[0033] 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 which is derivatized afterwards and its salts, and derivatized humic acid which is oxidized afterwards and its salts and mixtures thereof.

[0034] 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.

[0035] 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+} and Fe^{3+}. This capability is enhanced by oxidation of humic acid .

[0036] In the past no complex binding capability 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 is even superior to with sulphonic acid derivatized acrylic acid copolymer. Oxidized humic acid with 1350mg Ca ion binding capacity per gram has stronger complexation capability than any other commercially available builder currently as shown herewith below.

Comparison of Ca^{2+} Complex Binding Capacities of Builders:

[0037]

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

[0038] Calcium ion binding capacity in mg with respect to per gramm builder used in aqueous solutions is measured titrimetrically.

[0039] All formerly used builder compounds have their drawbacks such as polyphosphate, which are overfertilizing water sources. Polyacrylates are strong builders but due to their chemical origin some ecological reservations are still existing. Considering its builder strength, relatively small amounts of oxidized humic acid is needed which is both economically and environmentally advantageous.

[0040] The ideal builder should have strong earth alkaline metal cation capturing capacity, should be of organic origin and ecologically acceptable. By the search of builder with such capabilities 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.

[0041] 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.

[0042] 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 which are 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 than commercially already used builders. It is a good working , organic , with less ecological concern builder compound thus superior to already existing builders.

[0043] 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.

[0044] The presence of carboxylate and phenolate groups give humic acid the ability to form complexes with ions such as Mg2+, Ca2+, Fe2+, Fe3+.

[0045] This capability is enhanced by oxidation of humic acid , therefore oxidized humic acid is superior to the humic acid as builder. We assume that additional oxidized phenol and carboxylategroups formed during oxidizing procedure enhance the complexation capability . Our measurements 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 cleaning compositions regarding cleaning capabilities. We assume that oxidized humic acid has relatively more phenolate, carboxylate groups which are participating by complexation process.

[0046] 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.

[0047] Detergents are surfactants with cleaning properties in dilute solutions. To enhance the cleaning capability water hardness is to be reduced with water softeners which are builders. Water hardness is caused by the presence of earth alkali metal cations like Mg+ and Ca+ in water. In presence of these cations surfactants cannot reveal their full capability of encapsulating the dirt and removing it from the surface. Because earth alkaline metal cations build nonsoluble salts with surfactants and become inefficient. Therefore these cations are to be removed from water. This task is accomplished by adding builders to the cleaning compositions.

[0048] 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.

[0049] 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 .

[0050] The need to have builder with high binding capacity, less environmental concern and prefferably of organic origin to eliminate actuel and future concerns is fullfilled with the present invention.

[0051] According to first broad form of the present invention, there is provided cleaning compositions comprising oxidized humic acid, its salts and derivetives and their mixtures.

[0052] Oxidized humic acid used in cleaning 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 cleaning compositions have same performance, durability, foaming capacity, cleaning capacity and stability .The oxidized humic acid containing compositions of the present invention are equal or superior to the commercially available cleaning composition products.

[0053] In present invention used oxidized humic acid amounts 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 cleaning compositions of the present invention as well and last without degradation or negative effects for adequate time period .

[0054] According to present invention oxidised humic acid is used in fabric care compositions, dish cleaning compositions, home care compositions, personal care compositions in hard surface cleaning compositions

[0055] Oxidized humic acid of the present invention is used in cleaning compositions in liquid, solid and semisolid state as well. The application forms are including cream, gel, lotion, solution ,colloid ,suspension, powder, granul, tablet and capsul among other possibilities.

[0056] 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.

[0057] 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.

[0058] In the present invention ,oxidized humic acid is typically used in the form of aqueous solutions. Alternatively said oxidized humic acid is used in solid form such as powder or granule .

[0059] Typically, cleaning 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.

[0060] The amounts of oxidized humic acid used in the cleaning compositions according to the present invention may be varied depending on the use purpose and desired concentrations. The cleaning compositions of the present invention may include additional additives known in the art such as surfactants among others. Surfactants suitable for such use may be of anionic, cationic, nonionic and amphotheric nature .

[0061] A cleaning 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 cleaning composition of the present

invention.

[0062] Alternatively a cleaning composition of the present invention is prepared by mixing oxidized humic acid and surfactants and other desirable ingredients necessary in dry state to obtain solid cleaning composition of the present invention.

[0063] The present invention have applications on cleaning of fabrics, clothes, carpets, dishes, ceramic, glass, plastic, wood and metal surfaces and comparable stuffs and surfaces.

[0064] 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 1: Preparation of Oxidized Humic Acid Containing Laundry Composition

[0065]

Linear alkyl benzene sulfonic acid Sodium salt	7.3 %
Caustic soda	2.3 %
Oxidized humic acid	0.1 %
Water	as required to complete

[0066] Ingredients are mixed in water to obtain a solution.

[0067] The skilled person of the field is familiar with the ranges used in detergent formulations and further necessary ingredients may be added as needed.

Comparative Example 1 : Preparation of EDTA Containing Laundry Composition

[0068] Humic acid is replaced with commonly used complexation agent ethylene diamine tetra acetic acid tetrasodium salt Na4EDTA

Linear alkyl benzene sulfonic acid Sodium salt	7.3 %
Caustic soda	2.3 %
Na4EDTA	0.1 %
Water	as required to complete

Comparative Washing Tests

[0069] For the assessment of the effectiveness of oxidized humic acid containing compositions in comparison to oxidized humic acid substituted comparative compositions, washing tests with selected stains are carried out in the same conditions.

[0070] Tests are conducted via Scheffe Panel Score Test.

[0071] Accordingly, cotton fabrics stained with selected stains are cut equally . 3kg of stained cotton fabric is put in washing water having water hardness corresponding to 150ppm calcium ion Ca2+. 100g of oxidized humic acid containing solution of Example 1 is added and washed in automatic washing mashine at 40C and dried.

[0072] Same procedure is applied to 100g of Na4EDTA containing Comparative Example 1 solution .

[0073] Afterwards stain removing capacities of both washings are compared by eye sighting according to Scheffe Panel Score Units on the following scale:

0 No difference
1 I think this is better
2 I know this is a little better
3 I know this is much better
4 I know this is very much better

Comparative Washing Results of Example 1 and Comparative Example 1 Compositions of selected stains

Stains Comparative Scheffe values of Example 1/Comparative example 1

[0074]

foundation	2.13
caffee	0.63
barbecau sauce	2.00
mud	2.65
Salad sauce	1.63
Ketchup	2.0

[0075] As can be seen from comparative washing test results oxidized humic acid containing cleaning compositions are at least as good as comparative cleaning compositions, regarding cleaning capabilities, even better.

EXAMPLE 2: Preparation of Oxidized Humic Acid Containing Dishwashing Composition

[0076]

Linear alkyl benzene sulfonic acid sodium salt	14.6 %
Caustic soda	3.8 %
Oxidized humic acid	0.2 %
Water	as required to complete

[0077] Ingredients are mixed in water to obtain a solution .

[0078] The skilled person of the field is familiar with the ranges used in detergent formulations and further necessary ingredients can be added as needed.

Comparative Example 2: Preparation of EDTA Containing Dishwashing Composition

[0079] Humic acid is replaced with commonly used complexation agent EDTA having same functionality.

Linear alkyl benzene sulfonic acid sodium salt	14.6%
Caustic soda	3.8 %
EDTA	0.05 %
Water	as required to complete

Comparative Washing Tests

[0080] 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.

[0081] **No oil tests :** are conducted with water containing 0.5g of example 2 and comparative example 2 solution each in 2L water.

[0082] **Oil tests :** with 4 , 8 and 12 drops of oil each are conducted with 1g of example 2 and comparative example 2 solution each in 2L water.

[0083] In tests used water is containing 450 ppm calcium ion Ca2+ and test temperature is 25C.

[0084] Test sample is prepared by adding 1g cleaning composition in 2 Liter of water, adding oil drops and taking 200ml from this mixture in a glass cylinder having 4 cm inner diameter and 70cm of height. Glass cylinder is stoppered and revolved with 40 revolution/minute for 3 minutes. After stopping 10 seconds waited and height of foam is measured.

[0085] Measured foam heights are in proportional relationship to the cleaning capacity of respective dishwasher compositions.

Comparative Dish Washing Test Results

[0086]

Soil	Example 2 (foam height in cm)	Comparative Example 2 (foam heigth in cm)
No oil	26	21
4 drops of oil	26	18
8 drops of oil	22	8
12 drops of oil	8	4

[0087] As can be seen from tests, compositions containing oxidized humic acid are superior with respect to foaming capacity to non oxidized humic acid containing corresponding compositions, which is an indication of washing strength in dish washing composition.

Claims

1. Use of oxidized humic acid, its salts and derivatives or mixtures thereof, in cleaning compositions.
2. A cleaning composition according to claim 1, wherein cleaning composition is in liquid form.
3. A cleaning composition according to claim 1, wherein cleaning composition is in solid or semisolid form.
4. A cleaning composition according to claim 1, wherein cleaning composition is a fabric care composition, a dish cleaning composition, a home care composition, a personal care composition or a hard surface cleaning composition.
5. A cleaning composition according to claim 1, wherein cleaning composition is a dishwasher composition.
6. A cleaning composition according to claim 1, wherein cleaning composition is a laundry composition.
7. A cleaning composition according to claim 1, wherein cleaning composition is a hard surface cleaning composition.
8. A cleaning composition according to claim 1, comprising oxidized humic acid its salts and derivatives or mixtures thereof in liquid form.
9. A cleaning composition according to claim 1, comprising oxidized humic acid its salts and derivatives or mixtures thereof in solid or semisolid form.
10. A cleaning composition according to preceding claims, which further comprises a surfactant or surfactants.
11. An oxidized humic acid its salts and derivatives or mixtures thereof for use in the manufacture of a cleaning composition.
12. A cleaning composition as claimed in any preceding claims, having application on cleaning surfaces.
13. A cleaning composition as claimed in any preceding claims, having application preferably on fabrics, clothes, textiles, dishes, glass, metal, ceramic and carpets.

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

1. Use of oxidized humic acid, its salts and derivatives or mixtures thereof, in cleaning compositions.
2. A cleaning composition according to claim 1, wherein cleaning composition is in liquid form.
3. A cleaning composition according to claim 1, wherein cleaning composition is in solid or semisolid form.

4. A cleaning composition according to claim 1, wherein cleaning composition is a fabric care composition, a dish cleaning composition, a home care composition, a personal care composition or a hard surface cleaning composition.

5. A cleaning composition according to claim 1, wherein cleaning composition is a dishwasher composition.

6. A cleaning composition according to claim 1, wherein cleaning composition is a laundry composition.

7. A cleaning composition according to claim 1, wherein cleaning composition is a hard surface cleaning composition.

8. A cleaning composition according to claim 1, comprising oxidized humic acid its salts and derivatives or mixtures thereof in liquid form.

9. A cleaning composition according to claim 1, comprising oxidized humic acid its salts and derivatives or mixtures thereof in solid or semisolid form.

10. A cleaning composition according to preceding claims, which further comprises a surfactant or surfactants.

11. An oxidized humic acid its salts and derivatives or mixtures thereof for use in the manufacture of a cleaning composition.

12. A cleaning composition as claimed in any preceding claims, having application on cleaning surfaces.

13. A cleaning composition as claimed in any preceding claims, having application preferably on fabrics, clothes, textiles, dishes, glass, metal, ceramic and carpets.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 00 1600

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	15 December 2014	Pfannenstein, Heide

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 14 00 1600

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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