(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 623 455 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
18.03.2020 Bulletin 2020/12

(21) Application number: **19196827.0**

(22) Date of filing: **11.09.2019**

(51) Int Cl.:
C11D 1/65 *(2006.01)* ***C11D 3/04*** *(2006.01)*
C11D 3/34 *(2006.01)* ***C11D 3/37*** *(2006.01)*
C11D 3/40 *(2006.01)* *C11D 1/22* *(2006.01)*
C11D 1/62 *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **12.09.2018 IT 201800008545**

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(54) **DESCALING FORMULATION FOR WCS**

(57) A descaling formulation is described for application on the surface of bathroom fixtures, preferably for application on WCs.

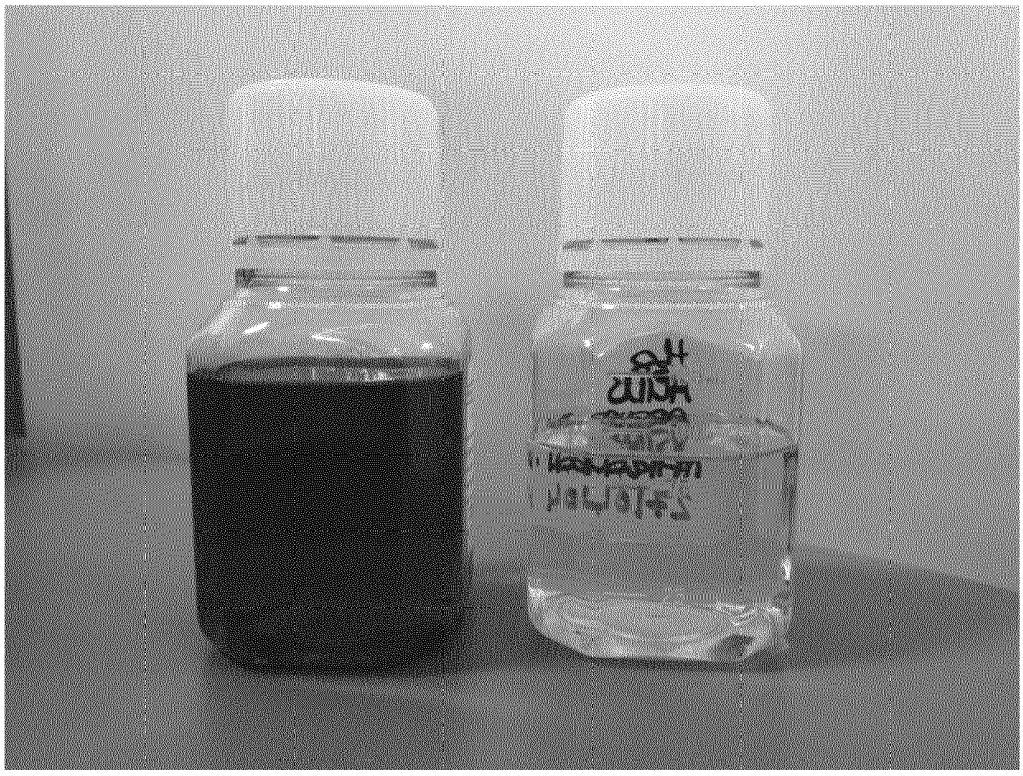

Figure 1

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Description

[0001] The present invention relates to a descaling formulation for application in WCs.

[0002] The descaling products for WCs that currently exist are products based on hydrochloric acid and are almost always formulated with rheology modifying systems to ensure a greater effectiveness on the vertical surfaces of the WC.

[0003] The flowing speed on the ceramic walls of the WC must in fact be reduced, thus increasing the contact time of the product with the limestone and thus obtaining the removal of a greater quantity of encrustation.

[0004] Traditional viscosifying systems are characterized by the presence of ethoxylated fatty amines and ethoxylated amine oxides and have a strong tendency to yellow under extreme pH conditions caused by the presence in the formulations of strong mineral acids, such as hydrochloric acid. Furthermore, over time, these viscosifying agents give the descaling formulation a dark yellow to reddish colour, and in order to remedy this colouring and obtain a product having a more attractive colour for the consumer, and above all a colour that does not change over time, blue or green dyes are added, that are capable of masking the dark yellow/red colouring.

[0005] Also as a result of their viscosity, the resulting formulations however tend to leave a very persistent colour on the glazed surface of bathroom fixtures. The complete elimination of this product residue and therefore colour, requires various flushings of wastewater with a consequent additional water consumption.

[0006] This has given rise to the need for a WC cleaning product, a descaler, which does not leave coloured residues on the surface of the WC after use. On the one hand, in fact, as mentioned above, it is essential to try to reduce the amount of water used to a minimum, thus avoiding water flushings only for the elimination of colour residues: this requirement is of primary importance within a global need for minimizing water waste; the expression of discontent by the users of descaling products due to the non-perfect removal of the product from the surface of the WC, with the consequent formation of coloured spots that disappear only after several water flushings, has led, on the other hand, to the search for a descaling formulation for WCs that does not have the above-mentioned drawbacks.

[0007] The simplest solution for solving the problem of colour residues, i.e. eliminating the dye from the formulation, is not feasible in fact, due to the poor aesthetic effect of the mixture obtained: yellow is not a desirable colour for this category of products, as it does not convey a sense of hygiene to the end user.

[0008] Another way of avoiding colour deposits on the walls of WCs is to use a white formulation that is then camouflaged with the ceramic of the WC. A similar solution must, however, take into account the inherent difficulty in covering a base tending to yellow: with time, the white formulation in any case tends to turn from white to beige and even to brown.

[0009] Furthermore, even if the end-user were to accept a colouring of the product that changes over time towards yellow/beige, it would in any case be extremely difficult to identify a pigmenting system capable of giving the formulation a white colour and resisting pH values lower than 1.

[0010] The most common white pigment, titanium dioxide, is not capable of withstanding the pH conditions of descaling products of WCs for long, and it dissolves completely in a few days. The fate of all the other mineral fillers (gypsum, carbonates, silicates) that can be used for the same purpose is similar.

[0011] The objective of the present invention is therefore to identify a descaling formulation for WC applications which overcomes the drawbacks of the formulations of the state of the art.

[0012] This and further objectives that will appear evident from the text of the present patent application have been achieved by the descaling formulation for WCs according to the present invention.

[0013] The present invention therefore relates to a descaling formulation for WCs characterized in that it comprises or consists of:

a) a viscosifying agent consisting of a cationic surfactant and an anionic surfactant selected, respectively, from quaternary ammonium salts and salts of strong aromatic organic acids;

b) a pigmenting agent consisting of, or comprising a colloidal aqueous dispersion of an inert organic polymer consisting of a styrene-acrylic copolymer, having an average molecular weight ranging from 300,000 to 800,000 Daltons, preferably equal to 500,000 Daltons, and a concentration of solids ranging from 20 to 50% by weight, preferably equal to 35% by weight; and

c) a descaling agent selected from hydrochloric acid, phosphoric acid, sulfuric acid or sulfamic acid, preferably hydrochloric acid.

[0014] More specifically, the quaternary ammonium salt can be selected from salts having general formula (I)

$$R_1R_2R_3R_4N^+\ Cl^- \qquad (I)$$

wherein R_1, R_2, R_3, R_4, the same as or different from each other, are alkyl or alkyl-aryl groups having a number of carbon atoms ranging from 1 to 30.

[0015] The quaternary ammonium salt is preferably selected from tallow-trimethylammonium chloride or hexadecylt-

rimethyl-ammonium chloride.

[0016] Tallow is a product of animal origin, consisting of a mixture of triglycerides of C_{14}-C_{18}, saturated and unsaturated, long-chain fatty acids.

[0017] The salt of a strong aromatic organic acid is preferably selected from sulfonates having general formula (II)

$$R_1\text{-Ar-}SO_3Na \qquad (II)$$

wherein R_1 is an alkyl group having a number of carbon atoms ranging from 1 to 30 and Ar is a phenyl group.

[0018] The salt of the strong aromatic organic acid is more preferably selected from dodecylbenzenesulfonic acid sodium salt, 4-methylbenzenesulfonic acid sodium salt and relative mixtures.

[0019] The weight ratio of quaternary ammonium salts/salts of strong aromatic organic acids ranges from 1,000:1 to 10:1, preferably from 5:1 to 4:1.

[0020] The viscosifying agent is present in the formulation according to the present invention in a quantity ranging from 0.1 to 10% by weight: more specifically, the cationic surfactant is present in a quantity ranging from 0.09 to 9% by weight and the anionic surfactant in a quantity ranging from 0.01 to 1% by weight with respect to the total weight of the descaling formulation.

[0021] The pigmenting agent is preferably a colloidal aqueous dispersion of an inert organic polymer, namely a styrene-acrylic copolymer, obtained by the polymerization of styrene and acrylic/methacrylic acid, having an average molecular weight ranging from 300,000 to 800,000 Daltons, preferably equal to 500,000 Daltons, and a concentration of solids ranging from 20 to 50% by weight, preferably equal to 35% by weight. The molecular weight is a number average molecular weight.

[0022] The pigmenting agent is present in the formulation according to the present invention in a quantity ranging from 0.01 to 5% by weight with respect to the total weight of the descaling formulation.

[0023] The descaling agent is selected from hydrochloric acid, phosphoric acid, sulfuric acid or sulfamic acid; it is preferably hydrochloric acid, more preferably aqueous hydrochloric acid at 33% by weight.

[0024] The descaling agent is present in the formulation according to the present invention in a quantity ranging from 0.1 to 60% by weight, in the case of HCl at 33% by weight.

[0025] The formulation according to the present invention may optionally also comprise a perfuming agent or fragrance in a quantity ranging from 0.01 to 1% by weight with respect to the total weight of the descaling formulation.

[0026] The descaling formulation for WCs according to the present invention preferably comprises or consists of

a) a viscosifying agent consisting of tallow-trimethylammonium chloride or hexadecyltrimethyl-ammonium chloride and a mixture of dodecylbenzenesulfonic acid sodium salt and 4-methyl-benzenesulfonic acid sodium salt, in a weight ratio quaternary ammonium salt /mixture of sodium salts ranging from 5:1 to 4:1;
b) a pigmenting agent consisting of a colloidal aqueous dispersion of a styrene-acrylic copolymer, having an average molecular weight of 500,000 Daltons and a concentration of solids equal to 35% by weight; and
c) a descaling agent which is aqueous hydrochloric acid at 33% by weight.

[0027] The descaling formulation for WCs according to the present invention more preferably consists of:

a) a viscosifying agent consisting of 1.5% by weight of tallow-trimethylammonium chloride or hexadecyl-trimethyl-ammonium chloride and 0.35% by weight of a mixture of dodecylbenzene sulfonic acid sodium salt and 4- methyl-benzenesulfonic acid sodium salt;
b) a pigmenting agent consisting of 0.6% by weight of a colloidal aqueous dispersion of a styrene-acrylic copolymer, having an average molecular weight of 500,000 Daltons and a concentration of solids equal to 35% by weight;
c) 41% by weight of aqueous hydrochloric acid at 33% by weight, as descaling agent;
d) 0.1% by weight of a fragrance,

the complement to 100 consisting of water.

[0028] The weight percentages always refer to the total weight of the descaling formulation for WCs according to the present invention.

[0029] A further object of the present invention therefore relates to the use of the descaling formulation according to the present invention for application on the surface of bathroom fixtures, preferably for application on the surface of WCs, as a descaling agent and detergent.

[0030] The technical difficulties previously indicated and typical of the formulations of the state of the art or possible alternative solutions to the technical problem considered, have very surprisingly been solved by the descaling formulation for WCs according to the present invention characterized by the presence of a particular viscosifying system with a high resistance to yellowing, combined with a pigmenting system resistant to low pH values, all without jeopardizing the

dissolution properties of the limestone of a traditional descaling formulation, i.e. based on hydrochloric acid or, more generally, on strong mineral acids.

[0031] The particular viscosifying system of the formulation according to the present invention is based on the combination of a cationic surfactant such as a quaternary ammonium salt and an anionic surfactant, deriving from a strong aromatic organic acid.

[0032] Quaternary ammonium salts are compounds known for their high chemical stability in a very wide pH range: more specifically, the stability is particularly high in an acid environment, whereas with extremely alkaline pHs degradation by Hofmann elimination may occur. The chemical stability evidently also results in a lower tendency towards yellowing, a phenomenon mainly caused by the presence of free amines.

[0033] The micelles that are formed in the presence of the cationic surfactant can be disturbed by the addition of a suitable hydrotrope, with the formation of rod-like micellar species and a simultaneous increase in the viscosity. It should in fact be borne in mind that a descaling formulation for WCs must be characterized by specific viscosity characteristics in order to be able to function and remove encrustations efficiently.

[0034] As the environment of the formulation is strongly acidic, a hydrotropic agent had to be identified among the salts of very strong acids that could not be protonated with the consequent formation of insoluble species.

[0035] Salts of carboxylic acids and organic phosphates were therefore excluded, whereas sulfates, theoretically excellent candidates, showed a tendency towards hydrolysis which made their use extremely non-recommendable.

[0036] Sulfonates, and in particular the sodium salt of dodecylbenzenesulfonic acid, surprisingly proved to be particularly effective.

[0037] It is important however to operate with the dosages defined above, in order to avoid the precipitation of species deriving from the formation of ionic pairs between oppositely charged surfactants.

[0038] Although the viscosifying system according to the present invention reaches a lower viscosity with respect to the traditional formulations based on ethoxylated amines, it guarantees in any case a correct adhesion of the descaling formulation according to the present invention to the walls of the WC and consequently an effective descaling effect.

[0039] It has also been surprisingly found that the descaling formulation according to the present invention can be characterized by a white pigmentation by the addition of a colloidal dispersion of inert organic polymers. This dispersion proved to be surprisingly stable even at a pH lower than 1.

[0040] More specifically, it is a colloidal aqueous dispersion of a styrene-acrylic copolymer which can be assimilated according to the INCI nomenclature with a polystyrene, i.e. having chemical properties similar to those of a polystyrene.

[0041] A fragrance can also be added to the aqueous mixture of hydrochloric acid, cationic surfactant, anionic surfactant and polystyrene dispersion, with a slight drop in the final viscosity.

[0042] The descaling formulation for WCs according to the present invention thus obtained has no performance differences, expressed as the quantity of calcium carbonate removed, with respect to traditional descaling products containing amines/ ethoxylated amine oxides and dyes.

[0043] It has the undoubted advantage, however, of keeping its white colouring (as shown in figures 1 and 2 discussed in the following examples) almost constant and not requiring unnecessary water flushings to remove the colour residues from the walls of the WC with a consequent significant water saving.

[0044] The following examples are provided for purely illustrative purposes.

[0045] In all the examples provided hereunder, the descaling formulation was prepared as follows:

- a mixer was loaded with all the deionized water necessary for the process, at room temperature;
- hydrochloric acid at 33% by weight was then added under stirring and under a suction hood;
- the cationic surfactant was subsequently added, depending on the composition, stirring until complete mixing;
- the anionic surfactant was then added in solid form, adding it slowly under stirring, until complete dissolution;
- the solution of styrene-acrylic inert polymer was subsequently added, stirring until a white homogeneous dispersion had been obtained;
- the fragrance was finally added, mixing for 15 minutes in order to obtain a complete dispersion of the oil in the aqueous phase.

[0046] In the examples, nine gel tablets were tested, whose qualitative and quantitative compositions are indicated in table 1 below.

Example 1

[0047] Base composition of the reference product of the state of the art, containing HCl, amines and ethoxylated amine oxides:

Composition in raw materials	% (w/w)
Demineralized water	57.00000
Hydrochloric acid 33%	41.00000
Ethoxylated oleic amine Trade-name: Arlypon VPC, Basf	1.50000
Unsaturated ethoxylated C_{16}-C_{18} and C_{18} alcohols, Trade-name: Arlypon VPC, Basf	0.50000

[0048] The product Arlypon VPC is a mixture of ethoxylated oleic amine and ethoxylated unsaturated C_{16}-C_{18} and C_{18} alcohols, in a 3: 1 weight ratio.

Example 2

[0049] Base composition of the formulation according to the present invention containing HCl, quaternary ammonium salts and sulfonates:

Composition in raw materials	%(w/w)
Demineralized water	57.15000
Hydrochloric acid 33%	41.00000
tallow-trimethylammonium chloride	1.50000
Mixture of dodecylbenzenrsulfonic sodium salt and 4-methyl-benzenesulfonic acid sodium salt Trade-name: Marlon ARL, Sasol	0.35000

Example 3

[0050] Base composition of the formulation according to the present invention containing HCl, quaternary ammonium salts and sulfonates:

Composition in raw materials	%(w/w)
Demineralized water	57.15000
Hydrochloric acid 33%	41.00000
hexadecyltrimethylammonium chloride	1.50000
Mixture of dodecylbenzenrsulfonic sodium salt and 4-methyl-benzenesulfonic acid sodium salt Trade-name: Marlon ARL, Sasol	0.35000

Example 4

[0051] Final formulation according to the present invention with the base formulation of Example 2:

Composition in raw materials	%(w/w)
Demineralized water	56.45000
Hydrochloric acid 33%	41.00000
tallow-trimethylammonium chloride	1.50000
Polystyrene dispersion	0.60000
Mixture of dodecylbenzenrsulfonic sodium salt and 4-methyl-benzenesulfonic acid sodium salt Trade-name: Marlon ARL, Sasol	0.35000

(continued)

Composition in raw materials	%(w/w)
Fragrance	0.10000

Example 5

[0052] Final formulation of the reference product of the state of the art, containing the traditional base of Example 1:

Composition in raw materials	%(w/w)
Demineralized water	56.89000
Hydrochloric acid 33%	41.00000
Ethoxylated oleic amine Trade-name: Arlypon VPC, Basf	1.50000
Unsaturated ethoxylated C16-18 and C18alcohols, Trade-name: Arlypon VPC, Basf	0.50000
Fragrance	0.10000
Dyes	0.01000

Example 6

[0053] The physico-chemical characteristics of the products of the previous examples 1-5 are indicated in the Table 1 below:

Table 1

Product	Titre HCl (% w/w)	Density (g/mL)	Viscosity (cPs)
Example 1	14.6	1.067	80
Example 2	14.7	1.064	46
Example 3	14.2	1.068	53
Example 4	13.7	1.061	37
Example 5	13.7	1.067	78

[0054] The acid titre is determined by classical volumetric titration with a standard solution of 0.1N NaOH and a phenolphthalein indicator.

[0055] The density is measured by means of a Mettler DA - 100 M microdensometer, injecting the sample directly into the U-tube of the instrument, after calibration with demineralized water.

[0056] The viscosity of the products is measured by a Ford cup with a 2 mm diameter hole, completely filling the instrument with the fluid under examination and measuring the time taken for its total emptying.

[0057] The following performance tests were then carried out comparing the final formulation of Example 4 according to the present invention and the final formulation of Example 1 according to the state of the art.

Performance tests

[0058] The descaling power of a WC cleaner was evaluated with two performance tests suitable for measuring how much $CaCO_3$ (limestone) is consumed over time.

Test 1: Marble cube test, which involves immersing a cube of white Carrara marble, having a known weight and size, in the descaling liquid for certain times (5, 30 and 60 minutes). After careful rinsing and drying of the cube, its weight is measured to determine the percentage of $CaCO_3$ consumed by the product.

Test 2: Marble slab test, which involves immersing a slab of white Carrara marble, having a known weight and size, in the descaling liquid for a time equal to 10 seconds; the slab is then placed in a vertical position on a grid to allow

the liquid to flow along the surface of the marble for a period of 10 minutes. After careful rinsing and drying of the slab, its weight is measured to determine the percentage of $CaCO_3$ consumed by the product. For both tests, the highest percentage of $CaCO_3$ removed corresponds to the best performance of the product.

[0059] The results of Test 1, performed on a marble cube, for the formulation of Example 4 in comparison with the formulation of Example 5, are indicated in Table 2:

Table 2

Product	Quantity of $CaCO_3$ removed (%)		
	5 minutes	30 minutes	60 minutes
Example 4	1.88	8.69	14.18
Example 5	1.5	6.5	13.8

[0060] The results of Test 2, performed on a marble slab, for the formulation of Example 4 in comparison with the formulation of Example 5, are indicated in Table 3:

Table 3

Product	Quantity of $CaCO_3$ removed (%) in 10 minutes
Example 4	0.245
Example 5	0.204

[0061] From the data shown in Tables 2 and 3, a slight improvement or at least a substantial performance identity between a descaling formulation according to the state of the art and a descaling formulation according to the present invention is also evident.

Example 7

[0062] The colour stability over time was then tested with respect to the base formulation according to the state of the art of Example 1 and the base formulation according to the present invention of Example 2, and for the final descaling formulation of Example 4 according to the present invention.

[0063] Figure 1 shows the two samples, the base formulation according to the state of the art of Example 1 (on the left) and the base formulation according to the present invention of Example 2 (on the right), stored at 40°C for three months: the different tendency towards yellowing of the base is evident. The base formulation according to the state of the art of Example 1 has a substantially brown colour, whereas the base formulation according to the present invention of Example 2 is still completely transparent.

[0064] Figure 2 shows the descaling formulation according to the present invention of Example 4, stored at 5°C (left), 20°C (center) and 40°C (right) for three months: the colour stability of the product is evident, which is white and remains white even after storage for three months at 40°C.

Claims

1. A descaling formulation for WCs **characterized in that** it comprises or consists of

a) a viscosifying agent consisting of a cationic surfactant and an anionic surfactant selected, respectively, among quaternary ammonium salts and salts of strong aromatic organic acids, the weight ratio of quaternary ammonium salts/salts of strong aromatic organic acids preferably ranging from 1,000: 1 to 10:1, even more preferably from 5:1 to 4:1;
b) a pigmenting agent consisting of, or comprising a colloidal aqueous dispersion of an inert organic polymer consisting of a styrene-acrylic copolymer, having an average molecular weight ranging from 300,000 to 800,000 Daltons, preferably equal to 500,000 Daltons, and a concentration of solids ranging from 20 to 50% by weight, preferably equal to 35% by weight; and
c) a descaling agent selected from hydrochloric acid, phosphoric acid, sulfuric acid or sulfamic acid, preferably hydrochloric acid.

2. The formulation according to claim 1, wherein the quaternary ammonium salt can be selected from salts having general formula (I)

$$R_1R_2R_3R_4N^+ Cl^- \qquad (I)$$

wherein R_1, R_2, R_3, R_4, the same as or different from each other, are alkyl or alkyl-aryl groups having a number of carbon atoms ranging from 1 to 30, and is preferably selected from tallow-trimethylammonium chloride or hexadecyltrimethylammonium chloride.

3. The formulation according to one or more of the previous claims, wherein the salt of a strong aromatic organic acid is selected from sulfonates having general formula (II)

$$R_1\text{-Ar-}SO_3Na \qquad (II)$$

wherein R_1 is an alkyl group having a number of carbon atoms ranging from 1 to 30 and Ar is a phenyl group, preferably selected from dodecylbenzenesulfonic acid sodium salt, 4-methylbenzenesulfonic acid sodium salt and relative mixtures.

4. The formulation according to one or more of the previous claims, wherein the viscosifying agent a) is present in a quantity ranging from 0.1 to 10% by weight, the cationic surfactant being present in a quantity ranging from 0.09 to 9% by weight and the anionic surfactant in a quantity ranging from 0.01 to 1% by weight with respect to the total weight of the descaling formulation.

5. The formulation according to one or more of the previous claims, wherein the pigmenting agent is a colloidal aqueous dispersion of an inert organic polymer, namely a styrene-acrylic copolymer, having an average molecular weight equal to 500,000 Daltons, and a concentration of solids equal to 35% by weight, in a quantity ranging from 0.01 to 5% by weight with respect to the total weight of the descaling formulation.

6. The formulation according to one or more of the previous claims, wherein the descaling agent is selected from hydrochloric acid, phosphoric acid, sulfuric acid or sulfamic acid, preferably hydrochloric acid, more preferably aqueous hydrochloric acid at 33% by weight.

7. The formulation according to one or more of the previous claims, wherein the descaling agent is aqueous hydrochloric acid at 33% by weight in a quantity ranging from 0.1 to 60% by weight.

8. The formulation according to one or more of the previous claims, further comprising a perfuming agent or fragrance in a quantity ranging from 0.01 to 1% by weight with respect to the total weight of the descaling formulation.

9. The formulation according to one or more of the previous claims, which comprises or consists of

a) a viscosifying agent consisting of tallow-trimethylammonium chloride or hexadecyltrimethyl-ammonium chloride and a mixture of dodecylbenzenesulfonic acid sodium salt and 4-methyl-benzenesulfonic acid sodium salt, in a weight ratio quaternary ammonium salt/mixture of sodium salts ranging from 5:1 to 4:1;
b) a pigmenting agent consisting of a colloidal aqueous dispersion of a styrene-acrylic copolymer, having an average molecular weight of 500,000 Daltons and a concentration of solids equal to 35% by weight; and
c) a descaling agent which is aqueous hydrochloric acid at 33% by weight .

10. The formulation according to one or more of the previous claims, which consists of

a) a viscosifying agent consisting of 1.5% by weight of tallow trimethylammonium chloride or hexadecyl-trimethylammonium chloride and 0.35% by weight of a mixture of dodecylbenzene sulfonic acid sodium salt and 4-methyl-benzenesulfonic acid sodium salt;
b) a pigmenting agent consisting of 0.6% by weight of a colloidal aqueous dispersion of a styrene-acrylic copolymer, having an average molecular weight of 500,000 Daltons and a concentration of solids equal to 35% by weight;
c) 41% by weight of aqueous hydrochloric acid at 33% by weight, as descaling agent;
d) 0.1% by weight of a fragrance,

the complement to 100 consisting of water.

11. Use of the descaling formulation according to one or more of the claims from 1 to 10, for application on the surface of bathroom fixtures, preferably for application on the surface of WCs, as descaling agent and detergent.

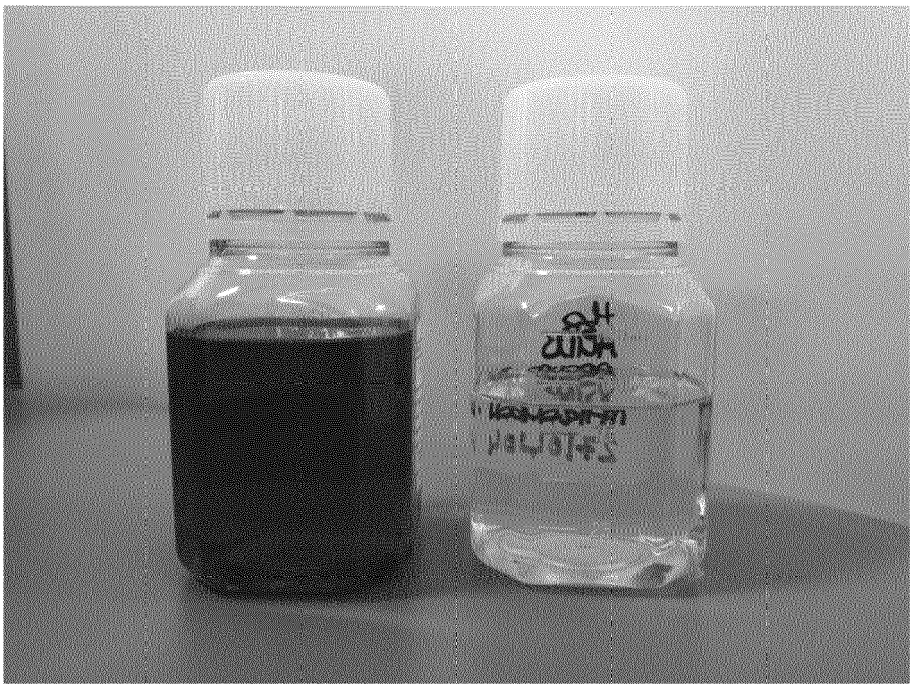

Figure 1

Figure 2

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EUROPEAN SEARCH REPORT

Application Number
EP 19 19 6827

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	EP 0 832 964 A1 (PROCTER & GAMBLE [US]) 1 April 1998 (1998-04-01) * page 1, line 5 - page 2, line 23 * * page 5, lines 22-41 * * page 7, line 49 - page 8, line 1 * * claims; examples *	1-11	INV. C11D1/65 C11D3/04 C11D3/34 C11D3/37 C11D3/40
A	GB 2 073 233 A (ARROW CHEM LTD) 14 October 1981 (1981-10-14) * page 2, lines 15-45; claims *	1-11	ADD. C11D1/22 C11D1/62
A	WO 99/27066 A1 (PROCTER & GAMBLE [US]) 3 June 1999 (1999-06-03) * page 1, lines 1-18 * * page 14, lines 6-11 * * claims; examples *	1-11	

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	7 November 2019	Péntek, Eric

CATEGORY OF CITED DOCUMENTS

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82