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(54) Solid product with scale-removing and anti-algae effect for sanitary fixtures and process for its preparation

(57) The present invention relates to a solid product with scale-removing and anti-algae effect for sanitary fixtures, comprising sulfamic acid, one or more surfactants and one or more binders. The invention also relates to a use of the product described herein as scale remover and anti-algae product for treating sanitary fixtures. The present invention also relates to a process for preparing the product described herein.

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Description

[0001] The present invention relates to a scale-removing and anti-algae product, to a use thereof for treating sanitary fixtures, and to a process for preparing such product.

[0002] One of the problems that usually occurs in sanitary fixtures such as toilet bowls or cisterns is the formation of scale. The term "scale" is used to reference deposits of calcium carbonate ($CaCO_3$) which form solid accumulations on the surfaces of metals, ceramic or plastics in contact with water or humidity and shorten the life and durability of the sanitary fixtures. The formation of scale, in addition to being unsightly, leads to a shorter life of the sanitary fixtures and moreover is unsanitary, since scale deposits constitute a medium for the formation of bacterial colonies.

[0003] In order to solve this problem, different products with an anti-scale action have been devised. These products can include those based on acids in liquid form, for example hydrochloric acid and hydrofluoric acid, alone or in combination with other acids. However, these acids are highly corrosive, and if copper salts are also present in the scale, they dissolve and reprecipitate onto the surfaces, causing local corrosion effects.

[0004] A second category of compounds utilizes active ingredients based on mixtures of inorganic and organic acids, which are less aggressive than the preceding ones. Among these acids, mention can be made of citric acid, maleic acid, glycolic acid and tartaric acid, alone or in combination with sulfuric acid or sulfamic acid. The action of these products is applied on the basis of a reduction of pH, which produces an environment which is unfavorable to the formation of scale. These products are usually in the form of liquids or tablets of compressed powders (tabs) to be dissolved in water. Although these products are less aggressive than those based on hydrochloric or hydrofluoric acid, they are however less effective, since their liquid formulation does not allow the application of the scale-removing action in a manner which is prolonged over time.

[0005] Moreover, in the specific field of anti-scale treatment for sanitary fixtures, compounds such as phosphonates, chelating systems or sequestrants are used which mostly have a preventive action against the deposition of scale and therefore do not apply a curative scale-removing action where scale has already deposited. Solid and liquid foaming agents for sanitary fixtures are also commercially available which have a preventive action and are based on inorganic acids, such as for example citric acid, or citric acid/sodium citrate buffer agents or phosphonates, which are however scarcely effective, with a bland scale-removing action.

[0006] Another common problem for sanitary fixtures is the formation of algae, vegetable compounds which usually form where water stagnation occurs. Algae can form within toilet cisterns in the form of filaments or green/brown marks on the walls and help to reduce the lifespan of cisterns. These filaments, especially in case of reduced use of the cistern, can cause problems in the operating mechanisms of the cisterns. Accordingly, as regards cisterns, the formation of algae is even more problematic than the formation of scale. Scale in fact affects predominantly cisterns made of ceramic and its formation is much smaller in the case of less expensive and accordingly more widespread plastic cisterns, the internal polystyrene linings and plastic operating mechanisms of which can be attacked scarcely by scale.

[0007] Chlorine-based products are very widespread for treatment against algae, but resorting to these toxic and polluting substances makes the products scarcely safe for the consumer and scarcely environmentally compatible.

[0008] There is, therefore, the need to provide a product with a scale-removing and anti-algae effect which is in a form adapted to allow prolonged effectiveness over time, not only of preventive nature but also of a curative nature, is characterized by high effectiveness against algae, is formulated so that it is not excessively aggressive against the surfaces of sanitary fixtures, and is not toxic for the consumer.

[0009] The aim of the present invention is to provide a product which has a superior scale-removing action than known anti-scale products and at the same time acts against the formation of algae.

[0010] Within this aim, an object of the invention is to provide a product which also has a detergent, sanitizing, fragrancing and coloring effect.

[0011] Moreover, another object of the invention is to provide a product which is capable of preventing the deterioration of sanitary fixtures.

[0012] Another object of the invention is to provide a product which is characterized by an action which is both preventive and curative and is prolonged over time.

[0013] Another object of the invention is to provide a product which is not aggressive with respect to the materials of which sanitary fixtures are made and is not toxic for the consumer.

[0014] Still another object of the invention is to provide a process which is simple to carry out and allows to prepare the previously cited product.

[0015] This aim and these and other objects, which will become better apparent hereinafter, are achieved by a solid product with a scale-removing and anti-algae effect for sanitary fixtures, which comprises sulfamic acid, one or more surfactants, and one or more binders.

[0016] The aim and objects of the invention are achieved also by a use of the product according to the invention as a scale-removing and anti-algae product for treating sanitary fixtures.

[0017] Moreover, the intended aim and objects are also achieved by a process for preparing the product according to the invention, which comprises the steps of:

a) mixing sulfamic acid, the one or more surfactants, the one or more binders, and optionally the one or

more additives so as to obtain a uniform mix,
b) giving the selected shape to the mix,
c) cooling the mix so as to obtain a solid product.

[0018] Further characteristics and advantages of the invention will become better apparent from the detailed description of an embodiment thereof, given by way of non-limiting example of its scope, and from the accompanying drawings, wherein:

Figure 1a is a photograph of a glass subjected to a scale-removing functionality test with a scale-removing product for comparison at the time of 0 hours;
Figure 1b is a photograph of a glass subjected to a scale-removing functionality test with the product according to the invention at the time of 0 hours;
Figure 1c is a photograph of a glass subjected to a scale-removing functionality test with a scale-removing product for comparison at the time of 72 hours;
Figure Id is a photograph of a glass subjected to a scale-removing functionality test with the product according to the invention at the time of 72 hours;
Figure 1e is a photograph of a glass subjected to a scale-removing functionality test with a scale-removing product for comparison at the time of 15 days;
Figure 1f is a photograph of a glass subjected to a scale-removing functionality test with the product according to the invention at the time of 15 days;
Figure 2a is a photograph of a toilet cistern after an anti-algae functionality test with a comparison scale-removing product;
Figure 2b is a photograph of a toilet cistern after an anti-algae functionality test with the product according to the invention.

[0019] According to the invention, the scale-removing and anti-algae product in solid form described here utilizes as an active principle a particularly active inorganic acid such as sulfamic acid in addition to one or more surfactants, which enhance the effect of sulfamic acid, and one or more binders, which are designed to amalgamate the components of the product in order to facilitate production procedures. Use of a product based on sulfamic acid characterized by a solid form allows to obtain a prolonged hygiene action over time with respect to products in which the sulfamic acid is present in liquid form.

[0020] In one embodiment according to the invention, the sulfamic acid can be in an amount from 1% to 80% by weight of the product. More preferably, the sulfamic acid can be in an amount from 10% to 30% by weight on the weight of the product. For example, the sulfamic acid can be in an amount equal to 19% by weight.

[0021] According to the invention, the scale-removing and anti-algae product in solid form can assume different forms, which make it suitable for use for treating sanitary fixtures. In particular, the product can assume the form of a rimblock, cistern block or effervescent block. The term "rimblock" or "wc rimblock" is used to reference a solid product with a square geometric shape which is inserted in an appropriate basket with a handle which can hang from the rim of a sanitary fixture. The term "cistern block" or "cistern wc block" designates a solid product, for example having a cubic or round geometric shape, which can be wrapped in a water-soluble film and introduced in the cistern of sanitary fixtures. Finally, the term "effervescent block" identifies a solid product, which has for example a cubic or round geometric shape, weighs approximately 20-25 g, and is characterized by the ability to dissolve rapidly due to its formulation, which comprises one or more effervescent agents.

[0022] In an embodiment according to the invention, the one or more surfactants can be selected from the group constituted by an anionic surfactant, a non-ionic surfactant, and an amphoteric surfactant.

[0023] Preferably, the anionic surfactant can be in an amount from 2% to 70% by weight on the weight of the product, the non-ionic surfactant can be in an amount from 1% to 40% by weight on the weight of the product, and the amphoteric surfactant can be in an amount from 1% to 20% by weight on the weight of the product.

[0024] The anionic surfactants have a detergent effect for the enamel of the sanitary fixtures and a foam-generating effect which corresponds to the amount with which the product according to the invention is formulated. Non-limiting examples of anionic surfactants can be surfactants of the group constituted by a sodium alkyl aryl sulfonate, a sulfonated sodium paraffin, a sodium alkyl sulfate, a sulfonated alpha-olefin, and mixtures thereof. In a preferred embodiment of the invention, the sodium aryl alkyl sulfonate is sodium dodecyl benzene sulfonate. In another preferred embodiment of the invention, the sodium alkyl sulfate can be sodium lauryl ethoxy sulfate.

[0025] Non-ionic surfactants are used mostly for their binding action on the different components of the product, thus giving the finished product consistency and hardness. They further have a moderate foaming effect. In the formulation of the product according to the invention, the non-ionic surfactant can be selected from the group constituted by a fatty acid alkanolamide, coconut monoethanolamide, coconut diethanolamide, an ethoxylated fatty alcohol, a polyalkylene glycol with a molecular weight from 200 to 6000, and mixtures thereof.

[0026] Another type of surfactants that can be part of the formulation of the product according to the invention is constituted by amphoteric surfactants. Non-limiting examples of this class of surfactants are sultaine, lauramidopropyl betaine, an imidazoline, an N-alkyl amino acid, alkyl amino dipropionate and a derivative of betaine.

[0027] As regards the one or more binders, they can be present in a quantity from 0.1 % to 10% by weight on the weight of the product. Preferably, the binders can be in a quantity from 0.5% to 2% by weight on the weight of the product. Moreover, the one or more binders can be selected from the group constituted by glycerin, propyl-

ene glycol, a polyethylene glycol, water, a wax, coconut monoethanolamide, a cetyl stearyl alcohol and a stearyl alcohol. The role of the binders is to provide a lubricating action and amalgamate the components of the product in times which are acceptable for industrial production.

[0028] The product according to the invention may further comprise other components in order to give the finished product particular properties, such as color, fragrance, effervescence and others. In particular, the product according to the invention can further comprise one or more additives selected from the group constituted by a color, a fragrance, an odor neutralizing agent, a sequestrant, a brightener, an effervescence generator, a disinfectant, an enzyme, a whitening agent, an anti-adhesion agent, a neutral salt, and mixtures thereof.

[0029] Preferably, the color can be in a quantity from 0.0001% to 1% by weight on the weight of the product when the product is in the form of rimblocks and from 1% to 10%, preferably 2% to 5%, by weight on the weight of the product when the product is in the form of cistern blocks which color the water; the fragrance can be present in a quantity from 1% to 20%, preferably 2% to 8%, by weight on the weight of the product; the odor neutralizing agent can be in a quantity from 0.1% to 3%, preferably 0.3% to 1%, by weight on the weight of the product; the sequestrant can be in a quantity from 0.5% to 5%, preferably 1% to 3%, by weight on the weight of the product; and the effervescence generator can be in a quantity from 5% to 40%, preferably 15% to 30%, by weight on the weight of the product.

[0030] The term "sequestrant" is used to reference a product which has a metal chelating action, which is capable of sequestering/locking the metals in a solution.

[0031] The term "brightener" is used to reference a product which has a scale-removing action capable of removing opaqueness from surfaces, for example by removing deposits of scale, thus improving the aesthetic appearance of the sanitary fixtures.

[0032] In one embodiment of the invention, the effervescence generator can be selected from the group constituted by sodium bicarbonate, citric acid, tartaric acid, and malic acid. Preferably, the effervescence generator can be sodium bicarbonate or citric acid, thanks to their low cost.

[0033] The product may of course further comprise also one or more neutral salts, such as for example sodium sulfate or sodium chloride, or in any case other substances usually used with a function of an inert filler in preparing products for treating sanitary fixtures.

[0034] The product according to the invention applies an anti-algae action, which is further facilitated by the pH with which such product is formulated. In particular, the product can have a pH ranging from 1.5 to 4. In a preferred embodiment, the product can have a pH ranging from 2 to 4, since a value of acidity of more than 2 makes the product less dangerous and allows it not to be classified as "corrosive" according to the indications of annex VI of Directive 67/548/EEC.

[0035] The product according to the invention can be used as scale-removing and anti-algae agent in treating sanitary fixtures. In particular, the term "sanitary fixtures "designates toilet bowls and cisterns.

[0036] The product according to the invention can be prepared by means of a particular production process, in which the sulfamic acid, the surfactants and the binders are processed in the form of a mix, which is then given the selected shape and solidified by cooling.

[0037] In the first passage of this process, the sulfamic acid, the surfactants and optionally the additives are mixed until a uniform mix is obtained. Subsequently, a geometric shape is imparted to the mix thus prepared for example by means of an extruder which has an outlet whose geometry (shape) is such as to give the specific shape to the product. This extrusion procedure uses one or more binders which can be selected from the group constituted by glycerin, propylene glycol, polyethylene glycol and water.

[0038] As an alternative to extrusion, another procedure adapted to impart to the mix a specific shape can consist in hot-mixing the components of the product and pouring the liquefied hot mix into appropriate molds, whose shape is such as to give the product the selected shape *(casting).* This casting uses binders which can be selected from the group constituted by a wax, coconut monoethanolamide, a stearyl alcohol and a stearic alcohol. Of course, the binders for casting can be replaced with other equivalent compounds which melt at temperatures which are compatible with the process according to the invention.

[0039] The mix extruded or poured into the molds is finally left to solidify simply by cooling. Cooling can consist simply in exposing the mix extruded or poured into the molds to ambient temperature, in particular in the case of the extrusion procedure. As an alternative, cooling can consist of a procedure in which the temperature of the product is lowered actively, for example by refrigeration or by applying a cold air stream, particularly in the case of the casting procedure, during which the mixture of the components of the product has been heated before being poured into the molds.

[0040] The process according to the invention is particularly versatile, since it is suitable to prepare all forms of the product, including the forms of rimblock, cistern block and effervescent block. This is possible because, by using the extrusion technique, the extruder can be equipped with an outlet whose shape is adapted to give the selected shape to the product; for example, the outlet of the extruder can have a shape which is adapted to give a shape of rimblock, cistern block or effervescent block. Likewise, by using the casting technique, the final form of the product can be determined by the geometric shape of the mold into which the mix is poured; for example, the mold can have a shape which is adapted to give the form of rimblock, block or effervescent block.

[0041] Moreover, the process according to the invention can comprise the additional passage of packaging

the solid product in a blister or water-soluble film.

Examples

[0042] By using the formulations indicated below, products in the form of rimblock (Table 1), cistern block (Table 2) and effervescent block (Table 3) have been prepared.

Table 1

Components	% w/w
Sulfamic acid in powder	19
Sodium dodecyl benzene sulfonate	48
Sodium sulfate	28.2
Fragrance	3
Sodium lauryl ethoxylate	1.5
Water	0.04
Color	0.17
Glycerin	0.08
pH (1%) rimblock = about 2	

Table 2

Components	% w/w
Sulfamic acid in powder	19
Sodium dodecyl benzene sulfonate	41
Sodium chloride	7.7
Sodium sulfate	8
Coconut monoethanolamide	20
Blue color	4.3
pH (1%) cistern block = about 2.	

Table 3

Components	% w/w
Sulfamic acid in powder	19
Sodium dodecyl benzene sulfonate	34
Sodium sulfate	9.9
Sodium bicarbonate	20
Citric acid	15
Blue color	0.1
Lauramidopropyl betaine	2
pH (1%) effervescent block = ranging from 3 to 4.	

[0043] Product functionality tests were carried out which were designed to measure its durability during the use of sanitary fixtures and its scale-removing and anti-algae effectiveness.

[0044] During the duration test, the product in cistern block form with the composition according to Table 2 (identified as T2) and a control product in cistern block form (identified as F4), characterized by the same composition as T2 but without sulfamic acid, were placed inside a toilet cistern and the total number of flushes required to consume the blocks was also recorded. The results are shown in the following table.

Table 4

Cistern block	total flushes
Cistern block T2	480
Cistern block F4	367

[0045] The product in cistern block form T2 was found to be superior to the cistern block F4 and showed no abnormal effects during the test, such as losses of material, maintaining a constant dissolving rate.

[0046] During the scale-removing functionality test, the cistern block T2 was used to prepare 100 g of aqueous solution with a concentration of 2.4 g/l. Likewise, a control sample with the cistern block F4 was prepared. Glasses with scale deposits were immersed in the two solutions for periods equal to 72 hours and 15 days and then were extracted from the solutions and rinsed. As can be seen from the comparison of Figures 1a-1f, after 72 hours the solution related to the cistern block T2 has removed almost completely scale in the upper part of the glass (Figure 1d) and after 15 days it had cleaned it completely (Figure 1f). On the contrary, the control sample F4 achieves inferior results, leaving the glasses scaled with scale (Figures 1c and 1e).

[0047] During the anti-algae functionality test, a product in cistern block form T2 and a product in cistern block form F4 were each placed in a toilet cistern and the cleaning and algae elimination effect was observed after performing 150 flushes. As can be seen from the comparison of Figures 2a and 2b, the cistern in which the cistern block T2 has been used (Figure 2b) is cleaner than the cistern of the cistern block F4 (Figure 2a), thus demonstrating the anti-algae efficiency of the product according to the invention.

[0048] In practice it has been found that the product according to the invention fully achieves the intended

aim, since the combination of sulfamic acid, surfactants and binders applies an effective scale-removing action and a considerable anti-algae effect.

[0049] Moreover, it has been found that the aim of providing a product which also has a detergent, sanitizing, fragrancing and coloring effect has been achieved, since the product according to the invention, by being able to be formulated with different additives, is capable of performing all of the effects mentioned above.

[0050] Moreover, the product according to the invention is capable of preventing the deterioration of sanitary fixtures, since the action of the sulfamic acid active ingredient prevents the deposits of scale and the algae from damaging the components of the sanitary fixtures.

[0051] Moreover, the product according to the invention is capable of applying an action which is prolonged over time due to the solid formulation with sulfamic acid.

[0052] Moreover, the product according to the invention can be provided in forms which are adapted for treating the different types of sanitary fixtures, since it can be prepared in the form of rimblocks, cistern blocks or effervescent blocks.

[0053] The product according to the invention is also not aggressive for the materials of which sanitary fixtures are made, is not toxic for the consumer and is environmentally compatible, since its components are in such quantities that they are not toxic and the characteristic pH of the product is such that the product is not corrosive.

[0054] Finally, the process according to the invention is simple to perform and low in cost, since it can use extrusion technology, which further makes the process suitable for preparing the product according to the invention in its different forms.

[0055] The product and the process thus conceived are susceptible of numerous modifications and variations, all of which are within the scope of the appended claims; all the details may further be replaced with other technically equivalent elements.

Claims

1. A solid product with scale-removing and anti-algae effect for sanitary fixtures, comprising sulfamic acid, one or more surfactants and one or more binders.

2. The product according to claim 1, wherein the sulfamic acid is in a quantity from 10% to 30% by weight on the weight of the product.

3. The product according to claim 1, wherein the one or more surfactants are selected from the group constituted by an anionic surfactant, a non-ionic surfactant and an amphoteric surfactant.

4. The product according to claim 3, wherein the anionic surfactant is present in a quantity from 2% to 70% by weight on the weight of the product.

5. The product according to claim 3, wherein the non-ionic surfactant is present in a quantity from 1% to 40% by weight on the weight of the product.

6. The product according to claim 3, wherein the amphoteric surfactant is in a quantity from 1% to 20% by weight on the weight of the product.

7. The product according to claim 3, wherein the anionic surfactant is selected from the group constituted by a sodium alkyl aryl sulfonate, a sulfonated sodium paraffin, a sodium alkyl sulfate, a sulfonated alpha-olefin, and mixtures thereof.

8. The product according to claim 7, wherein the sodium alkyl aryl sulfonate is sodium dodecyl benzene sulfonate.

9. The product according to claim 7, wherein the sodium alkyl sulfate is sodium lauryl ethoxy sulfate.

10. The product according to claim 3, wherein the non-ionic surfactant is selected from the group constituted by an alkanolamide of a fatty acid, coconut monoethanolamide, coconut diethanolamide, an ethoxylated fatty alcohol, a polyalkylene glycol with a molecular weight from 200 to 6000 and mixtures thereof.

11. The product according to claim 3, wherein the amphoteric surfactant is selected from the group constituted by sultaine, lauramidopropyl betaine, an imidazoline, an N-alkyl amino acid, alkyl amino dipropionate and a derivative of betaine.

12. The product according to claim 1, wherein the one or more binders are in a quantity from 0.1 % to 10% by weight on the weight of the product.

13. The product according to claim 1, wherein the one or more binders are selected from the group constituted by glycerin, propylene glycol, a polyethylene glycol, water, a wax, coconut monoethanolamide, a cetyl stearyl alcohol and a stearyl alcohol.

14. The product according to one or more of the preceding claims, **characterized in that** it further comprises an additive selected from the group constituted by a color, a fragrance, an odor neutralizing agent, a sequestrant, a brightener, an effervescence generator, a disinfectant, an enzyme, a whitener, a non-stick agent, a neutral salt and mixtures thereof.

15. The product according to claim 14, wherein the fragrance is in a quantity from 1% to 20% by weight on the weight of the product, preferably from 2% to 8%.

16. The product according to claim 14, wherein the odor neutralizing agent is in a quantity from 0.1% to 3%

by weight on the weight of the product, preferably 0.3% to 1%.

17. The product according to claim 14, wherein the sequestrant is present in a quantity from 0.5% to 5% by weight on the weight of the product, preferably 1% to 3%.

18. The product according to claim 14, wherein the effervescence generator is in a quantity from 5% to 40% by weight on the weight of the product, preferably 15% to 30%.

19. The product according to one or more of the preceding claims,
characterized in that it has a pH ranging from 1.5 to 4.

20. The product according to claim 19, **characterized in that** it has a pH ranging from 2 to 4.

21. The product according to one or more of the preceding claims, **characterized in that** it is in the form of a rimblock, cistern block or effervescent block.

22. The product according to claim 21, wherein the product is in the form of a rimblock and the color is in a quantity from 0.0001% to 1% by weight on the weight of the product.

23. The product according to claim 21, wherein the product is in the form of a cistern block and the color is in a quantity from 1% to 20% by weight on the weight of the product, preferably 2% to 5%.

24. Use of the product according to one or more of the preceding claims as scale remover and anti-algae agent for treating sanitary fixtures.

25. A process for preparing the product according to one or more of claims 1-23, comprising the steps of:

a) mixing sulfamic acid, the one or more surfactants, the one or more binders and optionally the one or more additives so as to obtain a uniform mix,
b) giving the selected shape to the mix,
c) cooling the mix so as to obtain a solid product.

26. The process according to claim 25, **characterized in that** the one or more binders are selected from the group constituted by glycerin, propylene glycol, a polyethylene glycol and water, and in which the chosen shape is imparted to the mix by extruding the mix by means of an extruder with an outlet whose shape is suitable for the shape to be imparted to the product.

27. The process according to claim 26, **characterized in that** the outlet of the extruder is adapted to impart to the product the shape of a rimblock, cistern block or effervescent block.

28. The process according to claim 25, **characterized in that**:

the sulfamic acid, the one or more surfactants, the one or more binders and optionally the one or more additives are hot-mixed;
the one or more binders are selected from the group constituted by a wax, coconut monoethanolamide, a cetyl stearyl alcohol and a stearyl alcohol;
and wherein the selected shape is imparted to the mix by pouring the mix into a mold having a shape which is suitable for the shape to be imparted to the product.

29. The process according to claim 28, **characterized in that** the mold has a shape which is adapted to impart to the product the shape of a rimblock, cistern block or effervescent block.

30. The process according to claim 25, **characterized in that** it further comprises the step of:

d) packaging the solidified product in a blister or in a water-soluble film.

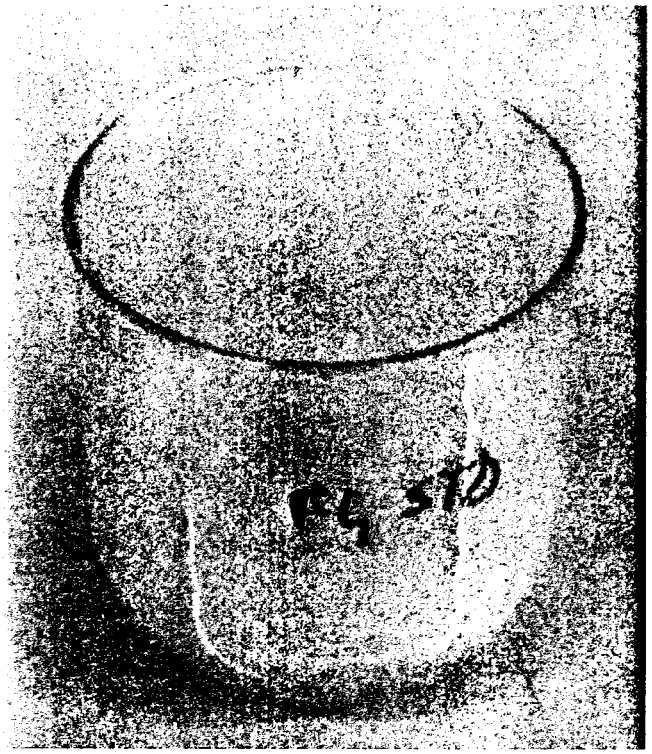

Fig. 1A

Fig. 1B

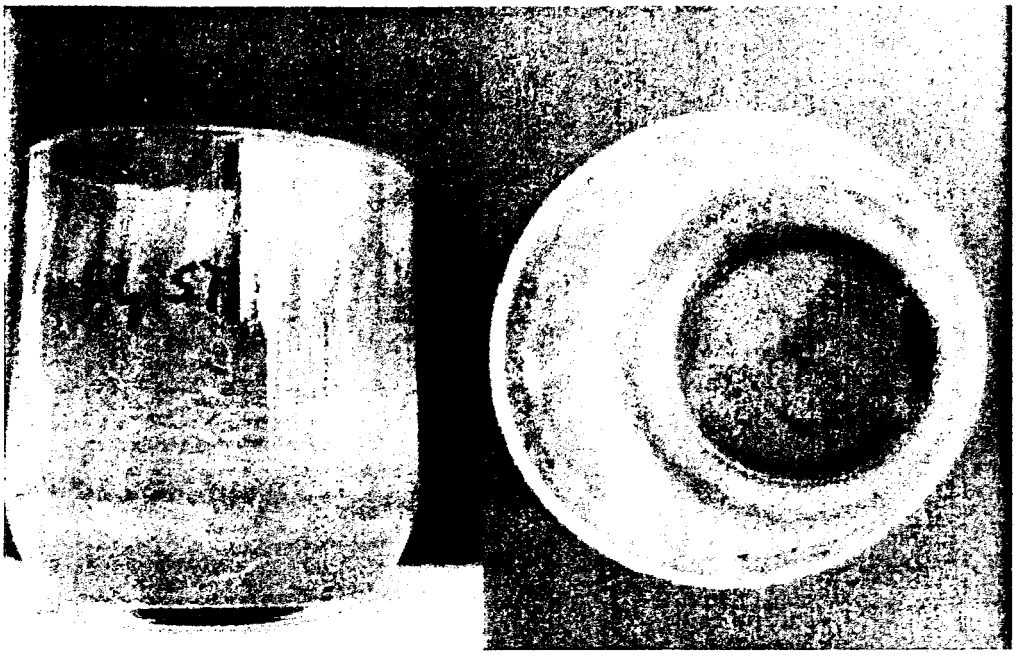

Fig.1C

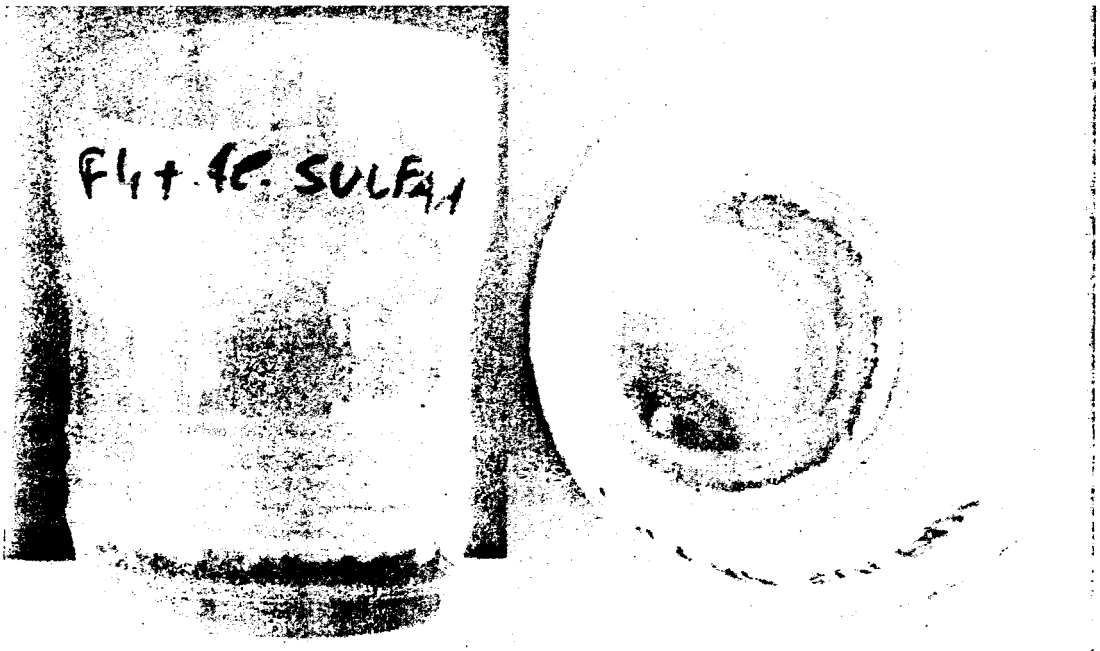

Fig. 1D

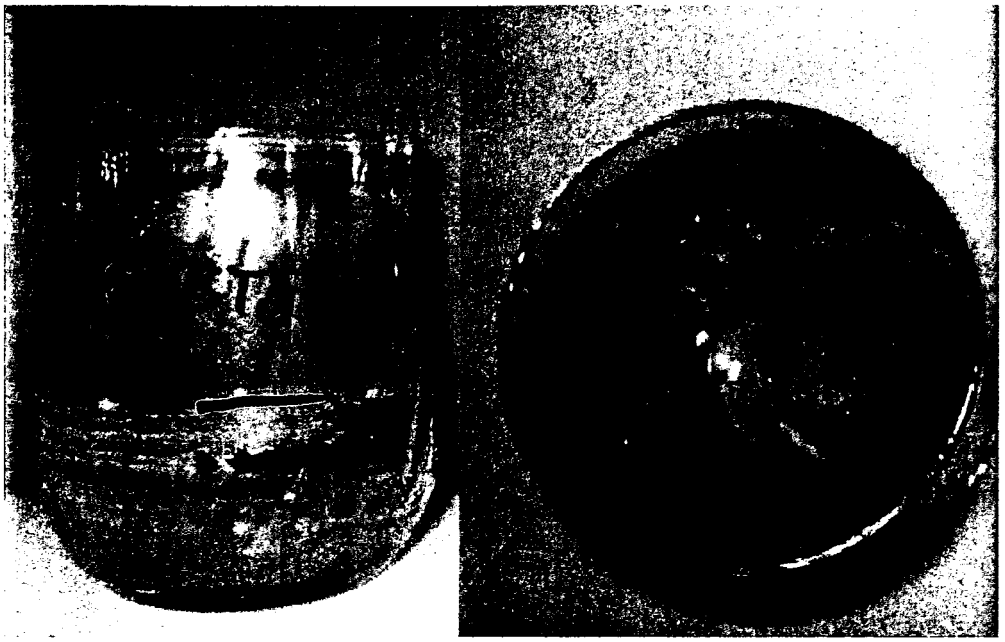

Fig. 1 E

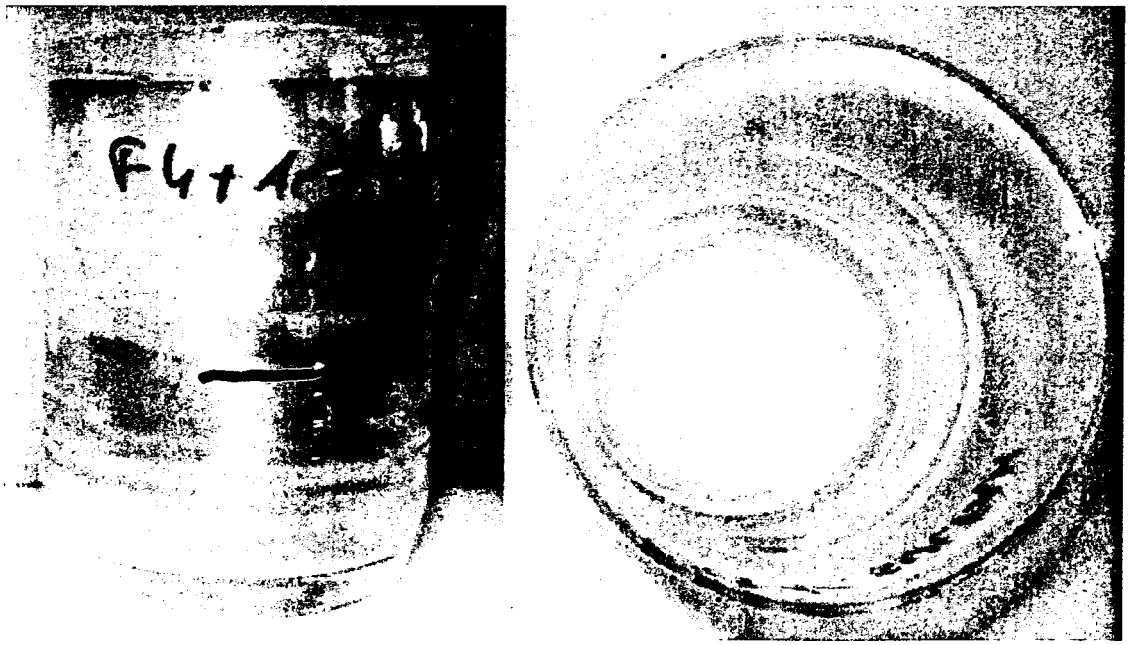

Fig. 1F

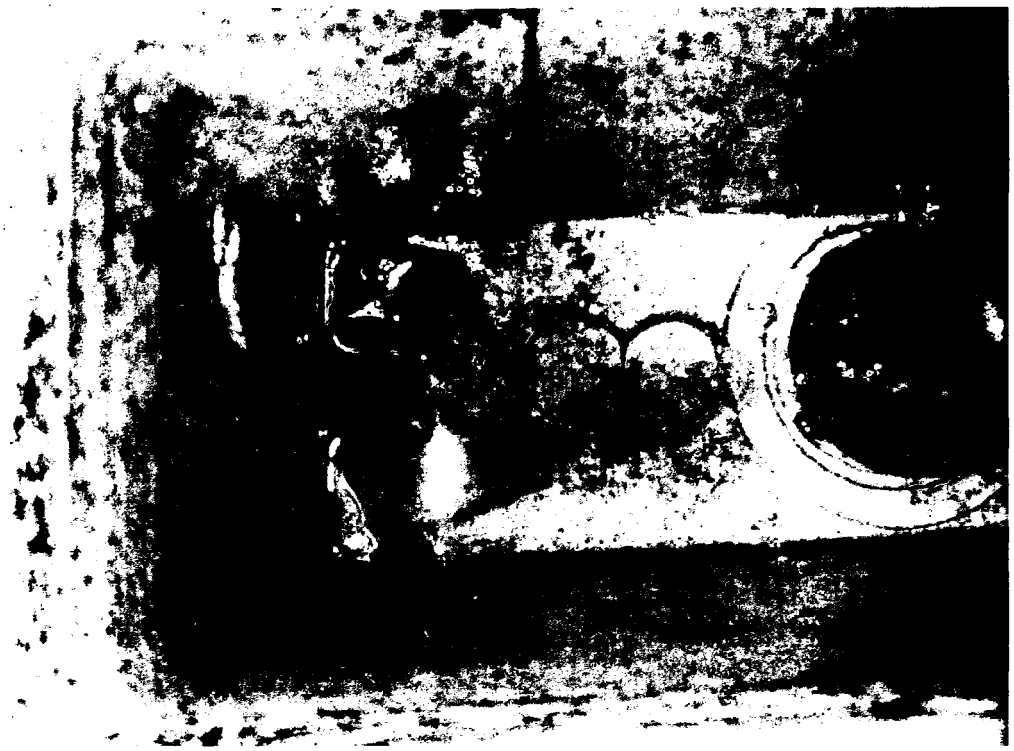

Fig. 2A

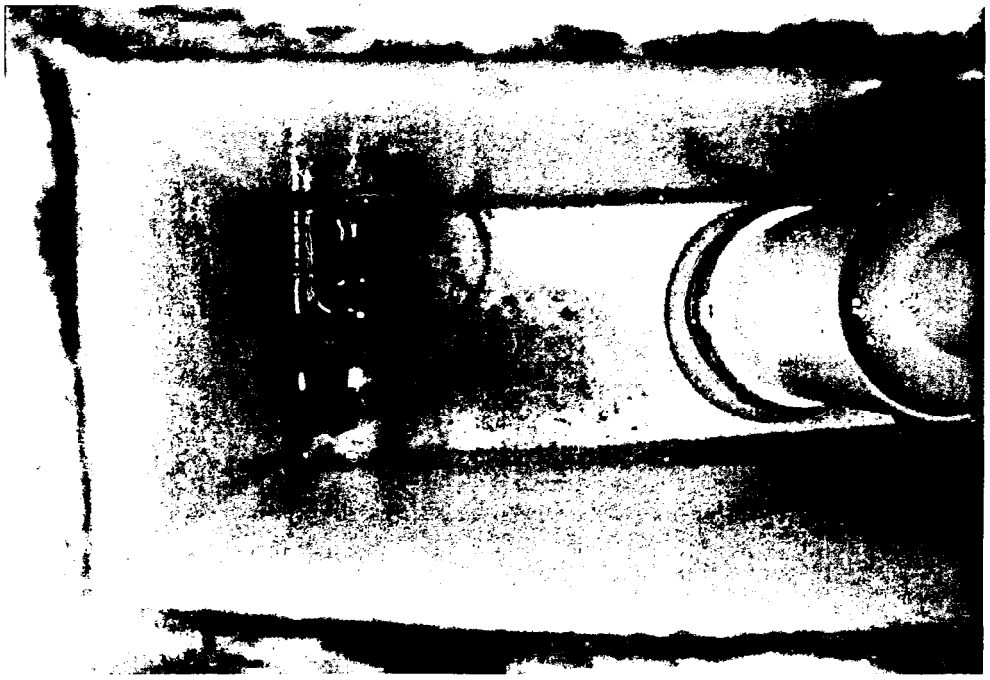

Fig. 2B

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 42 5793

DOCUMENTS CONSIDERED TO BE RELEVANT

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	21 May 2008	Péntek, Eric

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Application Number
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The present search report has been drawn up for all claims

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