Title: A STABILISED OZONE SOLUTION FOR USE IN CLEANING SYSTEMS

Abstract: The present invention relates to stabilised corrosion-inhibiting solutions of ozone, more particularly, to ozone confined in regions of a hydrophobic phase within an aqueous phase. Said stabilised solutions of ozone can be used in cleaning systems for removal of for example hydrophobic substances in water solution, bloodstains, rust, calcium carbonate (limestone), other calcium-containing precipitates, biofilm, cleaning and sterilising equipment used in biological and medical applications, and for wound care.
A stabilised ozone solution for use in cleaning systems

Technical Field Of The Invention
5 The present invention relates to stabilised corrosion-inhibiting solutions of ozone, more particularly, to ozone confined in regions of a hydrophobic phase within an aqueous phase. Said stabilised solutions of ozone can be used in cleaning systems for removal of for example hydrophobic substances in water solution, bloodstains, rust, calcium carbonate (limestone), other calcium-containing precipitates, biofilm, cleaning and sterilising equipment used in biological and medical applications, and for wound care.

Background of the Invention
New cleaning processes are continuously being developed. In order to optimise the process regarding environmental effects and cost it is desirable to meet certain criteria. The method should be efficient and only use a minimum amount of chemicals. It is also beneficial if many different types of unwanted substances and chemicals can be removed in the same process. The toxicity and environmental effects of the chemicals used should also be taken into account, and they should not form toxic by-products. The following chemicals are already well known and used in the industry for cleaning:

20 Surfactants form micelles or other mesomorphic states in water solutions with the hydrophobic part pointing into the micelle and the hydrophilic part pointing outwards. If hydrophobic dirt is present, e.g. oil, this will dissolve in the centre of the micelle where it is protected against the water. The micelles containing the hydrophobic dirt can then easily be rinsed away. Surfactants can therefore successfully be used to remove hydrophobic substances in water solution.

Organic acids, such as carboxylic acids like acetic or oxalic acid are used in industry to dissolve for instance bloodstains, rust, calcium carbonate as well as other calcium containing precipitates.

Ozone is a known powerful sterilant with many advantages; it has high and fast kinetics, it is not selective (like antibiotics) and it forms no toxic by-products (in contrast to for example chlorine).
It is also known to use cleaning solutions containing active cleaning substances encapsulated in a solution so as to form emulsions or microemulsions.

Numerous patents have been issued on cleaning systems having combined some of the above-mentioned components, a few of which are discussed below.

US-5 962 388 discloses acidic aqueous cleaning compositions, and particularly hard surface cleaning compositions, which contain alkyl or aryl sulphonate surfactant, selected hydrophobic cleaning solvent, polycarboxylic acid, and aqueous solvent system in solution and/or a micellar phase, the pH being between 2 and 4. These cleaning compositions have excellent soap foam removal and hard water deposit removal properties. Optionally, they also contain additional anionic sulphate surfactant, cationic surfactant, peroxide and/or hydrophilic polymer.

US-5 827 447 discloses a liquid bleaching agent composition comprising hydrogen peroxide, a surfactant and a bleach activator capable of yielding an organic peracid when reacted with hydrogen peroxide.

US-3 964 994 discloses hydrogen peroxide-containing micellar dispersions, i.e. systems containing peroxides, aqueous medium, and a surfactant. The hydrogen peroxide-containing micellar dispersions are then mixed with the liquid media in which hydrogen peroxide is to be used as a reactant or catalyst to effect intimate contact and dispersions of the hydrogen peroxide within the liquid media.


The above patents/patent applications disclose mixtures between amphiphiles and peroxides. However, the more potent oxidizing capacity of ozone in combination with its hydrophobic properties makes it more suitable for combining a disinfecting and cleaning action. Only JP-A-6313194 concerns mixtures with ozone. However, this patent application does not make use of
any buffers for stabilizing the pH and thereby lacks control of the sterilizing efficiency. In addition, no multi-action concerning decalcification and corrosion control is disclosed or provided.

It is previously known to stabilise ozone in solution, using amphiphiles, for sufficient time to render it useful for applications as those indicated above. It is also known to combine these components with organic carboxylic acids. The above-mentioned multi-action properties of the ozone can thus be used in order to provide a versatile cleaning system. However, usability of such stabilised ozone solutions is severely reduced because of their ability to oxidise or induce hydrolysis of organic polymeric materials, i.e. rubbers or plastic materials. So far, no one has presented any versatile cleaning system being devoid of said disadvantageous corrosive properties.

Thus, a cleaning system exhibiting anti-microbial, detergent and decalcifying effects, as well as corrosion-inhibiting effects with respect to organic polymeric materials, would thus be much desired. At present, such a corrosive-inhibiting cleaning agent is not known from the prior art.

**Summary of the invention**

In view of the problems associated with prior art cleaning systems comprising ozone compositions, there is a need for a stabilised ozone cleaning composition with which ozone can be stabilised for various periods of time, but in particular for extended use, and which also exhibit anti-microbial, detergent and decalcifying effects, as well as corrosion-inhibiting effects.

So far, the prior art has not presented any solution to this problem.

Therefore, one object of the invention is to provide a stabilised ozone solution that can be used for various periods of time, as well as for extended use.

The present invention achieves this object by stabilising ozone in a hydrophilic environment by using surfactants, an emulsion of a hydrophobic phase, or a combination of both.
Another object according to the present invention is to provide cleaning compositions using the stabilised ozone solutions, which cleaning solutions efficiently removes essentially all types of unwanted substances and bacteria, while being stable and having no negative impact on the environment.

A further object of the invention is to provide compositions that do not oxidise or induce hydrolysis of organic polymeric materials, i.e. rubbers or plastic materials.

None of the prior art compositions combine the qualities of surfactants, organic carboxylic acids and ozone, being a very powerful cleaning solution that can be used even in the presence of oxidation sensitive polymeric organic materials. It would remove hydrophobic substances (biofilm), calcium-containing precipitates, and also make the product sterilising.

In a further aspect the present invention provides a cleaning solution comprising the inventive compositions as the active component, used for removal of for example hydrophobic substances, bloodstains, rust, calcium carbonate, other calcium containing precipitates, biofilm and bacteria from an object. The cleaning solution can also be used for cleaning and sterilising equipment used in biological and medical applications, and for wound care.

In a further aspect the invention also provides a method of removing hydrophobic substances, bloodstains, rust, calcium carbonate (limestone), other calcium-containing precipitates, and biofilm, or any other type of dirt from an object, the method comprising the step of applying to said object a stabilised solution of ozone in water, wherein the ozone is confined in regions of a hydrophobic phase within a hydrophilic phase.

In a further aspect the invention also provides a method of cleaning and sterilising equipment used in biological and medical applications, the method comprising the step of applying to said equipment a stabilised solution of ozone in water, wherein the ozone is confined in regions of a hydrophobic phase within a hydrophilic phase.

In a further aspect the invention also provides a method of cleaning and sterilising a wound, the
method comprising the step of applying to said wound a stabilised solution of ozone in water, wherein the ozone is confined in regions of a hydrophobic phase within a hydrophilic phase.

**Brief Description of the drawings**

The present invention will now become more fully understood from the detailed description given herein, wherein reference is made to the accompanying drawings, in which,

Figure 1 compares the ozone concentration (as a function of time) in a solution of pure ozone and an ozone solution where SDS (sodium dodecyl sulphate) was added after 5.5 minutes,

Figure 2 compares the ozone concentration (as a function of time) in a solution of pure ozone and an ozone solution where dodecyl b-D-maltoside was added after 7.5 minutes,

Figure 3 compares the ozone concentration (as a function of time) in a solution of pure ozone and an ozone solution where dodecyl trimethyl ammonium was added after approximately 5 minutes,

Figure 4 compares the ozone concentration (as a function of time) in an aqueous ozone solution at two different concentrations of SDS,

Figure 5 compares the ozone concentration (as a function of time) in a solution of pure ozone and an ozone solution where an acetate and acidic acid solution was added after 5 minutes,

Figure 6 compares the ozone concentration (as a function of time) in a solution of pure ozone and an ozone solution where an oxalate and oxalic acid solution was added after 7 minutes,

Figure 7 compares the ozone concentration (as a function of time) in a solution of pure ozone at pH 5 and an ozone solution containing sodium acetate and SDS at pH 7,

Figure 8 compares the ozone concentration (as a function of time) in a solution of pure ozone at pH 5 and an ozone solution containing sodium oxalate and SDS at pH 6,
Figure 9 shows the $^{13}$C NMR spectrum of pure oxalate.

Figure 10 shows the $^{13}$C NMR spectrum of oxalate treated with ozone.

Figure 11 shows the $^{13}$C NMR spectrum of pure acetate.

Figure 12 shows the $^{13}$C NMR spectrum of oxalate treated with ozone.

**Detailed Description of preferred embodiments**

The present inventors have filed several patent applications covering systems, devices and methods using the sterilising effect of ozonised water solutions at exact concentration.

In addition to this sterilising effect, the present invention provide stabilised solutions of ozone, as well as cleaning solutions containing these stabilised solutions of ozone. These solutions can for example suitably be used for removing various types of dirt, cleaning and sterilising equipment used in biological and medical applications, and wound care.

The primary object of the invention is to provide a method to stabilise ozone in solution for various periods of time, but in particular for extended use.

The present invention achieves this object by stabilising ozone in a hydrophilic environment by using surfactants. Since surfactants have a hydrophobic and a hydrophilic part, it is possible in a hydrophilic environment to create surfactant microspheres having their hydrophilic parts pointing outwards towards the hydrophilic environment and their hydrophobic part pointing towards the centre of the microspheres. In a mixture of such microspheres and ozone in a hydrophilic environment, the hydrophobic ozone will take refuge to said spheres, whereby the depletion rate of ozone in a hydrophilic environment can be significantly reduced.

In one embodiment of the present invention, the surfactants are present in the solution in a mesomorphic phase or a liquid crystalline phase. The surfactants may be present in the solution as linear chains or as a phase that is, lamellar, hexagonal, cubic and micellar, or any other
mesomorphic state.

The present invention surfactants are selected from the group comprising anionic, non-ionic, neutral, amphoteric or zwitterionic and cationic surfactants and at least one surfactant is selected from the group comprising sodium dodecyl sulphate, dodecyl b-D-maltoside, dodecyl trimethyl ammonium acetate, 1,2-Dihexadecanoyl phosphatidylcholine, polyethylene glycol p-octylphenyl ether, betaine or sulphobetaine surfactants.

In another embodiment of the present invention, the ozone is stabilised in a hydrophilic environment by creating an emulsion or a microemulsion of a hydrophobic phase, e.g. oil. For short time stabilisation this can be done by sonication of a mixture of ozone, oil, and a hydrophilic phase. For extended ozone stability, a surfactant is also added to the mixture.

In a second aspect of the present invention there is provided a cleaning composition which is based on the discovery that it is possible to combine three potent cleaning agents, namely surfactants, acids, and ozone, into one solution that has the ability to remove essentially all types of unwanted substances and bacteria, while maintaining the cleaning composition in a stable state and without imparting corrosive properties to said cleaning composition.

Many polymeric materials, such as plastics and rubbers, contain polar functional groups or linkages. The presence of an amphiphile, with a polar and non-polar part, will orient the polar ends towards the polar constituents of a polymeric material. Ozone, being a highly hydrophobic molecule, in this way gets less access to the polymeric materials and consequently oxidation of induced hydrolysis is reduced.

Thus, in order to be able to efficiently remove calcium containing precipitates a cleaning composition is provided using a stabilised ozone solution and at least one acid and/or the salt thereof. The at least one acid is selected from the group of organic acids such as oxalic acid, acetic acid, or other carboxylic acids.

Both the ozone, the surfactants and the acids have an effect on and remove biofilm from objects
or surfaces.

In a further aspect the invention provides a method of removing hydrophobic substances, bloodstains, rust, calcium carbonate (limestone), other calcium-containing precipitates, and biofilm, or any other type of dirt from an object; cleaning and sterilising of equipment used in biological and medical applications; and wound care, the method comprising the step of applying to said object a stabilised solution of ozone in water, wherein the ozone is confined in regions of a hydrophobic phase within a hydrophilic phase.

The cleaning composition according to the present invention further comprises a biocompatible solvent, such as water or a hydrocarbon, or any other biocompatible solvent, including but not limited to alcohol solvents such as ethanol, with which the objects of the present invention may be achieved. However, water is preferred. The cleaning solution may also comprise auxiliary agents, such as dispersion agents, stabilisers, buffers, co-surfactants, or co-polymers.

However, several factors influence the stability of the ozone solutions and thus their usability, including amphiphile concentrations relative to aggregation conditions (CMC, Critical Micellar Concentration), additives and type of salts, pH and pH buffers present, as well as temperature. The multi-action of ozone solutions also requires the adequate combination of salt, pH and amphiphile.

If these parameters can be controlled, the highly aggressive oxidation properties of ozone can thus be significantly reduced, allowing exposure to materials which otherwise would readily be decomposed by ozone, with retained multi-action properties.

In the cleaning composition according to the present invention the molar ratio between the surfactant and ozone is 1:1 to 10000:1, preferably 10:1 to 1000:1, and more preferably 100:1 to 1000:1. The surfactant can constitute from about 0.05 wt% to about 40 wt% of the weight of water in the solution.

For maximum efficiency, the pH value in the cleaning solutions is below 5, and preferably below
4. pH buffers should offer a controlled pH in the range 4-5. The anionic, basic constituents of the pH buffer should not accelerate ozone decomposition or seriously affect phase behaviour of the amphiphile. Therefore, suitable pH buffers may only involve anions such as organic carboxylates, sulphates or phosphates. This is also true for any addition of salt, which should not, like in the case of the pH value, accelerate ozone decomposition or seriously affect phase behaviour of the amphiphile.

The inventive cleaning compositions are used at 0-100°C, and more preferably at 10-60°C, since the various effects are optimized (cleaning, sterilization in combination with decalcifying and non-corrosive effects) in those temperature intervals.

Now a more detailed description will be given of how the ozone stability, the compatibility of the active substances and their efficiency to remove dirt was determined.

**Ozone stability in the presence of SDS (anionic amphiphile)**

In Figure 1 it can be seen that an anionic amphiphile such as SDS has a positive effect on the stability of ozone. It prolongs the lifetime of ozone three to four fold as compared with a pure ozone solution at approximately the same pH.

\[
\text{Na}^+ \overset{\text{O}}{\underset{\text{O}}{\text{S}}} \overset{\text{O}}{\underset{\text{O}}{\text{(CH}_2\text{)}_{11}}} \overset{\text{O}}{\underset{\text{CH}_3}{\text{O}}}
\]

*Structure of SDS (sodium dodecyl sulphate)*

When the concentration of SDS is high, SDS is predominantly present in the form of linear molecules. When the concentration decreases the surfactants will predominantly change aggregation state into micelles. In Figure 4, when using the higher surfactant concentration, a significant increase in the lifetime of ozone can be seen. Aggregation of the surfactant will also change with temperature.

One of the surfactants, SDS, was tested at two different concentrations: Low concentration (0.1
mM), where the surfactant exists in micellar aggregates, and high concentration (200 mM), where the surfactant exists in the form of both micelles and linear (paraffinic) chains. Phase diagrams (not shown) show that SDS can occur in other forms as well, such as hexagonal, lamellar etc. However, in order to obtain these states the surfactant solution has to be heated.

The experiments show that ozone is depleted much faster in the presence of SDS in the state of both micelles and paraffinic chains than when SDS exhibits a predominantly micellar constitution, i.e. practically no paraffinic chains.

10 Ozone stability in the presence of dodecyl β-D-maltoside (neutral amphiphile)
As can be seen in Figure 2, a non-ionic amphiphile such as dodecyl β-D-maltoside has a stabilising effect on ozone. The depletion rate of ozone is about half the depletion rate of pure ozone solution at approximately the same pH.

\[
\text{Structure of dodecyl } \beta\text{-D-maltoside}
\]

15 Ozone stability in the presence of dodecyl trimethyl ammonium acetate (cationic amphiphile)
As can be seen in Figure 3, also a cationic amphiphile such as dodecyl trimethyl ammonium acetate has a stabilising effect on ozone. The lifetime time of ozone can be increased by approximately a factor of two when dodecyl trimethyl ammonium acetate is present in the solution.
Structure of dodecyl trimethyl ammonium acetate

The stability of ozone with respect to the different amphiphiles should not be directly compared, since pH is slightly different in the different experiments (pH has a very significant effect on the decomposition rate of ozone, since the rate-limiting steps involve reaction with OH⁻). Furthermore, as mentioned above, the amphiphiles can be aggregated in different types of mesomorphic states or liquid crystalline phases, which can affect their efficiency in stabilizing ozone.

Ozone stability in the presence of acetic and oxalic acid

As can be seen when studying Figures 5 and 6 (the graphs should not be directly compared as the pH varies slightly between the experiments), both oxalate and acetate have a positive effect on ozone stability and can therefore be used in a cleaning solution containing ozone without negatively influencing the stability of ozone, i.e. increasing the ozone depletion rate.

The aqueous solutions of the acids were analysed using ¹³C NMR and IR spectroscopy before and after treatment with ozone. Figures 9-12 show that no decomposition products have evolved after having mixed acids and the ozone, thus implicating that they do not react with each other.

The observation that oxalic acid does not react with ozone is not surprising since oxalate is being discussed as one of the end decomposition products when using an ozone aqueous purification systems for the treatment of biomass. For acetate, the same reaction pattern can be verified when studying the literature within the field, where it is mentioned to be an inhibitor of ozone depletion.

Instead of using an acid, it is also possible to use its corresponding salt. In the case of oxalic and acetic acid that would be oxalate and acetate, respectively. By adding an acid or its salt to the cleaning solution a double action is achieved through acidification and complexation. The main
effect is achieved by the lowering of the pH, but organic anions, such as oxalate and acetate, also enhances the dissolution process by complex formation.

**Ozone stability in the presence of both a surfactant and an acid solution**

An additional test was made to verify that the solution of mixed surfactant and acetate or oxalate would not affect the ozone stability. All three surfactants were tested with both oxalate and acetate, but only the results from SDS are presented here. However, the other surfactants show similar behaviour. It should be noted that the pH values for the test with acetate and oxalate were different (pH 7, respectively pH 6) and should therefore not be compared directly. The pure ozone solution has a lower pH (pH 5) and should therefore only be seen as a reference. Higher pH leads to faster ozone decomposition.

As can be seen in Figures 7 and 8, mixing SDS with sodium acetate and oxalate, respectively, does not increase the rate of decomposition of ozone. Instead, it indicates that a stabilisation occurs.

**Ozone stability in microemulsion**

Experiments showed that a microemulsion containing aniseed oil and SDS also could have a stabilising effect on ozone. The depletion rate of ozone is about half compared to pure water at the same pH.

**Removal of calcium carbonate**

When preparing a solution containing a saturated aqueous solution of CaCO₃, solid CaCO₃, and a solution of SDS, acetic acid, and sodium acetate, the CaCO₃ started to dissolve and the solution was clear after approximately 15 seconds. Thus, the surfactant and acid solution dissolves CaCO₃. However, for a successful result it is crucial to have an acidic solution. This holds also when ozone is present in the cleaning solution.

**Removal of biofilm**

In order to ensure that the solution of surfactant and acetic or oxalic acid, as well as ozone would be efficient towards a biofilm, a solution of acid and SDS was mixed with a vegetable oil. The
test showed that the surfactant solution, after being mixed with the acid and/or ozone, still had the ability to dissolve hydrophobic substances (in this case vegetable oil. Thus, it retains an effect against biofilm.

Thus, the present invention provides a cleaning solution combining three potent cleaning substances, namely ozone, surfactant and acetic or oxalic acid, which until now have not been shown to coexist without decomposing each other. The cleaning solution according to the present invention also exhibits improved ozone lifetime compared with a pure ozone solution. Furthermore, the inventive cleaning solution has also been shown to dissolve hydrophobic substances, i.e. exhibiting an ability to remove bio film, and successfully dissolve limestone.

Examples
The present invention will now be described more in detail with reference to the non-limiting examples presented below.

General details
Deionised water was used in all aqueous solutions. All experiments were made at room temperature, ~23°C. The variation of the temperature between the different experiments was relatively small and should not have any significant effect on the outcome. All tests were made at least twice in order to verify the reproducibility.

The following procedure was applied in the analysis of ozone concentration. Magnetic stirrer was used to obtain a homogeneous solution. The ozone concentration, pH and temperature were registered every 30 seconds, until ozone no longer could be detected.

The following equipment was used during the experiments:

- Ozone electrode: Fisher Rosemount 499A
- pH-electrode: ORION 9101SCE
- Thermometer: ORION 917006
- Ozone generator (water): Otre AB, 2000-1L
- Ozone generator (air): BMT Messtechnik, BMT802X
Ozone analyser (air): BMT Messtechnik, BMT963
IR-spectrophotometer: BIO-RAD, 375C
NMR: Bruker, DMX500

**Example 1. Ozone stability in the presence of different surfactants**
An aqueous ozone solution with a concentration of approximately 6 ppm was tapped directly from the ozone water generator into a beaker. The ozone electrode was used to register the changes in concentration. The surfactants (SDS, dodecyl b-D-maltoside, and dodecyl trimethyl ammonium acetate) were added to the ozone solution after roughly 6 minutes. The concentration of the surfactants was approximately 0.1 mM.

The cationic surfactant dodecyl trimethyl ammonium acetate used in this experiment had from the beginning (as commercialised) a different anion, namely Br⁻. However, the bromide reacted directly with ozone, and was therefore removed by metathetical reaction (in principal, a reaction between two salts where the anions change places, generally having its drive force in the fact that one of the products is insoluble in the solvent used): 0.1 g surfactant (2.16x10⁻⁴ mol Br⁻) was mixed with a 100 ml aqueous solution containing 0.05 g AgAc (3.0x10⁻⁴ mol Ag⁺). The solution was filtered to remove the formed precipitate, AgBr.

The results of the ozone stability test are shown in Figures 1-3, namely that the added surfactants increase the lifetime of ozone by a factor 2.

**Example 2. Ozone stability in the presence of different concentrations of SDS**
An aqueous ozone solution with a concentration of approximately 6 ppm was tapped directly from the ozone generator into a beaker. The ozone electrode was used to register the changes in concentration. SDS was added directly to the aqueous ozone solution, yielding solutions having concentrations of 0.1 mM and 200 mM with respect to SDS. The result is seen in Figure 4, namely that the higher concentration of SDS increases the lifetime of ozone by a factor 5 compared with the lower concentration.
Example 3. Ozone stability in the presence of acetic and oxalic acid

An aqueous ozone solution with a concentration of approximately 6 ppm was tapped directly from the ozone generator into a beaker. The ozone electrode was used to register the changes in concentration. Acetic or oxalic acid was added directly to the solution. The concentration of the acids was approximately 0.01M. The results are shown in Figures 5 and 6, namely that the addition of the acids to the ozone solution increase the lifetime of the ozone by a factor 2.

In order to verify that the organic acids had not been oxidised by ozone an additional test was made. 300ml of an aqueous solution of acid (0.1M, 30x10⁻³ mol) was bubbled with ozone for five hours. The gaseous concentration of ozone was ~ 100 g/m³. The airflow was 0.2 l/minute, which gives 1.2 g ozone/h (1.7x10⁻³ mol ozone/h). The aqueous solutions were analysed using ¹³C NMR and IR spectroscopy before and after treatment with ozone. The results are shown in Figures 9-12, namely that the peaks in the spectrograms of the pure acid solutions (Figures 9 and 11) had not changed their appearance after prolonged treatment with ozone (Figures 10 and 12).

Example 4. Ozone stability in the presence of surfactant and acid solution

An aqueous ozone solution with a concentration of approximately 6 ppm was tapped directly from the ozone generator into a beaker. The ozone electrode was used to register the changes in concentration. Acetic acid respective oxalic acid together with the surfactant was directly added to the ozone solution. The concentration of the acids was approximately 0.01 M and the concentration of the surfactants was 0.1 mM. The results are shown in Figures 7-8, namely that the lifetime of ozone increased with at least 50 % compared with a pure ozone solution.

Example 5. Ozone stability in microemulsion

A microemulsion containing approximately 0.2 wt% aniseed oil and 2 wt% SDS was manufactured. Ozone was introduced in the microemulsion in a concentration of approximately 4 ppm. By continuous measurement of the ozone concentration, the experiment showed that the emulsion had a positive effect on the ozone stability. Using a microemulsion, the depletion rate of ozone was about half the depletion rate in pure water at the same pH.

Example 6. Removal of calcium carbonate
An aqueous solution was saturated with CaCO$_3$ and filtrated. The solution (20 ml) was poured into a beaker and 0.05 g CaCO$_3$ was added. Another solution of SDS (1 mM), acetic acid (0.5 M), and sodium acetate (0.5 M) was prepared, and 5 ml was added to the first solution. The CaCO$_3$ started to dissolve and the solution was clear after approximately 15 seconds. When including ozone in the cleaning solution, the ozone concentration used was approximately 4 ppm.

**Example 7. Removal of biofilm**

In order to ensure that the solution of surfactant and acetic or oxalic acid would be efficient towards biofilm a test was made as follows:

A 20 ml solution of 10 mM acid and 7 mM SDS was poured into a beaker with a magnetic stirrer. Rape oil (brand Zeta) was dropped into the solution. At large excess of oil in comparison to the surfactant, the surfactant acid solution started to have difficulty dissolving the oil. When including ozone in the cleaning solution, the ozone concentration used was approximately 4 ppm.

**Example 8. Test of non-corrosiveness**

A polyurethane tubing was exposed to an 8.4 ppm solution of ozone in the absence as well as in the presence of buffered 10 mM SDS for 24 hours. The difference in polymer corrosion was easily observed as the tubing exposed to the non-buffered cleaning solution exhibited visual corrosive marks only after 24 hours contact.
Claims

1. A stabilised acidic aqueous solution of ozone, characterised in that the ozone is present in a hydrophilic phase comprised within a hydrophobic phase, and that the solution is corrosive-inhibiting.

2. A solution according to claim 1, characterised in that said hydrophobic phase comprises at least one surfactant.

3. A solution according to claim 2, characterised in that the surfactant is present in the solution either in a mesomorphic state or a liquid crystalline phase.

4. A solution according to any of claims 2-3, characterised in that the surfactant is present in the solution as linear chains or as a phase that is lamellar, hexagonal, cubic, or micellar.

5. A solution according to any of claims 2-4, characterised in that the at least one surfactant is selected from the group consisting of anionic, non-ionic, neutral, cationic, amphoteric and zwitterionic surfactants.

6. A solution according to any of claims 2-5, characterised in that the surfactant is selected from the group consisting of sodium dodecyl sulphate, dodecyl b-D-maltoside, dodecyl trimethyl ammonium acetate, 1,2-Dihexadecanoyl phosphatidylcholine, polyethylene glycol p-octylphenyl ether, betaine or sulphobetaine surfactants.

7. A solution according to any of claims 1-6, characterised in that said hydrophobic phase comprised within said hydrophilic phase is an emulsion or a microemulsion.

8. A solution according to any of claims 1-7, characterised in that it comprises at least one acid or a salt thereof.
9. A solution according to claim 8, characterized in that the acid is an organic acid.

10. A solution according to claim 9, characterized in that said organic acid is a carboxylic acid.

11. A solution according to claim 10, characterized in that said carboxylic acid is selected from the group consisting of oxalic acid and acetic acid.

12. A solution according to any of claims 1-11, characterized in that it comprises solvents such as water, hydrocarbons, or other biocompatible solvents.

13. A solution according to any of claims 1-12, characterized in that it comprises auxiliary agents, such as dispersion agents, stabilisers, co-surfactants or co-polymers.

14. A solution according to any of claims 2-13, characterized in that the molar ratio between the surfactant and ozone is 1:1 to 10000:1, preferably 10:1 to 1000:1, and more preferably 100:1 to 1000:1.

15. A solution according to any of claims 2-14, characterized in that the surfactant is present at a range of about 0.05 wt% to about 40wt%.

16. A solution according to any of claims 1-15, characterized in that the solution is used at 0-100°C, and more preferably at 10-60°C.

17. A solution according to any of claims 1-16, characterized in that the pH in the solution is below 6, and preferably below 3.

18. A solution according to any of claims 1-17, characterized in that the solution is buffered.

19. A solution according to claim 18, characterized in that the buffer is selected from the group comprising organic carboxylates, sulphates or phosphates.
20. A cleaning solution, **characterised in that** it comprises the solution according to claim 1 as the active component.

21. A cleaning solution according to claim 20, **characterised in that** said regions of hydrophobic phase comprise at least one surfactant, the molar ratio between the surfactant and ozone being 1:1 to 10000:1, preferably 10:1 to 1000:1, and more preferably 100:1 to 1000:1, wherein the surfactant constitutes up to 40 wt% of the weight of water in the solution, said cleaning solution further comprising an organic acid, and optionally further comprising auxiliary agents, which cleaning solution preferably is used at 10-60°C, and wherein the pH in the cleaning solution is below 5, and preferably below 4.

22. A method of removing stains from an object, **characterised in that** it comprises:
   - applying to said object the solution according to claims 1-20 or the cleaning solution according to claims 20-21.

23. A cleaning and sterilising equipment used in biological and medical applications, **characterised in that** it comprises:
   - applying to said equipment the solution according to claims 1-20 or the cleaning solution according to claims 20-21.

24. A method of cleaning and sterilising a wound comprising,
   - applying to said wound the solution according to claims 1-20 or the cleaning solution according claims 20-21.
SDS in ozone water

![Graph of SDS in ozone water](image)

**Fig. 1**

Dodecyl-b-D-Maltoside in ozone water

![Graph of Dodecyl-b-D-Maltoside in ozone water](image)

**Fig. 2**
Dodecyl trimethyl ammonium acetate

Fig. 3

Different concentrations of SDS in ozone water

Fig. 4
Acetate in ozone water

![Graph of Acetate in ozone water]

Fig. 5

Oxalate in ozone water

![Graph of Oxalate in ozone water]

Fig. 6
Sodium acetate + SDS in ozone water

Fig. 7

SDS+Oxalate in ozone water

Fig. 8
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or: to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C11D, A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, CHEM. ABS DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search: 17 February 2004

Date of mailing of the international search report: 18-02-2004

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## INTERNATIONAL SEARCH REPORT

**International application No.**

**PCT/SE 2003/001246**

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