



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 077 250 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
21.02.2001 Bulletin 2001/08

(51) Int. Cl.⁷: C11D 3/00, C11D 1/835,
C11D 3/02, C11D 3/08

(21) Application number: 00305606.6

(22) Date of filing: 03.07.2000

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 16.08.1999 GB 9919324

(71) Applicant: **Agroserv Limited
Warminster, Wiltshire, BA12 9 HT (GB)**

(72) Inventors:
• **Milne, Colin C.W.,
c/o Agroserv Limited
Bishopstrow, Warminster, Wilts BA12 9HT (GB)**
• **Barberio, Giacinto Giovanni,
c/o Agroserv Limited
Bishopstrow, Warminster, Wilts BA12 9HT (GB)**

(74) Representative:
**Matthews, Derek Peter
Frank B. Dehn & Co.,
European Patent Attorneys,
179 Queen Victoria Street
London EC4V 4EL (GB)**

(54) **Aqueous formulations**

(57) An aqueous composition comprising

- (i) at least one metal hydroxide and/or metal silicate;
- (ii) a surfactant mixture comprising at least one alkyl glucoside and at least one nonionic surfactant;
- (iii) a quaternary ammonium disinfectant;
- (iv) a hydrotroping agent; and
- (v) optionally a chelating agent

for use in the cleaning of milking and milk storage equipment such as bulk milk tanks, milk pipelines etc.

EP 1 077 250 A1

Description

[0001] This invention relates to cleaning formulations and in particular to formulations for use in the cleaning of milking and milk storage equipment such as bulk milk tanks, milk pipelines etc.

5 **[0002]** Traditionally, cleaning formulations for milking and milk storage equipment have been based on combinations of alkaline compounds (sodium hydroxide, potassium hydroxide, sodium carbonate) in solution with sodium hypochlorite for sanitising.

10 **[0003]** Whilst sodium hypochlorite is a very effective sanitising agent, its solutions do not wet surfaces very effectively and hence products have been developed to overcome this wetting problem. Surfactants have been found to increase wetting power and hence may be added to sodium hypochlorite formulations. However, only a limited number of surfactants are compatible with sodium hypochlorite and these surfactants are usually high foaming. Such high foaming formulations do not work well in certain environments such as cleaning in place (CIP) in milk and food pipeline systems.

15 **[0004]** Sodium hypochlorite solutions containing sodium hydroxide are alkaline and corrosive and hence are not suitable for use with milking equipment or milk storage systems comprising metals such as aluminium or zinc or soft metal alloys. The reaction between the formulation and metal may also produce hydrogen which may have a corrosive effect on equipment structures.

20 **[0005]** Moreover, some metals such as nickel, cobalt and copper, greatly accelerate the breakdown of sodium hypochlorite. Also, iron, which does not itself catalyse the breakdown of sodium hypochlorite, may act as a degradation promoter in the presence of any of the above metals. Thus, alkaline sodium hypochlorite solutions are not ideal for use in milking equipment or milk storage systems comprising nickel, cobalt, copper or iron alloys containing said metals. For example, stainless steel may contain nickel and cobalt as well as iron. Hence, although stainless steel is normally resistant to alkaline corrosion, prolonged contact with sodium hypochlorite solutions may cause corrosion and rusting due to the oxidation induced by the nickel or cobalt content.

25 **[0006]** Care must also be taken to ensure that sodium hypochlorite solutions do not come into contact with acids, thus generating harmful chlorine gas.

30 **[0007]** A range of alternative products have been developed which have disinfectant properties, for example products comprising quaternary ammonium compounds (cationics), amphoteric, iodine compounds, etc. None of these products are as efficient as formulations comprising sodium hypochlorite and most cannot be used in alkaline mixtures. Since a level of causticity is required to emulsify fats and ensure successful removal of protein deposits from milking equipment, such as bulk storage tanks, such alternative products are also not favoured.

35 **[0008]** It has now surprisingly been found that an alkaline formulation including surfactants, disinfectants, a hydrotroping agent and optionally a scale build-up retardant can provide efficacious sanitising with low foaming properties which is a real alternative to alkaline formulations containing sodium hypochlorite.

[0009] The invention thus provides an aqueous composition comprising

- (i) at least one metal hydroxide and/or metal silicate;
- (ii) a surfactant mixture comprising at least one alkyl glucoside and at least one nonionic surfactant;
- (iii) a quaternary ammonium disinfectant;
- (iv) a hydrotroping agent; and
- (v) optionally a chelating agent.

40 **[0010]** Preferred metal hydroxides are potassium hydroxide and especially sodium hydroxide. Preferred metal silicates are sodium silicate, especially sodium metasilicate. In a most preferred embodiment the alkalinity is provided by sodium hydroxide alone. Typically, the formulation contains 2 to 25%, preferably 5 to 15%, more preferably 6 to 10% by weight of the metal hydroxide and/or metal silicate component. Surprisingly it has been found that the surfactants, disinfectant and hydrotroping agent can tolerate these high levels of causticity.

45 **[0011]** The surfactant mixture comprises both an alkyl glucoside and a nonionic surfactant. Alkyl glucosides, also known as sugar lipids, are commercially available from a variety of suppliers and have a range of applications and properties. Alkyl glucosides are derived from glucose and possess alkyl substituents of differing chain length, for example C₃₋₁₄.

[0012] Nonionic surfactants are also widely available commercially. For example, alkoxylate surfactants of general formula R(O(CH₂)_m)_nOH where R is an alkyl group with an active hydrogen atom, e.g. an amine, alcohol, fatty acid, ester; m is 2 or 3, preferably 2; and n is 4 to 20 are commercially available. Mixed ethoxy and propoxy alkoxylates are

also readily available. A particularly useful combination of alkyl glucoside and ethoxylate surfactant is sold under the trade name Berol by Akzo-Nobel, specifically Berol LFG 61 or Berol DGR 81. Typically, the formulation of the invention contains 2 to 15%, preferably 5 to 9%, especially 5 to 7% by weight of the surfactant component. Other suitable surfactant mixtures will of course be readily determined by the person skilled in the art.

5 [0013] Quaternary ammonium disinfectants are also commercially available. They are typically of formula RN(CH₃)₃Cl where R is C₆₋₂₀ alkyl. One of the methyl groups is often replaced by a longer alkyl chain, e.g. a C₂₋₂₀ or C₆₋₂₀ alkyl chain, giving alternative quaternary ammonium disinfectants. A particularly useful quaternary ammonium disinfectant is dioctyldimethylammonium chloride which is sold under the trade name Bardac-LF by Lonza. Typically, the formulation of the invention contains 0.5 to 10%, preferably 1 to 7%, especially 2 to 5% by weight of the quaternary 10 ammonium disinfectant. Other suitable quaternary ammonium disinfectants will of course be readily determined by the person skilled in the art.

15 [0014] The hydrotroping agent may be a propionate, betaine or glycinate type of amphoteric surfactant and a range of such hydrotroping agents are again readily available in the market place. Particularly preferred hydrotroping agents include octylimino-dipropionate and sodium capryloimino-dipropionate. A particularly useful hydrotroping agent is that sold under the trade name Ampholak YJH-40 by Akzo-Nobel. Typically the formulation contains 1 to 10%, preferably 2 to 8%, especially 3 to 7% by weight of the hydrotroping agent. Other suitable hydrotroping agents will of course be readily determined by the person skilled in the art.

20 [0015] It may be necessary to employ a chelating agent in the formulations of the invention, especially in areas of hard water. When a chelating agent is included, this may conveniently be trisodium nitrilotriacetate (sodium NTA) or 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) or its sodium salts. Typically, the formulation of the invention contains 1 to 10%, preferably 2 to 8%, especially 3 to 5% by weight of the chelating agent. Other suitable chelating agents will of course be readily determined by the person skilled in the art.

25 [0016] The balance of the cleaning formulation of the invention is water. In use, the formulation is further diluted with water at a ratio of 200-300:1 water/cleaner.

25 [0017] It is preferred if sanitisation occurs at elevated temperature, e.g. 30°C, especially 75°C. This has been found to enhance the effectiveness of the sanitising formulation to bacteria.

[0018] The following non-limiting example serves to illustrate the invention.

Example 1

30 [0019] A tap water sample was inoculated with high numbers (10⁶) of *Bacillus cereus*. Another tap water sample was injected with high numbers of *E.Coli*. Both samples were divided into four separate tubes and a formulation comprising 7.5% by weight sodium hydroxide, 6.0% by weight Berol LFG61, 3.0% by weight Bardac LF, 4.5% by weight Ampholak YJH-40, 4% sodium NTA and 75% by weight water was added to a tube from each set to give a final dilution 35 of 1:300, 1:250 and 1:200 respectively. The remaining two tubes were kept as controls. All the tubes were incubated at 30°C for 10 minutes. The results are displayed in Table 1 below.

| 40 | Dilution of product | Organism | Count/ml Control | Count/ml After contact | percentage reduction |
|----|---------------------|-----------------|------------------|------------------------|----------------------|
| | 1:300 | <i>B.cereus</i> | 5000000 | 1400 | 99.97 |
| | 1:300 | <i>E.Coli</i> | 15000000 | <10 | 100 |
| 45 | 1:250 | <i>B.cereus</i> | 5000000 | 1600 | 99.97 |
| | 1:250 | <i>E.Coli</i> | 15000000 | <10 | 100 |
| | 1:200 | <i>B.cereus</i> | 5000000 | 2500 | 99.95 |
| 50 | 1:200 | <i>E.Coli</i> | 15000000 | <10 | 100 |

55 [0020] The results show that at 30°C the formulation was effective against *E. coli* and *B. cereus* at dilutions of 200:1, 250:1 and 300:1 with a better than 99.95% reduction. The product was very effective against *Bacillus cereus* which has the ability to produce spores which are resistant to some disinfectants. Moreover, the formulation gave very low foam levels.

[0021] It is anticipated that the formulations of the invention would be equally if not more effective at temperatures of 30°C and above.

Claims

1. An aqueous composition comprising
 - 5 (i) at least one metal hydroxide and/or metal silicate;
 - (ii) a surfactant mixture comprising at least one alkyl glucoside and at least one nonionic surfactant;
 - (iii) a quaternary ammonium disinfectant;
 - 10 (iv) a hydrotroping agent; and
 - (v) optionally a chelating agent.
- 15 2. A composition as claimed in claim 1 wherein the metal hydroxide and/or metal silicate is potassium hydroxide, sodium hydroxide and/or sodium silicate.
3. A composition as claimed in claim 1 or claim 2 comprising 2 to 25% by weight of the metal hydroxide and/or metal silicate.
- 20 4. A composition as claimed in any preceding claim wherein the nonionic surfactant is an alkoxylate surfactant of general formula $R(O(CH_2)_m)_nOH$ where R is an alkyl group with an active hydrogen atom; m is 2 or 3; and n is 4 to 20.
5. A composition as claimed in any preceding claim comprising from 2 to 15% by weight of surfactant.
- 25 6. A composition as claimed in any preceding claim wherein the quaternary ammonium disinfectant is of formula $RN(CH_3)_3Cl$ where R is C₆₋₂₀ alkyl.
7. A composition as claimed in any preceding claim comprising from 0.5 to 10% by weight of quaternary ammonium disinfectant.
- 30 8. A composition as claimed in any preceding claim wherein the hydrotroping agent is a propionate, betaine or glycinate amphoteric surfactant.
9. A composition as claimed in claim 8 wherein the hydrotroping agent is octylimino-dipropionate or sodium capryloimino-dipropionate.
- 35 10. A composition as claimed in any preceding claim comprising 1 to 10% by weight of hydrotroping agent.

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 5606

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) | | | | | | |
|---|---|---|---|-----------------|----------------------------------|----------|-----------|------------------|--------------------|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | | | | | | | |
| Y | US 4 240 921 A (KANIECKI THADDEUS J) 23 December 1980 (1980-12-23) * claims 1-3; examples 1,2 * --- | 1-7 | C11D3/00 C11D1/835 C11D3/02 C11D3/08 | | | | | | |
| Y | DATABASE WPI Section Ch, Week 198105 Derwent Publications Ltd., London, GB; Class D25, AN 1981-07092D XP002153269 & SU 735 630 B (EREV ZOOL VETER INS), 28 May 1980 (1980-05-28) * abstract * | 1-7 | | | | | | | |
| A | DATABASE WPI Section Ch, Week 199744 Derwent Publications Ltd., London, GB; Class D25, AN 1997-475604 XP002153270 & JP 09 221697 A (SHOWA DENKO KK), 26 August 1997 (1997-08-26) * abstract * | 1 | | | | | | | |
| A | DATABASE WPI Section Ch, Week 200025 Derwent Publications Ltd., London, GB; Class D25, AN 2000-291796 XP002153271 & RU 2 129 591 C (DAIRY IND RES INST), 27 April 1999 (1999-04-27) * abstract * | 1-3,5 | TECHNICAL FIELDS SEARCHED (Int.Cl.7) C11D | | | | | | |
| | | -/- | | | | | | | |
| <p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>20 November 2000</td> <td>Loiselet-Taisne, S</td> </tr> </table> | | | | Place of search | Date of completion of the search | Examiner | THE HAGUE | 20 November 2000 | Loiselet-Taisne, S |
| Place of search | Date of completion of the search | Examiner | | | | | | | |
| THE HAGUE | 20 November 2000 | Loiselet-Taisne, S | | | | | | | |
| CATEGORY OF CITED DOCUMENTS | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | | | | | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | | | | | | | | |



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 5606

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
| A | <p>DATABASE WPI Section Ch, Week 199503 Derwent Publications Ltd., London, GB; Class D25, AN 1995-020603 XP002153272 & RU 2 010 844 C (MOSC APPLIED BIOTECHN INST), 15 April 1994 (1994-04-15) * abstract *</p> <p>-----</p> | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.7) |
| <p>The present search report has been drawn up for all claims</p> | | | |
| Place of search | Date of completion of the search | Examiner | |
| THE HAGUE | 20 November 2000 | Loiselet-Taisne, S | |
| CATEGORY OF CITED DOCUMENTS | | <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p> | |
| <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> | | | |

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 30 5606

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-11-2000

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| US 4240921 | A | 23-12-1980 | NONE | |
| SU 735630 | B | 25-05-1980 | NONE | |
| JP 9221697 | A | 26-08-1997 | NONE | |
| RU 2129591 | C | 27-04-1999 | NONE | |
| RU 2010844 | C | 15-04-1994 | NONE | |