(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 December 2010 (23.12.2010)

PCT

(10) International Publication Number
WO 2010/147485 A1

(51) International Patent Classification:
C11D 7/26 (2006.01) *C11D 7/22* (2006.01)

(21) International Application Number:
PCT/NZ2010/000113

(22) International Filing Date:
15 June 2010 (15.06.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
577699 16 June 2009 (16.06.2009) NZ

(71) Applicant *(for all designated States except US)*: **DONAGHYS INDUSTRIES LIMITED** [NZ/NZ]; Unit D, 14-16 Sherffield, Harewood, Christchurch, 8053 (NZ).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **YERITSYAN, Karen** [NZ/NZ]; 6 Gibson Street, Wakari, Dunedin, 9010 (NZ).

(74) Agents: **SNOEP, Robert** et al.; CreateIP, 20 Bealey Avenue, PO Box 35-132, Shirley, Christchurch 8640 (NZ).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2010/147485 A1

(54) Title: ACID CLEANING COMPOSITION

(57) Abstract: The invention relates to an acid cleaning composition. In particular, an acid cleaning composition in the form of a stable liquid concentrate including at least 50 % by with of the following acids: (a) at least one organic acid with both alcohol and acid functionality; (b) at least one further organic acid with chelating properties; and (c) at least one further organic acid exhibiting reactions characteristic of carboxylic acids. This combination acts to provide strong cleaning activity and requires less acid concentration to achieve the same degree of cleaning effect as existing cleaning compositions.

ACID CLEANING COMPOSITION

STATEMENT OF CORRESPONDING APPLICATIONS

This application is based on the Provisional specification filed in relation to New Zealand Patent Application Number 577690, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

The invention relates to an acid cleaning composition. More specifically, the invention relates to an acid cleaning composition that utilises at least three organic acids which in combination act to provide strong cleaning activity and requires less acid concentration to achieve the same degree of cleaning effect as existing cleaning compositions.

BACKGROUND ART

The components of commercial cleaning compounds modify the nature of water so that it may efficiently penetrate, dislodge and carry away surface contamination that for the purposes of this specification is termed 'soil'.

Cleaning can be considered as a series of four steps:

1. Bringing the detergent solution into intimate contact with the soil to be removed by means of good wetting and penetrating properties;

2. Displacement of the solid and liquid soils from the surface to be cleaned by saponifying the fat, peptising the proteins and dissolving the minerals;

3. Dispersion of the soil in the solvent by dispersion, deflocculation or emulsification; and

4. Preventing re-deposition of the dispersed soil back onto the clean surface by providing good rinsing properties.

In addition to achieving these steps, it is desired that a good cleaner be:

1. Adequate for effectively softening water;
2. Quickly and completely dissolved;
3. Non-toxic;
4. Less corrosive;
5. Economical to use; and
6. Stable upon storage.

As should be appreciated, water alone acts as a good cleaning agent if enough external energy is put into the system. By way of illustration, the primary constituent of all dairy plant cleaners is water. Pure water presents no problem, but no dairy plant supply water is ideal as the water may be hard, may contain traces of contaminants or may contain fouling substances such as suspended matter. Water alone is therefore not always the ideal cleaning solution.

Cleaning compounds may be added to the water in order to decrease the external energy requirements by increasing the internal potential energy of the water. Addition of cleaning compounds also compensates for the above issues of water quality and in general avoids the need to individually tailor cleaning compounds for different water supplies as one compound can often be sufficient for a variety of applications.

The compounds required for adequate cleaning of food plant equipment generally are complex mixtures of chemicals combined to achieve a specific purpose.

Periodic cleaning and sanitising in dairy, food and beverage industries, in food preparation and service businesses are a necessary practice for product quality and public health. Residuals left on equipment surfaces or contaminants found in the process or service environment can promote the growth of micro-organisms.

Visual inspection of the equipment cannot ensure that surfaces are clean or free of micro-organisms. Antimicrobial treatments as well as cleaning treatments are therefore required for all critical surfaces in order to reduce microbial population to safe levels established by public health regulations. This process is generally referred to as 'sanitising' where the standard to be met is to result in a reduction in microbial population of at least 99.999 % (5 logs) for specified micro-organisms.

The antimicrobial efficacy of sanitising treatments is significantly reduced if the surface is not absolutely free of soil and other contaminants prior to the sanitising step. The presence of residual food soil and/or mineral deposits inhibits sanitising treatments by acting as physical barriers which shield micro-organisms lying within the organic or inorganic layer from the anti-microbial agent. Furthermore, chemical interactions between the anti-microbial agent and certain contaminants can disrupt the killing mechanism of the anti-microbial agent.

The selection of sanitiser/disinfectant is based on properties which need to be considered including: to be non toxic when used properly; to be harmless to the applied surfaces; to be fast acting, even in presence of organic matter; to be effective against all types of infectious agents (broad spectrum); to easily penetrate the material to be disinfected; to be stable; and to be compatible with the cleaners that are used.

Various chemicals exhibiting varying degrees of antimicrobial activity have been used in sanitising operations. Among these are short-chain monocarboxylic acids having less than 20 carbon atoms, quaternary ammonium compounds and

hexachlorophene compounds. These compounds have been admixed with various surfactants and water to yield aqueous sanitising solutions. Sanitisers containing halogens can be corrosive to metal surfaces of food plants and quaternary ammonium compounds, which also have been used, strongly adhere to sanitised surfaces even after copious rinsing and may interfere with desired microbial growth during food processing, e. g. fermentation.

Acid type cleaners are routinely used in at least the dairy industry for milkstone removal and also as part of the cleaning process on high temperature heat exchange equipment. By way of example, equipment in a dairy context that require cleaning include plate pasteurisers, tubular heaters, HTST pasteurisers, evaporators, UHT units, as well as in CIP cleaning of other milk processing and storage equipment. These types of equipment are routinely cleaned by a two-phase circulation system using an acid type cleaner in one phase. Using these cleaners allows for the removal of burnt on milk deposits thereby preventing milkstone formation.

A wide choice of acid type cleaners is available. They are blends of organic acids, inorganic acids, or acid salts usually with the addition of wetting agent. To be effective, acid type cleaners generally produce a pH of 3.0 or lower in the diluted solution. Other important characteristics of existing cleaners are that the cleaner should work well in hard as well as soft water and should show minimal corrosion on dairy plant metals. Acid cleaners also can combine the rinsing and sanitising steps.

Acid detergents can be very effective in solutions where soils fail to respond to alkaline cleaners. For many years, acids have been employed as milkstone removers in the dairy industry. In addition, acids have been extensively used in the dairy plant sanitation program, especially for cleaning high-temperature processing equipment such as. Application of acid maintains the equipment surface free of

mineral deposits and keeps stainless steel in good condition. Often acids are used as acidified rinses to ensure neutralisation of alkaline residues that may be left on equipment after insufficient rinsing of the alkaline cleaner.

There are various acidic cleaner sanitisers known in the art. Most of them can be combined in three classes: inorganic acids based; organic acids based; inorganic and organic acids blend based compositions.

The most popular inorganic acids are phosphoric, sulphuric, hydrochloric and nitric acids which should be recognised as being strong and corrosive acids. These strong acids are normally combined with a mild or weak acid, for example phosphoric acid, to soften the strong acid corrosive effect.

Examples of existing products on the market based on these groups of acids are Combat™ acid cleaner sanitiser manufactured by Donaghys Industries, based on a blend of sulphuric and phosphoric acids; Proclean CIP™ acid manufactured by Madison Chemicals Co, based on phosphoric and nitric acids.

Existing products have the disadvantages that they are highly corrosive and, where phosphoric acid is used there is potential for water phosphate contamination.

Recently, attention has been drawn to water contamination with phosphates. Many attempts have been done to decrease phosphate use and replace them with more environmentally friendly cleaners. By way of example Merck & Company Inc. reduced the use of phosphoric acid by 95% for cleaning glassware and replaced it with a citric acid based cleaner.

In the last twenty years more attention has been drawn to the potential use of organic acids as cleaning and sanitising compounds. Organic acids such as acetic, peroxyacetic, lactic, propionic and formic acids are the most common acid sanitisers. Examples of such compositions include: Citra Acid™ manufactured by

Epsilon Chemicals Ltd.; Perasan™ and Bioside HS™ manufactured by EnviroTech Chemicals, Inc.

These compounds work very well on stainless steel surfaces or where they may be in contact for a long time. Organic acids also have the advantage that they are safer acid cleaners and they also have anti-microbial properties as well. A disadvantage though is that organic acids tend to be weaker than inorganic acid cleaners described above and therefore a greater concentration and/or volume of organic acid is required to achieve the cleaning levels desired.

It should therefore be appreciated that it would be desirable to have a cleaner that utilised organic acids and which achieved the same level of cleaning properties as inorganic acids and ideally used lower concentrations and/or volumes of organic acid.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

All references, including any patents or patent applications cited in this specification are hereby incorporated by reference. No admission is made that any reference constitutes prior art. The discussion of the references states what their authors assert, and the applicants reserve the right to challenge the accuracy and pertinency of the cited documents. It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents form part of the common general knowledge in the art, in New Zealand or in any other country.

Throughout this specification, the word "comprise", or variations thereof such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements integers or steps, but not the

exclusion of any other element, integer or step, or group of elements, integers or steps.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

DISCLOSURE OF THE INVENTION

As noted above, the most commonly used formulations of acid cleaners are based on inorganic acid mixtures. These mainly consist of two acids, one of which is a strong acid, for example sulphuric acid, and a second acid which is a mild or weak acid, for example phosphoric acid. The main disadvantages of such formulations are that they are highly corrosive and are considered as a possible source of water contamination.

The inventors have found that by using a blend of organic acids with specific properties, it is possible to achieve excellent results in cleaning beyond that which was expected and avoid use of corrosive solutions and contamination sources. A further unexpected finding was that the specific combination of organic acids provided sufficient cleaning effects even when less (1/3rd less) concentrated than traditional acid cleaning solutions.

According to a first aspect of the invention there is provided an acid cleaning composition in the form of a stable liquid concentrate including at least 50% by weight of the following acids:

(a) at least one organic acid with both alcohol and acid functionality;

(b) at least one further organic acid with chelating properties; and

(c) at least one further organic acid exhibiting reactions characteristic of carboxylic acids.

As should be appreciated, the acids present in this invention are naturally occurring compounds, widely used in similar or other fields of application by themselves or as mixtures. In contrast to inorganic acids, organic acids are less corrosive, are not considered as a source of contamination of ground waters, safer to handle and transport, and show better performance.

In one embodiment, the organic acid with both alcohol and acid functionality may be glycolic acid. Glycolic acid has one of the smallest organic molecules with both acid and alcohol functionality, resulting in unique chemical attributes. Glycolic acid uses both the hydroxyl and carboxyl acid groups to form five-member ring complexes (chelates) with polyvalent metals. It readily forms typical salts with active metals, metal oxides and bases.

In one embodiment, the organic acid with chelating properties may be citric acid. Citric acid's ability to chelate metals makes it useful in soaps and laundry detergents. By chelating the metals in hard water, it lets these cleaners produce foam and work better without need for water softening. In a similar manner, citric acid is used to regenerate the ion exchange materials used in water softeners by stripping off the accumulated metal ions as citrate complexes.

In one embodiment, the organic acid exhibiting reactions characteristic of carboxylic acids may be oxalic acid. Oxalic acid is relatively strong despite being classified as a weak acid, with pKa_1=1.27 and pKa_2=4.28. Oxalic acid exhibits many of the reactions characteristic of other carboxylic acids. Oxalic acid also forms esters such as dimethyloxalate (melting point 52.5-53.5°C) and an acid chloride (oxalyl chloride).

Oxalic acid or ethanedioic acid ($C_2 H_2 O_4$) is a dicarboxylic acid and is present in many plants and vegetables, notably in those of the Oxalis and Rumex genera, where it often occurs in the cell sap of the plants as the potassium or calcium salt

(oxalate). Oxalic acid is also a product of the metabolism of many mould fungi. Several species of *Penicillum* and *Aspergillus* convert sugar into calcium oxalate with a 90% yield under optimum conditions. Oxalic acid is also made by passing carbon monoxide into concentrated sodium hydroxide (NaOH) or heating sodium formate in the presence of NaOH.

Oxalate, the conjugate base of oxalic acid, is an excellent ligand for metal ions. It usually binds as a bidentate ligand forming a 5-membered MO_2C_2 ring. An illustrative complex is potassium ferrioxalate, $K_3[Fe(C_2O_4)_3]$.

Advantageous properties of oxalic acid have given possibility to use this acid in different areas. For example, WO 91/08981 describes application of oxalic acid as a component for composition used for bleaching and washing animal tissue. US 3,993,575 describes the possibility to use oxalic acid for removal of tenacious soil, such as tarnish, discoloration, corrosion and oxidation products from vehicles. One reference[1] shows use of oxalic acid as an efficient catalyst in the condensation of 2-aminoaryl ketones with carbonyl compounds leading to the formation of quinolines in excellent yields under solvent free conditions.

Another reference[2] has shown, that oxalic acid can successfully be used to replace phosphoric acid for de-gumming vegetable oils with high phosphatide content prior to alkali refining, and as a result, alleviate the pollution problem with phosphate waste in cases where water purification by means of a chemical treatment process is not possible.

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[1] Chemical Monthly, volume 138, number 12/ December 2007, p. 1249-1252

[2] R. Ohlson and C. Svensson (Research Laboratory, AB Karshamns Oljefabriker, Karsshamn, Sweden) Journal of the American Oil Chemists' Society, Volume 53, Number 1, 1976, p.8-11.

US 4,316,752 shows that surface of metal, carbon steel galvanised steel and/or aluminium, can be modified by treating the metal surface with a dilute aqueous oxalic acid solution, and further treating the surface with a phosphotising bath, to improve the corrosion resistance of the metal surface.

Besides above described examples, further applications for oxalic acid include:

- Precipitating agent in rare-earth mineral processing;
- Bleaching agent in the textile activities, wood pulp bleaching;
- Rust remover for metal treatment;
- Used in commercial rust removers to remove rust stains from tubs and sinks;
- Grinding agent, such as marble polishing;
- Waste water treatment, removing calcium in water;
- Use in cleaning and sterilizing home-brewing equipment;
- Useful as a reducing agent for photography and ink removal;
- Used as purifying agent in pharmaceutical industry;
- Used by rock collectors to clean mineral specimens; and
- Remove food and rust stains from kitchen benches, plumbing fixtures and fabric.

Notwithstanding the above, there is little commercial use of oxalic acid in applications for cleaning processing equipment such as in dairy environments.

Preferably, the acid cleaning composition includes:

(a) 10-90% total acid by weight organic acid with both alcohol and acid functionality;

(b) 1-45% total acid by weight organic acid with chelating properties; and,

(c) 1-25% total acid by weight organic acid exhibiting reactions characteristic of carboxylic acids.

For the purposes of this specification, the term 'total acid' refers to the total concentration of acids in the composition. Further, the above concentration [%] for each component is calculated using the formula:

$$\%AcidA = 100 \times \frac{WeightAcidA}{Weightofsumofacids}$$

More preferably, organic acid with both alcohol and acid functionality may be glycolic acid included at a rate of about 30 to 80% total acid by weight, or about 35-70% of total acid content by weight, or about 40-70% of total acid by weight, or most preferably, about 50-60% of total acid content by weight.

More preferably, the organic acid with chelating properties may be citric acid present in amounts of about 10-40% of total acid content by weight, or about 25-37% of total acid content by weight, or more preferably in amounts of about 28-35% of total acid content by weight.

More preferably, the organic acid exhibiting reactions characteristic of carboxylic acid is oxalic acid present in an amount of about 5-20% of total acid content by weight, or about 10-15% of total acid content by weight, or more preferably in amount about 10-12 % of total acid content by weight.

In one embodiment determined by the inventor, the ideal composition in terms of cleaning capacity is determined in part by the oxalic acid concentration in the total

composition. In one embodiment, the oxalic acid concentration is about 2-7% by weight of total formulation calculated by the formula:

$$\%compositionoxalicacid = 100 \times \frac{Weightofoxalicacid}{TotalCompositionWeight}$$

More preferably, the inventor has found that the amount of oxalic acid is ideally about 5-6% by weight of total composition.

In one embodiment, the composition contains 40-70% glycolic acid, 28-35% citric acid and 2-7% oxalic acid by weight in the total composition.

Preferably, the acid cleaning composition has a ratio of acids approximate to:

(a) 3 to 7 parts by weight organic acid with both alcohol and acid functionality;

(b) 2 to 5 parts by weight organic acid with chelating properties; and,

(c) 0.25 to 1.75 parts by weight organic acid exhibiting reactions characteristic of carboxylic acids.

In one embodiment, the acid cleaning composition has a ratio of acids approximate to 5 parts glycolic acid, 3 parts citric acid and 1 part oxalic acid.

Preferably, the acid cleaning composition has a pH of less than 5. More preferably, sufficient acid is present to confer a pH of between approximately 1.0-3.5.

In further embodiments, the acid cleaning composition also includes further compounds selected from the group consisting of:

(a) further acids selected from organic or inorganic acids;

(b) at least one antimicrobial agent;

(c) at least one surfactant compound;

(d) and combinations thereof.

In one embodiment, further acids may be selected from the group consisting of: acetic, formic, phosphoric, sulphuric acids, and combinations thereof.

As noted above, the composition may include an anti-microbial agent or agents. By inclusion of such agents, the composition also gains additional sanitiser properties which may be equally effective on gram-negative and gram-positive micro-organisms and on yeast and moulds. Note that by virtue of the acid properties, the composition even without anti-microbial agent, still has sanitising properties. An advantage of the composition of the invention is that the antimicrobial activity of the composition is unaffected by water hardness which can be an issue in the art. In one embodiment, antimicrobial compound is included at a concentration of 3-10% of the total composition by weight.

In one embodiment, the anti-microbial agent or agents may include quaternary ammonium compounds (QAC). Non-limiting examples include didecyl dimethyl ammonium chloride; N-alkyl (C12-14) dimethyl benzyl ammonium chloride; N,N-bis (3-aminopropyl) dodecylamine; N-decyl-N-isononyl-N,N-dimethyl ammonium chloride, N-Isononyl- N,N,N-trimethyl ammonium chloride, decyl chloride blend.

As may be appreciated from the above, the various QAC's may be either:

a) First Generation: $C_6 H_5$ --CH_2 $N(CH_3)_2$ R alkyldimethylbenzyl ammonium chloride; or

b) Second Generation: $(C_2 H_5)C_6 H_5$ --CH_2 $N(CH_3)_2$ R alkyldimethylethylbenzyl ammonium chloride; or

c) Third Generation: $N(R)_2$ $(CH_3)_2$ R-dimethyl ammonium chloride

The anti-microbial agent may be from the quaternary ammonium chloride family including dialkyls from 6-18 carbon atoms ammonium chlorides, dialkyls from 1-4 carbon atoms ammonium chlorides. Preferably, didecyl dimethyl ammonium chloride, dioctyl dimethyl ammonium chloride, octyl decyl dimethyl ammonium chloride and alkyl (C_{14} -50%, C_{12} -40%, C_{16} -10%) dimethyl benzyl ammonium chloride, and combinations thereof.

In a yet further embodiment, the antimicrobial agent may be a combination of quaternary ammonium compounds consisting of the following blend in a 1:1:2:2.67 weight ratio respectively:

a) Didecyl dimethyl ammonium chloride;

b) Dioctyl dimethyl ammonium chloride;

c) Octyl decyl dimethyl ammonium chloride; and,

d) Alkyl (C_{14} -50% by weight, C_{12} -40% by weight, C_{16} -10% by weight) dimethyl benzyl ammonium chloride

During use as a disinfecting composition, the total levels of this blend (a-d) will preferably range from 500 to 1000ppm's (parts by weight per million).

In further embodiments, other quaternary materials that may be utilised are Tomah quaternaries (quaternary ammonium materials). Tomah quaternaries are based on the reaction of high molecular weight aliphatic tertiary amines with an alkylating agent such as methyl chloride. Quaternaries are more cationic and more stable to pH change than other amine-based surfactants such as ethoxylated amines or amine acetate salts. The different molecular configurations give different solubility, emulsification, and cationic strength properties. Most Tomah quaternaries can be represented by the formula:

$$RO(CH_2)_3\ N^+\ (CH_3)(C_2\ H_4\ OH)_2\ Cl^-$$

Where R is an aliphatic alkyl of hydrophobe (of 6-18 carbon atoms) Other useful quaternary ammonium materials are:

- Q-14-2 75% active isodecyloxypropyl dihydroxyethyl methyl ammonium chloride;
- Q-14-2PG 75% active isodecyloxypropyl dihydroxyethyl methyl ammonium chloride (supplied in propylene glycol);
  Q-17-2 75% active isotridecyloxypropyl dihydroxyethyl methyl ammonium chloride;
- Q-17-2PG 75% active isotridecyloxypropyl dihydroxyethyl methyl ammonium chloride (supplied in propylene glycol);
- Q-18-2(50) 50% active octadecyl dihydroxyethyl methyl ammonium chloride;
  Q-18-15 100% active octadecyl poly (15)oxyethylene methyl ammonium chloride;
  Q-D-T 50% active tallow diamine diquatemary;
- Q-DT-HG 70% active tallow diamine diquatemary (supplied in hexylene glycol);
- Q-C-15 100% active coco poly(15)oxyethylene methyl ammonium chloride; and
- Q-ST-50 50% active trimethyl stearyl quaternary ammonium material.

Yet further preferred antimicrobial compounds include polymeric ammonium quaternary compounds - polyquats, for example N,N-dimethyl-2-hydroxypropylammonium chloride polymer.

Yet another preferred antimicrobial compound are the poly-(hexamethylene-biguanite) hydrochloride (PHMB) based antimicrobial compounds. Given the fact that the PHMB molecule is cationic in nature, these antimicrobials formulate in a manner analogous to quaternary ammonium compounds.

In one embodiment, the surfactant compound is a non-ionic compound. The surfactant in the present invention may be present in an amount of about 0.1-15% by weight of the total composition, or in an amount of 0.1-12% by weight of the total composition, or in an amount of 0.2-5% by weight of the total composition, or preferably in an amount of 0.3-1% by weight of the total composition. Preferred surfactants may include:

1. Alcohol alkoxylates,
2. Nonylphenol ethoxylates
3. Ethylene oxide/propylene oxide block copolymers,

The inventors consider that a main advantage of this class of surfactants is that they are non-ionic and therefore miscible with anionic, cationic and other non-ionic surfactants; they do not react with cations, such as calcium and magnesium, which means they can be used in hard water; and they are fully resistant to non-oxidising acids in concentrations at which they are normally employed in applications.

Non-ionic surface active agents are usually the reaction product of an alkylene oxide, typically ethylene oxide, with an alcohol, alkylphenol, alkylamine, fatty acid or other appropriate compound having at least one active hydrogen atom. For most practical surface active agents the most common alcohols, amines and acids have a carbon chain length in the range C_8-C_{18} and the most common alkylphenols are nonylphenol and octylphenol. Dialkylphenols and trialkylphenols are also used in some specialised applications.

For the present invention the inventors have found that the most suitable non-ionic surfactants are alcohol alkoxylates and nonylphenol ethoxylates.

The versatility of alcohol alkoxylate based surfactants is such that they can be used to formulate acidic, alkaline and neutral cleaners that satisfy the most varied requirements. These types of surfactants generally perform well as emulsifiers, although some perform better than others. Their practical performance as emulsifiers can be gauged according to their hydrophilic – lipophilic balance, which correlates with their degree of ethoxylation. They are very effective wetting agents.

Still more preferably, the inventors have found that the most suitable surfactants from this range are alcohol alkoxylates with average molar mass 500-830g/mol, HLB value 14-16, degree of ethoxylation 8-10.

In one embodiment, a diluent may be added to the concentrate prior to use. Preferably, the diluent is food grade. In one embodiment the diluent is potable water. In one example, the concentrate may be added to the diluent at a ratio from 1:10 parts concentrate to diluent to 1:1500 parts concentrate to diluent, or in a ratio from about 1:100 to about 1:1300 or more preferably from about 1:500 to 1:1200 parts of concentrate to diluent.

Preferably, the acid cleaning composition concentrate may be diluted at a rate of less than 1.5mL concentrate per litre of diluent. More preferably, the dilution rate may be less than or equal to 1.0mL concentrate per litre of diluent.

A preferred embodiment of the solution of the present invention is a low foaming, acidic antimicrobial sanitising and/or cleaning solution prepared by diluting the composition as defined above with potable water in such ratio, that it comprises between about 1 to about 10000ppm, preferably from about 100 to about 8000ppm, most preferably from about 400 to about 6000ppm of the antimicrobial

agent or agents; and optionally, a sufficient amount of the detergent to induce surface wetting and soil removal and water as the balance of the composition.

Further, as noted above, synergies were noted form the mixture that were unexpected particularly around the lower concentration of concentrate required compared to what would have been expected in the art. The inventors also completed experiments using only two of the acids described and eliminating the third. The results were considerably less effective at cleaning and the same lower concentration result was not observed. The inventors understand that the synergy observed may be explained by the synergistic effect of the glycolic acid unique chemical properties, due to presence of hydroxyl and carboxyl groups, chelating properties of citric acid and the oxalic acid relatively strong dicarboxylic acid and able to play role as ligand. The different properties combine to form a cleaning composition that enhances the de-scaling and chelating properties of the acids individually.

It should be noted that oxalic acid is the only possible compound in which two carboxylic groups are joined directly, for this reason oxalic acid is one of the strongest organic acids. Unlike other carboxylic acids, oxalic acid is readily oxidised.

According to a further aspect of the present invention there is provided a method of producing an acid cleaning composition in the form of a diluted liquid by the steps of:

(a) preparing a liquid concentrate containing at least 50% by weight of total acid by mixing together:

i. at least one organic acid with both alcohol and acid functionality;

ii. at least one further organic acid with chelating properties;

iii. at least one further organic acid exhibiting reactions characteristic of carboxylic acids; and

(b) when used, diluting the concentrate with a diluent at a ratio of less than 1.5mL concentrate per litre of diluent.

Preferably, in the above method, the organic acid with both alcohol and acid functionality is glycolic acid.

Preferably, in the above method, the organic acid with chelating properties is citric acid.

Preferably, in the above method, the organic acid exhibiting reactions characteristic of carboxylic acids is oxalic acid.

In one embodiment, the composition produced in the method in step (a) includes:

(a) 10-90% by weight organic acid with both alcohol and acid functionality;

(b) 1-45% by weight organic acid with chelating properties; and,

(c) 1-25% by weight organic acid exhibiting reactions characteristic of carboxylic acids.

In one embodiment, mixing is completed in step (a) using ratios of acids approximate to:

(a) 3 to 7 parts by weight organic acid with both alcohol and acid functionality;

(b) 2 to 5 parts by weight organic acid with chelating properties; and,

(c) 0.25 to 1.75 parts by weight organic acid exhibiting reactions characteristic of carboxylic acids.

In one particular embodiment mixing is completed in step (a) using a ratio of acids approximate to 5 parts glycolic acid, 3 parts citric acid and 1 part oxalic acid.

Optionally, the method also includes the step of mixing in additional compounds selected from the group consisting of: further acids selected from organic or inorganic acids; at least one antimicrobial agent; at least one surfactant compound; and combinations thereof.

Preferably, the surfactant compound is a non-ionic compound.

Preferably, the diluent used in step (b) is water. In one embodiment, the concentrate is added to the diluent in step (b) at a ratio from 1 part concentrate to 10 parts diluent to 1 part concentrate to 1000 parts diluent.

According to a further aspect of the present invention there is provided the use of an acid cleaning composition concentrate substantially as hereinbefore described to clean dairy processing equipment.

According to a further aspect of the present invention there is provided the use of a diluted acid cleaning composition substantially as hereinbefore described to clean dairy processing equipment.

It should be appreciated from the above description that there is described a cleaning composition and method of manufacturing same. The advantages which should be apparent to those skilled in the art include:

- Good stability which does not change in a wide range of temperatures;
- Dissolves milkstone and removes rust spots;
- Easier transportation and storage, and more effective production. The same amount of formulation will give 1/3rd more final use solution at rate

1ml/L on dilution, than common inorganic acids based cleaner sanitisers, when used at recommended concentration rates as 1.5 ml/L;

- Minimal difference in cleaning effects between the invention and traditional inorganic acid cleaning mixtures even when the invention composition was used at lower rates than the art;

- The antimicrobial activity of the composition is unaffected by water hardness;

- The composition is a low foaming composition on dilution and application capable of removing intense flavour, e. g. of soft drinks. Commonly used acid cleaner sanitisers containing quaternary ammonium compounds as sanitising agents are known to produce foam, which sometimes makes it hard to dilute the concentrate to the appropriate level. This results in not having adequate concentration of active ingredient in final solution, for example, over diluting the solution because of an unclear border between liquid/foam phases;

- The composition also requires less water to rinse the residues such as foam off the surface after application, which has some environmental and economical effects;

- The composition is less corrosive than the art;

- The composition is more environmentally friendly than the art;

- Being highly concentrated with increased performance present invention has economical and environmental advantages, such as less packaging disposal, reducing shipping and handling costs, and biodegradability;

- The composition significantly accelerates scale removal approximately by up to 20%;
- The manufacturing process incorporates less corrosive raw materials, and generates no heat during production unlike art compositions such as those containing sulphuric acid;
- The formulation is safer to use on a wider range of applied surfaces; and
- All components of the invention are biodegradable and environmentally friendly.

BEST MODES FOR CARRYING OUT THE INVENTION

The invention is now described with reference to examples illustrating the composition and the advantages that the composition offers.

EXAMPLE 1

In this example a total of seven compositions were prepared with different concentrations of oxalic, citric and glycolic acids as shown in Table 1 below.

Table 1 – Composition Concentrations

Composition Number	Glycolic Acid (70% strength) Content [g/L]	Citric Acid Content [g/L]	Oxalic Acid Content [g/L]
1	250	150	50
2	250	120	55
3	300	100	30
4	200	170	60
5	270	120	55
6	270	200	20
7	150	200	60
8	162.5	75	25

All compositions contained antimicrobial compound in concentration of 50 g/L, and non ionic surfactant in amount of 5.1 g/L and were diluted at a rate of 1.5mL per litre of potable water.

The compositions were initially tested on their stability at both low and elevated temperatures.

None of the compositions showed stability issues at elevated temperature however, compositions 4 and 5 did not show the desired stability at low temperatures. Low temperature stability is important where the composition may be stored in cold conditions, for example in unheated storage warehouses or dairy sheds.

The compositions were tested for rust spot removal from applied surfaces. In this test, compositions 3 and 6 did not show satisfying results in rust spot removal from applied surfaces.

General cleaning ability was also assessed and composition 8 was not found to show the desired cleaning ability at the dilution rates tested.

Milk stone removal was then tested. Milk stones preparation was completed by the method described in the art[3].

In brief, the method involves cleaning type 302 stainless steel strips first with phosphoric acid based acid cleaner and then with alkaline cleaner, followed by thoroughly rinsing the steel strips in distilled water and drying. The strips were then weighed and placed so that lower parts of the strips were consecutively dipped into vessels containing: a) 250ppm available chlorine solution, b) raw whole

[3] Laboratory study of factors influencing milkstone formation" by Thaddeus Lewandowski, Pennsalt Chemical Corporation, Research and Development Division, Wyndmoor, Pennsylvania

milk, initially at 37°C and allowed to cool to room temperature during the test: c) potable water at room temperature, used as the first rinse; d) cleanser solution at 49°C, at 0.25%; e) a second water – rinse at 49°C. The exposed time of each strip to each liquid was 70 seconds, and transit time from liquid to liquid was 30 sec. This cycle was repeated 30 times, the milk being replaced with a fresh supply at 37°C after each 15 cycles. The milk was stirred mechanically during each cycle, about 5 minutes, before the strips were dipped into it. At the end of the exposure period, the strips were held at room temperature for 10 minutes and weighted. The amount of the formed milkstone was equal to the difference of weights of strips before and after experiment.

Working solutions of compositions 1, 2, 7 described above were prepared at dilution rate 1ml/L and 1.5ml/L in hot (75-85°C – recommended temperature for acid rinse procedure) water. The steel strips were dipped into the prepared diluted compositions for 60 seconds under constant mechanical stirring, rinsed with distilled water, dried and weighted to determine the amount of removed milkstone as a difference in strip weight.

The result was that there was no significant difference in cleaning ability of diluted samples at rate of 1ml/L compared to diluted samples at rate of 1.5ml/L.

In addition, it was found, that the best properties, from application and performance point of view, are shown by composition 1 although compositions 2 and 7 also gave useful results.

EXAMPLE 2

In this example, the performance of the invention composition to common inorganic acid based cleaning compositions was compared via a similar experiment to that described in Example 1 to test milk stone removal.

As a comparison, Combat™ acid sanitiser containing 170 g/L of phosphoric acid, 112g/L of sulphuric acid and 6.2g/L of anti-microbial compound, was used at the recommended dilution rate of 1.5ml/L. Working solutions were prepared in hot (75-85°C) and cold water.

The steel strips used were dipped into the prepared diluted compositions for 60 seconds under constant mechanical stirring, rinsed with distilled water, dried and weighed to determine the amount of removed milkstone as a difference in strip weight.

Composition 1 removed approximately 99.97% on average of formed milkstone, compared to Combat™ acid sanitiser, where the average milkstone removal was approximately 99.968%.

The results show that there was no reduction in performance by the invention composition, compared to a common inorganic acid based composition when used at recommended rates.

EXAMPLE 3

In this example, the reduction in foaming noted by the inventors is further described.

Commonly used acid cleaner sanitisers containing quaternary ammonium compounds as sanitising agent are known to produce foam. The foam may make it difficult to dilute the concentrate to an appropriate level and may result in not having adequate concentration of active ingredient in final solution. For example, over-diluting of the solution may occur because of an unclear border between liquid/foam phases.

The composition of the present invention in trials produces less foam compared to existing art compositions on dilution and application. This makes it easier to dilute the composition to an appropriate volume.

A further advantage is that, because there are fewer foam residues, less water is required to rinse the residues off the surface of treated equipment after application thereby reducing the processing water required and resulting in environmental and economical benefits.

EXAMPLE 4

As noted in the above description, the combination of organic acids identified by the inventors appears to have synergetic effects.

To illustrate the effects, various formulations were prepared using only two of above described acids in recalculated concentrations so that total amount of acids equals the original formulation total acids amount.

For example:

Formulation 1 included 214.28 kg per 1000L of glycolic acid and 120 kg per 1000L of citric acid;

Formulation 2 included 274.28 kg per 1000L of glycolic acid and 60 kg per 1000L of oxalic acid;

Formulation 3 (the invention) included glycolic, citric and oxalic acids in total equalling 334.28 kg per 1000L.

Subsequent experiments have shown that cleaning properties of the invention formulation was significantly improved over experimental formulations containing only two of above described acids. In addition, to achieve the desired degree of

cleaning, about 1/3rd less formulation was required for the invention compared to when formulations containing two acids are used.

EXAMPLE 5

Further working examples of glycolic, citric, oxalic acid containing compositions are now described in Tables 2 to 5 below.

Table 2 - Cleaner Composition 1

INGREDIENT	CONCENTRATION kg/1000L
Glycolic acid (70% strength)	214.28
Citric acid (anhydrous)	90
Oxalic acid	30
Barquat PQ-2™ anti-microbial[4]	120
Teric 9A2™ surfactant[5]	7
Water	To balance

Table 3 - Cleaner Composition 2

INGREDIENT	CONCENTRATION kg/1000L
Glycolic acid (70% strength)	142.85
Citric acid (anhydrous)	60
Oxalic acid	20
Acetic acid	40
Tecsol BAC50™ anti-microbial[6]	100
Water	To balance

[4] N,N-dimethyl-2-hydroxypropylammonium chloride

[5] C_9-C_{11} alcohol ethoxylate

[6] N-alkyl (C12-C14) dimethyl benzyl ammonium chloride

Table 4 - Cleaner Composition 3

INGREDIENT	CONCENTRATION kg/1000L
Glycolic acid (70% strength)	214.28
Oxalic acid	30
Citric acid (anhydrous)	90
Phosphoric acid (85% strength)	117.65
Bardac 2280™ anti-microbial[7]	64
Lutensol XL 100™ surfactant[8]	5
Water	To balance

Table 5 – Cleaner Composition 4

INGREDIENT	CONCENTRATION kg/1000L
Glycolic acid (70% strength)	357.14
Citric acid	150
Oxalic acid	50
Lonzabac 12.100™ anti-microbial agent[9]	14
Water	To balance

As should be appreciated from the above description and examples, the invention provides the advantages of at least:

[7] Didecyl dimethyl ammonium chloride

[8] Alcohol alkoxylate

[9] N,N-bis (3-aminopropyl) dodecylamine

- The manufacturing process incorporates less corrosive raw materials, and generates no heat during production, unlike sulphuric acid;
- The formulation is safer to use on a wider range of applied surfaces;
- All components of the invention are biodegradable and environmentally friendly;
- Formulations require less packaging and less hazardous material for disposal; and
- Formulations show good stability which does not change in a wide range of temperatures.

Further advantages of the present formulations include easier transportation and storage, and more effective production. The same amount of formulation will give approximately 1/3rd more final use solution at rate 1ml/L on dilution, than common inorganic acids based cleaners when used at recommended concentration rates as 1.5 ml/L.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof as defined in the appended claims.

WHAT WE CLAIM IS:

1. An acid cleaning composition in the form of a stable liquid concentrate including at least 50% by weight of the following acids:

   (a) at least one organic acid with both alcohol and acid functionality;

   (b) at least one further organic acid with chelating properties; and

   (c) at least one further organic acid exhibiting reactions characteristic of carboxylic acids.

2. An acid cleaning composition as claimed in claim 1, wherein the composition includes:

   (a) 10-90% total acid by weight organic acid with both alcohol and acid functionality;

   (b) 1-45% total acid by weight organic acid with chelating properties; and,

   (c) 1-25% total acid by weight organic acid exhibiting reactions characteristic of carboxylic acids.

3. An acid cleaning composition as claimed in claim 1 or 2, wherein the organic acid with both alcohol and acid functionality is glycolic acid.

4. An acid cleaning composition as claimed in claim 1 or 2, wherein the organic acid with chelating properties is citric acid.

5. An acid cleaning composition as claimed in claim 1 or 2, wherein the organic acid exhibiting reactions characteristic of carboxylic acids is oxalic acid.

6. An acid cleaning composition as claimed in any one of claims 1 to 3, wherein the organic acid with both alcohol and acid functionality is glycolic acid present in amounts of about 30 to 80% total acid by weight.

7. An acid cleaning composition as claimed in any one of claims 1 to 3, wherein the organic acid with both alcohol and acid functionality is glycolic acid present in amounts of about 35 to 70% total acid content by weight.

8. An acid cleaning composition as claimed in any one of claims 1 to 3, wherein the organic acid with both alcohol and acid functionality is glycolic acid present in amounts of about 40 to 70% total acid content by weight.

9. An acid cleaning composition as claimed in any one of claims 1 to 3, wherein the organic acid with both alcohol and acid functionality is glycolic acid present in amounts of about 50 to 60% total acid content by weight.

10. An acid cleaning composition as claimed in claims 1, 2 and 4, wherein the organic acid with chelating properties is citric acid present in amounts of about 10-40% of total acid content by weight.

11. An acid cleaning composition as claimed in claims 1, 2 and 4, wherein the organic acid with chelating properties is citric acid present in amounts of about 25-37% of total acid content by weight.

12. An acid cleaning composition as claimed in claims 1, 2 and 4, wherein the organic acid with chelating properties is citric acid present in amounts of about 28-35% of total acid content by weight.

13. An acid cleaning composition as claimed in claims 1, 2 and 5, wherein the organic acid exhibiting reactions characteristic of carboxylic acid is oxalic acid present in amounts of about 5-20% of total acid content by weight.

14. An acid cleaning composition as claimed in claims 1, 2 and 5, wherein the organic acid exhibiting reactions characteristic of carboxylic acid is oxalic acid present in amounts of about 10-15% of total acid content by weight.

15. An acid cleaning composition as claimed in claims 1, 2 and 5, wherein the organic acid exhibiting reactions characteristic of carboxylic acid is oxalic acid present in amounts of about 10-12% of total acid content by weight.

16. An acid cleaning composition as claimed in any one of claims 1, 2, and 5 wherein the amount of oxalic acid is about 5-6% by weight of total acid content by weight.

17. An acid cleaning composition as claimed in any one of claims 1 to 16, wherein the composition contains 40-70% glycolic acid, 28-35% citric acid and 2-7% oxalic acid by weight in the total composition.

18. An acid cleaning composition as claimed in any one of claims 1 to 17, wherein the acid cleaning composition has a pH of less than 5.

19. An acid cleaning composition as claimed in claim 18, wherein the pH is between 1.0 and 3.5.

20. An acid cleaning composition as claimed in any one of claims 1 to 19, wherein the acid cleaning composition also includes further compounds selected from the group consisting of:

(a) further acids selected from organic or inorganic acids;

(b) at least one antimicrobial agent;

(c) at least one surfactant compound;

(d) and combinations thereof.

21. An acid cleaning composition as claimed in claim 20 wherein the further acids are selected from the group consisting of: acetic, formic, phosphoric, sulphuric acids, and combinations thereof.

22. An acid cleaning composition as claimed in claim 20, wherein the antimicrobial compound is included at a concentration of 3-10% of the total composition weight.

23. An acid cleaning composition as claimed in claim 20 or 22 wherein the anti-microbial agent includes quaternary ammonium compounds (QAC).

24. An acid cleaning composition as claimed in claim 23, wherein the various QAC's are either:

a) First Generation: $C_6 H_5$ --CH_2 $N(CH_3)_2$ R alkyldimethylbenzyl ammonium chloride; or

b) Second Generation: (C2 H5)C6 H5 --CH2 N(CH3)2 R alkyldimethylethylbenzyl ammonium chloride; or

c) Third Generation: N(R)2 (CH3)2 R-dimethyl ammonium chloride.

25. An acid cleaning composition as claimed in any one of claims 20, 22 to 24 wherein the anti-microbial agent is from the quaternary ammonium chloride family including dialkyls from 6-18 carbon atoms ammonium chlorides, dialkyls from 1-4 carbon atoms ammonium chlorides.

26. An acid cleaning composition as claimed in a claim 25 wherein the quaternary ammonium chloride family is didecyl dimethyl ammonium chloride, dioctyl dimethyl ammonium chloride, octyl decyl dimethyl ammonium chloride and alkyl (C_{14} -50%, C_{12} -40%, C_{16} -10%) dimethyl benzyl ammonium chloride, and combinations thereof.

27. An acid cleaning composition as claimed in claims 23 to 26, wherein the antimicrobial agent is a combination of quaternary ammonium compounds consisting of the following blend in a 1:1:2:2.67 weight ratio respectively:

a) Didecyl dimethyl ammonium chloride;

b) Dioctyl dimethyl ammonium chloride;

c) Octyl decyl dimethyl ammonium chloride; and,

d) Alkyl (C14 -50% by weight, C12 -40% by weight, C16 -10% by weight) dimethyl benzyl ammonium chloride.

28. An acid cleaning composition as claimed in claim 27, wherein the total levels of this blend (a-d) is in the range from 500 to 1000ppm's (parts by weight per million).

29. An acid cleaning composition as claimed in claims 23 to 28, wherein other quaternary ammonium materials utilised are Tomah quaternaries represented by the formula:

$$RO(CH_2)_3\,N^+\,(CH_3)(C_2\,H_4\,OH)_2\,Cl^-$$

where R is an aliphatic alkyl of hydrophobe (of 6-18 carbon atoms).

30. An acid cleaning composition claimed in anyone of claims 20 to 29 wherein the antimicrobial compounds include polymeric ammonium quaternary compounds.

31. An acid cleaning composition as claimed in claim 20, wherein the antimicrobial compound is a poly-(hexamethylene-biguanite) hydrochloride (PHMB) based antimicrobial compound.

32. An acid cleaning composition as claimed in claim 20, wherein the surfactant compound is a non-ionic compound.

33. An acid cleaning composition as claimed in claim 20 or 32, wherein the surfactant is present in an amount of about 0.1-15% by weight of the total composition.

34. An acid cleaning composition as claimed in claim 20 or 32, wherein the surfactant is present in an amount of about 0.1-12% by weight of the total composition.

35. An acid cleaning composition as claimed in claim 20 or 32, wherein the surfactant is present in an amount of about 0.2-5% by weight of the total composition.

36. An acid cleaning composition as claimed in claim 20 or 32, wherein the surfactant is present in an amount of about 0.3-1% by weight of the total composition.

37. An acid cleaning composition as claimed in claims 20, 32 to 36 wherein the surfactants are selected from one of the following classes: Alcohol alkoxylates, Nonylphenol ethoxylates or Ethylene oxide/propylene oxide block copolymers.

38. An acid cleaning composition as claimed in claim 37, wherein the alcohol alkoxylates have average molar mass 500-830g/mol, HLB value 14-16 and degree of ethoxylation 8-10.

39. An acid cleaning composition as claimed in any one of claims 1 to 38, wherein the acid composition includes a food grade diluent.

40. An acid cleaning composition as claimed in claim 39, wherein the diluent is potable water.

41. An acid cleaning composition as claimed in claim 39 or 40, wherein the acid cleaning composition is diluted at a rate of less than 1.5mL concentrate per litre of diluent.

42. A method of producing an acid cleaning composition in the form of a diluted liquid by the steps of:

(a) preparing a liquid concentrate containing at least 50% by weight of total acid by mixing together:

i. at least one organic acid with both alcohol and acid functionality;

ii. at least one further organic acid with chelating properties; and

iii. at least one further organic acid exhibiting reactions characteristic of carboxylic acids; and

(b) when used, diluting the concentrate with a diluent at a ratio of less than 1.5mL concentrate per litre of diluent.

43. A method of producing an acid cleaning composition as claimed in claim 42, wherein the composition produced in the method in step (a) includes:

(a) 10-90% by weight organic acid with both alcohol and acid functionality;

(b) 1-45% by weight organic acid with chelating properties; and,

(c) 1-25% by weight organic acid exhibiting reactions characteristic of carboxylic acids.

44. A method of producing an acid cleaning composition as claimed in claims 42 or 43, wherein the method also includes the step of mixing in additional compounds selected from the group consisting of: further acids selected from organic or inorganic acids; at least one antimicrobial agent; at least one surfactant compound; and combinations thereof.

45. The use of an acid cleaning composition concentrate substantially as hereinbefore described to clean dairy processing equipment.

46. The use of a diluted acid cleaning composition substantially as hereinbefore described to clean dairy processing equipment.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000113

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C11D 7/26 (2006.01) *C11D 7/22* (2006.01)

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)
C11D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPODOC/WPI, CAPLUS, AGRICOLA & Keywords, oxalic, citric, glycolic, carboxylic and the like

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4357254 A (KAPILOFF et al) 02 November 1982 See abstract; col. 10, lines 10-55; Tables 3-4; Claim 7.	1-2, 4-5, 10, 13, 18-20, 32-37, 39-44
X	US 5154197 A (AULD et al) 13 October 1992 See Abstract; Table 2.	1, 18
X	US 3510351 A (van DILLEN et al) 05 May 1970 See abstract; col 4, lines 23-56, Etchant No. 6; claim 1.	1, 3 and 6
X	US 2006/0116306 A1 (PATIEN et al) 01 June 2006 See Tables 1-3; para. [0042]-[0043]	42-44

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 September 2010	20 SEP 2010
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **ANASTASIOS POLAS** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6225 6148

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000113

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1721961 A1 (THE PROCTER AND GAMBLE COMPANY) 15 November 2006 See Whole Document	1-44

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000113

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: **45-46**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 45 and 46 do not comply with Rule 6.2(a) because they rely on references to the description and/or drawings

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/NZ2010/000113

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	4357254	AU	81460/82	CA	1173336	EP	0069150
		NO	830915	US	4496470	WO	8202379
		ZA	8200178				
US	5154197	EP	0458533	JP	4227487		
US	3510351	DE	1546191	GB	1119680	JP	49027031
		ZA	656244				
US	2006116306	AU	2003285317	CA	2502420	DE	10257390
		EP	1567635	WO	2004053048		
EP	1721961	CA	2606452	EP	1721960	MX	2007014165
		US	2006287209	WO	2006124583		

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX