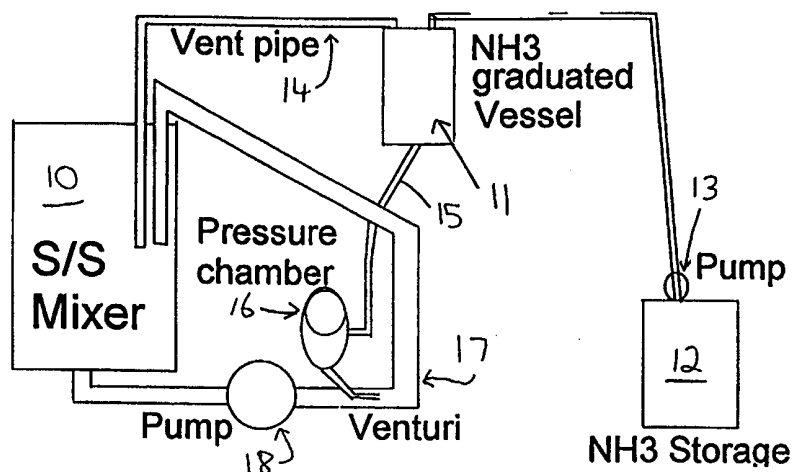




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/AU99/01094</p> <p>(22) International Filing Date: 8 December 1999 (08.12.99)</p> <p>(30) Priority Data: PP 7623 9 December 1998 (09.12.98) AU</p> <p>(71) Applicant (for all designated States except US): CAIRNSCORP TECHNOLOGY PTY LIMITED [AU/AU]; 221 Brisbane Street, Ipswich, QLD 4305 (AU).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): CAIRNS, Gerald, Joseph, Ward [GB/AU]; 221 Brisbane Street, Ipswich, QLD 4305 (AU).</p> <p>(74) Agent: CULLEN & CO.; Level 12, 240 Queen Street, Brisbane, QLD 4000 (AU).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>

(54) Title: CLEANING SOLUTIONS CONTAINING CITRIC ACID AND USES THEREOF



(57) Abstract

An aqueous ammoniated citric acid cleaning solution effectively cleans metal parts at room temperature. The solution is prepared by diluting a concentrated aqueous citric acid solution containing between 1-10 % ammoniation, the concentrated solution being prepared in a special way. Dilution of this specially prepared concentrated solution provides a working solution which is much more effective in cleaning metal parts than conventionally prepared citric acid solutions which require hot temperature applications to work effectively.

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CLEANING SOLUTIONS CONTAINING CITRIC ACID AND USES THEREOF

FIELD OF THE INVENTION

This invention relates to cleaning solutions containing citric acid
5 and various uses thereof and particularly relates to novel cleaning solutions
which can have an improved cleaning ability especially at lower temperatures.

BACKGROUND ART

Aqueous solutions of citric acid are well-known and are widely
used as a chemical cleaner in the removal of iron oxides from ferrous metals.
10 Aqueous citric acid solutions are widely used for cleaning steam generating
plant and chemical processing equipment and is a safe and effective acid
cleaner in a variety of metal finishing applications. It is used extensively for
cleaning stainless steel parts which are liable to stress corrosion cracking in
the presence of chloride ions and therefore cannot be cleaned with
15 hydrochloric acid.

Citric acid reacts with ferric oxide to form a water soluble
chelate. The most stable chelate is that containing one molecule of ferric ion
and one molecule of citrate ion. This means that for each part by weight of
ferric ion present, four parts by weight of citric acid is required. Exhaustion of
20 the citric acid cleaning solution therefore sometimes results in the
precipitation of ferric salts but it has been found that if an excess of 0.5% citric
acid is maintained, precipitation of the ferric salts can be reduced or avoided.

The dissolution of mill scale, operational scale, and bare metal
produces ferrous ions in solution. For example, soluble ferric ion in contact
25 with steel is reduced to ferrous ion, and most cleaning operations are
conducted in the absence of dissolved oxygen so that the ferrous ion is
usually present to a much larger extent than the ferric ion.

Steel and ferrous oxide react with aqueous citric acid to provide
a ferrous hydrogen citrate. The ferrous hydrogen citrate increases in
30 concentration during the citric acid cleaning process and eventually
precipitates as its solubility limit is reached.

To reduce the risk of precipitation, it is known to add ammonia

to citric acid solutions. It is known to add sufficient ammonia to a 3 to 5% citric acid solution to increase the pH to 3.5. At this pH, one of the three carboxylic acid hydrogens of the citric acid is neutralized. A relatively large amount of ammonia is added to a very dilute (3 to 5%) citric acid solution, and
5 it is found that this solution at pH 3.5 will dissolve rust more rapidly than citric acid. The reaction product is ferrous ammonium citrate (instead of ferrous hydrogen citrate), and the ferrous ammonium citrate is highly soluble and will not precipitate even when the pH of the solution is raised to about 10.

It is known to add 3 to 5% aqueous citric acid solutions to give a
10 pH of 5.6 to form a diammonium citrate.

Current conventional literature to the use of citric acid solutions and ammoniated citric acid solutions are to high temperature solutions in order to clean the metal parts within an acceptable period of time. Thus, the solutions are applied at temperatures in the range of 60°C to 95°C. Lowering
15 the temperature to room temperature or below does not provide a useful cleaning effect and the cleaning process takes far too long.

Several attempts have been made in order to speed up the cleaning process at lower temperatures. For instance, it is known to add small quantities (0.5 to 1.5%) of ammonium bifluoride as a catalyst which
20 allows the dilute citric acid cleaning solutions to be used at room temperature. However, the catalyst introduces fluoride into the solution which requires safe handling precautions when using this technique.

When cleaning large pieces of equipment, it has been difficult to date to properly clean the equipment by using hot dilute citric acid solutions
25 as the solution must be kept hot for a period of time and this requires large energy and capital inputs. Heated soak solutions, heated foams, hot steam or sprays have also been used but suffer from the same disadvantages. The use of fluoride catalysts require safe handling procedures and techniques and is generally not considered desirable.

30 Another disadvantage with dilute citric acid solutions is that the solution itself does not have a very long shelf life. In a fairly short period of time, the solution becomes contaminated with bacterial and fungal growth.

Another disadvantage with known ammoniated dilute citric acid solutions is the difficulty in forming the solution. To make up large volumes of dilute solution requires the addition of fairly large amounts of ammonium hydroxide and ammonium hydroxide is a toxic chemical and requires safe handling procedures. The resultant solution can easily liberate ammonia and cause poisoning and toxic effects to workers.

After much research and experimentation, an improved cleaning composition containing citric acid has now been developed and which may overcome at least some of the abovementioned disadvantages or provide the consumer with a useful or commercial choice.

OBJECT OF THE INVENTION

One form of the present invention is based on the realization that an ammoniated citric acid solution can be made more readily by adding ammonia to a saturated or near saturated aqueous citric acid solution as opposed to addition of ammonia to a dilute solution of citric acid.

Therefore, in one form the invention resides in a method for manufacturing an ammoniated concentrated citric acid solution which comprises gradual addition of ammonium hydroxide to a saturated or substantially saturated aqueous citric acid solution until a desired ammoniation level is obtained.

Citric acid has a solubility in water of 54% w/w at 10°C, 59.2% at 20°C, 64.3% at 30°C, 68.6% at 40°C, 70.9% at 50°C, 73.5% at 60°C, 76.2% at 70°C, 78.8% at 80°C, 81.4% at 90°C, and 84% at 100°C. The term "saturated aqueous citric acid solution" would be a term clearly evident to a person skilled in the art. The method need not be limited to a fully saturated aqueous citric acid solution but can include a substantially saturated or near saturated aqueous citric acid solution or concentrated citric acid solutions, it being appreciated that the citric acid solution is to be much more concentrated than the known method of ammoniating dilute citric acid solutions.

Although the concentrated citric acid solution can be ammoniated by ammonium hydroxide, it is envisaged that other types of

amines may be used to form an ammoniated concentrated citric acid solution.

In one form, the amount of ammonium hydroxide added is sufficient to provide an ammoniation of between 1 to 10%, and preferably an ammoniation of between 2 to 6% and most preferably an ammoniation of about 3.1%.

In another form, the invention resides in a concentrated cleaning composition comprising a saturated or substantially saturated aqueous acid solution which contains between 1 to 10% ammoniation. By saturated or substantially saturated is meant that the citric acid solution contains substantially as much citric acid as possible without appreciable precipitation occurring at the temperature of the solution. It is preferred that the solution contains between 2 to 6% ammoniation and most preferably about 3.1% ammoniation. It is preferred that ammonium hydroxide is used to ammoniate the citric acid solution.

The concentrated cleaning composition has several advantages. Firstly, the composition has an extremely long shelf life and has a reduced susceptibility to bacterial or fungal growth. The ammonia appears to stay stable within the citric acid solution and does not appear to be appreciably liberated over time. This minimizes the requirement for safe handling procedure and possible poisoning by liberated ammonia or amines.

In one form, the concentrated cleaning composition includes one or more additives which can function to improve the cleaning capability of the composition. The additives may include surfactants which can increase the rate of penetration of the scale or other impurities which are to be cleaned.

The surfactant can be based on salts of fatty acids by reacting mono and/or polyunsaturated fatty acids such as canola oil firstly with a minimum of potassium hydroxide followed by urea, sodium sulphate and sucrose in the cold, then with the addition of a triazole corrosion inhibitor compound such as benzotriazole or tolytriazole results in a corrosion inhibitor surfactant which not only reduces smutting of cleaned surfaces but also in acceleration of the reactivity of the solution at low ambient temperatures.

The concentrated cleaning composition, as described above, can be diluted with water to form a working solution. The dilution may be about 1 part of the concentrated composition to 8 parts of water. Working solutions may be between 1-20% w/w, and more preferably between 1-15% w/w.

While not wishing to be bound by theory, it appears that the diluted cleaning composition described above is superior to the known dilute 3 to 5% citric acid solutions which have been ammoniated and which cannot be stored because of susceptibility to bacterial and fungal attack.

The cleaning composition according to the invention has a much higher free acid present in the ammoniated saturated solution which allows much of the ions to exist in a ferrous state without precipitating. It appears that these ferrous ions take part in auto oxidation reactions with ferric ion in the scale which functions synergistically and improves the reaction capacity to the cleaning solution. This would not be available if all the ion was in the form of a chelate which would be the situation with the known citric acid solutions.

It is also found that the cleaning compositions according to the invention when diluted allow metal products to be cleaned at ambient temperature and within a suitable period of time and therefore heating of the solution is not essential. This in turn reduces or avoids the need to provide heaters and other high energy dependents and high cost equipment to heat and maintain the solution in a hot condition during the cleaning process.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a method of manufacturing an ammoniated concentrated citric acid solution in bulk.

Figures 2 and 3 illustrate the cleaning efficiency of the solutions

BEST MODE

Referring to Figure 1, a concentrated citric acid solution containing 600g of citric acid per litre of water is added to a stainless steel paddle mixer 10. Aqueous solution of ammonium hydroxide (225g per litre water) is metered into a large graduated polyethylene container 11 from a storage container 12 and via a pump 13. Container 11 has a gas overflow

vent pipe 14, which extends into mixer 10 and below the level of water in the mixer so that no gas escapes to the atmosphere during charging container 11 with the appropriate volume of ammonium hydroxide.

Once the required amount of ammonium hydroxide has been added to container 11, it passes through lower conduit 15 and via a valve to a pressure chamber 16. The pressure chamber forms a venturi junction with the main delivery pipe 17 on the output side of a circulating pump 18 which circulates the citric acid solution from mixer 10 in a closed loop through conduit 17 and back into the mixer. Ammonium hydroxide is gradually added to the circulating concentrated citric acid. The pressure chamber 16 helps to smooth out the gas or steam explosions which occur as the ammonium hydroxide comes into contact with the concentrated citric acid as the reaction is vigorously exothermic.

The method of manufacture results in an extremely low cost system which produces a highly concentrated solution of high specific gravity and which is ideally suited for packaging for commercial use. The method uses lower amine concentrations which have been shown to be effective and make the method of manufacture simple, safe and economical in large to small batch sizes. The system permits batches as large as 5,000 litres to be produced without the need for special heat exchange or other cooling devices.

Figures 2 and 3 illustrate the cleaning efficiency of the solutions.

The figures show photographs of rusted sample tags and illustrated the ammoniated citric acid solution effects on the removal of the rust from the tags.

Figure 2 shows, in the Y axis, the times that the tags were immersed in the solution while the X axis shows 4 different solutions. The first and second column in Figure 2 are known conventional solutions. The first column is a dilute (3 to 5%) ammoniated citric acid solution at pH 5.6 to form the diamine and at 24°C. The second column is a similar citric acid solution with less added ammonia to form the monoamine solution of pH 3.5.

The third column shows a concentrated citric acid solution made

by the method described above and diluted to 2.5% w/w. The fourth column shows the same solution but diluted to 1.88% w/w.

In Figure 2, the solutions in columns 3 and 4 had 1% surfactant additive the additive being described above.

5 In Figure 3, columns 1 and 2 are the same as with Figure 2 and columns 3 and 4 illustrate that the diluted solution according to the invention provides good cleaning properties at ambient temperate (24°C) but as well at a greatly reduced temperature of 10°C (see column 4). The fifth column shows a dilute monoamine at 1.88% w/w. The solutions according to the
10 embodiment and illustrated in columns 3 and 4 have 5% surfactant additive the additive being described above.

Careful observations of the sample tags illustrated in Figures 2 and 3 showed that the solutions according to the invention work faster than the traditional monoamine and diamine citric acid solutions. The surfactant
15 enhances protection of the parent metal from any corrosive effects of the solution. The surfactant according to the invention has a particular affinity for oxides and while components of the surfactant are hydrophobic, once in contact with the rust they react to form aqueous soluble species which assists in the penetration and removal of the scale.

20 The solutions according to the invention are distinguished from known citric acid solutions by the lesser amount of ammonia and therefore the higher free acid found in the solutions according to the invention.

It is found that approximately 3.1% ammoniation of the concentrated citric acid provides a rapid and effective method of producing a
25 concentrated solution which is stable and economic for commercial storage and for deployment as a diluted 12% working solution with water. This is superior to the conventional method of ammoniating 3 to 5% citric acid solutions which cannot be stored due to bacterial and fungal attack and therefore must be used when prepared.

30 The much higher free acid present in the solutions according to the invention allows much of the iron to exist in a ferrous state. The solution according to the invention is much more active at ambient temperatures and

down to about 15°C or less thereby saving energy and time.

The invention therefore provides a practical one-step cleaning procedure for metal parts or other parts requiring cleaning.

Previously known citric acid solutions react very slowly and
5 obtaining very clean metal surfaces suitable to accept various types of
coatings such as paint, and galvanized zinc was very difficult as the slow
rates of reaction permitted build-up of electrochemical polarization charges on
the cleaned surfaces such that by the time the whole surface scale was
removed, ionized solvated scale products were progressively attracted to the
10 cleaned surfaces thereby creating a heavily smutted surface which was
unsuitable for the application of coatings.

With respect to the surfactants according to an embodiment of
the invention, although it is well-known that polyunsaturated fats react
corrosively with rust and iron metal, by modifying the polyunsaturated fats as
15 described above, the corrosion effect is reduced remarkably without limiting
the reactivity with the oxides of iron.

The surfactant possesses the following properties:

- (a) Miscibility with water and wetting capacity in oily and dirty conditions.
- 20 (b) Reactivity with metal oxides rendering them either directly soluble in water or making them much more reactive with the amine citrate components of the solution.
- (c) Improving the cleanliness of the cleaned metal surface.
- (d) Inhibition of corrosivity to the parent metal cleaned surfaces.
- 25 (e) Acts synergistically with a working solution based on the 3.1% ammoniated concentrated citric acid solution to improve low ambient temperature reactivity.
- (f) Greatly improves the penetrating capacity of the solution as a whole.
- 30 (g) Has a citrate sparing effect reducing the rate of exhaustion of the working solution and extending the

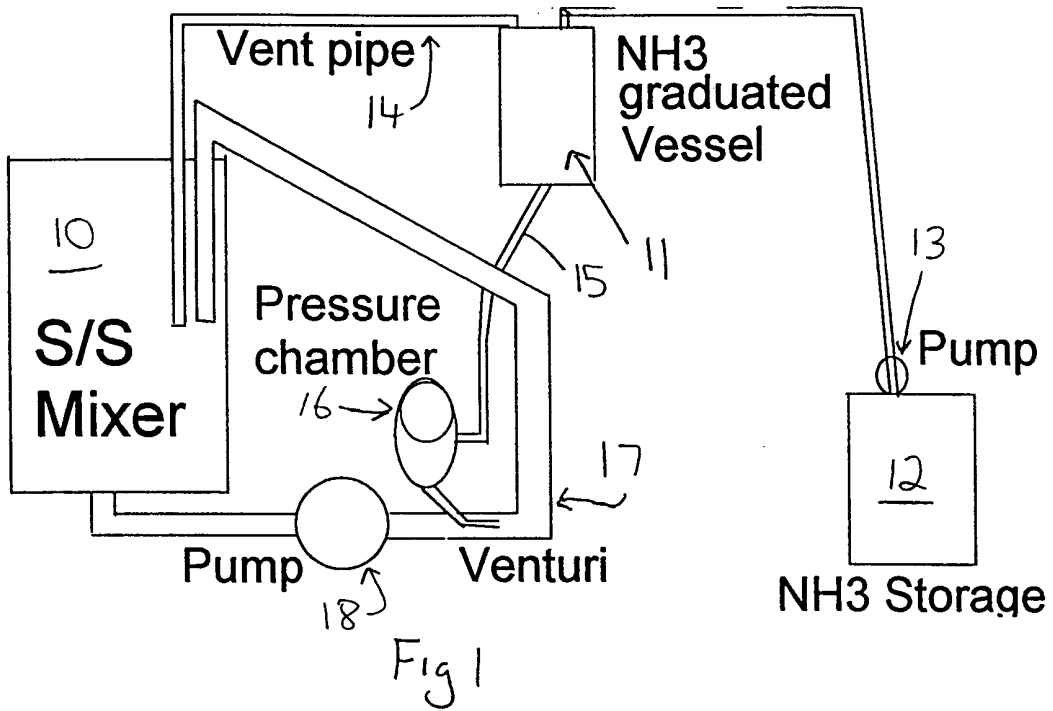
working life of any given solution. This significantly improves the economics by extending the capacity of the most expensive component of the solution namely citric acid.

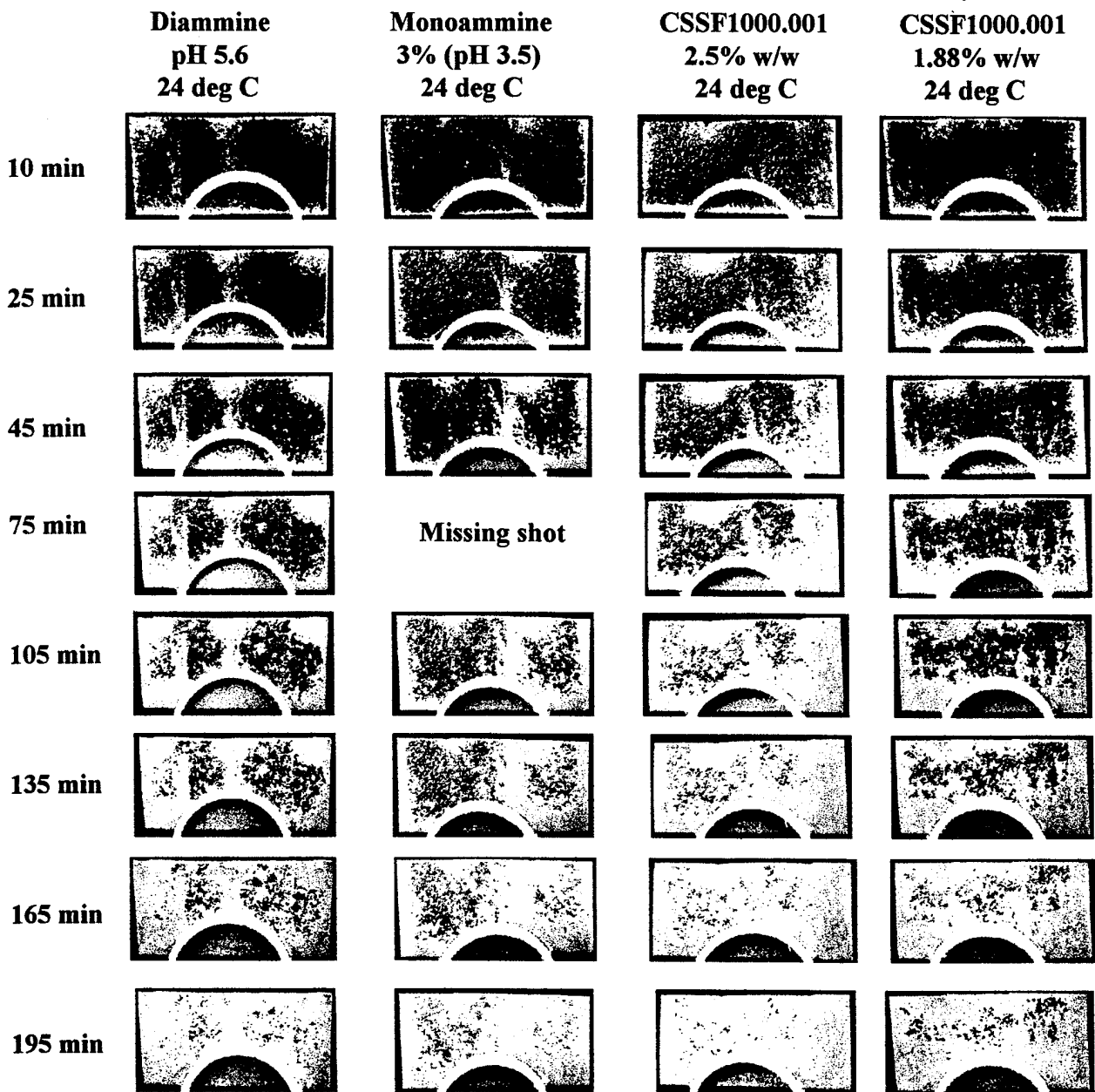
- 5 (h) Surfactant is workplace safe in keeping with the other components of the working solution, with a very low order of toxicity.
- (i) Complete biodegradability.
- 10 (j) Reduces flash rusting on removal from the solution by providing a degree of passivation of the cleaned metal surfaces.
- (k) Ambient temperature operation saving in time and energy.
- 15 (l) Single step cleaning procedure eliminating the traditional multi-stage cleaning operations again saving energy and time.

It should be appreciated that various other changes and modifications can be made to the embodiment described without departing from the spirit and scope of the invention.

CLAIMS:

1. A concentrated cleaning composition comprising a saturated or substantially saturated aqueous acid solution which contains between 1 to 10% ammoniation.
- 5 2. The composition of claim 1 wherein the solution contains between 2-6% ammoniation.
3. The composition of claim 2, wherein ammonium hydroxide is used as the ammoniation agent.
4. A cleaning solution for cleaning metal parts at ambient
10 temperatures, the solution being the solution of claim 1 diluted to between 1.5 -15% w/w with water prior to use.
5. The solution of claim 4, containing between 1-5%w/w of additives which is a salt of a fatty acid and a triazole.
6. A method for forming the cleaning solution of claim 1, the
15 method comprising the steps of gradual addition of ammonium hydroxide to a saturated or substantially saturated aqueous citric acid solution.
7. The method of claim 6, wherein a concentrated citric acid solution containing 600g of citric acid per litre of water is added to a mixer, an aqueous solution of ammonium hydroxide (225g per litre water) is metered
20 into a container from a storage container which has a gas overflow vent pipe which extends into the mixer and below the level of water in the mixer so that no gas escapes to the atmosphere during charging of the container with the appropriate volume of ammonium hydroxide, once the required amount of ammonium hydroxide has been added to the container , it passes through a
25 conduit and via a valve to a pressure chamber which forms a venturi junction with a main delivery pipe on the output side of a circulating pump which circulates the citric acid solution from the mixer in a closed loop and back into the mixer, the ammonium hydroxide being gradually added to the circulating concentrated citric acid, the pressure chamber functioning to smooth out the
30 gas or steam explosions which occur as the ammonium hydroxide comes into contact with the concentrated citric acid as the reaction is vigorously exothermic.





Preferred solution @ 24 & 7.5 deg C.

Fig 2

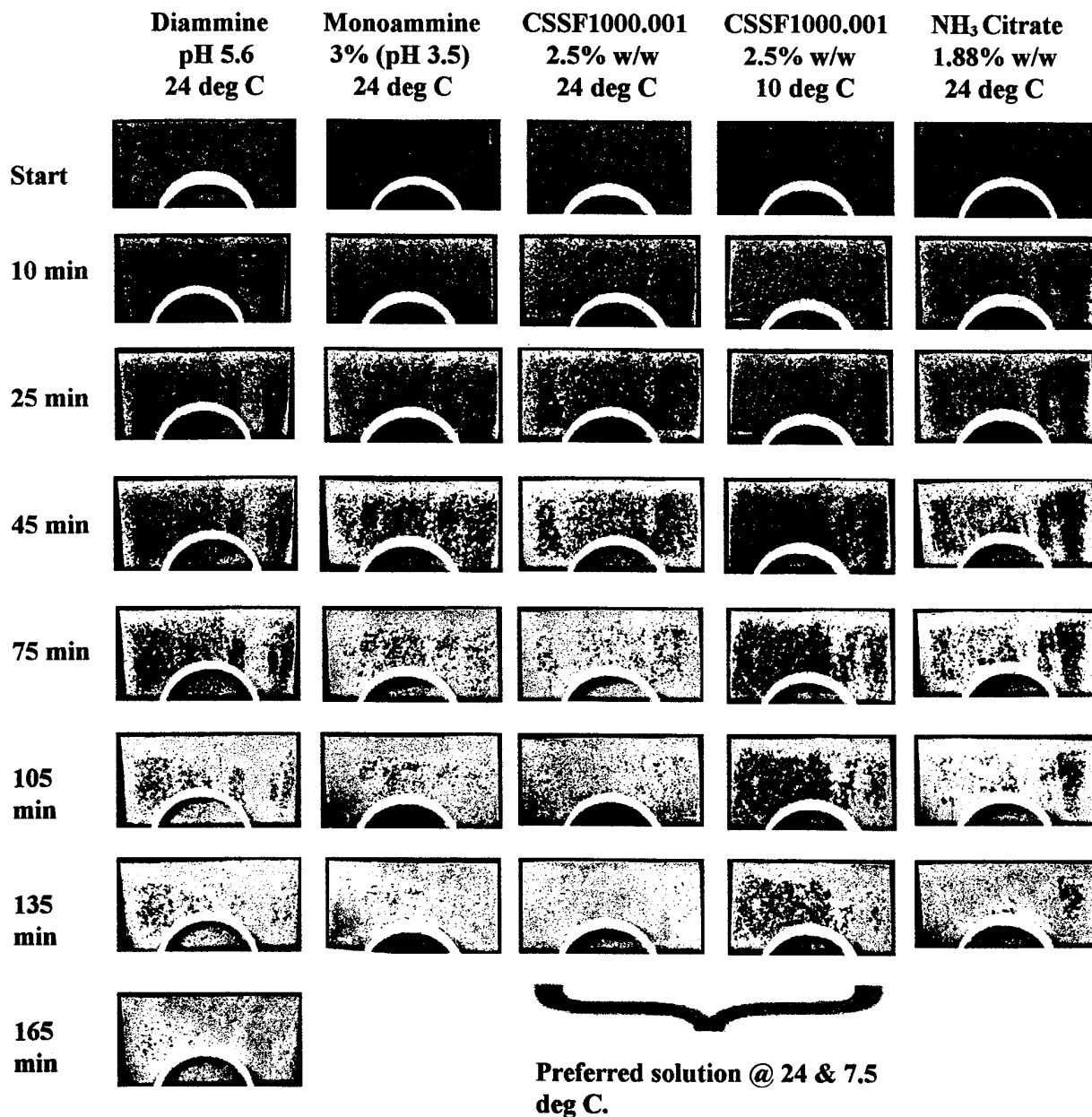
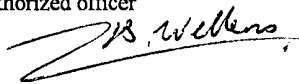


Fig 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 99/01094

A. CLASSIFICATION OF SUBJECT MATTER												
Int Cl ⁷ : C23G 1/02, 1/06, 1/08												
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) IPC ⁷ : AS ABOVE												
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Nil												
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Derwent on-line WPAT: IPC as above with key words ammon:												
C. DOCUMENTS CONSIDERED TO BE RELEVANT												
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.										
A	Derwent Abstract Accession No. 56119 D/31, Class E17, M12, JP, A, 56-072162 (Mitsubishi: Heavy Ind KK.) 16 June 1981 Whole document	1-7										
A	Derwent Abstract Accessopm No 56120 D/31, Class E17, M12, JP, A, 56-072163 (Mitsubishi: Heavy Ind KK.) 16 June 1981 Whole document	1-7										
A	US, A, 4452643 (Martin et al), 5 June 1984 Whole document	1-7										
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex												
<p>* Special categories of cited documents:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%;">"A" Document defining the general state of the art which is not considered to be of particular relevance</td> <td style="width: 30%;">"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</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"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</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" Document defining the general state of the art which is not considered to be of particular relevance	"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	"E" earlier application or patent but published on or after the international filing date	"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	"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)	"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	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed	
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"E" earlier application or patent but published on or after the international filing date	"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											
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"P" document published prior to the international filing date but later than the priority date claimed												
Date of the actual completion of the international search 08 February 2000		Date of mailing of the international search report 16 FEB 2000										
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/01094

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE, A1, 4212891 (Metasco Chemish - Technische Producte GmbH), 21 October 1993 Whole document	1-7
A	"Metals Handbook" 9th Ed., Vol 5 Surface Cleaning, Finishing, and Coating, American Society for Metals 1982, ISBN 0-87170-0115. Page 66	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU 99/01094

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					
DE	4212891	AU	39532/93	EP	589028	WO	9321362
END OF ANNEX							