

657971

Australian Patent  
Application No. 19956/92

**Australia**

Patents Act 1990

**NOTICE OF ENTITLEMENT**

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United States of America

being authorised by the Applicant(s)/Nominated Person(s) in respect of an application entitled:  
**SOAP COMPOSITIONS OF CARBOXYLIC ACIDS AND AMINES USEFUL  
IN REMOVAL AND PREVENTION OF SCALE**

state the following:-

1. The Applicant(s)/Nominated Person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):-

the applicant is the assignee of the invention from the actual inventors

~~2a.\* The Applicant(s)/Nominated Person(s) is/are the applicant(s) of the of the basic application(s) listed\* on the Patent Request\* in the Declaration under Article 8 of the PCT.~~

2b.\* The Applicant(s)/Nominated Person(s) is/are entitled to rely on the basic application(s) listed\* on the Patent Request\* in the Declaration under Article 8 of the PCT as follows:

The Applicant/Nominated Person is the assignee of the basic applicant

3.\* The basic application(s) listed \*on the Patent Request\* in the Declaration under Article 8 of the PCT is/are the application(s) first made in a Convention Country in respect of the invention.

~~4a.\* The Applicant(s)/Nominated Person(s) is/are the depositor(s) of the deposit(s) listed in the Schedule hereto.~~

~~4b.\* The Applicant(s)/Nominated Person(s) has/have the consent of \_\_\_\_\_, of~~

the depositor(s) of the deposit(s) listed in the Schedule hereto, to rely on that/those deposit(s).

DATED this TENTH. day of December 19 93

*Jerome H. Ludwig*  
(Signature)  
Jerome H. Ludwig  
Executive Vice President  
(Name & Title)

**AUSTRALIAN INDUSTRIAL  
PROPERTY ORGANISATION  
SYDNEY**

14 MAR 1994

\* Delete if not applicable  
IRN: 256080

INSTR. CODE: 64180



AU9219956

(12) PATENT ABRIDGMENT (11) Document No. AU-B-19956/92  
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 657971

- (54) Title  
SOAP COMPOSITIONS OF CARBOXYLIC ACIDS AND AMINES USEFUL IN REMOVAL AND PREVENTION OF SCALE
- International Patent Classification(s)  
(51)<sup>s</sup> C02F 005/12 C11D 009/26
- (21) Application No. : 19956/92 (22) Application Date : 11.05.92
- (87) PCT Publication Number : WO92/20629
- (30) Priority Data
- (31) Number (32) Date (33) Country  
700780 16.05.91 US UNITED STATES OF AMERICA
- (43) Publication Date : 30.12.92
- (44) Publication Date of Accepted Application : 30.03.95
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- (56) Prior Art Documents  
US 3095379  
US 4032460
- (57) Claim

1. A method for the removal of water scale deposits containing calcium or magnesium carbonate, oxide or hydroxide from a surface comprising providing a stoichiometric equivalent of an ~~weak~~ organic carboxylic acid with a corresponding stoichiometric equivalent of <sup>an</sup> ~~a~~ weak amine base in the presence of water to yield a 1:1 aqueous neutral soap reaction product, wherein an effective amount of free acid is present in solution to react with said calcium or magnesium carbonate, oxide or hydroxide present in water scale to form the respective metallic soap thereof;

treating a surface having said water scale deposits with an effective amount of said aqueous

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(10) 657971

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neutral soap reaction solution for reaction with said calcium or magnesium carbonate, oxide or hydroxide to form said soap; and

rinsing said treated surface with water to provide said surface with said deposits removed.

5. A method of removing and preventing in aqueous media scale containing calcium or magnesium carbonate, oxide or hydroxide, comprising .

adding to said aqueous media a neutral soap reaction product of a 1:1 stoichiometric equivalent of <sup>an</sup> ~~a weak~~ organic carboxylic acid and an ~~weak~~ amine base, wherein an effective amount of free acid is present in solution to react with said calcium or magnesium carbonate, oxide or hydroxide present in said aqueous media to form the respective metallic soap thereof.



INTERNATIONAL PUBLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : C02F 5/10</p>	<p>A1</p>	<p>(11) International Publication Number: WO 92/20629 (43) International Publication Date: 26 November 1992 (26.11.92)</p>
<p>(21) International Application Number: PCT/US92/03905 (22) International Filing Date: 11 May 1992 (11.05.92) (30) Priority data: 700,780 16 May 1991 (16.05.91) US (71) Applicant: H.E.R.C. INCORPORATED [US/US]; 1748 West Fillmore, Phoenix, AZ 85007 (US). (72) Inventors: HEATT, Allen, C. ; 1850 South Westwood, Mesa, AZ 85210 (US). LUDWIG, Jerome, H. ; 8840 North 57th Street, Paradise Vally, AZ 85253 (US). (74) Agents: JOSEPHIC, David, J. et al.; Wood, Herron &amp; Evans, 2700 Carew Tower, Cincinnati, OH: 45202 (US).</p>		<p>(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC (European patent), MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, RU, SD, SE, SE (European patent), SN (OAPI patent), TD (OAPI patent), TC (OAPI patent).</p> <p>Published With international search report. With amended claims.</p> <p>92 07 91</p>
<p>(54) Title: SOAP COMPOSITIONS OF CARBOXYLIC ACIDS AND AMINES USEFUL IN REMOVAL AND PREVENTION OF SCALE</p>		
<p>(57) Abstract</p> <p>A soap composition for the removal and prevention of scale in aqueous media comprising a 1:1 stoichiometric equivalent of an organic carboxylic acid and an amine base. The organic carboxylic acid is selected from the group consisting of hydroxy-acetic, citric, acetic, gluconic, salicylic, tartaric and benzoic, and mixtures thereof. The amine base is selected from the group consisting of monoisopropanolamine, diisopropanolamine, triisopropanolamine, monoethanolamine, diethanolamine, triethanolamine, diethylamine, and mixtures thereof.</p>		

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**SOAP COMPOSITIONS OF CARBOXYLIC ACIDS AND  
AMINES USEFUL IN REMOVAL AND PREVENTION OF SCALE**

**Background of the Invention**

Compositions for removal and prevention of scale are well developed in the patent art. "Scale" is a term that applies to deposits on surfaces such as bath tubs, shower tiles, cooling towers, heat ex-  
5 changers, evaporative coolers, swimming pools, fountains, hydraspas, water purification systems, and the like. Scale deposits usually include compounds such as metal carbonates, oxides and hydroxides which  
10 deposit on surfaces in contact with water generally as a result of exceeding the limit of solubility of such materials in water. A considerable number of patents have issued covering compositions for the removal or prevention of scale including U.S. Pats. Nos.  
15 3,447,965; 3,490,741; 3,639,279; 3,671,448; 4,435,303; 4,595,517; 4,686,067; 4,797,220 and 4,802,990. These patents are not the only patents related to the subject matter of this invention and they are not represented to be the most pertinent prior art. They  
20 are merely illustrative of various descaling and scale

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prevention compositions that have been disclosed in prior patents.

Many formulations disclosed in the above mentioned patents are acidic or alkaline in nature and have many disadvantages, such as irritation to the skin, eyes and mucous membranes during use. Additionally, prior formulations tend to react with the surfaces with which they come into contact during use including metal, ceramic and grout surfaces. Other known compositions tend to rapidly generate carbon dioxide gas as a result of their reaction with metal carbonate during use. Another disadvantage of current compositions is their potential reactivity with chlorine-containing materials with which they may be used to generate chlorine gas during use or storage.

In particular, for example, U.S. Pat. No. 4,797,220 discloses an aqueous composition of hydroxyacetic acid and triethanolamine at volume percentages of 0.7 to 10 of the acid to the amine with a 2 to 3.5 ratio being preferred. These compositions are highly acidic with pHs on the order of about 2-3 and can attack various metal surfaces, dissolve tile grout, react with chlorine-containing cleaners and irritate mucous membranes. While other alkaline compositions have been suggested, they suffer from similar disadvantages and are generally less effective.

In brief, there has been a continuing need for effective chemical compositions and processes for

removal and prevention of scale. There is a need for compositions that would minimise or eliminate the disadvantages associated with known compositions.

### Summary of the Invention

This invention is directed to aqueous compositions having long term descaling activity and to methods for the use of such compositions in the removal or prevention of scale. In accordance with this invention, a composition for the removal and prevention of scale in aqueous media comprises stoichiometric equivalents of an organic carboxylic acid and an amine base. These soap compositions of carboxylic acids and an amine base at a 1:1 stoichiometric ratio have effective and long term activity in removing and preventing scale precipitation. These soap compositions minimise or eliminate the disadvantages mentioned in the background of this invention.

In a first embodiment of the invention, there is provided a method for the removal of water scale deposits containing calcium or magnesium carbonate, oxide or hydroxide from a surface comprising:

- 15 providing a stoichiometric equivalent of an organic carboxylic acid with a corresponding stoichiometric equivalent of an amine base in the presence of water to yield a 1:1 aqueous neutral soap reaction product, wherein an effective amount of free acid is present in solution to react with said calcium or magnesium carbonate, oxide or hydroxide present in water scale to form the respective metallic soap thereof;
- 20 treating a surface having said water scale deposits with an effective amount of said aqueous neutral soap reaction solution for reaction with said calcium or magnesium carbonate, oxide or hydroxide to form said soap; and
- rinsing said treated surface with water to provide said surface with said deposits removed.

- 25 In a second embodiment of the invention, there is provided a method of removing and preventing in aqueous media scale containing calcium or magnesium carbonate, oxide or hydroxide, comprising:

- adding to said aqueous media a neutral soap reaction product of a 1:1 stoichiometric equivalent of an organic carboxylic acid and an amine base, wherein an effective amount of free acid is present in solution to react with said calcium or magnesium carbonate, oxide or hydroxide present in said aqueous media to form the respective metallic soap thereof.

The 1:1 stoichiometric soap compositions include an organic carboxylic acid such as hydroxyacetic, citric, acetic, gluconic, salicylic, tartaric, benzoic and others. The amine base of the composition is selected from the group of ammonia and organic amine bases such as monoethanolamine, triethanolamine, isopropanolamine, diethylamine, triisopropanolamine, tetraethanoethylenediamine, and others.



3a

The 1:1 soap compositions are especially adapted for use in aqueous systems to prevent or remove scale build-up. These compositions also have a long term descaling activity especially useful in tub

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and tile cleaners (industrial and household), water  
and oil well reclamation, water distribution system  
reclamation, cooling towers and heat exchangers,  
evaporative coolers, industrial cooling systems (such  
5 as chemical and plastic processing equipment, etc.),  
swimming pools, fountains, hydraspas, automotive  
radiators, hot water heating systems, distillation and  
reverse osmosis water purification systems and boil-  
ers. The environmental applications of this invention  
10 lead to the conservation of energy and water.

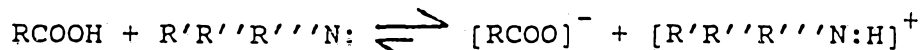
Compositions of this invention are organic  
in nature and generally are biodegradable, nontoxic  
and noncorrosive. Other advantages and benefits of  
this invention will be understood with reference to  
15 the following detailed description and examples.

#### DETAILED DESCRIPTION

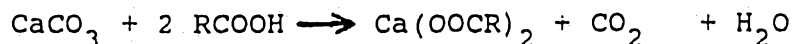
As stated above, the soap compositions of  
the present invention have 1:1 stoichiometric equi-  
valents of an organic carboxylic acid and an amine  
20 base. The effectiveness of aqueous solutions of these  
neutral soaps is believed to be due to their ability  
to solubilize magnesium and calcium carbonates which  
are predominant constituents of scale. The intrinsic  
character of the compositions is believed to contri-  
25 bute to their long term effectiveness in removing  
scale and preventing scale precipitation. The compo-  
sitions of this invention are soaps of weak acids and

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weak bases and are represented in aqueous equilibrium by the following Equation A:



If excess amine is used in a composition, the equilibrium will be shifted to the right resulting in less "free" acid available in solution and a slower reaction rate with metal carbonates as has been demonstrated by the examples hereinafter. Furthermore, as the acid is consumed when reacting with the metal carbonate, excess amine is formed as the equilibrium shifts to the left. With 1:1 stoichiometric soap compositions, the equilibrium is far to the right but there will be small amounts of "free" acid present in solution to react with magnesium, calcium or other metal carbonates, oxides and hydroxides to form the respective metallic soaps as represented by the following Equation B:



In view of the above reaction, the use level of a 1:1 soaps in a particular application of this invention may require respective organic carboxylic acids that produce calcium, magnesium or other metal soap derivatives that are relatively water soluble and do not precipitate out during use. Generally,

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magnesium soaps are more soluble than calcium soaps of carboxylic acids and the solubility of both increases substantially with an increase in temperature. For instance, the magnesium salt of hydroxyacetic acid increases in solubility from 7.9 to 29.8 gms per 100 gms water with an increase in temperature from 18°C to 100°C, whereas the corresponding calcium salt only increases in solubility from 1.2 to 4.6 gms over that same temperature range.

10                   The organic carboxylic acids (as represented by the R group of the above Equation A) suitable for use in compositions of this invention include aromatic, substituted aromatic, aliphatic, and substituted aliphatic acids. More preferably the organic acids are hydroxycarboxylic acids including hydroxyacetic, citric, gluconic and tartaric acid. Other organic carboxylic acids include acetic, salicylic and benzoic acids. An amine base of the 1:1 stoichiometric soap composition includes ammonia and organic amines (as represented by the R', R'' and R''' group of the above Equation B), preferably alkanolamines including monoethanolamine, triethanolamine, triisopropanolamine and isopropanolamine. Other aliphatic amines such as diethylamine may be employed. The organic carboxylic acids and amine components of the compositions of this invention are very well known with reference to the above identified patents that are listed in the background of this invention. These components have been

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used to make acidic compositions as stated above with respect to U.S. Pat. No. 4,797,220. Other alkaline compositions have been formulated containing these components. However, before this invention, these

5 carboxylic acids and amine bases were not used as 1:1 stoichiometric soaps for descaling purposes as set forth herein. The descriptions of these patents with respect to the component organic carboxylic acids and amines that may be reacted to form the soaps are

10 incorporated herein by reference.

The following examples further illustrate the practice of this invention and its present best modes.

15 EXAMPLE 1 - Reactivity of Soaps of Carboxylic Acids and Amine Bases with Magnesium Carbonate

0.1 equivalent of carboxylic acid (R-COOH) was reacted in 100 ml of water with 0.1 equivalent of amine base (R'-,R''-,R'''-N:) in a 400 ml beaker with magnetic stirring to yield a clear solution of the 1:1

20 soap.

1.00 g of magnesium carbonate, n-hydrate (J. T. Baker) powder was added to the aqueous soap solution with magnetic stirring and the beaker covered with aluminum foil. The slurry was then stirred,

25 sometimes heated as noted and observed.

The following results were obtained as reported in Table I.

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TABLE I

	<u>ACID</u>	<u>AMINE</u>	<u>OBSERVATIONS</u>
	A. Citric	Triisopropanol-amine	12 min. clear solution
5	B. Citric	Triethanolamine	45 min. clear solution
	C. Hydroxyacetic	Triisopropanol-amine	75 min. clear solution
10	D. Hydroxyacetic	Triethanolamine	75 min. clear solution
	E. Citric	Ammonia	95 min. clear solution
15	F. Acetic	Triethanolamine	120 min. light haze, clears overnight
	G. Hydroxyacetic	Ammonia	120 min. low haze, clears overnight
20	H. Gluconic	Isopropanolamine	60 min. moderate haze, heat to reflux-light haze
25	I. Salicylic	Triethanolamine	150 min. moderate haze, heat to reflux-low haze clears overnight
30	J. Tartaric	Triethanolamine	330 min. clear solution
	K. Benzoic	Triethanolamine	330 min. clear solution
	L. Hydroxyacetic	Diethylamine	48 hours-low haze, heat to reflux-clears

35 Note: moderate haze = notable change in slurry observed

low haze = stirrer can be seen through slurry

light haze = can see through slurry

clear solution = no slurry, clear and bright

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As evidenced by Table I, magnesium carbonate reacts with the 1:1 soaps of aliphatic or aromatic carboxylic acids and various amine bases or ammonia. As indicated, the rate of reaction of the 1:1 soaps increases with temperature as expected. Table I  
5 demonstrates that 1:1 soaps of this invention react with and dissolve one of the main components of scale very effectively.

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EXAMPLE 2 - Reactivity of Soaps of Carboxylic Acids  
and Amine Bases with Calcium Carbonate

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0.1 equivalent of carboxylic acid (R-COOH)  
was reacted in 100 ml of water with 0.1 equivalent of  
5 amine base (R'-,R''-,R'''-N:) in a 400 ml beaker with  
magnetic stirring to yield a clear solution of the 1:1  
soap.

1.00 g of calcium carbonate (EM Science)  
powder was added to the aqueous soap solution with  
10 magnetic stirring and the beaker covered with aluminum  
foil. The slurry was then stirred, sometimes heated  
as noted and observed.

The following results were obtained as  
reported in Table II.

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TABLE II

	<u>ACID</u>	<u>AMINE</u>	<u>OBSERVATIONS</u>
	A. Citric	Triisopropanol- amine	1 hr. clear solution
5	B. Citric	Triethanolamine	2 hrs. clear solution
	C. Hydroxyacetic	Triethanolamine	48 hrs., light, whispy precipi- tate. clears on warming
10			
	D. Hydroxyacetic	Triethanolamine	4 hrs. heavy slurry, no apparent change. Heat to reflux- clears
15			
	E. Acetic	Triethanolamine	Heat to reflux. Clears in 30 min.
20	F. Acetic	Triisopropanol- amine	Prolong heating to reflux per- iodically over 1½ hr. period results in clear solution.

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Table II demonstrates that calcium carbonate reacts slower than magnesium carbonate with the 1:1 soaps. If only a trace of calcium carbonate powder is added to an ammonium hydroxyacetate soap solution, the stirred slurry persists after 6 hours at room temperature but the mixture clears overnight indicating that the reaction is slow at room temperature. The citric acid/triisopropanolamine soap somewhat surprisingly provides fairly prompt reaction at room temperature by comparison. Furthermore, comparing Tables I and II, the citric acid/triisopropanolamine and the citric acid/triethanolamine soaps exhibit better response in comparison to other soaps and, thus, would be preferred in certain applications. For other applications where long term activity is desired, i.e., heat exchangers, the slower reacting soaps may be desired.

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EXAMPLE 3 - Reactivity of Soaps of Carboxylic  
Acids and Amine Bases with Excess  
Calcium Carbonate

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0.1 equivalent of carboxylic acid (R-COOH)  
5 was reacted in 100 ml of water with 0.1 equivalent of  
amine base (R'-,R''-,R'''-N:) in a 400 ml beaker with  
magnetic stirring to yield a clear solution of the 1:1  
soap.

5.00 gms of calcium carbonate (EM Science)  
10 powder was added to the aqueous soap solution with  
magnetic stirring and the slurry transferred to a jar  
and sealed. The slurries were then periodically  
shaken over a period of five days along with a control  
and maintained at room temperature. The slurries were  
15 then vacuum filtered and washed well with water. The  
filter cakes of unreacted calcium carbonate were air  
dried in an oven at 180°F followed by 250°F to con-  
stant weight.

The following results were obtained (cor-  
20 rected for the control) as reported in Table III.

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TABLE III

	<u>ACID</u>	<u>AMINE</u>	<u>GMS CALCIUM CARBONATE</u>
5	A. none	none	4.96 (99.2% recovered)
	B. Hydroxyacetic	Triethanolamine	4.46 (89.2% recovered)
	C. Acetic	Triethanolamine	4.71 (94.2% recovered)
10	D. Hydroxyacetic	Ammonia	4.44 (88.8% recovered)
	E. Salicylic	Triethanolamine	4.50 (90.0% recovered)

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Examples 1, 2 and 3 demonstrate that 1:1 soaps react with magnesium and calcium carbonate at room temperature and at elevated temperatures. The rates of reaction appear to vary depending upon the acid and/or the amine portion of the soap. Citric acid and hydroxyacetic acid appear to be the preferred carboxylic acids out of the ones listed. Triethanol-  
5 amine, triisopropanolamine and ammonia appear to be the preferred amines.

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EXAMPLE 4 - Comparative Reactivity of Alkali  
Metal Soaps of Carboxylic Acids  
with Magnesium Carbonate

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0.1 equivalent of hydroxyacetic acid was  
5 dissolved in 100 ml of water in a 400 ml beaker and  
reacted with 0.1 equivalent of 6 N sodium hydroxide  
solution with magnetic stirring.

1.00 g of magnesium carbonate, n-hydrate  
(J.T. Baker) powder was added to the aqueous 1:1 soap  
10 solution with magnetic stirring and the beaker covered  
with aluminum foil and the slurry stirred and ob-  
served.

After 48 hours there was no change in the  
heavy slurry observed. The slurry was then heated to  
15 reflux and still no change in the heavy slurry could  
be observed. There was apparently no reaction between  
the magnesium carbonate and the sodium hydroxyacetate  
soap solution. Soaps of alkali metal bases do not  
react with the alkaline earth carbonates. This is  
20 expected as alkali metal bases (hydroxides) are strong  
bases and react completely with the carboxylic acids,  
such as in Equation A above, and drive the reaction  
all the way to the right (soap) leaving no "free" acid  
available in solution.

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EXAMPLE 5 - Comparative Reactivity of Hydroxyacetic  
Acid Soap of Triethanolamine with  
Magnesium Carbonate in the Presence of  
Excess Triethanolamine

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5                   0.1 equivalents of hydroxyacetic acid were  
reacted with 0.2 equivalents of triethanolamine in 100  
ml of water in a 400 ml beaker with magnetic stirring.

                  1.00 gms of magnesium carbonate powder was  
added with magnetic stirring and the slurry observed.  
10                After 120 min. the slurry was still of moderate haze.  
(The slurry in a 1:1 soap solution clears in 75 min.  
See Example 1-D).

                  The slurry was then heated to reflux with  
magnetic stirring and the slurry cleared slowly. The  
15                increased level of free triethanolamine in the tri-  
ethanolamine/hydroxyacetic acid soap solution lowers  
the "free" hydroxyacetic acid concentration by shift-  
ing the equilibrium in the direction of the soap thus  
reducing the rate of reaction with magnesium carbonate  
20                because of the lower concentration of the "free"  
carboxylic acid.

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EXAMPLE 6 - Inhibition of Water Scale Formation and  
Precipitation During Concentration by the  
1:1 Soap of Hydroxyacetic Acid and  
Triethanolamine

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5                   5.7 ml of an aqueous solution of the 1:1  
soap of hydroxyacetic acid and triethanolamine con-  
taining 1.0 gm of the soap was added to 500 ml of tap  
water and the water concentrated to 100 ml by distil-  
lation.

10                   No solids were observed after concentration  
and the solution was crystal clear. On cooling to  
room temperature, no change was noted in the solution.

                  A control, without the 1:1 soap, resulted in  
substantial deposits on the sides of the distillation  
15                   vessel and the formation of an insoluble precipitate.  
The 1:1 soap solution of hydroxyacetic acid and  
triethanolamine is an effective agent to prevent water  
scale formation during concentration and would be  
beneficial in distillation, cooling towers, reverse  
20                   osmosis water purification systems, and the like.

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Neutral ionic and nonionic surfactants could assist in the removal of solids in water scale deposits in certain applications which utilize the 1:1 soap to break-up deposits by reacting with carbonates, oxides and hydroxides present. Furthermore, degreasing solvents, perfumes, odorants or masking agents might be advantageously employed in certain product formulations for particular end uses such as tub and tile cleaners.

10 EXAMPLE 7 - 1:1 Soap Evaluation in a Consumer  
Tub and Tile Product Formulation

A tub and tile formulation was prepared using an aqueous mixture of ammonia and triethanolamine in combination with hydroxyacetic acid in a 1:1 stoichiometric concentration along with other ingredients, i.e., odorizer, degreasing solvent, etc.

The formulation was sprayed on one half of a water spotted shower door and allowed to stand for one hour. The shower door was then rinsed with water and a comparison made between the treated and untreated door areas. The treated area of the door was clean and bright. The untreated area of the door remained spotted as at the beginning of the test. A tub and tile formulation utilizing the 1:1 soap of this invention was an effective agent for the removal of water scale deposits.

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Other modifications of the operating examples of this invention will become apparent to a person of ordinary skill in the art to achieve the benefits and advantages afforded by this invention.

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What is claimed is:

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01 July 1992

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1. A method for the removal of water scale deposits containing calcium or magnesium carbonate, oxide or hydroxide from a surface comprising  
providing a stoichiometric equivalent of an ~~weak~~ organic carboxylic acid with a corresponding stoichiometric equivalent of <sup>an</sup> ~~a~~ weak amine base in the presence of water to yield a 1:1 aqueous neutral soap reaction product, wherein an effective amount of free acid is present in solution to react with said calcium or magnesium carbonate, oxide or hydroxide present in water scale to form the respective metallic soap thereof;  
treating a surface having said water scale deposits with an effective amount of said aqueous neutral soap reaction solution for reaction with said calcium or magnesium carbonate, oxide or hydroxide to form said soap; and  
rinsing said treated surface with water to provide said surface with said deposits removed.



Substitute Sheet

2. The method of claim 1 wherein the organic carboxylic acid is selected from the group consisting of hydroxyacetic, citric, acetic, gluconic, salicylic, tartaric and benzoic, and mixtures thereof.

3. The method of claim 1 wherein the amine base is selected from the group consisting of ammonia, monoisopropanolamine, diisopropanolamine, triisopropanolamine, monoethanolamine, diethanolamine, triethanolamine, isopropanolamine, diethylamine and mixtures thereof.

4. The method of claim 1 wherein the organic carboxylic acid is hydroxycarboxylic and the amine base is an alkanolamine.



**SUBSTITUTE SHEET**

PCT/US92/0392e  
~~17 Dec~~  
01 July 1994

5. A method of removing and preventing in aqueous media scale containing calcium or magnesium carbonate, oxide or hydroxide, comprising adding to said aqueous media a neutral soap reaction product of a 1:1 stoichiometric equivalent of <sup>an</sup> ~~a~~-weak organic carboxylic acid and an ~~weak~~ amine base, wherein an effective amount of free acid is present in solution to react with said calcium or magnesium carbonate, oxide or hydroxide present in said aqueous media to form the respective metallic soap thereof.

6. The method of claim 5 wherein the organic carboxylic acid is selected from the group consisting of hydroxyacetic, citric, acetic, gluconic, salicylic, tartaric and benzoic, and mixtures thereof.



Substitute Sheet

7. The method of claim 5 wherein the amine base is selected from the group consisting of ammonia, monoisopropanolamine, diisopropanolamine, triisopropanolamine, monoethanolamine, diethanolamine, triethanolamine, diethylamine and mixtures thereof.

8. The method of claim 5 wherein the organic carboxylic acid is hydroxycarboxylic and the amine base is an alkanolamine.

9. The method of claim 5 comprising treating said deposits by spraying with said aqueous soap product.

10. A method for the removal of water scale deposits containing calcium or magnesium carbonate, oxide or hydroxide from a surface, which method is substantially as hereinbefore described with reference to any one of the Examples excluding the comparative Examples.

11. A method of removing and preventing in aqueous media scale containing calcium or magnesium carbonate, oxide or hydroxide, which method is substantially as hereinbefore described with reference to any one of the Examples excluding the comparative Examples.

**Dated 18 January, 1995**

**H.E.R.C. Incorporated**

**Patent Attorneys for the Applicant/Nominated Person**

**SPRUSON & FERGUSON**



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/03905

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (5): CO2F 5/10	US CL 252/82	
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
US	252/82, 117, 142, 180, 544, 546 134/2, 3 210/699, 700	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category *	Citation of Document, <sup>11</sup> with Indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X Y	US, A, 4,032,460 (ZILCH ET AL) 28 JUNE 1977, SEE COLUMN 3 LINES 22-60; EXAMPLE 26.	1-7 1-7
X Y	US, A, 3,095,379 (SCHWARTZ) 25 JUNE 1963, SEE COL. 1 LINES 31-43; COL. 2 LINES 45-52; COL. 2 LINE 57; COL. 3 LINE 8; EXAMPLE I AND II.	1-7 1-7
Y	US, A, 2,264,103 (TUCKER) 25 NOVEMBER 1941, PG. 1 RIGHT COLUMN LINES 22-25; PAGE 2 RIGHT COLUMN LINES 34-36; TABLES I AND II.	8-12
Y	US, A, 3,248,269 (BELL) 26 APRIL 1966, COL. 1 LINES 8-15; COL. 2 LINES 28-37, 50-53.	8-10,12
A	US, A, 3,447,965 (TEUMAC ET AL) 03 JUNE 1969, SEE ENTIRE DOCUMENT.	1-12
A	US, A, 3,639,279 (GANDNER) 01 FEBRUARY 1972, SEE ENTIRE DOCUMENT.	1-12
A	US, A, 4,250,048 (LEUESKIS) 10 FEBRUARY 1981, SEE ENTIRE DOCUMENT.	1-12
A	US, A, 4,303 (ABADI) 06 MARCH 1984, SEE ENTIRE DOCUMENT.	1-12
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
30 JUNE 1992	30 JUN 1992	
International Searching Authority	Signature of Authorizing Officer	
ISA/US	JAMES B. SILBERMAN	