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I/We ECOLAB INC.

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being the applicant(s) and nominated person(s) in respect of an application for a patent for an invention entitled FOAM SURFACE CLEANER (Application No. 36631/94), state the following:

1. The nominated person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):

THE NOMINATED PERSON IS THE ASSIGNEE OF  
THE ACTUAL INVENTORS.

2. The nominated person(s) has/have, for the following reasons, gained entitlement from the applicant(s) listed in the declaration under Article 8 of the PCT:

THE APPLICANT AND NOMINATED PERSON IS THE  
ASSIGNEE OF THE BASIC APPLICANTS.

3. The basic application(s) listed in the declaration under Article 8 of the PCT is/are the first application(s) made in a Convention country in respect of the invention.

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ECOLAB INC.

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on behalf of the applicant



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- (57) Claim

1. A method of stabilizing alkaline cleaning compositions using an adherent foam composition said foam composition comprising an alkalinity source, a vinyl polymer emulsion to provide an adherent foam, and a balance of water, said method comprising the step of adding said foam composition to said alkaline cleaner.

22. An adherent foam cleaning composition comprising:

- (a) an amount of alkaline cleaner effective in removal of soil; and
- (b) an adherent alkaline foam composition comprising:
- (i) an amount of alkalinity source effective to raise the pH of said foam cleaning composition;
  - (ii) an amount of vinyl polymer emulsion effective in providing an adherent foam;
- and
- (c) a balance of water.

36. A method of cleaning hard surfaces, said method comprising the step of applying a foaming alkaline cleaning composition comprising an alkaline cleaner and an adherent foam stabilizing composition, said adherent foam stabilizing composition comprising:

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- (a) An amount of alkalinity source effective to raise the pH of said composition;
- (b) an amount of vinyl polymer emulsion effective in providing an adherent foam; and
- (c) a balance of water.

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<p>(21) International Application Number: PCT/US94/02294 (22) International Filing Date: 3 March 1994 (03.03.94) (30) Priority Data: 08/069,601 1 June 1993 (01.06.93) US (71) Applicant: ECOLAB INC. [US/US]; Ecolab Center, St. Paul, MN 55102 (US). (72) Inventors: BESSE, Michael; 7450 Winnetka Heights, Golden Valley, MN 55427 (US). GUTZMANN, Timothy; 616 Crimson Leaf Court, Eagan, MN 55123 (US). KEPPERS, Roger; 42 Elizabeth Street, St. Paul, MN 55107 (US). RUHR, Richard; Route 2, Box 139, Buffalo, MN 55513 (US). (74) Agent: MAU, Michael, L.; Merchant, Gould, Smith, Edell, Welter &amp; Schmidt, 1000 Norwest Center, 55 East Fifth Street, St. Paul, MN 55101 (US).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, UA, UZ, VN, European patent: (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> <p><b>677653</b></p>	
<p>(54) Title: FOAM SURFACE CLEANER</p>		
<p>(57) Abstract</p> <p>The invention is a foam stabilizing composition which is used in conjunction with alkaline detergent products to produce a foam which is capable of clinging to vertical surfaces for extended time periods without breakdown or drying and ultimately rinse freely with water. The foam composition generally comprises an alkalinity source and a vinyl polymer. The invention also comprises a method of cleaning hard surfaces using the disclosed composition.</p>		

## FOAM SURFACE CLEANER

### Field of the Invention

The invention generally relates to alkaline surface  
5 cleaning compositions. More specifically, the invention  
relates to compositions and methods for improving  
alkaline detergents by providing a stabilized foam  
capable of remaining on vertical and horizontal surfaces  
for extended time periods which also rinses freely with  
10 water.

### Background of the Invention

Surface cleaning in any given environment is  
generally undertaken to maintain hygiene by removing  
15 residues left on the surface. Cleaning prevents  
contamination of substances, articles, and utensils as  
well as any other animate or inanimate objects such as  
food which may come in contact with the surface. While  
certain residues merely comprise carbonaceous debris,  
20 this debris may often provide a host or starting point  
for the growth of bacteria, microorganics, or other  
contaminants.

Additionally, surfaces may also be cleaned to  
maintain their serviceability and mechanical integrity  
25 during operation. In any given industrial or commercial  
setting, surfaces such as walls, floors, countertops, as  
well as, ranges, grills, ovens, mixing tanks, storage  
racks, and the like may all present difficult surfaces  
to clean and disinfect. Such structures may all, from  
30 time to time, contain surfaces which retain large  
residual contamination which is difficult to clean.  
Further, given the extended use that such equipment is  
subjected to, repeated cleaning is an ongoing problem.  
However, the frequency of such cleaning generally  
35 requires a high level of efficiency with minimal  
expenditure of human resources in the form of time and  
manpower.

For example, cleaners such as those useful in ovens  
often work by application to the intended surface for

extended periods of time. Current industrial detergents designed to be foam applied are capable of producing large levels of foam. However, when applied to soiled or cleaned vertical surfaces, for example, the foam  
5 begins to sag, collapse, and move toward the floor within minutes of application. Soil removal is often incomplete due to the limited contact time of the foam. As a result, repeated applications of the cleaner is often necessary. Another problem associated with  
10 current foaming detergents is the drying of the foam on the surface prior to rinsing. Premature drying may also require another detergent application to solubilize the remaining detergent residues and, ultimately, produce a clean, streak-free surface.

15 A number of cleaners have been developed for industrial and institutional surfaces. Gel compositions have been developed to clean and overcome the limited contact time between the detergent and soil associated with foam cleaning. These products utilize thickening  
20 agents to increase product to soil contact time in an attempt to improve soil removal. However, gel cleaners have some of the same limitations as foam cleaners including drying of the solution, poor rinseability, and poor visibility of the product once applied.

25 Past attempts at cleaning compositions include Verboom, U.S. Patent No. 4,477,365, which discloses the use of a composition containing an alkaline metal hydroxide, betaine, alpha olefin sulfonate, and hydrotropic agent. Schoenholz, U.S. Patent 3,808,051  
30 discloses a cleaning composition comprising an alkali metal salt of a weak organic acid, and a polyhydric alcohol which is used at a temperature of 250-550°F. Eisen, U.S. Patent 3,779,933 discloses a composition comprising an alkali metal hydroxide incorporating a  
35 nitrogen containing anionic surfactant, a thickening agent, and, optionally, a foam forming agent. Rink, U.S. Patent 4,135,947 discloses a water-based

composition having a pH of less than 10 and comprising carbon dioxide neutralized amines, water soluble solvents, and thickening agents. Heile, U.S. Patent 4,512,908 discloses an alkaline detergent composition comprising a chlorine source along with synthetic hectorright thickeners.

Generally, these prior compositions teach the use of alkaline cleaning constituents in a gelled or foaming state for use in applications such as ovens.

However, to date, these compositions have not been able to overcome problems including a lack of ease in rinseability, requirements for repeated application, and overall efficacy. As a result, a need exists for a alkaline stabilized foam for hard surface cleaning which provides the overall stability and cleaning requirements which allow application to any number of given surfaces.

#### Summary of the Invention

In accordance with a first aspect of the invention, there is provided a method of stabilizing alkaline cleaning compositions using an adherent alkaline foam which when combined with an alkaline cleaning composition produces an adherent foam which provides cleaning efficacy, rinseability, and surface adherence, wherein the foam comprises an emulsified vinyl polymer effective in providing an adherent foam, and water.

In accordance with an additional aspect of the invention, there is provided an adherent foam cleaner which comprises an adherent foam stabilizing additive of the invention combined with an alkaline cleaning agent such as a caustic cleaner, alkaline halogen cleaner, or solvated halogen cleaner.

In accordance with a further aspect of the invention, there is provided a method of cleaning surfaces comprising the step of applying a foaming cleaning composition to the intended surface. In accordance with a further aspect of the invention, there

is provided a cleaned surface resulting from use of the composition of the invention.

The composition of the invention comprises an alkali stable emulsified vinyl polymer a surfactant system along with various other adjuvants, and once combined with an alkaline cleaning agent a source of alkalinity. The composition displays physical properties such as rheology resulting in a long lasting foam having adhesion to non-horizontal surfaces. The long lasting foam permits the source of alkalinity in the cleaner to contact the soil for an extended period, and as a result, to promote the removal of soil. The foam is easily rinsed after sufficient time for removal of soil. The resulting foam composition allows application of the composition for extended periods of time allowing for the significant cleaning of vertical surfaces.

The invention may be used in conjunction with existing alkaline detergents to produce a foam which is capable of clinging to vertical and horizontal surfaces for extended time periods in excess of one hour without drying, and ultimately rinse freely with water. The invention overcomes the short comings of detergent systems by providing extended contact time (up to three hours on vertical surfaces), a highly visible stable foam, as well as providing a non-drying/free rinsing detergent.

#### Detailed Description of the Preferred Embodiments

The invention is a method of stabilizing alkaline cleaners using a viscous air entrained alkaline cleaning foam. The foam generally comprises a vinyl polymer or copolymer, as well as other optional adjuvants including surfactants, corrosion inhibitors, antimicrobial agents, builders, and the like. Once combined into a cleaning composition, the invention also comprises a foam stabilized cleaning composition as well as methods of





using this composition and the cleaned surfaces resulting therefrom.

#### The Polymeric Foam

The adherent foam of the invention comprises an emulsified polymer or copolymer matrix. The polymer matrix generally forms a net-like fabric that, once neutralized, becomes a thickened complex or system. This thickened composition provides adherence to the foam of the invention as well as lowering the flow characteristics of the composition. As a result, the thickened foam is capable of adhering without flow, on non-horizontal surfaces. Further, the polymeric matrix assists in entraining air in the foam of the invention. This entrained air, in turn, assists in providing adhesive character to the claimed composition. Further, the entrained air also assists in the breakdown of the foam once removal is desired.

In accordance with the invention, any number of vinyl compounds or monomers may be used to prepare the polymer or copolymer matrix used in the invention. Generally, vinyl polymers useful in the invention include polymers derived from vinyl acetals, vinyl acetates, vinyl alcohols, vinyl chlorides, vinyl ether monomers and polymers, n-vinyl monomers and polymers, vinyl fluorides, and the like.

Especially useful are vinyl polymers prepared from acrylic acid and its derivatives. Acrylic acid ( $\text{CH}_2 = \text{CHCO}_2\text{H}$ ) is a moderately strong carboxylic acid which is colorless liquid with an acrid odor. Generally acrylates are derivatives of both acrylic and methacrylic acid. Acrylic polymers and copolymers which may be used in the composition of the invention include alkyl acrylates such as methacrylate, ethylacrylate, propylacrylate, isopropylacrylate, and butylacrylate, isobutylacrylate, tertbutylacrylate, hexylacrylate, heptylacrylate, 2-heptylacrylate, 2-ethylhexylacrylate, 2-

ethylbutylacrylate, dodecylacrylate, hexadecylacrylate, 2-ethoxyethylacrylate, cyclohexylacrylate, and mixtures thereof.

Other vinyl polymers which may be used include  
5 vinyl acyl ethyl polymers; n-vinyl amide polymers; styrene polymers including vinyl benzene polymers; vinyl butyryl polymers including vinyl acetyl polymers; vinyl carbazole polymers; vinyl ester polymers including vinyl acetate polymers, as well as other vinyl esters of  
10 normal saturated aliphatic acids including formic, propanoic, butyric, valeric, caproic, and the like; vinyl esters of aromatic acids including benzoic, chlorobenzoic, nitrobenzoic, cyanobenzoic, and naphthoic; as well as vinyl ether polymers.

15 Hydrophilic monomers may also be utilized to produce the vinyl polymer in of the invention include acids and acid-esters of alpha, beta-unsaturated carboxylic acids such as methacrylic acid, acrylic acid, itaconic acid, aconitic acid, crotonic acid, mesaconic  
20 acid, carboxyethyl acrylic acid, maleic acid, fumaric acid and the like.

Synthetic polymers resulting from polymerization of many of the preceding monomers which are useful as foaming agents in the invention include generally,  
25 polyvinyl alcohol (with varying degrees of hydrolysis), ethylene/acrylic acid copolymers, ethylene/maleic anhydride copolymers, and styrene/maleic anhydride copolymers among others.

Those skilled in the art will realize that the  
30 preceding compounds and polymers are only exemplary of compounds and polymers which may be used as foam



stabilizing agents in the composition of the present invention and this list should not be viewed as limiting.

Preferably, the vinyl polymer comprises a polyacrylate/polymethacrylate copolymer. Rohm & Haas as  
5 Accusol 820 or Alco gum -SL70 available from Alco chemical. The concentration of the foaming polymer used in the composition of the present invention will generally range from about 0.15 to 10 wt-%, preferably  
10 range from about 0.2 to 8 wt-%, and most preferably range from about 0.5 to 6 wt-% depending on the characteristics to be imparted to the resulting foam.

#### The Surfactant System

The composition of the invention may also comprise a  
15 surfactant system. The surfactant system bolsters the cleaning efficacy of the composition and functions as a penetrant to add wettability to the composition allowing easy dissolution and solubilization of the composition of the invention. Further, the surfactant system also  
20 facilitates solubilization of fatty soils and lowers surface tension, thus adding surface activity to the composition.

Specifically, surfactants function to alter surface tension in the resulting compositions, provide sheeting,  
25 (aid in viscosity building) action, assist in soil removal and suspension by emulsifying soil and allowing removal through a subsequent flushing or rinse. Any number of surfactants may be used including organic surfactants such as anionic surfactants, zwitterionic or  
30 amphoteric surfactants, cationic surfactants and nonionic surfactants.

Anionic surfactants are useful in removing oily soils. Anionic surfactants include alkyl carboxylates, such as sodium and potassium carboxylates, alkyl  
35 sulfates, alkyl ether sulfates, alkyl benzene sulfonates, alkyl sulfonates, sulfonated fatty acid esters and the like.

Amphoteric or zwitterionic surfactants are also useful in providing detergency, emulsification, wetting and conditioning properties. Representative amphoteric surfactants include N-coco-3-aminopropionic acid and  
5 acid salts, N-tallow-3-iminodipropionate salts. As well as N-lauryl-3-iminodipropionate disodium salt, N-carboxymethyl-N-cocoalkyl-N-dimethylammonium hydroxide, N-carboxymethyl-N-dimethyl-N-(9-octadecenyl)ammonium hydroxide, (1-carboxyheptadecyl)trimethylammonium  
10 hydroxide, (1-carboxyundecyl)trimethylammonium hydroxide, N-cocoamidoethyl-N-hydroxyethylglycine sodium salt, N-hydroxyethyl-N-stearaminoglycine sodium salt, N-hydroxyethyl-N-lauramido- $\beta$ -alanine sodium salt, N-cocoamino-N-hydroxyethyl- $\beta$ -alanine sodium salt, as well  
15 as mixed alicyclic amines, and their ethoxylated and sulfated sodium salts, 2-alkyl-1-carboxymethyl-1-hydroxyethyl-2-imidazolinium hydroxide sodium salt or free acid wherein the alkyl group may be nonyl, undecyl, or heptadecyl. Also useful are 1,1-bis(carboxymethyl)-  
20 2-undecyl-2-imidazolinium hydroxide disodium salt and oleic acid-ethylenediamine condensate, propoxylated and sulfated sodium salt. Amine oxide amphoteric surfactants are also useful. This list is by no means exclusive or limiting.

25 Cationic surfactants may also be used including quaternary ammonium compounds such as N-alkyl(C<sub>12-18</sub>) dimethylbenzyl ammonium chloride, N-tetradecyldimethylbenzyl ammonium chloride monohydrate, N-alkyl(C<sub>12-14</sub>) dimethyl 1-naphthylmethyl ammonium chloride  
30 available commercially from manufacturers such as Stepan Chemical Company.

Preferably, when present, the surfactants used in the invention comprise one or more nonionic surfactants.

35 Nonionic surfactants which are useful in the invention include polyoxyalkylene nonionic detergents such as C<sub>8-22</sub> normal fatty alcohol-ethylene oxides or propylene oxide condensates, (that is the condensation

products of one mole of fatty alcohol containing 8-22 carbon atoms with from 2 to 20 moles of ethylene oxide or propylene oxide); polyoxypropylene-polyoxyethylene condensates having the formula  $\text{HO}(\text{C}_2\text{H}_4\text{O})_x(\text{C}_3\text{H}_5\text{O})_y\text{H}$  wherein  
 5  $(\text{C}_2\text{H}_4\text{O})_x$  equals at least 15% of the polymer and  $(\text{C}_3\text{H}_5\text{O})_y$  equals 20-90% of the total weight of the compound; alkylpolyoxypropylene-polyoxyethylene condensates having the formula  $\text{RO}-(\text{C}_3\text{H}_5\text{O})_x(\text{C}_2\text{H}_4\text{O})_y\text{H}$  where R is a  $\text{C}_{1-15}$  alkyl group and x and y each represent an integer of from 2 to  
 10 98; polyoxyalkylene glycols; butyleneoxide capped alcohol ethoxylate having the formula  $\text{R}(\text{OC}_2\text{H}_4)_y(\text{OC}_4\text{H}_9)_x\text{OH}$  where R is a  $\text{C}_{3-13}$  alkyl group and y is from about 3.5 to 10 and x is an integer from about 0.5 to 1.5; benzyl ethers of polyoxyethylene and condensates of alkyl  
 15 phenols having the formula  $\text{R}(\text{C}_6\text{H}_4)(\text{OC}_2\text{H}_4)_x\text{OCH}_2\text{C}_6\text{H}_5$  wherein R is a  $\text{C}_{5-20}$  alkyl group and x is an integer of from 5 to 40; and alkyl phenoxy polyoxyethylene ethanols having the formula  $\text{R}(\text{C}_6\text{H}_4)(\text{OC}_2\text{H}_4)_x\text{OH}$  wherein R is a  $\text{C}_{3-20}$  alkyl group and x is an integer from 3 to 20.

20 Preferably, nonionics such as nonyl phenol ethoxylates, and linear alcohol ethoxylates may be used in the invention. The surfactants may be used at concentrations ranging from about 0.00005 wt-% to 1 wt-%, preferably about 0.0001 wt-% to 1 wt-%, most  
 25 preferably about 0.0002 wt-% to 0.5 wt-%.

#### Adjuvants

The foam composition of the invention may also comprises any number of other adjuvants, such as alkalinity source corrosion inhibitors, sanitizers,  
 30 builders, and the like.

Corrosion inhibitors may be used to prevent the composition of the invention from facilitating corrosion of the surface to which it is applied. Exemplary corrosion inhibitors include silicates such as sodium  
 35 metasilicate, and potassium metasilicate as well as thiazoles such as benzotriazole, tolytriazole, and mercapto benzothiazol. Generally, the concentration of



the corrosion inhibitor will range from about 0.01 to 5 wt-%, preferably from about 0.1 to 3 wt-%, and most preferably from about .5 to 2 wt-%.

In order to prevent the formation of precipitates or other salts, the foam cleaning composition of the present invention may generally comprise builders, and chelating agents or sequestrants such as phosphates, phosphonates, acrylic polymers, and compounds such as EDTA or derivatives thereof.

Generally, sequestrants are those molecules capable of coordinating the metal ions commonly found in service water and thereby preventing the metal ions from interfering with the functioning of deterative components with the composition. The number of covalent bonds capable of being formed by a sequestrant upon a single hardness ion is reflected by labeling the sequestrant as bidentate (2), tridentate (3), tetridentate (4), etc. Any number of sequestrants may be used in accordance with the invention. Representative sequestrants include salts of amino carboxylic acids, phosphonic acid salts, water soluble acrylic polymers, among others.

Suitable amino carboxylic acid chelating agents include n-hydroxyethyliminodiacetic acid, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA). When used, these amino carboxylic acids are generally present in concentrations ranging from about 1 wt-% to 25 wt-%, preferably from about 5 wt-% to 20 wt-%, and most preferably from about 10 wt-% to 15 wt-%.

Other suitable sequestrants include water soluble acrylic polymer to condition the wash solutions under end use conditions. Such polymers include polyacrylic acid, polymethacrylic acid, acrylic acid-methacrylic acid copolymer, hydrolyzed polyacrylamide, hydrolyzed methacrylamide, hydrolyzed acrylamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed

polymethacrylonitrile, hydrolyzed acrylonitrile methacrylonitrile copolymers, or mixtures thereof.

Water soluble salts or partial salts of these polymers such as these respective alkali metal (for example, 5 sodium or potassium) or ammonium salts can also be used.

The weight average molecular weight of the polymers is from about 4000 to about 12000. Preferred polymers include polyacrylic acid, the partial sodium salts of polyacrylic acid or sodium polyacrylate having an 10 average molecular weight within the range of 4000 to 8000. These acrylic polymers are generally useful in concentrations ranging from about 0.5 wt-% to 20 wt-%, preferably from about 1 wt-% to 10 wt-%, and most preferably from about 1 wt-% to 5 wt-%.

15 Also useful as sequestrants are phosphonic acids and phosphonic acid salts. In addition to conditioning the water, organic phosphonic acids and phosphonic acid salts provide a grease dispersing character. Such useful phosphonic acids include, mono, di, tri and 20 tetra-phosphonic acids which can also contain groups capable of forming anions under alkaline conditions such as carboxy, hydroxy, thio and the like. Among these are phosphonic acids having the formula  $R_1N[C_2PO_3H_2]_2$  or  $R_2C(PO_3H_2)_2OH$  wherein  $R_1$  may be a -(lower) 25 alkylene]N[CH<sub>2</sub>FO<sub>3</sub>H<sub>2</sub>]<sub>2</sub> or a third (CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>) moiety; and wherein  $R_2$  is selected from the group consisting of C<sub>1</sub>-C<sub>6</sub> alkyl.

The phosphonic acid may also comprise a low molecular weight phosphonopolycarboxylic acid such as 30 one having about 2-4 carboxylic acid moieties and about 1-3 phosphonic acid groups. Such acids include 1-phosphono-1-methylsuccinic acid, phosphonosuccinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid.

When used as a sequestrant in the invention, 35 phosphonic acids or salts are present in a concentration ranging from about 0.25 wt-% to 15 wt-%, preferably from about 1 wt-% to 10 wt-%, and most preferably from about

1 wt-% to 5 wt-%.

Any number of chemical agents having microbial efficacy may be used in the invention. Representative compositions which could be used as antimicrobial agents  
5 in the invention include commonly available aldehydes such as formaldehyde and glutaraldehyde; iodophors such as iodine-nonionic surfactant complexes, iodine-polyvinyl pyrrolidone complexes, iodine-quaternary ammonium chloride complexes and amphoteric iodine-amine  
10 oxide complexes and the like; organic chlorine releasing agents such as cyanurates, cyanuric acids, and dichlorocyanuric dihydrates which are commercially available from FMC and Monsanto as their CDB and ACL product lines, respectively; fatty acids such as  
15 decanoic acid and the like; anionic surfactants such as dodecylbenzene sulfonic acid and sodium 1-octane sulfonate; phenols such as o-phenylphenol, 2,4,5-trichlorophenol, and 2,3,4,6-tetrachlorophenol commercially available from sources such as Dow Chemical  
20 Company and Mobay Chemical Company.

Also useful as antimicrobials in the invention are cationic surfactants including quaternary ammonium chloride surfactants such as N-alkyl( $C_{12-18}$ ) dimethylbenzyl ammonium chloride, N-alkyl( $C_{14-18}$ )  
25 dimethylbenzyl ammonium chloride, N-tetradecyldimethylbenzyl ammonium chloride monohydrate, N-alkyl( $C_{12-14}$ ) dimethyl 1-naphthylmethyl ammonium chloride available commercially from manufacturers such as Stepan Chemical Company.

30 When present, an antimicrobial agent must have a concentration effectively necessary for the required action to be provided. Generally, the concentration of antimicrobial agent may range from about .005 to 0.2 wt-%, preferably from about 0.005 to 0.15 wt-%, and most  
35 preferably from about 0.01 to 0.1 wt-%. Preferably, the antimicrobial agent comprise a mixture of sorbic acid and benzoic in the foam stabilizing composition at a



concentration of about 0.05 wt-% and 0.15 wt-%, respectively.

#### FOAM FORMULATION

In preparation, the vinyl polymer emulsion is combined with a source of alkalinity such as a hydroxide salt, carbonate, phosphate, amine or mixture thereof. The purpose of the alkalinity source is to neutralize the often acidic character of the vinyl polymer and reduce the amount of alkalinity scavenged from the alkaline cleaner with which the foam will later be combined. The foam may be neutralized with any number of alkalinity sources, including those disclosed below, to attain a pH of about 4 to 6, preferably about 4 to 5.5, and most preferably about 4.5 to 5.5.

Once neutralized a preservative system may be introduced into the composition along with any other adjuvants desired for use in the foam or cleaner. A summary of concentrations for the foam is provided below in Table 1.

of TABLE 1 (Wt-% as a percentage foam composition)

	<u>useful</u>	<u>working</u>	<u>preferred</u>
Vinyl Polymer	8-30	10-25	12-22
Surfactant	0.1-5	0.15-3	0.25-2
Alkalinity (pH)	4-6	4-5.5	4.5-5.5
Antimicrobial	0.025-0.5	0.05-0.4	0.1-0.3
Water	q.s	q.s.	q.s.

30

#### Cleaning Compositions

The foam stabilizing additive may be used in combination with any number of cleaning compositions such as alkaline or caustic cleaners, halogenated alkaline cleaners, and solvated alkaline cleaners among others. Alkaline or caustic cleaners may be based upon any number of alkali or alkaline earth metal hydroxides,



such as for example sodium hydroxide (caustic).

In order to achieve an alkaline pH, the cleaning composition generally requires an alkalinity source.

5 This higher pH increases the efficacy of soil removal and sediment breakdown when the chemical is placed in use and further facilitates the rapid dispersion of soils.

The source of alkalinity also functions to raise the  
10 pH of the form of the invention. The effect of this pH increase is to thicken the composition from a water thin complex to a foam capable of entraining air and adhering to horizontal and vertical surfaces.

The general character of the alkalinity source is  
15 limited only to those chemical compositions which have a greater solubility. That is, the alkalinity source should not contribute metal ions which promote the formation of precipitates or film salts. Exemplary alkalinity sources include silicates, hydroxides,  
20 phosphates, amines, and carbonates. Amines useful in accord with this invention include monoethanol, diethanol, and triethanol amines. Generally, when an amine compound is used or the alkalinity source, the concentration of the amine may range from about 0.10  
25 wt-% to 5 wt-%, preferably from about 0.10 wt-% to 4.5 wt-%, and most preferably from about 0.25 wt-% to 3 wt-%.

Silicates useful in accord with this invention  
include alkaline metal ortho, meta-, di-, tri-, and  
30 tetrasilicates such as sodium orthosilicate, sodium sesquisilicate, sodium sesquisilicate pentahydrate, sodium metasilicate, sodium metasilicate pentahydrate, sodium metasilicate hexahydrate, sodium metasilicate octahydrate, sodium metasilicate nanohydrate, sodium  
35 disilicate, sodium trisilicate, sodium tetrasilicate, potassium metasilicate, potassium metasilicate hemihydrate, potassium silicate monohydrate, potassium

disilicate, potassium disilicate monohydrate, potassium tetrasilicate, potassium, tetrasilicate monohydrate, or mixtures thereof.

5 Generally, when a silicate compound is used as the alkalinity source in the invention, the concentration of the silicate will range from about 0.5 wt-% to 8 wt-%, preferably from about 0.5 wt-% to 5 wt-%, and most preferably from about 0.5 wt-% to 3 wt-%.

10 Alkali metal hydroxides have also been found useful as an alkalinity source in the invention. Alkali metal hydroxides are generally exemplified by species such as potassium, sodium, and lithium hydroxide salts as well as other alkali hydroxide salts. Mixtures of these species may also be used. When present, the alkaline  
15 hydroxide concentration generally ranges from about 0.25 wt-% to 10 wt-%, preferably from about 0.5 wt-% to 8 wt-%, and most preferably from about 1 wt-% to 5 wt-%.

An additional source of alkalinity includes carbonates. Alkali metal carbonates which may be used  
20 in the invention include sodium carbonate, potassium carbonate, sodium or potassium bicarbonate, or sesquicarbonate, among others. Preferred carbonates include sodium and potassium carbonates. When carbonates are used, the concentration of these agents  
25 generally ranges from about 0.5 wt-% to 12 wt-%, preferably from about 1 wt-% to 10 wt-%, and most preferably from about 1.5 wt-% to 8.5 wt-%.

Phosphates which may be used as an alkalinity source in accordance with the invention include cyclic  
30 phosphates such as sodium or potassium orthophosphate, alkaline condensed phosphates such as sodium or potassium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate, and the like. In using phosphates, the concentration will generally range from about 1 wt-%  
35 to 20 wt-%, preferably from about 1 wt-% to 10 wt-%, and most preferably from about 2 wt-% to 8 wt-%.

Combinations of these alkalinity sources may also be

used. The pH of the composition, in use solution, ranges from about 6.5 to 14, preferably from about 7 to 14, and most preferably from about 7.5 to 14.

5

TABLE 2 (Wt-% as a percentage of total cleaning composition)

	<u>Constituent</u>	<u>Useful</u>	<u>Working</u>	<u>Preferred</u>
	<u>Alkalinity Source</u>			
10	Hydroxide Salts	0.25-10	0.5-8	1-5
	Silicates	0.5-8	0.5-5	0.5-3
	Carbonates	0.5-12	1-10	1.5-8.5
	Phosphates	1-20	1-10	2-8
	Amines	0.10-5.0	0.10-4.5	0.25-3.0

TABLE 2 (Cont.) (Wt-% as a percentage of total cleaning composition)

	<u>Useful</u>	<u>Working</u>	<u>Preferred</u>
5 <u>Constituent</u>			
<u>Vinyl Polymer Emulsion</u>	0.15-10	0.2-8	0.5-6
10 <u>Surfactant</u>	0.00005-1.0	0.0001-1.0	0.0002-0.5
<u>Antimicrobial</u>	0.005-0.2	0.005-0.15	0.01-0.1

Halogenated alkaline cleaners may comprise any number of alkalinity sources such as those useful with the adherent foam of the invention. In addition to providing cleaning efficacy, halogens may be used to disinfect, sanitize or otherwise enhance the antimicrobial character of the surface of application. Additionally, a halogen source may also be present such as chlorine, bromine, iodine, or fluorine among others.

Another cleaning composition with which the foam of the invention may be used is solvated (organic) cleaners having an organic character. Generally, organic solvents function to dissolve, suspend, or otherwise charge the physical properties of materials intended to be removed by the cleaners. Exemplary families of organic solvents include amines, olephinic compounds, short chain and long chain carboxylic acids, and alcohols including mono-, di-, and tri- functional alcohols among other compounds. Again any of the alkalinity sources mentioned earlier may be used with the invention. Organic cosolvents preferred for use in these compositions include mono-, di-, and polyfunctional alcohols. A summary of the concentrations, of cleaning compositions may be found in Table 3.

TABLE 3 (Wt-% as a percentage of total cleaning composition)

	<u>useful</u>	<u>working</u>	<u>preferred</u>
5 foam stabilizing additive	1.0-10.0	1.50-9.0	2.0-8.0
cleaning composition	0.05-20.0	0.05-18.0	0.1-15.0
water	q.s.	q.s.	q.s.

The formulated composition may be applied through any number of means known to those of skill in the art such as single and multiple container foam applicators like Klenzade Model K and 2S Foamers available from Ecolab Inc.

15 Working Examples

The invention will be further described by reference to the following detailed examples.

Foam Stabilizing Composition

20 A foam stabilizing composition was formulated having the following constituents and concentration.

FORMULA 1

	<u>Raw Material</u>	<u>Wt%</u>
	Distilled water	49.50
25	NaOH (50% w/v)	0.20
	Sorbic acid	0.05
	Benzoic acid	0.15
	Hidacid Pyranine dye, (CI #59040)	0.10
30	Acrylic Copolymer emulsion*	50.0

\*(Acusol 820-Rohm and Haas Co, or Gum SL-70 Alco Chemical Co.)

Various detergent compositions were then formulated as seen by Detergent Compositions A through E.

Detergent Composition A

	<u>Percent (Wt-%)</u>	<u>Raw Material</u>
	32.30	Soft Water
	0.10	EDTA
5	31.20	Sodium Hydroxide 50% (w/v)
	6.40	Organic chelant
	30.00	Sodium Hypochlorite

10 Detergent Composition B

	<u>Percent (Wt-%)</u>	<u>Raw Material</u>
	89.20	Sodium Hydroxide (50% w/v)
	4.35	Soft Water
	0.75	Nonionic Surfactant
15	0.10	Organic Chelant
	5.60	40% Sodium Gluconate

Detergent Composition C

	<u>Percent (Wt-%)</u>	<u>Raw Material</u>
	51.70	Deionized Water
20	1.40	Organic Chelant
	40.00	Sodium hydroxide 50%
	1.00	Nonionic surfactant
	2.00	Amine Oxide
	4.00	Amphoteric surfactant

25 Detergent Composition D

	<u>Percent (Wt-%)</u>	<u>Raw Material</u>
	69.9	Soft Water
	1	Versene 100 (EDTA)
	7.5	TKPP, 60% (w/v)
30	1.6	NaOH, 50% (w/v)
	1	Sodium Metasilicate, Anhy.
	3	Anionic Surfactant
	5	Nonionic Surfactant
35	3	Phosphate Ester
	8	Glycol Ether

Detergent Composition E

	<u>Raw Material</u>	<u>Wt %</u>
5	50% NaOH	96.45
	50% Gluconic acid	2.50
	Soft Water	1.00
	Nonionic Surfactant	0.05

The foam stabilizing composition was then combined  
 10 with the various Detergent Compositions (A through E)  
 and tested.

Working Example 1

Foam stabilizing Composition with Detergent  
 Composition A.

15 In a 44 liter (fifteen gallon) foam application  
 pressure vessel, 1,136 grams of Formula 1 was mixed with  
 17,059 grams of Soft Water. To this mixture was added,  
 while stirring, 730.0 grams of detergent composition A  
 containing over 10% NaOH and over 3% sodium  
 20 hypochlorite. The vessel was pressurized to  $443 \times 10^{-4}$   
 Kg/sq mm (63 p.s.i.) and the air-liquid controls  
 adjusted to 1/4 turn open air - 1 and 1/2 turns open  
 liquid. The resulting air-solution combination was  
 applied to vertical stainless steel walls as a rich foam  
 25 with a finished thickness of 1.27 - 0.64 cm (0.5 - 0.25  
 inches). This foam did not flow off the wall, but  
 instead remained as applied without collapse for ten  
 minutes. After forty minutes the foam still provided  
 100% coverage of the area to which it was applied with  
 30 only slight collapse. At this time, the foam was rinsed  
 off with cold water at low pressure and the Foam was  
 found to rinse off easily and completely.

Working Example 2

Foam stabilizing composition with Detergent  
 35 Composition B.

In a 44 liter (fifteen gallon) foam application  
 pressure vessel, 310 grams of Formula 1 was combined  
 with 15,900 grams soft water. To this mixture was  
 added, while stirring 1,510 grams of Detergent





Composition B with over 40% NaOH, a nonionic surfactant and chelating agents. The vessel was pressurized to  $443 \times 10^{-4}$  Kg/sq mm (63 p.s.i.) with air and the air-liquid controls adjusted to 1 and 1/2 turns open liquid and 1/4  
5 turn open air. The resulting air-solution combination was applied to vertical stainless steel walls as a dry foam with a finished thickness of 2.54 - 3.81 cm (1.0 - 1.5 inches).

This foam did not flow off the wall, but  
10 instead remained as applied without collapse for ten minutes with 100% coverage of the wall at this time. At 15 minutes after application the areas with a 3.81 cm (1.5") thick foam coating had sagged slightly but the wall remained 100% covered by the foam. At 20 minutes  
15 after application the foam had sagged sufficiently to clear 10% of the stainless steel wall of foam but the remainder of the wall was still coated. This foam was rinsed off with low pressure cold water and the foam was found to rinse easily and completely at this time.

20

Working Example 3

Foam stabilizing composition with Detergent Composition C.

With a dual intake wall mounted foam unit (Model K low pressure/standard pressure produced by  
25 Ecolab Incorporated) the combination of Formula 1 with a highly alkaline self foaming detergent with a blend of amphoteric surfactants and a level of NaOH in excess of 15% was tested for dynamic mixing and production of the stable alkaline foam. The unit operated by allowing a  
30 flow of water through a venturi to aspirate concentrated products into the stream of water and subsequent to their mixing inlets air under pressure into the fluid stream. With a concentration of Formula 1 equivalent to 7.5% and 1.6% of the Detergent Composition C determined  
35 by flow rate of the water and draw rate of the concentrates, the unit Model K LP/SP produced a very thick clinging foam on vertical stainless steel walls



which did not flow off the walls upon application. After 75 minutes the foam was found to be still 80% as foam with 20% collapsed but 100% coverage of the application area. The foam was easily rinsed off with  
5 low pressure hot water rinse 54.4°C (130 degrees F).

Working Example 4

Foam stabilizing composition with Detergent Composition D.

In a 44 liter (fifteen gallon) foam application  
10 pressure vessel 570 grams of Formula 1 was mixed with 17,700 grams of soft water. To this mixture was added, with stirring, 630 grams of Detergent Composition D with a water soluble solvent, anionic and nonionic  
surfactants. The vessel was pressurized to  $436 \times 10^{-4}$   
15 Kg/sq mm (62 p.s.i.) and the air-liquid controls adjusted to 1 and 1/2 turns open liquid, 1/8 turn open air. The resulting air-liquid combination was applied to stainless steel walls as a very wet foam which did not flow off the wall but instead flowed to an even foam  
20 coating of 0.32 cm (1/8 inch) thick. At 10 minutes after foam application there was no change in foam appearance with 100% coverage of stainless steel wall surface. At thirty minutes after foam application, a slight thinning of foam thickness was visible but the  
25 stainless steel wall surface was still coated 100% by the foam. Foam rinsed with low pressure cold water at this time. The foam was easily rinsed off.

Working Example 5

Foam stabilizing composition with Detergent  
30 Composition E.

In a 44 liter (fifteen gallon) foam application pressure vessel 1,140 grams of Formula 1 was mixed with 15,830 grams soft water. To this mixture was added, while stirring, 1,960 grams of a Detergent Composition E  
35 with NaOH content in excess of 45% NaOH. The vessel was pressurized to  $443 \times 10^{-4}$  Kg/sq mm (63 p.s.i.) and the air-liquid controls adjusted to 1/4 turn open air and 2



turns open liquid. The resulting air-solution combination was applied to vertical stainless steel walls with a finished thickness of 2.54 - 5.08 cm (1-2 inches). At 15 minutes after application there was 100% coverage with no change in foam appearance. At 25 minutes after application of the foam 95% of the area was covered with the remaining foam having slid to the floor. The foam rinsed easily with cold water low pressure rinse.

10

Comparative Example 1

In a 44 liter (fifteen gallon) foam application pressure vessel 1,890 grams of a detergent composition C was combined with 17,030 grams of soft water, the solution was stirred to mix. The vessel was pressurized to  $443 \times 10^{-4}$  Kg/sq mm (63 p.s.i.) with air and the air-liquid controls adjusted to 1 and 1/2 turns open liquid and 1/8 turn open air. The resulting air-solution combination was applied to vertical stainless steel walls. The foam produced was thick and wet and immediately upon application began to flow downward. At 10 minutes after application of the foam to the wall 95% of the wall was clear of any foam coating and the remaining area had a thin coating of foam. At fifteen minutes the 5% of the wall which had a thin foam coating at 10 minutes was coated with film without foam characteristics.

25



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of stabilizing alkaline cleaning compositions using an adherent foam composition said foam composition comprising an alkalinity source, a vinyl  
5 polymer emulsion to provide an adherent foam, and a balance of water, said method comprising the step of adding said foam composition to said alkaline cleaner.
2. The method of claim 1 wherein said alkalinity source comprise an alkali or alkaline earth hydroxide.
- 10 3. The method of claim 1 wherein said alkalinity source is selected from the group consisting of a silicate, a hydroxide, a phosphate, a carbonate, an amine, and mixtures thereof.
- 15 4. The method of claim 1 wherein said alkalinity source is present in a concentration ranging from about 0.10 wt-% to 12 wt-%.
5. The method of claim 1 wherein said vinyl polymer emulsion comprise one or more acrylic monomers.
- 20 6. The method of claim 1 wherein said vinyl polymer emulsion comprises one or more monomers selected from the group consisting of a vinyl acetal monomer, a vinyl acetate monomer, a vinyl alcohol monomer, a vinyl chloride monomer, a vinyl ether monomer, an n-vinyl monomer, a vinyl fluoride monomer, and mixtures thereof.
- 25 7. The method of claim 5 wherein said acrylic monomers are selected from the group consisting of acrylate, methylacrylate, ethylacrylate, propyl acrylate, isopropylacrylate, butylacrylate, sesquibutylacrylate, isobutylacrylate, tertbutylacrylate, hexylacrylate,  
30 heptylacrylate, 2-heptylacrylate, 2-ethylhexylacrylate, 2-



ethylbutylacrylate, dodecylacrylate, hexadecylacrylate, 2-ethoxyethyl acrylate, and mixtures thereof.

5 8. The method of claim 1 wherein said vinyl polymer comprises an ester of an alpha, beta-unsaturated carboxylic acid.

10 9. The method of claim 8 wherein said alpha, beta unsaturated carboxylic acid ester is selected from the group consisting of a methacrylic acid ester, an acrylic acid ester, an itaconic acid ester, an aconitic acid ester, a crotonic acid ester, a mesaconic acid ester, a carboxyethyl acrylic acid ester, a maleic acid ester, a fumaric acid ester, and mixtures thereof.

15 10. The method of claim 1 wherein said vinyl polymer emulsion is present in a concentration ranging from about 0.15 wt-% to 10 wt-%.

20 11. The method of claim 1 wherein said foam composition comprises a surfactant.

25 12. The method of claim 11 wherein said surfactant is selected from the group an anionic surfactant, a cationic surfactant, an amphoteric surfactant, a nonionic surfactant, and mixtures thereof.

30 13. The method of claim 11 wherein said surfactant is present in a concentration ranging from about 0.00005 wt-% to 1.0 wt-%.

35 14. The method of claim 12 wherein said surfactant comprises a nonionic surfactant present in a concentration ranging from about 0.00005 wt-% to 1.0 wt-%.



15. The method of claim 1 wherein the adherent foam composition comprises from about 0.01 wt-% to 0.5 wt-% of an alkalinity source from about 12.0 wt-% to 22 wt-% of a vinyl acrylic polymer from about 0.25 wt-% to 2 wt-% of a nonionic surfactant and a balance of water, wherein the pH of the composition is at about pH 4.5, said method comprising the step of adding said adherent foam to an alkaline cleaning composition.

16. The method of claim 15 wherein said alkalinity source comprise an alkali or alkaline earth metal hydroxide.

17. The method of claim 15 wherein said alkalinity source is selected from the group consisting of a hydroxide, a phosphate, a carbonate, an amine, and mixtures thereof.

18. The method of claim 15 wherein said vinyl acrylic polymer comprises one or more acrylic monomers selected from the group consisting of methylacrylate, ethylacrylate, propyl acrylate, isopropylacrylate, butylacrylate, sesquibutylacrylate, isobutylacrylate, tertbutylacrylate, hexylacrylate, heptylacrylate, 2-heptylacrylate, 2-ethylhexylacrylate, 2-ethylbutylacrylate, dodecylacrylate, hexadecylacrylate, 2-ethoxyethyl acrylate, and mixtures thereof.

19. The method of claim 15 wherein said vinyl acrylic polymer comprises an ester of an alpha, beta-unsaturated carboxylic acid.

20. The method of claim 19 wherein said alpha, beta unsaturated carboxylic acid ester is selected from the group consisting of a methacrylic acid ester, an acrylic acid ester, an itaconic acid ester, an aconitic acid ester,



a crotonic acid ester, a mesaconic acid ester, a carboxyethyl acrylic acid ester, a maleic acid ester, a fumaric acid ester, and mixtures thereof.

21. The method of claim 15 wherein said composition  
5 additionally comprises a surfactant selected from the group  
an anionic surfactant, a cationic surfactant, an amphoteric  
surfactant, a nonionic surfactant, and mixtures thereof.

22. An adherent foam cleaning composition comprising:  
10 (a) an amount of alkaline cleaner effective in  
removal of soil; and  
(b) an adherent alkaline foam composition comprising:  
(i) an amount of alkalinity source effective to  
15 raise the pH of said foam cleaning  
composition;  
(ii) an amount of vinyl polymer emulsion  
effective in providing an adherent foam;  
and  
(c) a balance of water.

23. The composition of claim 22 wherein said alkaline  
20 cleaner is selected from the group consisting of an  
alkaline solvated detergent, an alkaline halogenated  
detergent, an alkaline detergent, and mixtures thereof.

24. The composition of claim 22 wherein said  
25 composition comprises from about 0.50 to 20.0 wt-% of  
alkaline cleaner.

25. The composition of claim 22 comprising from about  
0.15 wt-% to 10.0 wt-% adherent foam.

26. The composition of claim 25 wherein said adherent  
30 alkaline foam alkalinity source comprise an alkali or  
alkaline earth hydroxide.



27. The composition of claim 22 wherein said adherent alkaline foam alkalinity source is selected from the group consisting of a silicate, a hydroxide, a phosphate, a carbonate, an amine, and mixtures thereof.

5 28. The composition of claim 27 wherein said adherent alkaline foam alkalinity source is present in a concentration ranging from about 0.1 wt-% to 12.0 wt-%.

10 29. The composition of claim 22 wherein said adherent foam vinyl polymer emulsion comprise one or more acrylic monomers.

30. The composition of claim 29 wherein said vinyl polymer emulsion comprises a polyacrylate-polymethacrylate copolymer emulsion.

15 31. The composition of claim 22 wherein said adherent foam vinyl polymer emulsion is present in a concentration ranging from about 0.15% wt-% to 10.0 wt-%.

32. The composition of claim 22 comprising a surfactant.

20 33. The composition of claim 32 wherein said surfactant is selected from the group an anionic surfactant, a cationic surfactant, an amphoteric surfactant, a nonionic surfactant, and mixtures thereof.

25 34. The composition of claim 32 wherein said surfactant is present in a concentration ranging from about 0.00005 wt-% to 1.0 wt-%.

35. The composition of claim 32 wherein said surfactant comprises a nonionic surfactant present in a concentration ranging from about 0.00005 wt-% to 1.0 wt-%.





36. A method of cleaning hard surfaces, said method comprising the step of applying a foaming alkaline cleaning composition comprising an alkaline cleaner and an adherent foam stabilizing composition, said adherent foam  
5 stabilizing composition comprising:

- (a) An amount of alkalinity source effective to raise the pH of said composition;
- (b) an amount of vinyl polymer emulsion effective in providing an adherent foam; and
- 10 (c) a balance of water.

37. The method of claim 36 wherein said adherent foam alkalinity source comprise an alkali or alkaline earth hydroxide.

38. The method of claims 36 wherein said alkaline cleaning composition is selected from the group consisting of an alkaline cleaner, an alkaline halogenated cleaner, a solvated alkaline cleaner and mixtures thereof.  
15

39. The method of claim 36 wherein said adherent foam comprises a polyacrylate-polymethacrylate vinyl polymer emulsion.  
20

40. The method of claim 36 wherein said foaming alkaline cleaning composition comprises from about 0.15 wt-% to 10.0 wt-% adherent foam stabilizing composition.

41. The method of claim 36 additionally comprising the steps of:  
25

- (a) formulating the foaming alkaline cleaning composition of claim 39;
- (b) applying said composition to a surface; and
- (c) removing said composition after an extended time  
30 period.



42. The cleaned surface resulting from the method of claim 36.

DATED THIS 4TH DAY OF FEBRUARY 1997

ECOLAB INC.

5 By its Patent Attorneys:

GRIFFITH HACK  
Fellows Institute of Patent  
Attorneys of Australia

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# INTERNATIONAL SEARCH REPORT

Inter. Application No  
PCT/US 94/02294

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 5 C11D3/37

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 5 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 practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indications, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 72, no. 26, 29 June 1970, Columbus, Ohio, US; abstract no. 134467, Z. NIESPODZIEWANSKI 'Foam for purification of metal, ceramics, and plastic surfaces' see abstract & PL, A, 58 991 (INST. TECH. BUDOWLANJEI) ---	1, 7, 11-13, 24
A	US, A, 3 321 408 (B.R. BRIGGS) 23 May 1967  see column 2, line 21 - line 50; example 12  ---	24, 25, 34-36
A	US, A, 3 296 147 (E.M. GATZA) 3 January 1967  see claims; examples  ---	24-26, 29-31, 35, 36
	-/--	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

4 October 1994

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INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/02294

2.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE, A, 27 33 619 (HENDRICKS & SOMMER) 2 February 1978  see claims; example -----	24, 32-36, 39, 45

**INTERNATIONAL SEARCH REPORT**

...information on patent family members

Inter national Application No

PCT/US 94/02294

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
PL-A-58991		NONE	
US-A-3321408		NONE	
US-A-3296147		AU-A- 4884664 GB-A- 1021957	
DE-A-2733619	02-02-78	AT-A- 345947 GB-A- 1542027	10-10-78 14-03-79