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**WO 02/094973 A1**

(54) Title: BIO-ACTIVE DE-INKING OR CLEANING FOAM

(57) Abstract: A foamable aqueous liquid product comprising an aqueous liquid and a stabilising agent, a surfactant, optionally a viscosity modifier, an enzyme and optionally a preservative, which is void of organic solvent and having particular utility in the printing and graphic arts industries.

## BIO-ACTIVE DE-INKING OR CLEANING FOAM

The invention relates to bio-active foams, formulations, manufacture thereof and uses therefor. The foams may be used in cleaning and/or removing spills of inks, dyes, organic matter such as vegetable and/or animal oils and fats, hydrocarbons and paints in the printing, graphics and manufacturing industries and in domestic and/or industrial food preparation.

### **Background to the Invention**

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Small volume ink spills (for example < 5 litres) in printing works or graphic art studios are typically cleaned up with a conventional adsorbant such as sawdust or Perlite <sup>TM</sup> a trade mark and product available in the UK from Zetmeelbedrijven de Bijenkorf B.V (The Netherlands). However, the residues which persist require further treatment so as to remove them. Typically, the residues are mobilised either with an organic solvent such as white spirits or with vegetable oils. The drawbacks in using an organic solvent is that it can be a dermatological and/or respiratory irritant, moreover the solvent vapours given off can be harmful and create a potential fire risk in a work environment. In the instance of using a vegetable oil, once it has been applied to the residue it often produces a slippery surface and therefore creates a potential workplace hazard. A further problem with using organic solvents and/or oils as ink clean up products is that the ink is not completely mobilised where the surface to be cleaned is microporous (e.g. concrete) so typically clean up products only serve to drive the ink further into the surface.

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### **Statement of the Invention**

In its broadest aspect, the invention provides a bio-active foam comprising at least one enzyme so as to assist in the breakdown of substrates such as lipids, oils, fats and/or grease.

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According to a further aspect of the invention, there is provided a foamable aqueous liquid containing a surfactant and an enzyme.

5 According to a yet further aspect of the invention, there is provided a foamable aqueous liquid product comprising a stabilising agent, a surfactant, optionally a viscosity modifier, an enzyme and optionally a preservative. The foamable aqueous liquid product does not have to, and preferably does not, contain any organic solvents.

## 10 Detailed Description of the Invention

The present invention is concerned with the use of an aqueous liquid-based foam carrier for the carriage of a bio-active enzyme. The foam advantageously acts to hold onto the substrate where the foam is applied thereby improving efficiency of targeting. In addition, the foam provides a gas/liquid environment above the substrate surface so as to enhance the rate of enzymatic degradation of specific organic species on the substrate. Preferably, the aqueous liquid component is water and more preferably distilled water. The water acts to solubilise/disperse the various components of the foamable liquid.

20

The stabilising agent is preferably a fatty acid. Suitable examples of fatty acids include stearic acid and/or sodium dodecyl sulphate (syn. lauryl sulphate). The function of the stabilising agent in the foamable aqueous liquid is to stabilise the foam once it has been formed with the help of the surfactant component. Those products suitable for use as a fatty acid must also contain a base so as to neutralise the fatty acid(s) whereby salts/soaps are formed. Preferably, the base is triethanolamine or another triolkanolamine. Irrespective of whether the stabilizing agent is a fatty acid, the product may optionally contain an acid, base or buffer as a pH modifier.

30

Preferably, the surfactant is a non-ionic surfactant which may optionally include an anionic surfactant; more preferably the non-ionic surfactant is a polyoxyethylene such as Brij™, available in the UK from Aldrich Chemical Company. Suitable surfactants which are anionic, for example includes sodium n-dodecyl sulphate or lauroylsarcosine sodium salt. Anionic surfactants are known to remove carbohydrate and protein type soils, whereas non-ionic surfactants are especially useful in removing greasy and oily food soils. Therefore, one embodiment of the invention is a mixture of surfactants to clean and remove complex soil types found on food preparation work surfaces and kitchen utensils. The surfactant not only aids in the dissolution or dispersion of the soil but also aids in the initial foaming of the aqueous liquid and is useful in stabilising the foam once it has formed.

Preferably, the viscosity modifier, when present, is a gum or the like, such as xanthan gum and is present in preferred embodiments so as to thicken the foamable liquid and thus retard drainage from the formed foam.

Preferably, the preservative, when present, is an antioxidant and/or an antibacterial agent and also acts to retard degradation of fats and other organic materials.

The foamable aqueous liquid product comprises at least one enzyme preferably selected from the group consisting of catalase, cellulase, cholesterol esterase, esterase, lipase, papain, peroxidase, phosphatase and protease. It will be appreciated that where the foamable aqueous liquid is to be used to remove lipid or ester films from solid substrates or surfaces, lipases and esterases enzymes are of particular utility.

The foam is preferably produced by aeration and more preferably by a suitable a propellant or blowing agent, such as a butane/propane mix, for example, A46 hydrocarbon.

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In the case of oil-based film in contact with a solid (often porous) substrate, while not wishing to be bound by theory, the mode of action of the foam in removing the lipid layer is believed to be as described in the following paragraphs:

5 Once the foam is deposited onto the spill/oil film, it begins to undergo gravitational separation. The aqueous liquid, enzyme(s) and surfactant component parts of the foam drain towards and onto the surface of the spill/oil film. However, because the film is hydrophobic, the aqueous medium is unable to penetrate through the film to separate it from the underlying solid surface. It is therefore believed thought that due  
10 to the presence and biological activity of the enzymes in the aqueous liquid the enzymatic action starts to “thin” the spill/oil film at the interface, allowing the aqueous liquid to penetrate the oil film and separate it from the underlying solid surface. The process is assisted by the presence of surfactants. As a consequence of the enzymatic action, the film can be lifted from the solid surface in small “crazy  
15 paving” type fragments.

Once the film fragments are separated from the solid substrate they begin to float up (oil being lighter than water) through the aqueous medium and to some degree (if they are small enough) through the lamellae of the foam, so that they are trapped at  
20 the gas/liquid interface. The foam is thus believed to act advantageously in several ways: i) as a targeting aid; ii) as a reservoir for the enzyme(s) and surfactant; iii) as a controlled means of dispensing enzyme and surfactant to the oil film surface and; iv) as a trap for the released oil film fragments.

25 Preferably, the foamable aqueous liquid product is contained within and dispensed from a pressurised container or canister. These containers/canisters may be reusable and capable of being re-pressurised. Alternatively, in the instance of providing a fixed installation, the foamable aqueous liquid may be contained within a tank/storage vessel and piped/dispensed under pressure from a directing nozzle to the  
30 area/ apparatus in need of cleaning.

The viscosity of the foamable aqueous liquid is desirably selected so that the liquid is able to drain from the lamellae of the foamed liquid in a slow controlled manner. If the viscosity is low then the rate of drainage (gravitational separation) will be fast and the foam will collapse quickly. On the other hand, if the viscosity is high, then the rate at which the enzyme drains onto the oil film will be slow and the speed at which the oil film fragments rise through the liquid to the foam will also be slow. Preferably, the foamable aqueous liquid has a viscosity in the range 2 to 10 centipoise.

Generation of the foam is achieved by pressurising the aqueous liquid with a liquified "blowing agent" in a canister. When the pressure is released via a nozzle, the liquid blowing agent becomes dissolved in the foam liquid and expands as it gassifies. Ideally, the blowing agent is uniformly mixed/dispersed with the foam liquid so that bubbles of relatively uniform size are produced from the foamable liquid ideally resulting in a formed foam with a bubble size within a specific size range in order to effect stability of the formed product. If there are a wide range of bubble diameters within the foam this can lead to instability and rapid foam collapse. The bubble size is desirably selected to be quite small e.g. 200  $\mu\text{m}$  so as to effect efficient "trapping" of oil film fragments. Preferably, the formed foam has bubbles of diameter within the range of 100-1000  $\mu\text{m}$  (for example 100-500  $\mu\text{m}$ , e.g. about 200  $\mu\text{m}$ ) and more preferably the standard deviation is within the range  $\pm 10-30\%$  and more preferably still  $\pm 20\%$ .

According to a further aspect of the present invention there is provided a formulation comprising about 80 to 90 wt.% of an aqueous medium, about 5 to 15 wt.% of a stabilising agent, about 2 to 5wt.% of a base, about 1 to 5 wt.% of a surfactant, about 0.05 to 0.5 wt.% of a viscosity modifier, an enzyme in the range of 0.1 to 1.0 wt.%, and optionally about 0.01 to 0.05 wt.% of a preservative, the formulated product being in the form of a foamable liquid. The formulation may contain up to 5 wt.%, preferably up to 3 wt.% and more preferably up to 1 wt.%, of other additives or components. The percentages of all components add up to 100%.

Preferably, the foam is formed by aeration with a propellant/blowing agent, such as foam 2 to 5 wt.% of a butane/propane mix (e.g. A46 hydrocarbon). Typically, the preferred concentration of enzyme within the formulation varies between 0.1 and 1.0% by weight and its selection is dependent on a user's requirements.

5

According to a yet further aspect of the invention there is provided a liquid having foam-forming characteristics obtainable by:

- (i) dispersing a viscosity modifier in an aqueous medium;
- 10 (ii) adding a surfactant and a stabilising agent to the mixture;
- (iii) adding a neutralising agent and optionally adding a further stabilising agent to the mixture;
- (iv) adding a preservative to the mixture and;
- (v) adding at least one enzyme to the mixture.

15

The invention therefore includes a liquid having the characteristics of a foamable liquid obtained by the above method.

Preferably, the above mentioned steps may be performed sequentially as steps (i) to 20 (v), simultaneously or in a variety of combinations either separately or in combination, the sequences of which is not intended to limit the scope of the method.

Preferably, when the resulting mixture is completed, it is provided in a container from where it may be dispensed under pressure. It will be appreciated that the 25 foamable liquid is aerated in order to form the foam and that aeration may be by agitation or by passing an appropriate blowing agent/propellant therethrough, preferably under pressure.

According to a yet further aspect of the invention there is provided use of a foamable 30 liquid as hereinbefore described for use as a cleaning product in the printing and graphic arts industries.

The foamable liquid of the present invention is of particular use where it can be used to "wash-up" i.e. clean print machine rollers and to clean small scale spill residues of oil-based and quick-set inks in printing works. It will be appreciated from the foregoing that the foamable liquid of the present invention does not have to contain  
5 any volatile organic solvents and therefore may be safe for use in the workplace within the terms of the European Union Volatile Organic Compounds (VOC) Directive and the Environmental Protection Agency and OSHA regulations in the United States. Indeed, if used in conjunction with UV polymerisable inks, the foam clean up system advantageously constitutes a completely solvent-free printing  
10 system.

According to a yet further aspect of the invention there is provided use of a foamable liquid as herein before described for use in the food preparation and manufacturing industries. Preferably, the foamable liquid and formed foam are non-toxic and non-  
15 hazardous when in use.

The foam may also be used as an industrial and/or domestic cleaning agent in the manufacture, retail and preparation of foods as a de-greasing agent for surfaces such as, for example, counters, floors and walls in addition to use as a cleaning agent in  
20 conventional and microwave ovens. The foams are of particular use in de-greasing/removing oil films from food preparation equipment and in the removal of solid oil residues, at room temperature from worktops and food preparation surfaces.

According to a yet further aspect of the invention there is provided use of a foamable  
25 liquid as herein before described for use in removing lubricating and diesel oil-spill residues, grease residues and non-dried, oil-based paint residues after small scale spills. The foams are of particular use in removing such spill/residues from flat and porous surfaces.

30 Typically, in preparing the foamable liquid of the present invention, the viscosity modifier (when used) is dispersed in the aqueous liquid under action of mild heat.



The surfactant may be added at the same time or after the viscosity modifier has dispersed. The surfactant, if solid, is allowed to melt and the stabilising agent and base added to the mixture with stirring. When the mixture has cooled to a temperature below which denaturation of the particular enzymes employed and can occur, e.g. below 37°C and especially about 30°C or below, the enzyme(s) may be added and optionally the preservative may be included in the mixture. The mixture can then be dispensed into appropriate containers for subsequent use.

Specific aspects of the present invention are disclosed in even greater detail in the following examples. The examples are illustrative only, and are not intended to limit the scope thereof in any respect. All parts and percentages are provided in weight percent unless otherwise stated.

### Example 1

Xanthan gum (1.2 g) is dispersed completely in water (845 ml) by mixing vigorously. The mixture is then heated to a temperature of about 60°C. Next, Brij 35™ (21.5 g) is added and mixed until completely melted. Subsequently, stearic acid (65 g) is added and mixed until it has completely dissolved. The mixture is then warmed to about 75°C and triethanolamine (37 ml) poured in and mixed. Then lauryl sulphate (29g) is added for about 0.5h until all the components have combined thoroughly. The mixture is cooled to about 30°C and BHT (0.2 g) is added. The enzyme lipase (0.5 wt. %) derived from porcine pancreas is then added and entire mixture is mixed well to dissolve the enzyme. During the preparation, mixing is carried out at a low speed in order to minimize foaming.

The final mixture is cooled to 20°C and dispensed into appropriate vessels/cans. A blowing agent is used (A46 hydrocarbon at 3.2 wt.%) to act as a propellant. For portable systems, the foamable liquid preparation is contained and dispensed in pressurised canisters or alternatively dispensed into larger refillable re-pressurisable canisters. For fixed, static applications the foamable liquid is contained within a tank

and piped under pressure to dispensing nozzles on, for example, a large printing machine.

Table 1

BASIC SOAP-STABILISED FOAMABLE LIQUID FORMULATION		
<i>Component</i>	<i>Conc.</i>	<i>Weight %</i>
Distilled water	845ml	84.5
Stearic acid	65g	6.5
Triethanolamine (99% LFG90)	37ml	3.7
Sodium dodecyl sulphate (syn. lauryl sulphate)	29g	2.2
Brij 35™ (surfactant)	21.5g	2.2
Xanthan gum	1.2g	0.1
Butylated hydroxytoluene	0.2g	0.02
Lipase (ex porcine pancreas)	5g	0.5

5

**Example 2**

The composition of Example 2 was prepared in the same way as Example 1 but the enzyme was an esterase (0.5 wt. %), derived from porcine liver.

10

Table 2

BASIC SOAP-STABILISED FOAMABLE LIQUID FORMULATION		
<i>Component</i>	<i>Conc.</i>	<i>Weight %</i>
Distilled water	845ml	84.5
Stearic acid	65g	6.5
Triethanolamine (99% LFG90)	37ml	3.7
Sodium dodecyl sulphate (syn. lauryl sulphate)	29g	2.2
Brij 35™ (surfactant)	21.5g	2.2
Xanthan gum	1.2g	0.1
Butylated hydroxytoluene	0.2g	0.02
Esterase (ex porcine liver)	5g	0.5

Both lipase (Example 1) and esterase (Example 2) enzymes have been trialled within the Basic Soap-Stabilised Foamable Liquid Formulation.

For the removal of thin vegetable oil films, the addition of 0.5% by weight lipase is  
5 more efficient in terms of speed of removal and percentage removal of the film, than 0.5% by weight esterase.

While it is considered that esterase does have value in specific applications (eg. certain mineral oils) it is envisaged that lipase will be adopted as a standard enzyme  
10 for the application of the foam to most commercial-scale cleaning applications.

### Example 3

An experiment to test the efficacy of the foamable liquid was conducted using the  
15 formulation of Example 1 compared to a control which comprised the formulation of Example 1 without the enzyme.

An ink film was applied to the rough sides of frosted microslides by spreading a thixotropic ink onto its surface. The ink was spread onto the slide so that the fissures  
20 on the rough surface filled up with the ink and produced an even layer was produced. The thickness of the ink layer was approximately 20  $\mu\text{m}$ . Experiments were performed within a 25 by 12.5 cm square polypropylene box. Ink coated slides were supported so that they rested approximately 25 mm above the base of the box. In this way intimate contact with the foam was achieved whilst avoiding contact with the  
25 solution in the bottom of the box which results from drainage from the foam.

Each Foam (Example 1 and Example 1 minus enzyme) was scooped into a separate polypropylene box on top of the ink-coated slides. After a predetermined time ( $t=0$  h and 89hrs) the slides were removed from the boxes and the surfaces freed from  
30 adherent foam. The residual ink was monitored photographically and using a densitometric technique. A third box with no foam was used as a further control.

Image analysis by densitometry was as follows: the slides bearing the ink layers were placed on a photographic light box and a black card mask with a rectangular aperture of the same dimensions as the deposited ink layer was placed over the slide. A video camera was focused on the slide/mask and the intensity of light transmitted was recorded. The video camera was connected to a Joyce/Loebel Magiscan image analyser to perform the densitometry measurement. The results are tabulated below. Values are given as transmittance so that black i.e. no transmittance would have a value of 0 whereas white i.e. complete transmittance would have a value of 100. Thus, the higher the densitometer transmittance value the more effective the cleaning.

Treatment Time (hours)	Control (No foam)	Example 1 without enzyme	Example 1 with enzyme
0	0.24	0.34	0.34
89	0.24	9.23	17.76

With reference to the Figures, there is shown a control microslide (Figure 1 B) covered with an ink film which received no treatment. Figure 1A illustrates an ink film coated microslide to which the foam formulation of Example 1 without the presence of an enzyme was applied whereas Figure 1C illustrates an ink film coated microslide to which the foam formulation of Example 1 including an enzyme ( 0.1% lipase) has been applied.

The results demonstrate that addition of the enzyme to the foam formulation greatly improves the ability and efficacy of the foam to lift ink spills compared to foam without an enzyme. In addition, following treatment with Example 1 foam with enzyme the residual ink film on the microslide was much "looser" and more amenable to being washed off in a water stream.

25

#### Example 4

The foamable liquid formulation incorporating 0.5% lipase and contained in a 400ml. pressurised canister has been tested in our kitchens and in large scale food preparation areas. The foam has been successfully used to remove both liquid and solid (crystalline) oil/grease films at room temperature (RT).

The substrates tested included: vinyl flooring; stainless steel worktops/food preparation surfaces; melamine (*Formica*) worktops/food preparation surfaces; glass oven doors;

The types of residues tested included: films of vegetable oil (liquid at RT); films of animal fats (solid at RT); Cocoa butter (solid at RT);

The foam was deposited directly from the 400ml. pressurised canister and onto the surface of the residue. In some cases, the surface was vertical (eg. oven doors) and the foam had sufficiently high cohesive properties to remain on the surface without any slippage. The foam was left for about 4min. then gently removed/swept from the substrate using a flat straight edge such as a soft plastic flat-edge spatula or rubber flat-edged 'squeegee'. It was unnecessary to apply undue pressure to the spatula or 'squeegee' onto the substrate, but only sufficient to effectively sweep away the foam bulk.

Our results showed that as the foam was removed, the oil/fat film could be seen to have lifted from the substrate and be trapped within the structure of the foam.

After the foam had been removed, the substrate had a dry, oil-free surface to the touch. The foam was effective in the removal of both solid (eg. cocoa butter) and liquid (eg. vegetable oil) films.

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Those skilled in the art having the benefit of the teachings of the present invention as herein above set forth, can effect numerous modifications thereto. These modifications are to be construed as being encompassed within the scope of the present invention as set forth in the appended claims.

### Claims

1. A foamable aqueous liquid product comprising: an aqueous liquid, a stabilising agent, a surfactant, optionally a viscosity modifier and an enzyme.  
5
2. A product according to claim 1 further comprising a preservative.
3. A product according to either claim 1 or 2 void of any organic solvents.
- 10 4. A product according to any preceding claim wherein the aqueous liquid acts to solubilise/disperse various components within the foamable aqueous liquid product.
5. A product according to claim 4 wherein the aqueous liquid is water.  
15
6. A product according to claim 5 wherein the water is distilled.
7. A product according to any preceding claim wherein the stabilising agent acts to stabilise the foam once it has been formed.  
20
8. A product according to claim 7 wherein the stabilising agent comprises a fatty acid.
9. A product according to claim 8 wherein the fatty acid comprises stearic acid  
25 and/or sodium dodecyl sulphate.
10. A product according to any preceding claim further comprising a base.
11. A product according to claim 10 wherein the base is triethanolamine.  
30

12. A product according to any preceding claim further comprising an acid or buffer as a pH modifier.
13. A product according to any preceding claim wherein the surfactant comprises a non-ionic surfactant.
14. A product according to claim 13 wherein the non-ionic surfactant is polyoxyethylene.
15. A product according to claim 14 wherein the polyoxyethylene is Brij™.
16. A product according to any preceding claim wherein the surfactant comprises an anionic surfactant.
17. A product according to claim 16 wherein the anionic surfactant is selected from sodium n-dodecyl sulphate or lauroylsarcosine sodium salt.
18. A product according to any preceding claim wherein the viscosity modifier acts to thicken the foamable aqueous liquid and product thus retard drainage from the formed foam.
19. A product according to claim 18 wherein the viscosity modifier is xanthan gum.
20. A product according to claim 2 or any of claims 3 to 19 when dependent thereon wherein the preservative is an antioxidant and/or an antibacterial agent which acts to retard degradation of fats or other organic materials.
21. A product according to any preceding claim wherein the enzyme is selected from the group consisting of a catalase, cellulase, cholesterol esterase,



esterase, lipase, papain, peroxidase, phosphatase and protease and mixtures thereof.

- 5 22. A product according to any preceding claim provided as a foamable aqueous liquid product is contained within and dispensable from a pressurised container or canister.
23. A product according to claim 22 wherein the container/canister is reusable and capable of being re-pressurised.
- 10 24. A product according to any one of claims 1 to 21 provided in a fixed installation whereby foamable aqueous liquid product is contained within a tank/storage vessel and can be piped/dispensed under pressure from a directing nozzle to an area/ apparatus that needs to be cleaned.
- 15 25. A product according to any preceding claim wherein the foamable aqueous liquid product has a viscosity in the range 2 to 10 centipoise.
- 20 26. A product according to any preceding claim wherein the formed foam has bubbles of diameter within the range of 100 to 1000  $\mu\text{m}$ .
27. A product according to claim 26 wherein the bubble diameter has a standard deviation in the range  $\pm 10\text{-}30\%$ .
- 25 28. A product according to claim 26 wherein the bubble diameter has a standard deviation of  $\pm 20\%$ .
- 30 29. A foamable aqueous liquid formulation comprising about 80 to 90 wt.% of an aqueous liquid, about 7 to 12 wt.% of a stabilising agent, about 2 to 5 wt.% of a base, about 1 to 3 wt.% of a surfactant, and optionally about 0.05 to 0.5

wt.% of a viscosity modifier, an enzyme in the range of about 0.1 to 1.0 wt.%, percentages of all components add up to 100%.

- 5 30. A formulation according to claim 29 further comprising about 0.01 to 0.05 wt.% of a preservative
31. A formulation according to either claim 29 or 30 containing up to 5 wt.% of other additives or components.
- 10 32. A formulation according to claim 31 containing between 1 to 3 wt.% of other additives or components.
33. A formulation according to any one of claims 29 to 32 further including any one or more of the features recited in any one or more of claims 1 to 31.
- 15 34. A formulation according to any one of claims 29 to 33 wherein the foam is formed by aeration with a 3.2 wt.% propellant/blowing agent.
35. A method for obtaining a foamable aqueous liquid comprising the steps of:
- 20
- (i) dispersing a viscosity modifier in an aqueous liquid;
  - (ii) adding a surfactant and a stabilising agent;
  - (iii) adding a neutralising agent and optionally adding a further stabilising agent;
  - 25 (iv) adding a preservative and;
  - (v) adding at least one enzyme.
36. A method according to claim 35 wherein steps are performed sequentially as steps (i) to (v), simultaneously, or in a variety of combinations either
- 30 separately or in combination.

37. A product or formulation according to any one of claims 1 to 35 comprising a foamable aqueous liquid formulation obtainable by the method according to either claim 36 or 37.
- 5 38. Use of a foamable aqueous liquid formulation according to any one of claims 1 to 35 as a cleaning product in printing and graphics industries.
39. Use of a foamable aqueous liquid formulation according to any one of claims 1 to 35 as a cleaning product in food preparation and manufacturing  
10 industries.
40. Use of a foamable aqueous liquid formulation according to any one of claims 1 to 35 as a cleaning product for removing lubricating and diesel oil-spill residues, grease residues and non-dried, oil-based paint residues after small  
15 scale spills.
41. A method of cleaning a surface comprising applying a foamable aqueous liquid product according to any one of claims 1 to 28 or a foamable aqueous liquid formulation according to any one of claims to 29 to 35 to the surface  
20 so as to remove lipids, fats and/or grease.

25

30



Fig 1A



Fig 1B

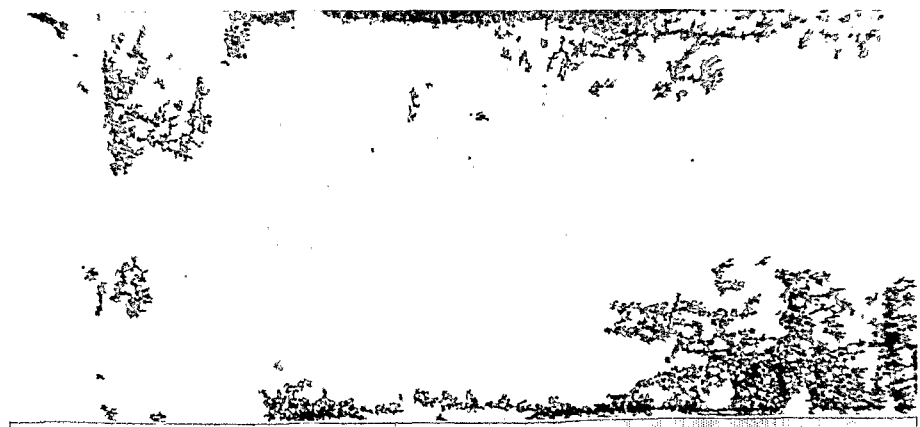


Fig 1C

## INTERNATIONAL SEARCH REPORT

PCT/GB 02/02297

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C11D17/00 C11D11/00 C11D3/386

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 C11D C23G

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)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 998 342 A (SCOVILLE ET AL) 7 December 1999 (1999-12-07)  column 2, line 14 -column 6, line 62 examples 1,3 claims 1-6	1, 2, 4-12, 16-18, 20-41
X	EP 0 839 905 A (PROCTER & GAMBLE) 6 May 1998 (1998-05-06)  page 1, line 40 - line 42 page 5, line 46 - line 48 page 6, line 11 - line 13 page 6, line 53 - line 57 example 1 claims 1-6	1-8, 12-23, 35-37

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

PCT/GB 02/02297

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 781 212 A (SMILLIE W) 25 December 1973 (1973-12-25)  column 2, line 32 - line 33 column 2, line 64 - line 65 column 6, line 36 - line 45 example 1  ----	1, 2, 4-6, 10, 11, 13, 16, 18, 21-23, 25-28, 37, 40, 41
X	US 4 561 998 A (WERTZ JEAN-LUC H M ET AL) 31 December 1985 (1985-12-31)  example 2  ----	1, 2, 4-8, 10-14, 16, 20, 21, 25-28
X	EP 0 450 702 A (UNILEVER NV (NL)) 9 October 1991 (1991-10-09)  page 6, line 42 - line 46 page 7, line 22 - line 35 examples 5, 11  ----	1-8, 10-16, 21, 25-28, 35-37
A	US 6 066 614 A (ORLANDINI ET AL) 23 May 2000 (2000-05-23) column 4, line 15 - column 6, line 39 examples 2-4 claims 1, 2, 14  ----	1-41
A	GB 2 273 893 A (UNILEVER PLC) 6 July 1994 (1994-07-06) page 20, line 6 - line 13 example 3  ----	1-41
A	US 4 242 377 A (ROBERTS ET AL) 30 December 1980 (1980-12-30) column 5, line 1 - line 2 column 8, line 36 - column 10, line 30 examples 1-3  ----	1-41
A	US 5 102 573 A (HAN SHAW-LIN ET AL) 7 April 1992 (1992-04-07) column 1, line 10 - line 62 example D column 11, line 53 - line 54 claims 1, 3-6, 9, 11, 13, 14, 16  ----	1-41
A	US 3 532 599 A (COOPERMAN ISADORE NATHAN) 6 October 1970 (1970-10-06) claim 1  ----	1-41
	-/--	

## INTERNATIONAL SEARCH REPORT

PCT/GB 02/02297

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 902 225 A (MONSON JAMES A)            11 May 1999 (1999-05-11)            column 5, line 61 -column 6, line 29            column 7, line 25 - line 44            examples 3,4            claim 1</p> <p style="text-align: center;">---</p>	1-41
A	<p>US 5 204 016 A (HAMILTON C R ET AL)            20 April 1993 (1993-04-20)            column 2, line 58 - line 68            column 5, line 48 -column 6, line 28            column 6, line 21 - line 22            example 1            claims 1,5,10-14</p> <p style="text-align: center;">---</p>	1-41
A	<p>US 4 587 030 A (CASEY SHERYL K)            6 May 1986 (1986-05-06)            column 1, line 12 - line 18            column 3, line 62 -column 5, line 23            example II            claims 1,2,17</p> <p style="text-align: center;">-----</p>	1-41

## INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB 02/02297

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5998342	A	07-12-1999	US 6235692 B1	22-05-2001
EP 0839905	A	06-05-1998	EP 0839905 A1 BR 9712883 A JP 2000508370 T WO 9820100 A1	06-05-1998 01-02-2000 04-07-2000 14-05-1998
US 3781212	A	25-12-1973	NONE	
US 4561998	A	31-12-1985	AT 22920 T AU 559791 B2 AU 1488883 A CA 1208519 A1 DE 3366958 D1 EP 0095205 A1 FI 831832 A ,B, GR 78820 A1 IE 55427 B1 JP 1785137 C JP 4077038 B JP 59025894 A MX 162610 A	15-11-1986 19-03-1987 01-12-1983 29-07-1986 20-11-1986 30-11-1983 25-11-1983 02-10-1984 12-09-1990 31-08-1993 07-12-1992 09-02-1984 31-05-1991
EP 0450702	A	09-10-1991	AU 629116 B2 AU 7399091 A BR 9101381 A CA 2039630 A1 EP 0450702 A2 JP 2033324 C JP 4227699 A JP 7057877 B ZA 9102545 A	24-09-1992 10-10-1991 26-11-1991 07-10-1991 09-10-1991 19-03-1996 17-08-1992 21-06-1995 30-12-1992
US 6066614	A	23-05-2000	EP 0812904 A2 CA 2257955 A1 EP 0906390 A1 WO 9747714 A1	17-12-1997 18-12-1997 07-04-1999 18-12-1997
GB 2273893	A	06-07-1994	NONE	
US 4242377	A	30-12-1980	NONE	
US 5102573	A	07-04-1992	AU 608589 B2 AU 1444188 A CA 1306921 A1 DK 194888 A EP 0286075 A2 FI 881655 A MX 167442 B NO 881526 A NZ 224148 A PT 87179 A ,B ZA 8802423 A	11-04-1991 13-10-1988 01-09-1992 11-10-1988 12-10-1988 11-10-1988 23-03-1993 11-10-1988 26-02-1991 01-05-1988 27-12-1989
US 3532599	A	06-10-1970	US 3813342 A	28-05-1974
US 5902225	A	11-05-1999	AU 3896395 A AU 5590296 A	02-05-1996 10-10-1996



# INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB 02/02297

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5902225	A	WO 9611162 A1	18-04-1996
US 5204016	A	20-04-1993 JP 5502900 T WO 9015858 A1	20-05-1993 27-12-1990
US 4587030	A	06-05-1986 AU 558507 B2 AU 2999584 A CA 1224998 A1 EP 0130786 A2 NZ 208598 A JP 1723311 C JP 4007400 B JP 60051800 A	29-01-1987 10-01-1985 04-08-1987 09-01-1985 12-11-1986 24-12-1992 10-02-1992 23-03-1985