1 Publication number:

0 354 011 **A1**

1

EUROPEAN PATENT APPLICATION

(2) Application number: 89307842.8

(9) Int. Cl.⁵: **C 11 D 1/62** C 11 D 3/00, C 11 D 1/835

22 Date of filing: 02.08.89

(39) Priority: 04.08.88 GB 8818593

Date of publication of application: 07.02.90 Bulletin 90/06

Designated Contracting States: AT BE CH DE ES FR GB GR IT LI LU NL SE 7 Applicant: Albright & Wilson Limited 210-222 Hagley Road West Oldbury Warley West Midlands B68 0NN (GB)

2 Inventor: Martin, Clifford George 10 Oak Bank Whitehaven Cumbria CA28 6HY (GB)

(74) Representative: Savidge, Roger Gordon Madgwick et al. c/o Albright & Wilson Limited 1 Knightsbridge Green London SW1X 7QD (GB)

Fabric conditioners.

A fabric conditioning composition comprises water, a cationic fabric conditioner having two C₁₅₋₂₂ alkyl and/or alkenyl groups and sufficient of a non-ionic, amphoteric or semipolar surfactant to lower the viscosity of the composition.

Description

10

15

20

25

30

35

40

45

50

55

60

FABRIC CONDITIONERS

Fabric conditioners are widely used to soften fabrics after washing in anionic detergents. As used herein the term refers to cationic organic compounds such as amine salts or quaternary nitrogen compounds, all of which have two long chain (e.g. C₁₅₋₂₂) alkyl and/or alkenyl groups, and especially two C₁₆₋₁₈ alkyl and/or alkenyl groups (e.g. tallowyl, oleyl, palmityl and/or stearyl groups).

Among the types of fabric conditioners which have been used are included quaternary ammonium salts and, in particular, distearyl dimethyl ammonium chloride, amido imidazoline salts, quaternised amido imidazolines, amido amine salts quaternised amido amines and ethoxylated amido amines. The amido imidazoline salts and quaternised amido imidazolines may be derived from amido amines by cyclisation. For convenience therefore, amido amine salts, amido imidazoline salts and their quaternised and/or alkoxylated derivatives are referred to collectively herein as "amido amine derivatives". Although they are only very sparingly soluble in water, fabric softeners can be fairly easily dispersed to form dilute aqueous dispersions with concentrations of up to about 20%. However a major problem encountered in the handling and formulation of fabric conditioners is the high viscosity of even the more dilute of such aqueous dispersions.

This is a particular problem for the manufacturer who supplies cationic fabric conditioners in bulk to the formulator, since it is difficult to obtain concentrated dispersions of fabric conditioners in a readily pourable and stable form. The manufacturer is thus concerned to reduce the viscosity of the bulk products, and at the same time to maintain and, if possible increase the relative concentration, in order to reduce the cost and inconvenience of transporting and storing large volumes of water.

The problem for the formulator is more complicated. There is an obvious need for a compromise between increased cost per unit volume and greater difficulty in pouring, on the one hand and increased effectiveness, per unit volume, on the other as the concentration is increased. However, consideration must also be given to the prejudice of the consumer who believes that more viscous products are necessarily more concentrated and therefore more effective, and may purchase a more viscous, but more dilute product despite its being less cost effective and harder to pour.

Control of viscosity, both in concentrated products, and on dilution, is therefore of crucial importance in making and formulating fabric conditioners.

The formulator normally sells compositions containing 3 to 7% fabric conditioner which represents the maximum concentration at which the formulation is sufficiently pourable, although higher concentrations e.g. up to about 15% can be achieved by adding trace amounts, usually of the order 100 to 1,500ppm, of calcium ion, e.g. as calcium chloride, which tends to reduce the viscosity. Concentrations greater than about 20% can only be achieved by using water soluble organic solvents. Manufacturers who need to achieve concentrations of greater than 50%, preferably 75 to 90%, for efficient distribution to the formulators, have therefore had to make substantially anhydrous concentrates in organic solvents such as lower alcohols. In practice the solvent most commonly used is isopropanol, which is expensive, flammable, odourous and may produce undesirable effects in the final formulation, such as variation of dispersion viscocity on ageing. Isopropanol has, however, generally been considered essential to obtain a pourable and concentrated composition.

The concentrate containing the water miscible solvents can be dispersed by stirring in hot water and blended with colouring, perfumes and traces of soluble calcium salts such as calcium chloride, in order to obtain a pourable formulation acceptable to the consumer. Nonionic surfactants or fatty alcohols are sometimes added to improve the dispersibility of the composition.

The difficulty of handling concentrates, the need to use hot water and the disadvantages of solvent, have all led manufacturers for many years to look for alternative ways of preparing concentrates, but hitherto without success. It is possible to alleviate some of the problems by using an unsaturated or partly unsaturated feedstock such as oleyl or soft tallow to provide the long chain alkyl/alkenyl group of the fabric conditioner and products have been prepared using feedstocks of a high iodine value (ie high degree of unsaturation).

Unfortunately it has been found that the higher the iodine value of the feedstock; the poorer is the fabric softening effect, and the more prone is the product to oxidation leading to discolouration and malodour.

Our pending British patent Application No. 8719083 describes a novel physical state of aqueous cationic fabric conditioners which enables them to be obtained as mobile creams of high concentration. We discovered that when electrolytes were included in certain critical concentrations in aqueous dispersion of cationic fabric conditioners a characteristic spherulitic structure was obtained, which typically underwent spontaneous creaming. The cream was a mobile concentrated aqueous dispersion with good fabric softening properties, which was rapidly dispersible in cold water by stirring or shaking.

Creams having a similar structure and composition to those obtained by allowing a dilute system to cream can also be prepared directly by mixing an electrolyte solution with the concentrate, until the desired cream concentration is achieved. However the properties of products so prepared are usually inferior to those obtained by actual creaming of a diluted solution. In general we have found that creams according to our aforesaid British Patent Application could be identified by a characteristics spherulitic appearance under the optical microscope. However the mobility of many of the creams was less than ideal and some fabric conditioners do not readily form creams of commercially useful concentration.

In particular when perfumes are added to fabric conditioner creams, unacceptable high viscosities are often

observed.

We have now discovered that small amounts e.g. typically 0.1 to 2% of surfactants, especially non-ionic amphoteric surfactant, substantially reduce the viscosity of fabric conditioners. This makes it possible to achieve higher concentrations with acceptable mobility. This discovery is surprising. Surfactants have previously been included in non-cream fabric conditioner formulations, but have normally been used in proportions of 3% - 5% by weight of the composition or more than 1:20 of the weight of fabric conditioner to improve the stability and/or dispersibility of the concentrates. Such high concentrations of surfactant have not hitherto been observed to improve mobility to any significant extent and usually increase the viscosity.

The concentrations of surfactant used according to our invention are substantially less than would be expected to have any useful effect on dispersibility. We have discovered that when surfactants are added progressively to fabric conditioners in concentrations of less than 2% based on the weight of the composition or less than 1:3 based on the weight of fabric conditioner the mobility typically rises to a maximum value with increasing surfactant concentration and then falls until, at the conventionally used concentrations of 3% or over, the mobility is generally less than that of the unmodified fabric conditioner.

The concentration of surfactant required for optimum mobility depends on the particular choice of fabric conditioner and of surfactant.

Our invention therefore provides a fabric conditioning cream composition substantially as described in our aforesaid British Patent specification, comprising water, a cationic fabric conditioner having two C_{15-22} alkyl and/or alkenyl groups and sufficient of an nonionic, amphoteric or semipolar surfactant to lower the viscosity of the composition.

Preferably the proportion of surfactant is less than 2% based on the total weight of the composition, more preferably less than 1.5% especially less than 1% e.g. less than 0.5%. The amount of surfactant is preferably less than 1:20 based on the weight of cationic fabric conditioner especially less than 1:30 most preferably less than 1:35.

Preferably the concentration of surfactant is greater than 0.01% based on the total weight of the composition, especially greater than 0.05%, e.g. greater than 0.1% usually greaten the 0.2% most preferably greater than 0.5%. Preferably the proportion of surfactant by weight of fabric conditioner is greater than 1:200 especially greater than 1:150 more preferably greater than 1:100 typically greater than 1:80 greater than 1:50 more especially greater than 1:40.

The invention is practically applicable to lowering the viscosity of creamed fabric softeners of the type described in our aforesaid British Patent Application, which contain electrolytes, such as calcium, chloride, in concentrations greater than 0.3% and usually 1 to 15% by weight of the composition.

We prefer to use as surfactants, according to our invention non-ionic surfactants such as alcohol alkoxylates or polyalkoxylated carboxylic acids, polyalkoxylated amines, polyalkoxylated glycol or glycerol esters, polyalkoxylated sorbitan esters or alkanoamides.

In each case the alkylene oxide groups are preferably ethylene oxides, or less preferably, propylene oxide, or a mixture of ethylene oxide propylene oxide. Other surfactants that may be used include amine oxides, imidazolines, amido amines and quaternary ammonium salts or benzalkonium salts having in each case one long chain (e.g. C_{8-20}) alkyl group, any other alkyl groups being less than C_{5} , preferably methyl. Alternatively the surfactant may be a betaine or sulphobetaine.

We prefer to use a fabric conditioner quaternised imidazoline fabric conditioners having two long chain, e.g. C 15-20, alkyl and/or alkenyl groups such as ditallowyl or distearyl imidazolinium methosulphate. Unquaternised imidazolinium salts, having two C15-20 alkyl groups are also useful as are mono or di-alkylated diamidoammonium salts having two C1-4 alkyl groups and two C15-20 alkyl groups. Examples include bis (tallowamindoetyl) ammonium, or bis (stearylamidoethyl) ammonium, mono or di-methosulphates. Tetra alkyl ammonium fabric conditioners such as dimethyl ditallowyl ammonium chloride are improved by addition of surfactants according to our invention, as are ditallowyl or distearyl benzalkonium or pyridinium salts or alkoxylated (e.g. ethoxylated) amido amines or imidazolines, such as bis (tallowamidoethyl) mono (1 to 8 mole) polyoxyethylammonium salt or quaternised ammonium salts.

For all the foregoing fabric conditioners the counter ion is usually chloride, sulphate, phosphate methosulphate, ethosulphate, or an organic ion such as formate, acetate, citrate, tartrate, or lactate.

The C15-22 groups (usually predominantly C16 and/or C18 groups) are preferably straight chain or less preferably branched chain alkyl groups, which may contain a proportion, preferably minor, of alkenyl groups such as oleyl groups. For maximum softening we prefer to use hard tallow or other alkyl groups having an iodine number less than 10, preferably less than 5. However for ease of manufacture the partially unsaturated feedstocks are more usually selected.

Commercial fabric conditioning compositions require to be perfumed. However, many perfumes have a major effect on the rheological properties of fabric conditioner creams, causing very large increases in viscosity. Addition of traces of surfactant according to our invention can substantially alleviate this problem.

It is also useful to add suspended solids, such as furned silica or bentonite to fabric conditioning creams. Typically for example, bentonite may be added in concentrations of 0.01 to 3% by weight e.g. 0.05 to 2% especially 0.1 to 1%. Such additions adversely affect the rheological properties of the cream. The presence of surfactant according to our invention alleviates such adverse effects.

The invention is illustrated by the following examples:

65

60

10

15

20

25

30

35

50

55.

Example 1

5

15

20

25

30

An initial concentrate consisting of a 90% by weight solution of ditallowyl imidazolinium methosulphate in isopropanol was added to a solution of 5% by weight calcium chloride in water at 60°C and stirred for 15 minutes to give a 15% by weight active dispersion.

After the dispersion had been allowed to stand for 7 days, a mobile cream was separated from a clear aqueous phase.

The cream contained 42.3% by weight total solids (57.7% loss of weight on drying) and 0.9% by weight isopropanol. Samples of the cream were each mixed with 1% by weight various surfactants. The results were analysed using the Herschel-Bulkley model for the initial and dynamic Yield Points and the Bingham Body Model for the Plastic Yield and Plastic Viscosity, averaged over the range: 0 to 700 sec. ⁻¹ shear and are shown in the Table 1. The results were obtained at 20°C using a cone with a horizontal angle of 2° and base diameter of 4cm and a plate with a 56.6u gap.

Example 2

The method of example 1 was used to prepare creams for various fabric conditioners each of which was mixed incrementally with small concentrations of each two surfactants.

The surfactants used were both ethoxylated synthetic C₁₂₋₁₅ alcohols. The Yield points and viscosities were measured as described in example 1 and are reported in table 2.

Example 3

(A) A fabric conditioning cream comprising 30% ethoxylated bis(tallowyl) methyl metho sulphate and 7.5% CaCl₂ had a viscosity of 112 mPs measured on the "Carrimed viscometer. Addition of 1% by wt. of an coconut alkyl amido propyl dimethylamino betaine surfactant sold as its sodium salt under the Registered Trademark "EMPIGEN" BS reduced the viscosity to 85 mPs.

(B) When 1% by wt. of a commercial perfume, formulated for use in fabric conditioners was added to the cream of paragraph (A) above in the absence of the surfactant the viscosity rose to 535 mPs. The addition of 1% by weight of the surfactant reduced the viscosity to 294 mPs.

(C) When 3% by wt. of bentonite was added to the fabric conditioner composition of paragraph (A) above the viscosity rose to 769 mPs. Addition of 1% surfactant lowered the viscosity to 571 mPs.

35

40

45

50

55

60

65

TABLE 1

| IMIDAZOLINE FABRIC CONDITIONER | CARRIMED RHEOMETER 1- 20°C 2°CONE 4cm DIAMETER 56.6 MICRON GAP | | | | |
|---|--|--|------------------------------|----------------------------------|--|
| + 1% SURFACTANT | v | USED | | | |
| | HERSCHEL-B | ULKLEY | BINGHAM | | |
| SURFACTANT | INITIAL YIELD Nm-2 | DYNAMIC YIELD Nm- ₂ | PLASTIC YIELD Nm-2 | PLASTIC VISCOSITY Pa.s | |
| laurylsorbitan 20 mole ethoxylate | 0.5371 | 0.3792 | 3.142 | 0.0559 | |
| C ₁₂₋₁₄ amidopropyl - betaine (30% Active) | 10.74 | 0.8373 | 5.555 | 0.0582 | |
| oleyl sorbitan - 20 mole ethoxylate | 0.5371 | 0.3316 | 3.520 | 0.06301 | |
| C ₁₂₋₁₈ alkylethoxy- dimethyl amine oxide (25% Active) | 1.432 | 1.384 | 4.894 | 0.07099 | |
| lauryl 3 mole - ethoxylate | 1.074 | 0.8997 | 4.109 | 0.07416 | |
| Nonylphenol 9 mole - ethoxylate | 0.7162 | 0.669 | 3.405 | 0.0740 | |

TABLE 1 Contd. (2)

| IMIDAZOLINE FABRIC CONDITIONER | CARRIMED RHEOMETER 1- 20°C 2°CONE 4cm DIAMETER 56.6 MICRON GAP | | | | |
|--|--|--------------------------------|--|----------------------------------|--|
| + 1% SURFACTANT | VISCOSITY MODEL USED | | | | |
| | HERSCHEL-B | ULKLEY | BINGHAM | | |
| SURFACTANT | INITIAL YIELD Nm ⁻² | DYNAMIC YIELD Nm ⁻² | PLASTIC YIELD Nm ⁻² | PLASTIC VISCOSITY Pa.s | |
| Noylphenyl 12 mole ethoxylate | 0.7162 | 0.669 | 3.405 | 0.0740 | |
| conconutamido propyl- dimethylamine oxide (31% Active) | 2.238 | 2.253 | 11.40 | 0.0881 | |
| C ₁₆ allkyltrimethyl-\ ammonium metho- sulphate (30% active) | 2.507 | 2.253 | 7.232 | 0.1098 | |
| Cetostearyl 11 mole- ethoxyate | 1.790 | 1.464 | 6.247 . | 0.124 | |
| C ₁₂₋₁₄ alkyldimethl hydroxethyl ammonium chloride (30% Active) | 2.865 | 2.392 | 7.121 | 0.1258 | |

TABLE 1 Contd. (3)

| IMIDAZOLINE FABRIC CONDITIONER | CARRIMED RHEOMETER 1- 20°C 2°CONE 4cm DIAMETER 56.6 MICRON GAP | | | | | |
|---|--|--------------------------------|--------------------------------|------------------------|--|--|
| + 1% SURFACTANT | v | VISCOSITY MODEL USED | | | | |
| | HERSCHEL-B | HERSCHEL-BULKLEY BINGHAM | | | | |
| SURFACTANT | INITIAL YIELD Nm ⁻² | DYNAMIC YIELD Nm ⁻² | PLASTIC YIELD Nm ⁻² | PLASTIC VISCOSITY Pa.s | | |
| Cetostearyl 6 mole - ethoxylate | 2.507 | 1.945 | 7.298 | 0.1361 | | |
| C ₁₅ alkyl 3 mole - ethoxylate | 1.432 | 1.336 | 4.97 | 0.1370 | | |
| Lauric Diethanolamide | 2.865 | 2.638 | 7.853 | 0.1453 | | |
| Laurylalcohol | 8.116 | 9.846 | 18.22 | 0.1699 | | |
| Coconut Monoethano- lamide | 3.223 | 2.760 | 7.8 | | | |
| C ₁₂₋₁₄ alkyl dimethl -carboxyethyl- ammonium chloride | | | | | | |
| (30% Active) | 3.223 | 2.675 | 7.630 | 0.1828 | | |
| No surfactant | 4.774 | 4.044 | 19.66 | 0.1842 | | |

TABLE 2

| SAMPLE AND ADDITIVE | INITIAL YIELD Nm ⁻² | DYNAMIC YIELD Nm ⁻² | PLASTIC YIELD Nm ⁻² | PLASTIC VISCOSITY Pa.s |
|---|--|--|--|----------------------------------|
| 30% bis(tallowamido- ethyl) methyl ammonium methosulphate ÷ 7.5% CaCl ₂ | 19.68 | 18.88 | 25.70 | 0.6334 |
| "+ 0.55% C ₁₂₋₁₅ - alcohol 3 mole - ethoxylate | 9.599 | 9.106 | 21.10 | 0.0412 |
| " ÷ 1.0% " " " " | 7.758 | 7.059 | 18.34 | 0.0832 |
| " + 2.0% " " " " | 7.758 | 6.826 | 18.81 | 0.0497 |
| " + 0.5% C ₁₂₋₁₅ alcohol 9 mole ethoxylate | 2.148 | 1.854 | 10.05 | 0.0505 |
| " + 1.0% " " " " | 2.507 | 2.239 | 9.467 | 0.0528 |
| "÷ 2.0% " " " " | 2.865 | 2.480 [| 9.921 | 0.0505 |

TABLE 2 Contd. (2)

| SAMPLE AND ADDITIVE | INITIAL YIELD Nm ⁻² | DYNAMIC YIELD Nm ⁻² | PLASTIC YIELD Nm ⁻² | PLASTIC VISCOSITY Pa.s |
|--|--------------------------------|--------------------------------|--------------------------------------|------------------------------|
| 30% tallow amido- imidazoline acetate + 7.5% CaCl ₂ - (Iodine Value of tallow = 20) | 47.74 | 46.58 | 58.59 | 5.99 |
| ÷ 0.5% C ₁₂₋₁₅ - alcohol 3 mole ethoxylate | 41.78 | 39.38 | 72.51 | 2.432 |
| + 1.0% " " " | 55.22 | 52.93 | 79.16 | 5.012 |
| + 2.0% " " " | 62.66 | 58.74 | 89.17 | 6.531 |
| + 0.5% C ₁₂₋₁₅ alcohol 9 mole ethoxylate | 38.79 | 38.3 | 71.64 | 1.029 |
| + 1.0% " " " " . | 41.78 | 41.1 | 74.71 | 1.028 |
| ÷ 2.0% " " " " | 32.82 | 30.59 | 72.16 | 0.526 |

TABLE 2 Contd. (3)

| SAMPLE AND ADDITIVE | INITIAL YIELD Nm ⁻² | DYNAMIC YIELD Nm ⁻² | PLASTIC YIELD Nm ⁻² | PLASTIC VISCOSITY Pa.s |
|---|--|--|--|--|
| | | | | |
| Ethoxylated bis- (tallowamidoethyl)- methyl ammonium metho- sulphate + 15% CaCl ₂ | 2.387 | | 5.557 | 2.895 |
| + 0.5% C ₁₂₋₁₅ - alcohol 3 mole ethoxylate | 1.79 | 1.406 | 6.685 | 1.268 |
| + 1.0% " " " " " · | 2.089 | 1.519 | 2.948 | 2.023 |
| + 2.0% " " " " | 1.492 | 0.9346 | 1.816 | 0.6169 |
| + 0.5% C ₁₂₋₁₅ alcohol 9 mole ethoxylate | 1.194 | 1.107 | 3.134 | 0.154 |
| ÷ 1.0% " " " ; | 1.492 | 1.268 | 3.881 | 0.270 |
| ÷ 2.0% " " " " | 1.194 | 1.067 | 2.01 | 0.196 |

TABLE 2 Contd. (4)

| | | <u></u> | ······································ | |
|--|--|--|--|----------------------------------|
| SAMPLE AND ADDITIVE | INITIAL YIELD Nm ⁻² | DYNAMIC YIELD Nm ⁻² | PLASTIC YIELD Nm ⁻² | PLASTIC VISCOSITY Pa.s |
| | | | | |
| Ethoxylated bis - | | | | |
| (tallowamidoethyl)- | - | | ļ | |
| methyl ammonium metho | | | | |
| sulphate + 7.5% CaCl ₂ | 1.79 | 1.335 | 6.925 | 0.1656 |
| + 0.55 "C ₁₂₋₁₅ alcohol | | 1 |] | . |
| 3 mole - ethoxylate | 1.79 | 1.374 | 5.697 | 0.1044 |
| | 1 | | | |
| + 1.0% " " " " | 1.492 | 1.611 | 5.356 | 0.1080 |
| | ! | | | |
| + 2.0% " " " " | 1.492 | 1.34 | 4.626 | 0.1383 |
| + 0 5% (alcohol | | | | |
| + 0.5% C ₁₂₋₁₅ alcohol 9 mole ethoxylate | 1.492 | 1 1.295 | 5.2 | 0.063 |
| , more ennoymane | 1.734 | 1 1.233 | 1 3.2 | 1 0.003 |
| + 1.0% " " " " , | 1.194 | 1 1.085 | 5.095 | 0.056 |
| | j | | j | i |
| + 2.0% " " " " | 1.194 | 0.9120 | 4.286 | 0.048 |
| | | 1 | 1 | 1 |

50

45

5

Claims

55

60

65

2. A composition according to claim 1 wherein the surfactant is present in a proportion of from 0.01 to 2% based on the weight of the composition.

3. A composition according to claim 2 wherein said surfactant is present in a proportion of 0.1 to 1.5% by weight of the composition.

4. A composition according to any foregoing claim wherein the proportion of surfactant is from 1:200 to

^{1.} A fabric conditioning cream composition comprising water, a cationic fabric conditioner having two C_{15-22} alkyl and/or alkenyl groups and from 1 to 15% by weight of electrolyte characterised in that the cream contains a quantity of nonionic, amphoteric or semi polar surfactant sufficient to lower the viscosity of the composition.

1:20 based on the weight of the cationic fabric conditioner.

- **5.** A composition according to the claim 4 wherein the proportion of surfactant is from 1:80 to 1:30 based on the weight of cationic fabric conditioner.
- **6.** A composition according to any forgoing claim wherein said surfactant is a poly alkoxylated fatty alcohol, alkyl phenol, fatty acid or sorbitan ester.
 - 7. A composition according to any of claims 1 to 5 when said surfactant is a betaine or sulpho betaine.
- 8. A composition according to any foregoing claim wherein said fabric conditioner is an imidazolinium salt or quaternised in imidazolinium salt.
 - 9. A composition according to any foregoing claim containing an effective amount of perfume.
 - 10. A composition according to any foregoing claim containing from 0.01 to 3% by weight of bentonite.

EUROPEAN SEARCH REPORT

EP 89 30 7842

| | | | | | EP 89 30 /8 |
|--|---|---|---|---|---|
|] | DOCUMENTS CONS | IDERED TO BE R | ELEVANT | | |
| Category | Citation of document with of relevant p | indication, where appropriat assages | | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| Х | FR-A-2 528 864 (COMPANY) * whole document * | OLGATE-PALMOLIVE | 1- | -4,6,9 | C 11 D 1/62 C 11 D 3/00 C 11 D 1/835 |
| A | EP-A-0 013 780 (PCOMPANY) * examples; claims | | 1- | -6,8,9 | |
| | DE-A- 888 535 (LI ASSOCIES S.A.) * whole document * | ESIEUR-COTELLE & | 1- | -6,8,9 | |
| | EP-A-0 303 473 (Al LTD.) * whole document *; (Cat. D) | | | -10 | |
| A | EP-A-0 165 138 (S ⁻ * claims; examples | TEPAN EUROPE) * | 1- | 6,8,9 | |
| | EP-A-0 060 003 (PR COMPANY) * claims * | ROCTER & GAMBLE | 1- | 6,8,9 | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| P,A | EP-A-0 280 550 (UN * whole document * | NILEVER NV) | 1- | 6,8,9 | C 11 D |
| | | | | | |
| | | | | | · |
| | | | | | |
| | | | | | |
| | The present course was at be | noon duouse ver for -11 -1-1 | | | |
| | The present search report has been place of search | Date of completion of | the search | | Francisco |
| BEI | RLIN | 31-10-1989 | į. | PELL | Examiner I-WABLAT B |
| X : partic Y : partic docum A : techn O : non- | ATEGORY OF CITED DOCUME cularly relevant if taken alone cularly relevant if combined with an ment of the same category lological background written disclosure nediate document | E : ear aft D : dot L : do: | ory or principle und lier patent documen er the filing date nument cited in the ument cited for oth mber of the same p | at, but publis application er reasons | hed on, or |