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(54) Title: ALKALINE CLEANERS BASED ON ALCOHOL ETHOXY CARBOXYLATES

(57) Abstract

An alkaline cleaner composition comprising an alkyl or alkylaryl ethoxy carboxylate, a strong chelating agent and a source of alkalinity, its manufacture and use in removing greasy soil from hard surface areas is described. The compositions are especially effective in removing lime-soaps in such greasy soil especially on institutional and commercial kitchen floors.

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ALKALINE CLEANERS BASED ON ALCOHOL ETHOXY CARBOXYLATES

BACKGROUND OF THE INVENTION

The present invention is related to an alkaline cleaner for removal of greasy soil from hard surface areas. It is especially effective in removing not only the grease but also lime-soaps found in institutional, and commercial kitchens and other food preparation environments. Prior to the present invention, the combination of food greases and lime-soaps have been difficult to clean from hard surfaces such as ceramic floor tiles or countertops. This difficulty apparently is due to unsaturated portions of materials being partially cross-linked which upon aging further polymerize.

Most lime-soap dispersants previously described contain sulfated, sulfonated or phosphonated compounds. Alkyl or alkylaryl ethoxy carboxylates are known in the art as mild surfactants for use in liquid detergent compositions. They have been described as being poor in grease cutting and require the use of other surfactants to achieve the desired cleaning. For example, international patent application, publication number WO92/08777 describes a light-duty dishwashing detergent composition containing an alkyl ethoxy carboxylate surfactant and calcium or magnesium ions and a moderate complexing agent. It was therefore surprising to find that alkyl and alkylaryl ethoxy carboxylates of the present invention are effective in removing greasy soil containing lime-soaps when such active ingredients are combined with a strong chelating agent and a source of alkalinity.

SUMMARY OF THE INVENTION

Accordingly the present invention includes an alkaline cleaner for removing greasy soil containing

lime-soaps from hard surfaces such as quarry or ceramic floor tiles in commercial and institutional kitchens.

The alkaline cleaner composition comprises:

(1) an effective detersive amount of alkyl or alkylaryl ethoxy carboxylates of the formula

$$R - O - (CH_2CH_2O)_n(CH_2)_m - CO_2X$$

wherein R is a C_8 to C_{22} alkyl group or R^1 in which R^1 is a C_4-C_{16} alkyl group,
n is an integer of 1-20,
m is an integer of 1-3, and
X is hydrogen, sodium, potassium, lithium ammonium, or an amine salt selected from monoethanolamine, diethanolamine and triethanolamine;

(2) an effective amount of a strong chelating agent;

(3) an effective amount of a source of alkalinity, and

(4) a diluent.

The cleaner composition can be sold as a concentrate or in the form of a dilute aqueous solution. The concentrate is preferred when sold to restaurants and institutions. Application of the concentrate is then carried out by known dilution methods.

DETAILED DESCRIPTION

As utilized herein including the claims, the term "wt%" refers to the weight proportion based upon the total weight of the composition.

The alkaline cleaner composition may be in solid or liquid form. In liquid form, the composition is preferably sold as a concentrate and used as a dilute aqueous solution. The composition includes an effective detersive amount of an alkyl or alkylaryl ethoxy carboxylate, an effective amount of a chelating agent and an effective amount of a source of alkalinity. The

composition also contains a diluent. The diluent for a concentrate may be water, alcohol, or an aqueous alcohol mixture. In dilute form, the diluent is water. The composition may further contain a water conditioning agent and other typical detergent additives such as dyes, perfumes, grease cutting solvents, and the like.

By effective detersive amount is meant an amount of active ingredient required to remove grease and lime-soap dirt from a hard surface.

By an effective amount of a strong chelating agent is meant the amount required to remove the alkaline earth salts (Ca or Mg) from the water hardness used in ordinary cleaning of floor tiles and grouts. The use of chelating agents also help break up the lime-soaps under alkaline conditions and can release soaps that can help in the cleaning process.

By effective amount of a source of alkalinity is meant enough alkaline materials to break apart semi-polymerized soils formed from the fats and lime-soaps which are on hard surfaces, e.g. floor surfaces, through cooking processes. The unsaturated portions of some fats are partially cross-linked and upon aging the soils can be further polymerized. Thus highly alkaline materials such as caustics or strong amines are helpful in breaking these apart.

As a preferred aqueous alkaline cleaning composition, alkyl and alkylaryl ethoxy carboxylates can be present in an amount ranging from about 0.1 to 20 wt%, the strong chelating agent being in the range of about 1-20 wt% and the source of alkalinity being in the range of about 0.5-30 wt%.

More preferred aqueous compositions comprise:

(1) about 1-5 wt% of alkyl or alkylaryl ethoxy carboxylate;

(2) about 10-15 wt% of a strong chelating agent, and

(3) about 2-12 wt% of a source of alkalinity.

The source of alkalinity is normally higher in the above range when the composition is used for commercial and institutional kitchen floors. Since the composition is useful for cleaning ceramic surfaces, the composition may also be applied in diluted form in cleaning household bathroom tiles as well as bathroom tiles in commercial locations. In this aspect, the percentage of source of alkalinity would be closer to the bottom of the above range, e.g. on or about the 2% level.

Preferred alkyl or alkylaryl ethoxy carboxylates of the above formula are those where n is an integer of 4 to 10 and m is 1.

Also preferred carboxylates are those alkyl carboxylates where R is a C_8-C_{16} alkyl group. Most preferred of the alkyl ethoxy carboxylates are those where R is a C_{12}-C_{14} alkyl group, n is 4 and m is 1.

In the alkylaryl series, a preferred embodiment is where R is of the formula R^1- in which R^1 is a C_6-C_{12} alkyl group. Most preferred is a carboxylate where R^1 is a C_9 alkyl group, n is 10 and m is 1.

The alkyl and alkylaryl carboxylates may be purchased as surfactants from commercial sources. Alternatively, they can be made by known synthetic methods starting with a fatty alcohol in the alkyl ethoxy carboxylate series.
This fatty alcohol can be monitorily reacted with ethylene oxide to prepare the required number of ethoxy linkages. The resulting ethoxy alcohol is then further reacted with a halo carboxylic acid such as, for example, halo-acetic acid, halo-propionic acid or halo-butyric acid to form the desired carboxylate.

In the alkylaryl series, an alkylated phenol can be reacted in the same manner with ethylene oxide and further with the halo carboxylic acid to form the desired carboxylate.

As an example of commercially available carboxylates, Emcol CLA-40, a C_{12-14} alkyl polyethoxy (4)

carboxylic acid, and Emcol CNP-110, a C_9 alkylaryl polyethoxy (10) carboxylic acid are available from Witco Chemical. Carboxylates are also available from Sandoz, e.g. the product Sandopan® DTC, a C_{13} alkyl polyethoxy (7) carboxylic acid.

The second active component in the alkaline cleaner composition is a strong chelating agent preferably in the form of its alkaline metal salt such as potassium or preferably the sodium salt. Chelating or sequestering agents are those molecules capable of coordinating the metal ions commonly found in hard water and thereby preventing the metal ions, eg. Ca and Mg, from interfering with the functioning of the detersive component of the composition. Strong chelating agents are aminopolycarboxylic acids such as, for example, nitrilotriacetic acid (NTA), ethylenediamine tetracetic acid (EDTA), N-hydroxyethyl-ethylenediamine triacetic acid (HEDTA), and diethylene-triamine pentaacetic acid (DTPA). The preferred chelating agent is ethylenediamine tetracetic acid (EDTA) in the form of its tetrasodium salt.

The third active component of the present alkaline cleaner composition is a source of alkalinity which can be an organic source or an inorganic source. Organic sources of alkalinity are often strong nitrogen bases including, for example, ammonia (ammonium hydroxide), monoethanolamine, monopropanolamine, diethanolamine, dipropanolamine, triethanolamine, tripropanolamine, and the like.

The inorganic alkaline source contained in the alkaline cleaners of this invention is preferably derived from sodium or potassium hydroxide. The preferred form is commercially available sodium hydroxide, which can be obtained in aqueous solution of concentrations of about 50 wt%.

As preferred sources of alkalinity, ammonia or ammonium hydroxide, monoethanolamine and sodium

hydroxide in 50 wt% aqueous solution is preferred. Most preferred is a combination of the three.

The composition of the present invention is manufactured in either a concentrate formulation or dilute aqueous formulation. All formulations are prepared initially in concentrated form by combining the ingredients in a mixing vessel and mixing the components creating a homogeneous liquid composition.

The resulting concentrate may be diluted and bottled for household purposes for cleaning bathroom tiles.

Preferably, the concentrate is sold as such for institutional and commercial settings which require a significant amount of the compositions. The purchased concentrated composition is then diluted to the proper strength at the site where they will be used. Systems for diluting concentrates are well known in the art and are normally employed by a wide variety of users, e.g. hotels, hospitals, restaurants, etc. Dispensing systems may cover a wide range in terms of complexity. The method of dilution may be rather simple and manual or require operator experience. A preferred method for dispensing a concentrate is described in U.S. Patent 5,033,649 which is incorporated herein by reference. The solution storage and dispensing apparatus has a container with two inlet ports for two different types of liquid e.g. a water and the liquid cleaning concentrate. The inlet ports for the two different types of liquid accommodate two inlet lines which transport the liquid into the container. The inlet lines are each removably interconnected to their respective liquid sources and container inlet ports. The container has a suitable proportioning means, such as an aspirator, permanently mounted inside of it.

The following examples illustrate in more detail the present invention but are not limiting thereon. The alkaline cleaner compositions of the present invention

were compared with other known surfactants. The data demonstrated the superiority of the present compositions in removing soil containing grease and lime-soaps from hard surfaces such as found in commercial and institutional kitchen floors.

EXAMPLES

Typical Restaurant Floor Soil:

Samples of greasy soil from seven local restaurants were collected. These samples were scraped from the grout lines between tiles. Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analyses were made on these soil samples. The results are shown in Table 1. The soils are quite similar, and average 30-40% fats (unsaturated fatty triglycerides), 20-30% Ca or Mg fatty salts, 15-20% proteins, and the remainder being glucosides and inorganics.

The presence and levels of fats, proteins, glucosides, and inorganics were expected. What was truly surprising was the high amounts of free fatty acids, which were complexed as the alkaline earth (Ca or Mg) salts. The free fatty acids were apparently generated from high temperature cooking (deep frying, etc.) on the triglycerides. The alkaline earth ions were either from the floor tile or grout, or from the water hardness in the water used for cleaning.

These alkaline earth salts of fatty acids, commonly called lime-soaps, are not only extremely insoluble in water but also very hydrophobic and not wetted by water, making their removal difficult.

Table 1. FTIR analyses of grout samples

Glucosides & Restaurant Inorganics	Fats	Fatty Salts	Proteins
McGoverns remainder	30-40	10-20	10-20
Back Street remainder	30-40	10-20	20-30
Parker House remainder	<5	10-15	30-40
Awadas remainder	10-20	20-30	<10
St. Clair Broiler remainder	50-60	10-20	<15
Pannekoeken remainder	50-60	20-30	15-20
Razzberrys remainder	20-30	20-30	30-40
AVERAGE remainder	30-40	20-30	15-20

* Results are in percent.

The fats reported are unsaturated fatty triglycerides (NMR).

Floor Cleaner Soil Removal Lab Test:

A model floor soil was designed based on the above study of several restaurant floor soil samples. This simulated floor soil and the subsequent floor soil removal laboratory test procedure were used to test various cleaners.

PROCEDURE: Quarry tiles soiled with a special Ca soil mixture are baked at two different temperatures: 300°F for 1-1/2 hours and 200°F for 3 hours. The tiles are read on the Relative Spectral Reflectance machine before running a test. The tiles are then measured after Gardner Straight Line treatment.

The Gardner Straight Line Washability apparatus, model WG 6700 is used to clean standard soiled tiles with standard pressure and stroke of a swatch towel,

using dilution concentrations of detergents.

APPARATUS AND MATERIALS:

1. Gardner Straight Line apparatus with plastic template, 21-15/16" x 6-15/16" x 1/8". One hole 6 x 6".
2. Relative Spectral Reflectance machine.
3. Cream, solid quarry tile, 6 x 6" panels. Supplier: Color Tile, St. Paul, MN.
4. Swatch towel, 6 x 6".
5. Scour pad, 6 x 6".
6. Paint brush, 1" width, to deliver 5.0 gm of soil.
7. 6 x 6" stainless steel plate with screws.
8. Stainless steel disc. (825 gm).

CALCIUM SOIL FORMULA:

Powdered milk	16.67%
Corn oil	29.50%
Ca Linoleate	10.00%
Ca Oleate	6.67%
Ca stearate	3.33%
Red Iron Oxide	0.50%
IPA 99% (isopropyl alcohol)	33.33%

Ca SOIL MIXING PROCEDURE: Add the ingredients in order into a 800 ml plastic beaker. Blend them well with a spatula before mixing. The soil mixture will be mixed with the Tekmar mixer for 5 to 10 minutes. Mix until uniform. Cover the beaker with plastic wrap. Do not leave soil uncovered for any length of time as the IPA evaporates. the minimum batch size is about 500 gm for adequate mixing with the Tekmar.

TILE SOILING PROCEDURE:

1. Stir the soil well before applying (a small amount of IPA may be added if the soil has dried somewhat). Apply 5.0 gm of soil (a balance can be used) with a paint brush to the tile surface.
2. The tiles will be baked at two different temperatures at 300°F for 1-1/2 hours and 200°F for 3 hours.

SOIL REMOVAL TEST PROCEDURE:

1. Make up typically at 2 oz/gal (1.5 wt.%) of each product to be tested.
2. Screw the swatch and a green scouring pad together in the stainless steel plate. Put Stainless steel disc weight on top.
3. Place soiled tile into the plastic template inside the Washability apparatus.
4. Transfer 200 gm of test solution into the Washability apparatus pan.
5. Start the machine immediately, washing the tiles for 150 cycles at 300°F and 100 cycles at 200°F conditions.
6. Remove tiles and rinse with cool water.
7. Allow the tiles to air dry.
8. Have a final reading as Delta Reflectance for the tiles following the same procedure as before.

9. Also, make visual estimates for percents soil removal in this test.

CALCULATIONS:

Delta Reflectance is determined by the final reading (R2) and the initial reading (R1)

Delta Reflectance = R2 - R1

Visual soil removal estimates are used to complement the delta reflectance readings.

Visual estimates can be graded with a scale that is comfortable to the operator. For example, one can use a scale of 0 to 100 percent removal or use a scale of 1 to 4.

1 = 0 - 25%
2 = 25 - 50%
3 = 50 - 75%
4 = 75 - 100%

Floor Soil Removal Test Results and Discussion:

Table 2 show 8 formulations labeled Modified OASIS 111-1 to 8. These were designed to be compared with an Ecolab liquid alkaline floor cleaner product, OASIS 111. The formulations were also designed to have roughly matching costs. The formulations were made up by mixing the ingredients named in Table 2 for each OASIS numbered sample in distilled (D1) water. Each formulation contains the same percentages of perfume and dyes - pine perfume, 0.1 wt%; Acid Green 25, an anthraquinone dye, 0.005 wt%; Yellow 8 BR (Acid Yellow 23), 0.006 wt%. OASIS 111 and modified OASIS 111-1 contain HF-055, an alcohol ethoxylate of a C_{12} - C_{14} alcohol and 18 mole ethylene oxide adduct, Ecolab, as an active ingredient. OASIS 111-2 and 111-3 contain in varying amounts as active ingredients a combination of Rewoteric AMB - 14, cocamido propylbetaine, Rewo Chemical Group, Steol CS-460, sodium laureth sulfate, Stepan Chemical Co., and Supra 2, lauryldimethylamine oxide, Ecolab. The latter combination is known to remove loose (non-polymerized) grease. Finally, samples labelled OASIS 111-4 to 111-8

contain as an active ingredient an alcohol ethoxy carboxylate of the present invention, EMCOL CNP-110, having the formula C_9H_{19} 0 - $(CH_2CH_2O)_{10}$ CH_2COOH, available from WITCO Chemical Corp. The lab floor soil removal test results are shown at the bottom of Table 2.

The test results generally show the superiority of Emcol CNP-110, an excellent lime-soap dispersant, over HF-055, and the combination of Rewoteric AMB-14/Steol CS-460/Supra 2.

TABLE 2

		MODIFIED							
RAW MATERIAL	OASIS 111	OASIS 111-1	OASIS 111-2	OASIS 111-3	OASIS 111-4	OASIS 111-5	OASIS 111-6	OASIS 111-7	OASIS 111-8
D1 WATER (BALANCE)									
NaOH, 50%	2.0	2.0	2.0	2.0	2.0	2.0	10.0		6.0
RU SILICATE	3.0								
MEA, 99%	6.0	6.0	6.0		6.0			8.0	6.0
NH4OH, 30% NH3	2.0	2.0	2.0	2.0	2.0				
BUTYL CELLOSOLVE	4.0								
HF-055	3.0	3.0							
REWOTERIC AMB-14			2.0 (0.6)	5.5 (1.65)					
STEOL CS-460			0.5 (0.3)	1.375 (0.83)					
SUPRA 2			0.5 (0.15)	1.375 (0.41)					
EMCOL CNP-110				(1.30)	2.0 (2.60)	4.0 (2.34)	3.6 (1.30)	2.0 (1.30)	2.0
VERSENE 100	7.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0
DYE & PERFUME (q.s.)									

NOTE: NUMBERS IN PARENTHESES ARE % OF SURFACTANTS ADJUSTED TO 100% ACTIVITY.

TABLE 2 cont.

		MODIFIED							
RAW MATERIAL	OASIS 111	OASIS 111-1	OASIS 111-2	OASIS 111-3	OASIS 111-4	OASIS 111-5	OASIS 111-6	OASIS 111-7	OASIS 111-8
RELATIVE % REMOVAL OF SOIL BAKED AT 300°F FOR 1.5 HOURS; PRODUCT TESTED AT 1.5%.									
1ST SERIES	35.0	46.0	42.0	28.0					
2ND SERIES	35.0	50.0			65.0	30.0	50.0	52.0	60.0
RELATIVE % REMOVAL OF SOIL BAKED AT 200°F FOR 3.0 HOURS; PRODUCT TESTED AT 1.5%.									
1ST SERIES	12.0	19.0	17.0	9.6					
2ND SERIES	12.0	12.0			15.0	15.0	25.0	15.0	20.0

Lime Soap Dispersing Test:

In this test, the abilities of various reputedly good lime-soap dispersants were compared with the alkaline cleaner compositions of the present invention in removing pre-formed calcium stearate, calcium oleate, and calcium linoleate in aqueous solution. The concentration of the surfactants used was 2 wt% and the concentration of the lime-soap used was 0.2%. The surfactants tested were:

	Trade Name / Manufacturer
Sodium laureth sulfate	Steol CS-460 / Stepan
Cocamidopropyl hydroxy sultaine	Varion CAS-W / Sherex
Alkylated naphthalene sulfonate, sodium salt	Morwet D-425 / Witco
C_{12}-C_{14} Alkyl polyethoxy (4) carboxylic acid	Emcol CLA-40 / Witco
C_9 Alkylaryl polyethoxy (10) carboxylic acid	Emcol CNP-110 / Witco

The test results indicate that Steol CS-460, Varion CAS-W, and Morwet D-425 have very minimal lime-soap removing abilities. On the other hand, the test results show Emcol CLA-40 and Emcol CNP-110 of the present invention to be excellent lime-soap removal agents and also good solubilizing agents (fraction of the lime-soap is solubilized in solution, not just suspended from precipitating).

CLAIMS

1. An alkaline cleaner composition comprising:
(1) an effective detersive amount of alkyl or alkylaryl ethoxy carboxylates of the formula:

$$R - O - (CH_2CH_2O)_n(CH_2)_m - CO_2X$$

wherein R is a C_8 to C_{22} alkyl group or R^1 in which R^1 is a C_4-C_{16} alkyl group,
n is an integer of 1-20,
m is an integer of 1-3, and
X is hydrogen, sodium, potassium, lithium or ammonium;
(2) an effective amount of a strong chelating agent;
(3) an effective amount of a source of alkalinity, and
(4) a diluent.

2. The composition of Claim 1, wherein n is an integer of 4-10 and m is 1.

3. The composition of Claim 1, wherein an effective detersive amount of alkyl ethoxy carboxylates is used.

4. The composition of Claim 3, wherein R is a C_8-C_{16} alkyl group.

5. The composition of Claim 4, wherein R is a C_{12}-C_{14} alkyl group, n is 4 and m is 1.

6. The composition of Claim 1, wherein the chelating agent is selected from ethylenediaminetetraacetic acid and nitrilotriacetic acid and alkali metal salts thereof.

7. The composition of Claim 1, wherein the alkaline source is selected from monoethanolamine, diethanolamine, triethanolamine, potassium hydroxide, sodium hydroxide, ammonia, ammonium hydroxide and mixtures thereof.

8. The composition of Claim 5, wherein the chelating agent is the tetrasodium salt of ethylenediaminetetraacetic acid.

9. The composition of Claim 5, wherein the alkaline source is selected from monoethanolamine, sodium hydroxide, ammonium hydroxide and mixtures thereof.

10. The composition of claim 1, wherein an effective detersive amount of alkylaryl ethoxy carboxylates is used.

11. The composition of Claim 10, wherein R is R^1 in which R^1 is a C_6-C_{12} alkyl group.

12. The composition of Claim 11, wherein R^1 is a C_9 alkyl group, n is 10 and m is 1.

13. An aqueous alkaline cleaner composition comprising:
(1) about 0.1-20 wt% alkyl or alkylaryl ethoxy carboxylates of the formula;

$$R - O - (CH_2CH_2O)_n(CH_2)_m - CO_2X$$

wherein R is a C_8 to C_{22} alkyl group or R^1 in which R^1 is a C_4-C_{16} alkyl group,
n is an integer of 1-20,
m is an integer of 1-3, and
X is hydrogen, sodium, potassium, lithium or ammonium;
(2) about 1-20 wt% of a strong chelating agent, and
(3) about 0.5-30 wt% of a source of alkalinity.

14. The composition of Claim 13 comprising:
(1) about 1-5 wt% of alkyl or alkylaryl ethoxy carboxylates;
(2) about 10-15 wt% of a strong chelating agent, and
(3) about 2-12 wt% of a source of alkalinity.

15. The composition of Claim 14 comprising:
(1) alkyl ethoxycarboxylates of the formula
$R\text{-}O\text{-}(CH_2CH_2O)_4CH_2CO_2X$
wherein R is a C_{12}-C_{14} alkyl group;
(2) tetrasodium salt of ethylenediaminetetraacetic acid, and
(3) monoethanolamine, sodium hydroxide, ammonium hydroxide or a mixture thereof.

16. The composition of Claim 14 comprising:
(1) alkylaryl ethoxy carboxylates of the formula
$R^1 \quad O\text{-}(CH_2CH_2O)_{10}CH_2CO_2X$
in which R^1 is a C_9 alkyl group;
(2) tetrasodium salt of ethylenediaminetetraacetic acid, and
(3) monoethanolamine, sodium hydroxide, ammonium hydroxide or a mixture thereof.

17. A method for removing greasy soil containing lime-soaps from hard quarry or ceramic surfaces comprising applying to said surface a dilute aqueous alkaline cleaner composition which comprises in concentrate form:
(1) about 0.1-20 wt% alkyl or alkylaryl ethoxy carboxylates of the formula;
$R - O - (CH_2CH_2O)_n(CH_2)_m\text{-}CO_2X$
wherein R is a C_8 to C_{22} alkyl group or R^1 in which R^1 is a C_4-C_{16} alkyl group,
n is an integer of 1-20,
m is an integer of 1-3, and

X is hydrogen, sodium, potassium, lithium or ammonium;

(2) about 1-20 wt% of a strong chelating agent, and

(3) about 0.5-30 wt% of a source of alkalinity.

18. The method of Claim 17 wherein the aqueous alkaline cleaner composition comprises:

(1) about 1-5 wt% of alkyl or alkylaryl ethoxy carboxylates;

(2) about 10-15 wt% of a strong chelating agent, and

(3) about 2-12 wt% of a source of alkalinity.

19. The method of Claim 17 wherein the aqueous alkaline cleaner composition comprises:

(1) alkyl ethoxycarboxylates of the formula

$$R\text{-}O\text{-}(CH_2CH_2O)_4CH_2CO_2X$$

wherein R is a C_{12}-C_{14} alkyl group;

(2) tetrasodium salt of ethylenediaminetetraacetic acid, and

(3) monoethanolamine, sodium hydroxide, ammonium hydroxide or a mixture thereof.

20. The method of Claim 17 wherein the aqueous alkaline cleaner composition comprises:

(1) alkylaryl ethoxy carboxylates of the formula

$$R^1 \qquad O\text{-}(CH_2CH_2O)_{10}CH_2CO_2X$$

in which R^1 is a C_9 alkyl group;

(2) tetrasodium salt of ethylenediaminetetraacetic acid, and

(3) monoethanolamine, sodium hydroxide, ammonium hydroxide or a mixture thereof.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/06 C11D3/30 C11D3/33 C11D3/02

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)
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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 indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NL,A,7 107 579 (HUNTER DOUGLAS) 5 December 1972 see claims; example ---	1-7,13, 14
X	GB,A,2 076 010 (SANDOZ PRODUCTS LTD) 25 November 1981 see claims 1-4,27-30; example 8 ---	1-5,7, 9-11,13
A	EP,A,0 121 286 (CHEM Y) 10 October 1984 see page 2, line 24 - page 3, line 25; examples --- -/--	1-4,7,9

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
2 August 1995	7. 08. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Grittern, A

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9338 Derwent Publications Ltd., London, GB; Class A96, AN 93-299874 & JP,A,05 214 362 (LION CORP) , 24 August 1993 see abstract -----	1-5

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INTERNATIONAL SEARCH REPORT

Intern nal Application No
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
NL-A-7107579	05-12-72	NONE		
GB-A-2076010	25-11-81	BE-A-	888761	12-11-81
		CH-A-	647543	31-01-85
		DE-A-	3118527	27-05-82
		FR-A,B	2482619	20-11-81
		JP-A-	57008298	16-01-82
		NL-A-	8102259	01-12-81
		US-A-	4399050	16-08-83
EP-A-0121286	10-10-84	NL-A-	8301168	16-10-84
		CA-A-	1222427	02-06-87