Section 29 (1)
Regulation 3.1 (2)

AUSTRALIA

Patents Act 1990

673379

NOTICE OF ENTITLEMENT

We, HENKEL CORPORATION, of 140 Germantown Pike, Suite 150, Plymouth Meeting, PA 19462, UNITED STATES OF AMERICA, being the applicant in respect of Application No. 50061/93 state the following:-

The Persons nominated for the grant of the patent has entitlement from the actual inventors by assignment.

The person nominated for the grant of the patent has entitlement from the applicant of the application listed in the declaration under Article 8 of the PCT by assignment.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

8 August 1996

.....

Richard H. Baddeley
Registered Patent Attorney

AU9350061

(12) PATENT ABRIDGMENT (11) Document No. AU-B-50061/93
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 673379

(54) Title
HARD SURFACE CLEANERS BASED ON APG, DICARBOXYLIC ACID AND PINE OIL

International Patent Classification(s)
(51)[5] C11D 001/08 C11D 003/18 C11D 003/20 C11D 003/22
C11D 003/43 C11D 003/44

(21) Application No. : 50061/93 (22) Application Date : 16.08.93

(87) PCT Publication Number : WO94/05751

(30) Priority Data

(31) Number	(32) Date	(33) Country
938734	31.08.92	US UNITED STATES OF AMERICA

(43) Publication Date : 29.03.94

(44) Publication Date of Accepted Application : 07.11.96

(71) Applicant(s)
HENKEL CORPORATION

(72) Inventor(s)
ALLEN D URFER; VIRGINIA [illegible] ROWITZ

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

It has been found that hard surface cleaners which contain terpenes such as d-limonene or pine oil must incorporate such substances as isopropyl alcohol or glycol ethers. However, these types of compounds also impart high VOC

(Volatile Organic Compounds) values to the compositions. Commercial products which exhibit high VOC values are coming under increasing scrutiny and restriction by federal and state regulatory statutes.

CLAIM

1. A hard surface cleaning composition comprising: (a) an alkyl polyglycoside of the formula I

$$R_4O(R_5O)_a(Z)_b \quad I$$

wherein R_4 is a monovalent organic radical having from about 6 to about 30 carbon atoms; R_5 is divalent alkylene radical having from 2 to 4 carbon atoms; Z is saccharide residue having 5 or 6 carbon atoms; a is a number having a value from 0 to about 12; b is a number having a value greater than from 1 to about 6; (b) from 1 to 50% by weight of the composition pine oil; and (c) a dicarboxylic acid having from about 3 to about 40 carbon atoms.

.../2

6. A hard surface cleaning composition comprising: (a) an alkyl polyglycoside of the formula I

$$R_4O(R_5O)_a(Z)_b \quad I$$

wherein R_4 is a monovalent organic radical having from about 6 to about 30 carbon atoms; R_5 is divalent alkylene radical having from 2 to 4 carbon atoms; Z is saccharide residue having 5 or 6 carbon atoms; a is a number having a value from 0 to about 12; b is a number having a value from 1 to about 6; (b) from 1 to 50% by weight of the composition pine oil; (c) a dicarboxylic acid having from about 3 to about 40 carbon atoms; and, (d) a terpene other than pine oil.

673379
OPI DATE 29/03/94 APPLN. ID 50061/93
AOJP DATE 28/06/94 PCT NUMBER PCT/US93/07569
AU9350061

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C11D 1/08, 3/18, 3/20
C11D 3/22, 3/43, 3/44

A1

(11) International Publication Number: WO 94/05751

(43) International Publication Date: 17 March 1994 (17.03.94)

(21) International Application Number: PCT/US93/07569

(22) International Filing Date: 16 August 1993 (16.08.93)

(30) Priority data:
07/938,734 31 August 1992 (31.08.92) US

(71) Applicant: HENKEL CORPORATION [US/US]; 140 Germantown Pike, Suite 150, Plymouth Meeting, PA 19462 (US).

(72) Inventors: URFER, Allen, D. ; 1210 Jarvis Lane, Lansdale, PA 19446 (US). LAZAROWITZ, Virginia, L. ; 103 Kimberly Way, Hatfield, PA 19440 (US).

(74) Agent: DRACH, John, E.; Henkel Corporation, 140 Germantown Pike, Suite 150, Plymouth Meeting, PA 19462 (US).

(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: HARD SURFACE CLEANERS BASED ON APG, DICARBOXYLIC ACID AND PINE OIL

(57) Abstract

Concentrated hard surface cleaning compositions containing pine oil and/or terpenes and nonionic and/or anionic surfactants can be obtained as clear liquids which remain clear when diluted with water.

"HARD SURFACE CLEANERS BASED ON APG, DICARBOXYLIC ACID AND PINE OIL"

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to hard surface cleaning compositions which contain pine oil.

2. Description of the Related Art

Hard surface cleaning compositions are a relatively specialized category of cleaning compositions. A hard surface cleaning composition is specifically designed or formulated such that it can be applied to a soiled hard surface of interest (e.g., glass, painted walls, woodwork, etc.) and removed therefrom (for example as by wiping with a dry or damp cloth) without a subsequent rinsing operation and without leaving a significant or unsightly residual film upon the surface after cleaning. In many instances, hard surface cleaners contain substances which will aid in cutting grease such as pine oil or terpenes. One of the problems associated with formulating hard surface cleaning compositions which contain pine oils and/or terpenes is the difficulty in solubilizing the pine oils and/or terpenes. It has been found that hard surface cleaners which contain terpenes such as d-limonene or pine oil must incorporate such substances as isopropyl alcohol or glycol ethers. However, these types of compounds also impart high VOC

(Volatile Organic Compounds) values to the compositions. Commercial products which exhibit high VOC values are coming under increasing scrutiny and restriction by federal and state regulatory statutes.

U.S. 5,025,069 teaches a low irritant, mild detergent composition which comprises, as essential components: (a) an alkyl glycoside; (b) a surface active agent containing sulfate and/or sulfonate group; (c) an amine oxide; (d) an ethoxylated surface active agent at a specific ratio; (e) a terpene type hydrocarbon; and, (f) 3-isothiazolone or its derivative. A technical information bulletin published by Stepan Company, Northfield, Ill, teaches the use of d-limonene in concentrated, all purpose cleaning formulations. The formulations contain d-limonene and nonionic and/or anionic surfactants. There is no teaching of compositions containing alkyl polyglycosides as the nonionic surfactant. There is also no teaching of compositions which contain a combination of a terpene such as d-limonene and pine oil. Prior to the present invention, it had been observed that hard surface cleaners comprised only of pine oil and a nonionic and/or an anionic surfactant, without other components such as those found in the prior art, did not give clear, single phase product whether concentrated, or diluted with water. Prior to the present invention it was necessary to formulate hard surface cleaning compositions which contain pine oil and only nonionic and/or anionic surfactants by incorporating compounds which impart high VOC values to the compositions such as isopropyl alcohol and glycol ethers in order to solubilize the pine oil. Thus, a need exists for a hard surface cleaning composition containing pine oil or pine oil in combination with one or more terpenes which does not contain materials which are volatile organic compounds such as isopropyl alcohol and glycol ethers which impart high VOC values to the cleaning compositions.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided concentrated hard surface cleaning compositions containing pine oil or pine oil and terpenes and nonionic and/or anionic surfactants which are clear liquids and which remain clear when diluted with water. Such compositions contain a dicarboxylic acid, an alkyl polyglycoside, and pine oil or pine oil and a terpene such as d-limonene and avoid the use of compounds which impart high VOC values to the compositions such as isopropyl alcohol and glycol ethers.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

Any commercial pine oil, such as steam-distilled, sulfate, or synthetic pine oil can be used in the composition according to the invention without affecting the clarity of the concentrated or diluted versions of the compositions according to the invention. The amount of pine oil, terpene, or combinations of pine oil and one or more terpenes which can be used in the compositions according to the invention will vary depending upon the use of the hard surface cleaning composition and will vary from 1% to 50% by weight of the total composition weight.

The dicarboxylic acids which can be used are those which have a minimum of 3 carbon atoms such as malonic acid and a maximum of 40 carbon atoms such as dimer acids which are the reaction product of the dimerization of two unsaturated carboxylic acids. For example, a typical dimer which can be used in the practice of the instant invention acids useful in the present invention is a C-36 dicarboxylic acid such as Westvaco™ H-240 obtained by the dimerization of two moles of a C-18 unsaturated monocarboxylic acid, such as oleic acid or linoleic acid, or mixtures thereof, e.g., tall oil

AUSTRALIAN 13 PATENT OFFICE

fatty acids. Examples of dimer acids include but are not limited to Westvaco H240, Empol ® 1004, Empol ® 1007, Empol ® 1008, and Empol ® 1016. Azelaic acid, a linear dicarboxylic acid having 9 carbon atoms can also be used. The dicarboxylic acid can be used in any amount which is effective to clarify a mixture of pine oil and an alkyl polyglycoside and will typically be in the pine oil: dicarboxylic acid weight ratio range of 1:1- to 10:1.

The alkyl polyglycosides which can be used in the hard surface cleaning compositions according to the invention have the formula I

$$R_4O(R_5O)_a(Z)_b \quad I$$

wherein R_4 is a monovalent organic radical having from about 6 to about 30 carbon atoms; R_5 is divalent alkylene radical having from 2 to 4 carbon atoms; a is a number having a value from 0 to about 12; b is a number having a value from greater than 1 to about 6. APG® and/or Plantaren™ surfactants are commercially available materials and may be obtained from Henkel Corporation, Ambler, PA., 19002. Examples of APG™ and/or Plantaren™ surfactants include but are not limited to:

1. Glucopon™ 225 - an alkylpolyglycoside in which the alkyl group contains 8 to 10 carbon atoms.
2. APG™ 325 - an alkyl polyglycoside in which the alkyl group contains 9 to 11 carbon atoms.
3. Glucopon™ 625 - an alkyl polyglycoside in which the alkyl groups contains 12 to 16 carbon atoms.
4. APG™ 300 - an alkyl polyglycoside substantially the same as the 325 product above but having a different average degree of polymerization.
5. Glucopon™ 600 - an alkylpolyglycoside substantially the same as the 625 product above but having a different average degree of polymerization.
6. Plantaren™ 2000 - a C_{8-16} alkyl polyglycoside.
7. Plantaren™ 1300 - a C_{12-16} alkyl polyglycoside.

AUSTRALIAN PATENT OFFICE

8. Plantaren™ 1200 - a C_{12-16} alkyl polyglycoside.

9. APG® 225 - an alkyl polyglycoside substantially the same as Glucopon™ 225 in which the alkyl group contains 8 to 10 carbon atoms.

AUSTRALIAN PATENT OFFICE

Other examples include alkyl polyglycoside surfactant compositions which are comprised of mixtures of compounds of formula I wherein Z represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; a is zero; b is a number from 1.8 to 3; and R^4 is an alkyl radical having from 8 to 20 carbon atoms. The composition is characterized in that it has increased surfactant properties and an HLB in the range of about 10 to about 16 and a non-Flory distribution of glycosides, which is comprised of a mixture of an alkyl monoglycoside and a mixture of alkyl polyglycosides having varying degrees of polymerization of 2 and higher in progressively decreasing amounts, in which the amount by weight of polyglycoside having a degree of polymerization of 2, or mixtures thereof with the polyglycoside having a degree of polymerization of 3, predominate in relation to the amount of monoglycoside, said composition having an average degree of polymerization of about 1.8 to about 3. Such compositions can be prepared by separation of the monoglycoside from the original reaction mixture of alkyl monoglycoside and alkyl polyglycosides after removal of the alcohol. This separation may be carried out by molecular distillation and normally results in the removal of about 70-95% by weight of the alkyl monoglycosides. After removal of the alkyl monoglycosides, the relative distribution of the various components, mono- and poly-glycosides, in the resulting product changes and the concentration in the product of the polyglycosides relative to the monoglycoside increases as well as the concentration of individual polyglycosides to the total, i.e. DP2 and DP3 fractions in relation to the sum of all DP fractions. Such compositions are disclosed in copending application serial number 07/810,588, filed on 12/19/91, the entire contents of which are incorporated herein by reference. The amount of the alkyl polyglycoside which can be used will vary with the amount of pine oil and can be determined by one of ordinary skill in the art. The amount will typically be in the alkyl polyglycoside: pine

oil weight ratio range of 1:10 to 10:1.

The terpenes which can be used in the compositions according to the invention are monoterpene hydrocarbons and oxygenated mono- and bicyclic terpenes. Examples of monocyclic monoterpene hydrocarbons include but are not limited to α-pinene, α-fenchene, camphene, β-pinene, d-limonene, l-limonene, d,l-limonene, and the like. Examples of oxygenated mono- and bicyclic terpenes include but are not limited to fenchone, α-fenchol, camphor, borneol, isoborneol, citronellol, and the like. The preferred terpene is d-limonene. Pine oil may be used in combination with monoterpene hydrocarbons and/or oxygenated mono- and bicyclic terpenes in the compositions according to the invention.

One preferred embodiment of the composition according to the invention is a hard surface cleaning composition comprising: (a) from about 1% to about 40 % by weight of an alkyl polyglycoside of the formula I

$$R_4O(R_5O)_a(Z)_b \quad I$$

wherein R_4 is a monovalent organic radical having from about 6 to about 30 carbon atoms; R_5 is divalent alkylene radical having from 2 to 4 carbon atoms; Z is saccharide residue having 5 or 6 carbon atoms; a is a number having a value from 0 to about 12; b is a number having a value from 1 to about 6; (b) from about 2% to about 50% by weight of pine oil; and (c) from about 2% to about 40% by weight of a dicarboxylic acid having from about 3 to about 40 carbon atoms. Another preferred embodiment of the composition according to the invention is a hard surface cleaning composition comprising: (a) from about 1% to about 40 % by weight of APG® 225; (b) from about 2% to about 50 % by weight of pine oil; and (c) from about 2% to about 40% by weight of Westvaco™ H240.

The following examples are meant to illustrate but not to limit the invention.

EXAMPLE 1

The data listed in Table 1 illustrate the effect of

solubilizing pine oil in hard surface cleaning compositions by incorporating a dicarboxylic acid such as Westvaco™ H-240 and APG®225 and does not contain alcohols or glycol ethers. The compositions containing the dicarboxylic acid and the alkyl polyglucoside afford clear liquids in both the concentrated and dilute forms.

Table 1

	COMPOSITION[9]								App[10]	
#	PO[1]	CDEA[2]	APG®[3]	SLS[4]	SXS[5]	DCA[6]	257[7]	LR[8]	C	D
1	40	20	20	---	---	---	---	---	M	-
2	25	25	25	---	---	---	---	---	G	-
3	33	33	17	---	---	---	---	---	G	-
4	42	8	21	---	---	---	---	8	M	-
5	15	---	10	10	6	6	---	---	C	C
6	23	---	13	---	---	15	13	---	C	C

1- Pine Oil
2- Nitrene™ 11230, a Cocoyl Diethanolamide.
3- APG® 225, 50% solids.
4- Sodium Lauryl Sulfate (29% actives)
5- Sodium Xylene Sulfonate (40% actives)
6- Westvaco H-240 (40% actives)
7- N-25-27 is Neodol-25-7
8- LR is Lorol™ 1214.
9- Parts by weight
10 Appearance- C-concentrate; D-diluted with water; M-milky; G-gel; C-clear. Dilutions were made only if the concentrated form of the formulation was clear.

EXAMPLE 2

The composition of formulation 7, given in parts by weight of each component, contained both pine oil and d-limonene in hard surface cleaning formulation and illustrates the effect of incorporating a dicarboxylic acid such as Westvaco H-240 and APG®225 on the solubility and hence, the clarity of a formulation. This composition, which contained the dicarboxylic acid and the alkyl polyglucoside but no alcohols or glycol ethers, afforded a clear liquid in both the concentrated and dilute forms.

Formulation 7

28 pine oil
5.5 d-limonene
17 APG® 225
5.5 Neodol 25-7
44 Westvaco H-240

What is claimed is:

1. A hard surface cleaning composition comprising: (a) an alkyl polyglycoside of the formula I

$$R_4O(R_5O)_a(Z)_b \quad I$$

wherein R_4 is a monovalent organic radical having from about 6 to about 30 carbon atoms; R_5 is divalent alkylene radical having from 2 to 4 carbon atoms; Z is saccharide residue having 5 or 6 carbon atoms; a is a number having a value from 0 to about 12; b is a number having a value from 1 to about 6; (b) pine oil; and (c) a dicarboxylic acid having from about 3 to about 40 carbon atoms.

2. The composition of claim 1 wherein said alkyl polyglycoside is APG® 225.

3. The composition of claim 1 wherein said dicarboxylic acid is Westvaco™ H-240.

4. A hard surface cleaning composition comprising: (a) from about 1% to about 40 % by weight of an alkyl polyglycoside of the formula I

$$R_4O(R_5O)_a(Z)_b \quad I$$

wherein R_4 is a monovalent organic radical having from about 6 to about 30 carbon atoms; R_5 is divalent alkylene radical having from 2 to 4 carbon atoms; Z is saccharide residue having 5 or 6 carbon atoms; a is a number having a value from 0 to about 12; b is a number having a value from 1 to about 6; (b) from about 2% to about 50% by weight of pine oil; and (c) from about 2% to about 40% by weight of a dicarboxylic acid having from about 3 to about 40 carbon atoms.

5. A hard surface cleaning composition comprising: (a) from about 1% to about 40 % by weight of APG® 225; (b) from about 2% to about 50 % by weight of pine oil; and (c) from about 2% to about 40% by weight of Westvaco™ H240.

AUSTRALIAN 13 PATENT OFFICE

6. A hard surface cleaning composition comprising: (a) an alkyl polyglycoside of the formula I

$$R_4O(R_5O)_a(Z)_b \quad I$$

wherein R_4 is a monovalent organic radical having from about 6 to about 30 carbon atoms; R_5 is divalent alkylene radical having from 2 to 4 carbon atoms; Z is saccharide residue having 5 or 6 carbon atoms; a is a number having a value from 0 to about 12; b is a number having a value from 1 to about 6; (b) from 1 to 50% by weight of the composition pine oil; (c) a dicarboxylic acid having from about 3 to about 40 carbon atoms; and, (d) a terpene other than pine oil.

7. The composition of claim 6 wherein said alkyl polyglycoside is APG® 225.

8. The composition of claim 6 wherein said dicarboxylic acid is Westvaco™ H-240.

9. The composition of claim 6 wherein said terpene is d-limonene.

AUSTRALIAN PATENT OFFICE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07569

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C11D 1/08, 3/18, 3/20, 3/22, 3/43, 3/44

US CL :252/162, 170, 174.17, 174.19, DIG. 14

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)

U.S. : 252/162, 170 174.17, 174.19, DIG. 14

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 practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,663,071 (BUSH ET AL.) 05 MAY 1987 see col. 4, lines 47-62; col. 12, lines 32-33; col. 14, lines 23-26; Example X.	1-8
Y	US,A, 5,073,293 (DEGUCHI ET AL.) 17 DECEMBER 1991 see col. 1, lines 8-14; col. 2, lines 18-57; col. 4, lines 48-63.	1-9
Y	US,A, 5,025,069 (DEGUCHI ET AL.) 18 JUNE 1991 see col. 1, lines 8-14; col. 2, lines 19-37; col. 5, line 57- col. 6, line 14.	1-9

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
10 SEPTEMBER 1993	12 NOV 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer for PAUL LIEBERMAN Telephone No. (703) 308-2520

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07569

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP,A, 2-32197 (KAO K.K.) 01 February 1990 see page 2, claims 1 and 2; page 7, paragraph 2; page 8, paragraph 2.	1-9
Y	JP,A, 1-182400 (KAO KK) 20 July 1989 see page 2, claim 1(d) and (e); page 4, paragraph 1; page 9, paragraph 1.	1-9
Y	JP,A, 1-144495 (KAO KK) 06 June 1989 see page 2, claim 1; page 7, paragraph 1; page 8, last paragraph - page 9, first paragraph.	1-9
Y	JP,A, 3-269097 (KAO CORPORATION) 29 November 1991 see page 2, claim 1 (a) and (b); see page 8, paragraph 2.	1-9
A	US,A, 4,414,128 (GOFFINET) 08 November 1983 see entire docuement in general.	1-9
A	US,A, 4,976,885 (WISOTZESKI ET AL.) 11 December 1990 see abstract; col. 3, lines 65-68; col. 5, lines 59-64.	1-9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07569

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

Automated Patent System: PINE(W) OIL#, ?TEPINEOL?, TERPENE(W) ALCOHOL#,? GLYCOSIDE?, ?GLUCOSIDE?, DI(W)CARBOXYLIC OR DICARBOXYLIC, WEST(W)VACO? OR WESTVACO?, ?LIMONENE? DETERG?/TI OR CLEAN?/TI.