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(71) Applicant: BASF CORPORATION Mount Olive, New Jersey 07828-1234 (US) (72) Inventors:

· Kerobo, Charles O. Southfield, Michigan 48075 (US)

· Welch, Michael C. Woodhaven, Michigan 48183 (US)

· Gessner, Suzanne M. Ypsilanti, Michigan 48197 (US)

· Patterson, Sonia J. Detroit, Michigan 48207 (US)

· Roberts, Glenis Wyandotte, Michigan 48192 (US)

(74) Representative:

Abel, Manfred et al **BASF Aktiengesellschaft** Patentabteilung ZDX - C6 67056 Ludwigshafen (DE)

(54)Aqueous based solvent free cleaner compositions containing two nonionic surfactants

(57) The present invention relates to an aqueous based, solvent free cleaning or degreaser composition, comprising (a) alcohol alkoxylate with a fatty alcohol moiety, (b) polyoxyalkylene block copolymer, and (c) a fatty alcohol having an oxyethylate moiety.

Description

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[0001] The present invention relates to an aqueous based solvent free cleaning or degreaser composition comprising at least two non-ionic surfactant components which effectively clean oils and greases from a variety of surfaces.

[0002] The demand for cleaning and degreasing formulations for a myriad of cleaning applications is well known. Target applications range from the light cleaning of printed electronic circuit boards to the cleaning of used automotive parts. Many formulations for these purposes contain varied levels of volatile solvents to efficiently degrease surfaces. Many heavy duty degreasing operations use heated solvent baths.

[0003] Recent concerns for environmental and toxicological effects of solvents and solvent baths have caused a full search for aqueous degreasing systems without solvent. Few surfactant based systems have been successful without at least a minor amount of solvent, for the dual purpose of cleaning and defoaming. Hence, industrial and institutional cleaning operations that require degreasing must reconcile their desire to be socially conscious with the need to remain effective.

[0004] The use of glycol ether solvents or cycloalkanes in cleaning compositions, in combination with anionic and/or nonionic surfactants, are known in the art. Examples of such systems may be found in Wittel et al., EP 376367; Kao Corporation, JP 3062096; Lyubarskay et al., SU 1300041; Bedo et al., SU T56873; and Dudesek et al., CS 220985.

[0005] Bobsein, et al, US Pat. No. 4,663,082, teach a high pH water based industrial cleaning composition comprising a series of anionic surfactants, builders and alkalinity agents. In addition, the patentees teach the use of phosphate builders and chelating agents.

[0006] Henkel AG World Organization Patent No. 91/10718 discloses a composition requiring at least one anionic surfactant and at least one monocarboxylic acid.

[0007] European Patent No. 0392394B1 issued to the Nippon Paint Co. of Japan teaches a degreasing composition and a surfactant package comprising a nonionic surfactant of the polyoxyalkylene ether type with a phosphate polyethylene oxide adduct. This mix is combined with a necessary amount of alkali builder of varying types. However, the phosphate moiety is responsible for increasing the generation of foam. Finally, residual phosphorous is an environmental concern. The nominal amount of alkali builder also results in a caustic solution.

[0008] Further, European Patent No. 0084411A1 assigned to Albright & Wilson Limited teaches the use of a wide variety of nonionic surfactants or a phosphate ester with an alkanolamide and solvent US 5,536,438, discloses a cleaning composition containing four nonionic surfactants (fatty alcohol ethoxylates) of different HLB values; US 5,518,648 discloses a dishwashing composition comprising 2 nonionic surfactants of the alcohol alkoxylate type and a block copolymer of EO/PO; US 5,382,376, discloses a detergent composition comprising: (a) EO/PO/EO block copolymer, (b) cosurfactants such as EO/PO/EO block copolymers with a hydrophobic moiety, (c) hydrophobic solvents such as alkylbenzenes; US 5,049,376 discloses a detergent composition comprising surfactants selected from anionic, zwitterionic, cationic and nonionic; non phosphate builders, EO/PO block copolymers, and a polycarboxylate polymer.

[0009] Finally, US 5,501,816 (US '816) discloses ternary surfactant blends comprising: alcohol alkoxylate with a fatty alcohol moiety, alkyl phenol alkoxylates and alkyl oxyethylate. US '816 also discloses that the addition of polycarboxylate polymers enhances the efficacy of the degreaser compositions.

[0010] Applicants have surprisingly discovered an at least diblend cleaning and degreasing composition that provides safe and effective cleaning power. Further, the present invention does not require the use of polkycarboxylates to enhance cleaning efficacy.

[0011] An aqueous based solvent free cleaning or degreaser composition has been found comprising at least two, preferably two nonionic surfactant components, wherein said nonionic surfactant components are selected from the group consisting of:

1. 0.15% - 5% of an alcohol alkoxylate with a fatty alcohol moiety having the Formula:

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, m is within the range of about 0 to 14, n is within the range of about 0 to 14, o is within the range of about 0 to 14, p is within the range of about 0 to 14, and R' is -- CH_3 , -- CH_2 CH_3 , and mixtures thereof, R" is -- CH_3 , -- CH_2 CH_3 , and mixtures thereof, and R" is -- CH_3 , -- CH_3 hydroxyalkyl group and mixtures thereof; or

2. 0.15% - 5% of a fatty alcohol moiety having the formula:

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$$R - (CH_2CHO)_x - (CH_2CH_2O)_y - (CH_2CHO)_z - R'''$$
 R''
 R''

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, x is within the range of about 0 to 14; y is within the range of about 3 to 14; z is within the range of about 0 to 20; R' is -CH₃, -CH₂CH₃, and mixtures thereof, R" is -CH₃, -CH₂CH₃, and mixtures thereof, and R" is -OH, -CH₃, -O-C₃-C₁₈ hydroxyalkyl group and mixtures thereof; or

3. 0.15% - 5% of a fatty alcohol having oxyethylate moieties having the Formula:

R (O
$$CH_2$$
 CH_2) $_x$ OH

wherein R=C₁₀-C₁₃ branched or straight chain alkyl group and x is within the range of about 4 to 10, or

4. 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C, preferably of about 10°C to about 40°C, most preferably of about 15°C to about 25°C, having the Formula I:

$$Y[(EO/A)_{m}(A)_{n}H]_{x}$$
 (I)

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (1) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (2) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight range is from about 1,000 to 20,000, or

5. 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C, preferably of about 10°C to about 40°C, most preferably of about 15°C to about 25°C, having the Formula II:

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$
 (II)

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (1) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (2) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound alone in Formula II and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight range is from about 1,000 to 20,000, or

6. 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud

point in a 1 weight percent aqueous solution of about 10°C to about 100°C, preferably of about 10°C to about 40°C, most preferably of about 15°C to about 25°C, having the Formula III:

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x}$$
 (III)

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (1) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (2) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound alone in Formula and III and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight range is from about 1,000 to 20,000, or

7. 0.15% - 5% of an alkyl phenol alkoxylate having the Formula:

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wherein P is phenyl group, R is a C_8 or C_9 branched or straight chain alkyl group, m is within the range of about 3 to 12, and n is within the range of about 0 to 12. Preferably the oxyethylate range or value of m will range from about 3 to 12 moles, and more preferably desirably from about 8 to 12 moles. Other oxyalkylation may be incorporated as desired.

[0012] The above formulation may optionally also contain about 0.005 to 1%, preferably 0.01 to 0.5 %, of at least one polycarboxylate polymer (8) of the following Formula:

wherein X=H, Na or similar alkali or alkaline earth metal, A=H, COOH, COONa or similar alkali or alkaline earth metal salts, A' is COOH, COONa, or similar alkali or alkaline earth metal salts, or --OCH₃ or an alkyl group having a chain length of about 4 to 20 carbon atoms, A"=H or CH₃, and m and n are numbers such that the monomer ratio is within the range of about 10:1 to 1:10 and the total molecular weight of the polymer is within the range of about 1,000 to 70,000.

Preparation of the Cleaning or Degreaser Composition of the Present Invention

[0013] The cleaning or degreaser composition of the present invention is prepared by blending any two or more of components (1), (2), (3), (4), (5), (6), or (7) according to methods known to those skilled in the art. These components are also known as nonionic surfactants.

The Alcohol Alkoxylate with a Fatty Alcohol Moiety

[0014] The alcohol alkoxylate with a fatty alcohol moiety has the following Formula:

$$R[OCHCH_2)_m/(OCH_2CH_2)_n][(OCH_2CH_2)_o/(OCH_2CH_2)_p]R'''$$
 R''

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, m is within the range of about 0 to 14, n is within the range of about 0 to 14, o is within the range of about 0 to 14, p is within the range of about 0 to 14, and R' is --CH₃, --CH₂ CH₃, and mixtures thereof, and R''' is --OH, --CH₃, --O--C₃ -C₁₈ hydroxyalkyl group and mixtures thereof. R''' can be, for example, --O--C₄ H₉. In a preferred embodiment, the oxyethylate level or value of n plus o will range from about 5 to 12, and even more preferably from about 4 to 10. The oxypropylate level or value of m plus p will preferably be about 4 to 14. Those skilled in the art may find that butylene oxide may also be incorporated into the alcohol alkoxylate.

[0015] A preferred alcohol alkoxylate with a fatty alcohol moiety has a carbon chain (R) of

 C_{12-15} with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, where m=1.5, n=1, o=9, and p=3.5. Said preferred alcohol alkoxylate with a fatty alcohol moiety is known as PLURAFACTM D25, and is available from BASF Corporation, Mt. Olive, NJ. Another preferred alcohol alkoxylate with a fatty alcohol moiety is INDUSTROLTM DW 5 which has a C_{8-10} carbon chain length (R) with approximately 10 moles oxyethylate and approximately 14 moles oxypropylate, wherein n=1, o=9, m=7, and p=7.

[0016] The alcohol alkoxylate with a fatty alcohol moiety will make up about 0.15 to 5.0% by weight of the total degreaser composition. More preferably, this component will comprise about 17 to 3.3% by weight of the total composition, and even desirably will be present in an amount of about 0.5 to 2% by weight of the total formulation.

2. The Fatty Alcohol Component

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[0017] The fatty alcohol component has the following Formula:

wherein R is a C₈ to C₁₈ branched or straight chain alkyl group, x is within the range of about 0 to 14; preferably 1 to 10; most preferably 1 to 6; y is within the range of about 3 to 20, preferably 3 to 10, most preferably 3 to 6; z is within the range of about 0 to 20, preferably 3 to 10, most preferably 3 to 5; R' is -CH₃, -CH₂CH₃, and mixtures thereof, R" is -CH₃, -CH₂CH₃, and mixtures thereof, and R" is H, -OH, -CH₃, -O-C₃-C₁₈ hydroxyalkyl group and mixtures thereof. Preferably, R' = CH₃ and CH₂CH₃, R" = CH₃ and CH₂CH₃, and R" = H.

[0018] The preferred fatty alcohol moiety is: PLURAFAC® LF7000 surfactant, which has a C_{16-18} carbon chain length (R) with approximately four moles of oxyethylate and approximately nine moles of oxypropylate. The most preferred fatty alcohol moiety is PLURAFAC® LF1200 surfactant, which has a C_{9-11} carbon chain length (R) with approximately nine moles of oxyethylate and one mole of oxybutylate.

[0019] The fatty alcohol component will comprise about 0.15 to 5% by weight of the total degreaser composition. More preferably, this component will comprise about 0.17 to 3.3% by weight of the total composition, and most preferably in an amount of about 0.5 - 2% by weight of the total formulation.

3. The fatty alcohol having oxyethylate moieties component.

[0020] The fatty alcohol having oxyethylate moieties has the following Formula:

R (O
$$CH_2$$
 CH_2)_x OH

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wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and x is within the range of about 4 to 10.

[0021] Preferred fatty alcohols having oxyethylate moieties are available from BASF Corporation, Mt. Olive, NJ, under the tradename ICONOLTM TDA 10, wherein R=13 and x=10 and ICONOLTM DA 4, wherein R=10 and x=4.

[0022] The fatty alcohol having oxyethylate moieties will comprise about 0.15 to 5% by weight of the total degreaser composition. More preferably, this component will comprise about 0.17 to 3.3% by weight of the total composition, and most preferably in an amount of about 0.5 - 2% by weight of the total formulation.

4. The Polyoxyalkylene Block Copolymer of Formula I

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[0023] The polyoxyalkylene block copolymer is a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of most preferably about 15°C to about 25°C having the Formula I:

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$$Y[(EO/A)_m(A)_nH]_x$$
 I

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (1) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (2) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound either alone in formulas II and III or in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26.

[0024] In Formula I, A is preferably oxypropylene or oxybutylene, most preferably, oxypropylene. The molecular weight of Formula I is from about 1,000 to 12,000, most preferably from 1,000 to 5,000, and most preferably from about 1,000 to 2,500.

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5. The Polyoxyalkylene Block Copolymer of Formula II

$$Y[(A)_O(EO)_m(A)_nH]_x$$

ΙI

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[0025] wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (1) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (2) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound either alone in Formulas II and III or in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26.

[0026] In Formula II, A is preferably oxypropylene or oxybutylene, most preferably, oxypropylene. The molecular weight of Formula II is from about 1,000 to 12,000, most preferably from 1,000 to 5,000, and most preferably from about 1,000 to 2,500. In the most preferred embodiment of Formula II, A is oxypropylene and the molecular weight is about 2,500.

6. The Polyoxyalkylene Block Copolymer of Formula III

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x}$$
 III

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[0027] wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (1) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (2) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound either alone in Formulas II and III or in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26.

[0028] In Formula III, A is preferably oxypropylene or oxybutylene, most preferably, oxypropylene. The molecular weight of Formula III is from about 1,000 to 12,000, most preferably from 1,000 to 5,000, and most preferably from about 1,000 to 2,500.

7. The alkyl phenol alkoxylate component

[0029] The alkyl phenol alkoxylate component has the following Formula:

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P—
$$(OCH_2CH_2)_m(OCHCH_2)_nOH$$
R
 CH_3

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wherein R is a C_8 or C_9 branched or straight chain alkyl group, m is within the range of about 3 to 12, and n is within the range of about 0 to 12. Preferably the oxyethylate range or value of m will range from about 3 to 12 moles, and more preferably desirably from about 8 to 12 moles. Other oxyalkylation may be incorporated as desired. In the above Formula, P represents a phenyl group.

[0030] Preferred alkyl phenol alkoxylates are available from BASF as ICONOL[™] OP 10 and ICONOL[™] NP4. ICONOL[™] OP10 is an octyl-phenol ethoxylate having a carbon chain length of 8 and an oxyethylate value of 10 moles. The oxypropylate or n value is zero. ICONOL[™] NP4 is a nonylphenol ethoxylate with a carbon chain length of 9 and an oxyethylate value of 4.

[0031] The alkyl phenol alkoxylate component will make up about 0.15 to 5.0% by weight of the total cleaner composition. More preferably, this component will comprise about 0.17 to 3.3% of the total composition, and even desirably will be present in an amount of about 0.5 to 2% by weight of the total formulation.

[0032] The relative ratios of the 2 nonionic surfactants may range from about 1:1 to about 1:2 to about 1:2 and fractional combination thereof (e.g. 0.5:1.5). In a preferred embodiment, there will be equal weight concentrations of each nonionic surfactant component.

45 [0033] The remainder of the cleaning or degreaser composition will comprise water.

[0034] The preferred diblend compositions are:

- 1) Component 1 + Component 2
- 2) Component 1 + Component 3
- 3) Component 1 + Component 4
- 4) Component 1 + Component 5
- 5) Component 1 + Component 6
- 6) Component 1 + Component 7

55 [0035] Other useful diblend compositions include, but are not limited to:

- 1) Component 1 + Component 6
- 2) Component 1 + Component 7

- 3) Component 2 + Component 3
- 4) Component 2 + Component 4
- 5) Component 2 + Component 5
- 6) Component 2 + Component 6
- 7) Component 2 + Component 7

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- 8) Component 3 + Component 4
- 9) Component 3 + Component 5
- 10) Component 3 + Component 6
- 11) Component 3 + Component 7
- 12) Component 4 + Component 5
- 13) Component 4 + Component 6
- 14) Component 4 + Component 7
- 15) Component 5 + Component 6
- 16) Component 5 + Component 7
- 17) Component 6 + Component 7

[0036] In a preferrred embodiment, the present invention relates to an aqueous based, solvent free cleaning or degreaser composition, comprising on an weight basis:

(1) about 0.15% - 5% of at least one alcohol alkoxylate with a fatty alcohol moiety selected from the group of compounds of the formula:

$$R[OCHCH_2)_m/(OCH_2CH_2)_n][(OCH_2CH_2)_o/(OCH_2CH_2)_p]R'''$$

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, m is within the range of about 0 to 14, n is within the range of about 0 to 14, o is within the range of about 0 to 14, p is within the range of about 0 to 14, and R' is -- CH_3 , -- CH_2CH_3 , and mixtures thereof, R" is -- CH_3 , -- CH_2CH_3 , and mixtures thereof, and R" is -- CH_3 , --

(2) about 0.15 - 5.0% of one fatty alcohol moiety of the formula:

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, x is within the range of about 0 to 14; y is within the range of about 3 to 14; z is within the range of about 0 to 20; R' is $-CH_3$, $-CH_2CH_3$, and mixtures thereof, R" is $-CH_3$, $-CH_2CH_3$, and mixtures thereof, and R" is $-CH_3$, $-CH_3$, $-CH_3$, $-CH_3$, and mixtures thereof;

(3) about 0.15 - 5% of at least one fatty alcohol having oxyethylate moieties ot the formula:

R (O
$$CH_2$$
 CH_2) $_x$ OH

wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and x is within the range of about 4 to 10; and water.

In another preferred embodiment, the present invention relates to an aqueous based, solvent free cleaning or degreaser composition, comprising on a weight basis:

(1) about 0.15% - 5% of at least one alcohol alkoxylate with a fatty alcohol moiety selected from the group of com-

pounds of the formula:

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(4/5/6) about 0.15 % - % % of a nonionic sufactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 40°C selected from the group consisting of at least one of the polyoxyalkylens having the Formulas:

$$Y[(EO/A)_m(A)_nH]_x$$
 (I)

 $Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$ (II)

$$Y[(A)_o(EO/A)_m(A)_nH]_x$$
 (III)

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound either alone in Formulas II and III or in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reacted to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26. The molecular weight range of polyoxyalkylene copolymers encompassed by Formula I, II, III is about 1,000 to 20,000.

The most preferred polyoxyalkylene copolymers useful in the practice of this embodiment are represented by Formula II. Specifically, in Formula II, A is preferably oxypropylene or oxybutylene, most preferably, oxypropylene. The molecular weight of Formula II is from about 1,000 to 12,000, most preferably from 1,000 to 5,000 and most preferably from about 1,000 to 2,600.

(3) about 0.15% - 5% of at least fatty alcohol having oxyethylate moieties of the following Formula:

R (O
$$CH_2$$
 CH_2) $_{x}$ OH

wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and x is within the range of about 4 to 10; and water.

In another preferred embodiment, the present invention relates to an aqueous based, solvent free cleaning or degreaser composition, comprising on a weight basis:

(4/5/6/) about 0.15% - 5% of a nonionic surfactant characterized as block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 40°C selected from the group consisting of at least one of the polyoxyalkylenes having the formulas:

$$Y[(EO/A)_m(A)_nH]_x$$
 (I)

$$Y[(A)_o(EO)_m(A)_nH]_x$$
 (II)

$$Y[(A)_{O}(EO/A)_{m}(A)_{D}H]_{X}$$
 (III)

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound either alone in Formulas II and III or in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reacted to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26. The molecular weight range of polyoxyalkylene copolymers encompassed by Formula I, II, III is about 1,000 to 20,000.

The most preferred polyoxyalkylene copolymers useful in the practise of this embodiment are represented by Formula II. Specifically, in Formula II, A is preferably oxypropylene or oxybutylene, most preferably, oxypropylene. The molecular weight of Formula II is from about 1,000 to 12,000, most preferably form 1,000 to 5,000 and most preferably from about 1,000 to 2,600.

(7) about 0.15% - 5.0% of one alkyl phenol alkoxylates of the following Formula:

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wherein R is a C_8 or C_9 branched or straight chain alkyl group, m is within the range of about 3 to 12, and n is within the range of about 0 to 12. Preferably the oxyethylate range or value of m will range from about 3 to 12 moles, and more preferably desirably from about 8 to 12 moles. Other oxyalkylation may be incorporated as desired. In the above Formula, P represents a phenyl group.

(3) about 0.15% - 5% of at least one fatty alcohol having oxyethylate moieties of the following Formula:

R (O
$$CH_2$$
 CH_2) $_{x}$ OH

wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and x is within the range of about 4 to 10; and water.

In another preferred emodiment, the present invention relates to an aqueous based, solvent free cleaning or degreaser composition, comprising on a weight basis:

(5a) about 0.15% to 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene polymer having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging from about 1,000 to 12,000 having the Formula IIa:

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$
 (IIa)

wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms, A represents propylene oxide (i.e. oxyproylene), wherein up to 15 percent by

weight of A is reacted directly with said organic compound in Formula I and 75 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26.

(6) about 0.15% to 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging form about 1,500 to 15,000 having the Formula III:

$$Y[(A)_{O}(EO/A)_{m}(A)_{n}H]_{x}$$
 (III)

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wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms, A represents propylene oxide selected from the group consisting of propylene oxide (oxypropylene) butylene oxide (oxybutylene) or tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in admixture wieth ethylene oxide in Formula II and 75 percent by weight or more of A is subsequently to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26.

(5b) about 0.15% to 5% of a nonionic sufactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging form about 1,000 to 10,000 having the Formula IIb:

$$Y[(A)_o(EO)_m(A)_nH]_x$$
 (IIb)

wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms, A represents butylene oxide (i.e. oxybutylene) wherein up to 25 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26. water.

In another preferred embodiment, the present invention relates to an aqueous based, solvent free cleaning or degreaser composition, comprising on a weight basis:

(5) about 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging from about 1,000 to 12,000 having the Formula II:

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$
 (II)

wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms, A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide or tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in Formula I and 75 percent by weight or more of A is subsequently reacted to produce the said polymer; within the range of about 0 to 26.

(6) about 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging from about 1,500 to 15,000 having the Formula III:

$$Y[(A)_o(EO/A)_m(A)_nH]_x$$
 (III)

wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms, A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide or tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in admixture with ethylene oxide in Formula Ii and 75 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26.

(3) about 0.15% - 5% of at least one fatty alcohol having oxyethylate moieties of the following formula:

R (O
$$CH_2$$
 CH_2) $_{x}$ OH

wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and x is within the range of about 4 to 10; and water.

[0037] It has also been found that the binary combination of the above combination of nonionic surfactants or any combination of the nonionic sufactants (1) to (7) may optionally contain at least one polycarboxylate based polymer or copolymer further enhances the efficacy of the degreaser composition.

[0038] Preferably, the polycarboxylate polymer or copolymer has the following Formula:

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wherein X=H, Na or similar alkali or alkaline earth metal, A=H, COOH, COONa or similar alkali or alkaline earth metal salts, A' is COOH, COONa, or similar alkali or alkaline earth metal salts, or --OCH₃ or an alkyl group having a chain length of about 4 to 20 carbon atoms, A"=H or CH₃, and m and n are numbers such that the monomer ratio is within the range of about 10:1 to 1:10 and the total molecular weight of the polymer or copolymer is within the range of about 1,000 to 70,000. (Unless otherwise specified, all molecular weights herein are expressed in terms of weight average molecular weight, or M(w)).

[0039] Polyacrylic acid having the above Formula is useful as the polycarboxylate additive. An excellent copolymer having the above Formula is acrylic acid/maleic acid copolymer. Those skilled in the art may also find that certain mixtures of polymers and copolymers according to the Formula heretofore set forth may also may utility as part of the cleaning or degreaser composition, and therefore these are also within the scope of the invention.

[0040] Illustrative methods for preparing the various useful polycarboxylate polymers and copolymers of the invention may be found in Burke et al., US Pat. No. 5,126,068, incorporated herein by reference.

[0041] An especially preferred monomer ratio for the polycarboxylate copolymer is about 1:1. A monomeric ratio within the range of about 3:1 to 1:3 is also preferred. A preferred molecular weight range is about 1,000 to 25,000, and even more preferably from about 8,000 to 12,000.

[0042] Especially useful copolymers as part of the cleaning or degreaser composition include the following structures. A polycarboxylate copolymer with a molecular weight of about 12,000, and X=Na, A=COONa, A'=C₅ H₁₁, A"=CH₃ and the monomeric ratio is about 1:1 (Polycarboxylate A in the examples). A polycarboxylate copolymer with a molecular weight of about 70,000, X=Na, A=COONa, A'=OCH₃, A"=H and the monomeric ratio is about 1:1. In addition, polyacrylic acid with a molecular weight of about 8,000, where X=Na is also effective as part of the invention. This polyacrylic acid may be obtained from BASF Corp. under the tradename of SOKALAN™ PA 30 CL.

[0043] The polycarboxylate polymer or copolymer as part of the invention is added to the cleaning or degreaser composition in amounts of about 0.005 to 1% by weight based upon the total weight of the composition. Preferably, the polymer or copolymer will comprise from about 0.01 to 0.5% of the total formulation.

The Utility of the Present Invention

[0044] The cleaning or degreaser composition according to the various embodiments of the invention is extremely useful in industrial, institutional, and household cleaning and degreasing of hard surfaces, including but not limited to, glass, ceramic, rigid and flexible hard surfaces and metal, especially automotive parts. The cleaning or degreaser composition may be applied by methods including but not limited to dipping, soaking, wiping, sonicating, spraying, and especially pressure spray washing. Further, the cleaning or degreaser composition may be applied at a wide range of temperatures from about 40 to 200°F.

[0045] While the invention has been described in each of its various embodiments, it is to be expected that certain modifications thereto may be made by those skilled in the art without departing from the true spirit and scope of the invention as set forth in the specification and the accompanying claims.

[0046] All percentages are weight percent unless otherwise indicated.

[0047] The following non limiting examples illustrate the utility of the present invention:

15 Example 1

Meat Packing Equipment Cleaning Composition

[0048]

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1. 0.17 to 3.3% of Component 1 - an alcohol alkoxylate with a fatty alcohol moiety having the Formula:

wherein $R=C_{12-15}$ with approximately 10 moles of oxyethylate and approximately 5 moles total of oxypropylate, where m=15, n=1, o=9, and p=3.5.

2. 0.17 to 3.3% of Component 2 - a fatty alcohol having the Formula:

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$$R-(CH_2CHO)_x-(CH_2CH_2O)_y-(CH_2CHO)_z-R'''$$
 R'

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wherein R is C₉₋₁₁ with approximately 9 moles of oxyethylate and one mole of oxybutylate.

45 Example 2

Household Hard Surface Cleaner

[0049]

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1. 0.5 to 2% of Component 1 - an alcohol alkoxylate with a fatty alcohol having the Formula:

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$$\begin{array}{c} \text{R}\left[\text{OCHCH}_2\right)_{\mathfrak{m}}/\left(\text{OCH}_2\text{CH}_2\right)_{\mathfrak{n}}\right]\left[\left(\text{OCH}_2\text{CH}_2\right)_{\mathfrak{o}}/\left(\text{OCH}_2\text{CH}_2\right)_{\mathfrak{p}}\right]\text{R'''} \\ \\ \\ \text{R'} \end{array}$$

wherein R=C₁₂₋₁₅ with approximately 10 moles of oxyethylate and approximately 5 moles total of oxypropylate, where m=15, n=1, o=9, and p-3.5.

2. 0.5% to 2.0% of Component 3 - a fatty alcohol having oxyethylate moieties having the Formula:

R (O CH_2 CH_2)_X OH

wherein R=13 and x=10.

Example 3

Carpet Cleaning Composition

25 [0050]

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1. 0.5 to 2.0% of Component 1 - an alcohol alkoxylate with a fatty alcohol having the Formula:

$$\begin{array}{c} \text{R}\left[\text{OCHCH}_2\right)_{\text{m}}/\left(\text{OCH}_2\text{CH}_2\right)_{\text{n}}\right]\left[\left(\text{OCH}_2\text{CH}_2\right)_{\text{o}}/\left(\text{OCH}_2\text{CH}_2\right)_{\text{p}}\right]\text{R'''} \\ \\ \\ \text{R'} \end{array}$$

wherein $R=C_{12-15}$, with approximately 10 moles of oxyethylate and approximately 5 moles total of oxypropylate, where m=1.5, n-1, o=9, and p=3.5.

2. 0.5 to 2.0% of Component 4 - a polyoxylakylene block copolymer of Formula I.

$$Y[(EO/A)_m(A)_nH]_X$$

wherein A=oxypropylene, and the molecular weight is 1,900.

Example 4

Industrial Degreasing Composition

[0051]

1. 0.17 to 3.3% of Component 1 - an alcohol alkoxylate with a fatty alcohol moiety:

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wherein R- C_{12-15} , with approximately 10 moles of oxyethylate and approximately 5 moles total of oxypropylate, where m=1.5, n=1, o=9, and p=3.5.

2. 0.17 to 3.3% of Component 5 - a polyoxyalkylene block copolymer of Formula II:

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$
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wherein A=oxypropylene and the molecular weight is 2,500.

Example 5

Meat Packing Equipment Cleaning Composition

[0052]

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1. 0.17 - 3.3% alcohol alkoxylate with a fatty alcohol moiety (a) has the follwing formula:

wherein the carbon chain length (R) is C_{12-15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, wherein further, m=1.5, n=1, o=9 and p=3.5.

2. 0.17 - 3.3% fatty alcohol of the formula:

wherein the carbon chain lenght (R) is C_{16-18} with approximately four moles of oxyethylate and approximately nine moles of oxypropylate.

3. 0.17 - 3.3% fatty alcohol having oxyethylate moieties having the following formula:

wherein R=13 and x=10.

Example 6

Household Hard Surface Cleaner

5 **[0053]**

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1. 0.5 - 2.0% alcohol alkoxylate with a fatty alcohol moiety having the formula

wherein the carbon chain length (R) is C_{12-15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, where further, m=1.5, n=1, o=9, and p=3.5.

2. 0.5 - 2.0% fatty alcohol moiety of the formula:

$$R-(CH_2CHO)_x-(CH_2CH_2O)_y-(CH_2CHO)_z-R'''$$
 R'
 R'

wherein the carbon chain length (R) is C_{9-11} with approximately nine moles of oxyethylate and one mole of oxybutylate;

3. 0.5 - 2.0% fatty alcohol having oxyethylate moieties having the following formula:

R (OCH
$$_2$$
CH $_2$) $_x$ OH

wherein R=13 and x=10.

Example 7

40 Carpet Cleaning Composition

[0054]

1. 0.5 - 2.0% alcohol alkoxylate with a fatty alcohol moiety having the formula

wherein the carbon chain length (R) is C_{12-15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, where further, m=1.5, n=1, o=9, and p=3.5.

2. 0.5 - 2.0% fatty alcohol moiety of the formula:

wherein the carbon chain length (R) is C_{16-18} with approximately four moles of oxyethylate and approximately nine moles of oxypropylate.

3. 0.5 - 2.0% fatty alcohol having oxyethylate moieties having the following formula:

$$R(OCH_2CH_2)_{x}OH$$

wherein R=10 and x=4.

8. 0.01 - 0.5% polycarboxylate polymer of the formula:

x=H, A=H, A' is COOH, A"=H and m and n are numbers such that the monomer ratio is within the range of about 10:1 to 1:10 and the total molecular weight of the polymer or copolymer is within the range of about 1,000.

Example 8

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Industrial Degreasing Composition

[0055]

1. 0.17 - 3.3% alcohol alkoxylate with a fatty alcohol moiety (a) has the following formula:

wherein the carbon chain length is C_{12-15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, where further, m=1.5, n=1, o=9, and p=3.5.

2. 0.17 - 3.3% fatty alcohol moiety of the formula:

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wherein the carbon chain length (R) is C_{16-18} (R) with approximately four moles of oxyethylate and approximately nine moles of oxypropylate.

3. 0.17 - 3.3% fatty alcohol having oxyethylate moieties having the following formula:

wherein R=10 and x=4.

20 Example 9

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Meat Packing Equipment Cleaning Composition

[0056]

1. 0.17 - 3.3% alcohol alkoxylate with a fatty alcohol moiety selected from the group of compounds of the Formula:

wherein R is a C_{12} to C_{15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, wherein further, m is 1.5, n is 1, o is 9, p is 3.5.

5. 0.17 - 3.3% polyoxyalkylene block copolymer of Formula II:

$$Y[(A)_o(EO)_m(A)_nH]_x$$

wherein A = oxypropylene and the molecular weight is about 2,500.

3. 0.17 - 3.3% fatty alcohol having oxyethylate moieties of the Formula:

wherein R = 10 and x = 4.

Example 10

Household Hard Surface Cleaning Composition

[0057]

1. 0.5 - 2% alcohol alkoxylate with a fatty alcohol moiety selected from the group of compounds of the Formula:

R[OCHCH₂)_m/(OCH₂CH₂)_n][(OCH₂CH₂)_o/(OCH₂CH₂)_p]R'''
| R''

wherein R is a C_{12} to C_{15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, wherein further, m is 1.5, n is 1, o is 9, p is 3.5.

5. 0.5 - 2% of a polyoxyalkylene block copolymer of the Formula II:

 $Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$

wherein A = oxypropylene and the molecular weight is about 2,600.

3. 0.5 - 2.0% of a fatty alcohol having an oxyethylate moiety of the Formula:

 $R(OCH_2CH_2)_{x}OH$

wherein R = 13 and x = 10.

Example 11

Household Carpet Cleaning Composition Comprising:

35 **[0058]**

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1. 0.5 - 2% alcohol alkoxylate with a fatty alcohol moiety selected from the group of compounds of the Formula:

 $R[OCHCH_2)_m/(OCH_2CH_2)_n][(OCH_2CH_2)_o/(OCH_2CH_2)_p]R'''$

wherein R is a C_{12} to C_{15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, wherein further, m is 1.5, n is 1, o is 9, p is 3.5.

5. 0.5 - 2% of a polyoxyalkylene block copolymer of the Formula II:

$$Y[(A)_{O}(EO)_{m}(A)_{n}H]_{X}$$

wherein A = oxypropylene and the molecular weight is about 1,900.

3. 0.5 - 2.0% of a fatty alcohol having an oxyethylate moiety of the Formula:

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wherein R = 10 and x = 4.

8. 0.01 - 0.5% polycarboxylate polymers having the Formula:

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COOX A H A''

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wherein x=H, A=H, A' is COOH, A"=H and m and n are numbers such that the monomer ratio is within the range of about 10:1 and the total molecular weight of the polymer or copolymer is about 1,000.

Example 12

25 Industrial Degreasing Composition

[0059]

1. 0.17 - 3.3% alcohol alkoxylate with a fatty alcohol moiety selected from the group of compounds of the Formula:

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wherein R is a C_{12} to C_{15} branched or straight chain alkyl group with approximately 10 moles total of oxyethylate and approximately 5 moles total of oxypropylate, wherein further, m is 1.5, n is 1, o is 9, p is 3.5.

4. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula II:

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$$Y[(A)_o(EO)_m(A)_nH]_x$$

wherein A = oxypropylene and the molecular weight is about 2,200.

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3. 0.17 - 3.3% of a fatty alcohol having an oxyethylate moiety of the Formula:

R (OCH
$$_2$$
CH $_2$) $_x$ OH

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wherein R = 13 and x = 10.

Example 13

Meat Packing Equipment Cleaning Equipment

5 [0060]

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5. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula II:

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$

wherein A = oxypropylene and the molecular weight is about 2,500.

7. 0.17 - 3.3% of an alkyl phenol alkoxylate has the following Formula:

P—
$$(OCH_2CH_2)_m (OCHCH_2)_nOH$$

|

R

 CH_3

wherein R = 8, and the oxyethylate value (m) is 10 moles and the oxypropylate (n) value is zero.

3. 0.17 - 3.3% of a fatty alcohol having oxyethylate moieties of the Formula:

wherein R is a 13 and x is 10.

35 Example 14

Household Hard Surface Cleaning Composition

[0061]

5. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula II:

$$Y[(A)_o(EO)_m(A)_nH]_x$$

wherein A = oxypropylene and the molecular weight is about 2,600.

7. 0.5 - 2.0% of an alkyl phenol alkoxylate has the following Formula:

P—
$$(OCH_2CH_2)_m (OCHCH_2)_nOH$$

R

 CH_3

wherein R = 9 and the oxyethylate (m) is 4 and the oxypropylate (n) value is 0.

3. 0.5 - 2.0% of a fatty alcohol having oxethylate moieties of the Formula:

$$R(OCH_2CH_2)_{x}OH$$

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10

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wherein R is 10 and x is 4.

Example 15

Carpet Cleaning Composition

[0062]

5. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula II:

$$Y[(A)_o(EO)_m(A)_nH]_x$$

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wherein A is oxypropylene and the molecular weight is 1,900.

7. 0.5 - 2.0% of an alkyl phenol alkoxylate has the following Formula:

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P— (OCH₂CH₂)
$$_{\rm m}$$
 (OCHCH₂) $_{\rm n}$ OH $_{\rm R}$

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wherein R = 9 and the oxyethylate (m) value is 4 and the oxypropylate (n) value is 0.

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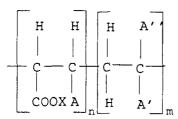
3. 0.5 - 2.0 % of a fatty alcohol having oxyethylate moieties of the Formula:

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wherein R is 10 and x is 4.

8. 0.01 to 0.5 % polycarboxylate polymer of the Formula:

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wherein the molecular weight is about 12,000, and X=Na, A=COONa, A'=C₅H₁₁, A"=CH₃ and the monomeric ratio is about 1:1.

Example 16

Industrial Cleaning Composition

5 [0063]

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5. 0.17 - 3.3 % of a polyoxyalkylene block copolymer of the Formula II:

wherein A=oxypropylene and the molecular weight is 2,200.

7. 0.17 - 3.3% of an alkyl phenol alkoxylate has the following Formula:

P— (OCH₂CH₂)
$$_{\rm m}$$
 (OCHCH₂) $_{\rm n}$ OH $_{\rm R}$ CH₃

wherein R=9 and the oxyethylate (m) value is 4 and the oxypropylate (n) value is 0.

3. 0.17 to 3.3% of a fatty alcohol having oxyethylate moieties of the Formula:

$$R(OCH_2CH_2)_{x}OH$$

wherein R is 10 and x is 4.

Example 17

Meat Packing Equipment Cleaning Equipment

40 [0064]

5a. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula IIa,

wherein A=oxypropylene and Formula IIa has a molecular weight of 1,900.

6. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula III,

$$Y[(A)_o(EO/A)_m(A)_nH]_x$$

wherein A=oxypropylene and Formula III has a molecular weight is 2,000.

5b. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula Ilb,

 $Y[(A)_{O}(EO)_{m}(A)_{n}H]_{x}$

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wherein A=oxybutylene and Formula IIb has a molecular weight is 2,500.

Example 18

Household Hard Surface Cleaning Composition

[0065]

5a. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula IIa,

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$

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wherein A=oxypropylene and Formula IIa has a molecular weight is 2,600.

6. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula III,

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$$Y[(A)_{O}(EO/A)_{m}(A)_{n}H]_{x}$$

wherein A=oxypropylene and the molecular weight of Formula III is 3,100.

5b. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula Ilb,

$$Y[(A)_{\circ}(EO/A)_{m}(A)_{n}H]_{x}$$

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wherein A=oxybutylene and Formula IIb has a molecular weight of 1,900.

Example 19

Carpet Cleaning Composition

[0066]

5a. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula IIa,

$$Y[(A)_o(EO)_m(A)_nH]_x$$

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wherein A=oxypropylene and Formula IIa has a molecular weight of 2,100.

6. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula III,

$$Y[(A)_{O}(EO/A)_{m}(A)_{n}H]_{x}$$

wherein A=oxypropylene and the molecular weight of Formula III is 4,500.

5b. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula Ilb,

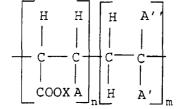
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$$Y[(A)_o(EO)_m(A)_nH]_x$$

wherein A=oxybutylene and Formula IIb has a molecular weight of 2,500.

8. 0.01 to 0.5 % polycarboxylate polymer of the Formula:

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wherein the molecular weight is about 12,000, and X=Na, A=COONa, A'=C₅H₁₁, A"=CH₃ and the monomeric ratio is about 1:1.

Example 20

Industrial Cleaning Composition

[0067]

5a. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula IIa,

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$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$

wherein A=oxypropylene and Formula IIa has a molecular weight of 2,600.

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6. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula III,

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x}$$

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wherein A=oxypropylene and the molecular weight of Formula III is 3,600.

5b. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula Ilb,

 $Y[(A)_o(EO)_m(A)_nH]_x$

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wherein A=oxybutylene and Formula IIb has a molecular weight of 5,500.

Example 21

Meat Packing Equipment Cleaning Equipment

5 [0068]

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5. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula II,

$$Y[(A)_{O}(EO)_{m}(A)_{n}H]_{x}$$

wherein A=oxypropylene and the molecular weight of Formula II is 1,900.

6. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula III,

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x}$$

wherein A=oxypropylene and the molecular weight of Formula III is 4,090.

3. 0.17 - 3.3% of a fatty alcohol having oxyethylate moieties of the Formula:

$$R(OCH_2CH_2)_{x}OH$$

wherein R is 13 and x is 10.

Example 22

Household Hardsurface Cleaning Composition

35 **[0069]**

5. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula II,

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$$Y[(A)_{O}(EO)_{m}(A)_{n}H]_{x}$$

wherein A=oxypropylene and the molecular weight of Formula II is 2,600.

6. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula III,

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x}$$

wherein A=oxybutylene and the molecular weight of Formula III is 3,500.

3. 0.5 - 2.0% of a fatty alcohol having oxyethylate moieties of the Formula:

$$R(OCH_2CH_2)_{x}OH$$

wherein R is 10 and x is 4.

Example 23

5 Carpet Cleaning Composition

[0070]

5. 0.5 - 2.0% of a polyoxyalkylene block copolymer of the Formula II,

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$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$

- wherein A=oxypropylene and the molecular weight of Formula II is 2,200.
 - 6. 0.5 2.0% of a polyoxyalkylene block copolymer of the Formula III,

20 $Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{X}$

wherein A=oxypropylene and the molecular weight of Formula III is 4,500.

3. 0.5 - 2.0% of a fatty alcohol having oxyethylate moieties of the Formula:

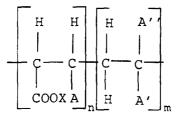
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wherein R=10 and x is 4.

8. 0.01 to 0.5 % polycarboxylate polymer of the Formula:

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wherein the molecular weight is about 12,000, and X=Na, A=COONa, A'=C₅H₁₁, A"=CH₃ and the monomeric ratio is about 1:1.

Example 24

50 Industrial Cleaning Composition

[0071]

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5. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula II,

 $Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$

wherein A=oxypropylene and the molecular weight of Formula II is 1,900.

6. 0.17 - 3.3% of a polyoxyalkylene block copolymer of the Formula III,

 $Y[(A)_{O}(EO/A)_{m}(A)_{n}H]_{x}$

wherein A=oxypropylene and the molecular weight of Formula III is 2,600.

3. 0.17 - 3.3% of a fatty alcohol having oxyethylate moieties of the Formula:

wherein R is 10 and x is 4.

Claims

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- 1. An aqueous based solvent free cleaning or degreaser composition comprising at least two nonionic surfactant components, wherein said two nonionic surfactants are selected from the group consisting of:
 - (1) 0.15% 5% of an alcohol alkoxylate with a fatty alcohol moiety having the Formula:

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, m is within the range of about 0 to 14, n is within the range of about 0 to 14, o is within the range of about 0 to 14, p is within the range of about 0 to 14, and R' is --CH₃, --CH₂ CH₃, and mixtures thereof, R" is --CH₃, --CH₂ CH₃, and mixtures thereof, and R" is --OH, --CH₃, --O--C₃ -C₁₈ hydroxyalkyl group and mixtures thereof; or

(2) 0.15% - 5% of a fatty alcohol moiety having the Formula:

R-
$$(CH_2CHO)_x$$
- $(CH_2CH_2O)_y$ - $(CH_2CHO)_z$ -R'''
R'

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, x is within the range of about 0 to 14; y is within the range of about 0 to 20; R' is -CH₃, -CH₂CH₃, and mixtures thereof, R" is -CH₃, -CH₂CH₃, and mixtures thereof, and R" is -OH, -CH₃, -O-C₃-C₁₈ hydroxyalkyl group and mixtures thereof; or

(3) 0.15% - 5% of a fatty alcohol having oxyethylate moieties having the Formula:

R (O
$$CH_2$$
 CH_2) $_X$ OH

wherein $R=C_{10}-C_{13}$ branched or straight chain alkyl group and x is within the range of about 4 to 10; or

(4) 0. 15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of 10°C to 100°C having the Formula I:

5 $Y[(EO/A)_m(A)_nH]_x$ (I)

> wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight range is from about 1,000 to 20,000, or

> (5) 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of 10°C to 100°C having the Formula II:

$$Y[(A)_{O}(EO)_{m}(A)_{M}H]_{X}$$
 (II)

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wherein. Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound alone in Formula II and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight range is from about 1,000 to 20,000, or

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(6) 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of 10°C to 100°C having the Formula III:

40 $Y[(A)_o(EO/A)_m(A)_nH]_x$ (III)

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wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound alone in Formula and III and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight range is from about 1,000 to 20,000, or

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(7) 0.15% - 5% of an alkyl phenol alkoxylate having the Formula:

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wherein P is phenyl group, R is a C_8 or C_9 branched or straight chain alkyl group, m is within the range of about 3 to 12, and n is within the range of about 0 to 12.

- 2. An aqueous based, solvent free cleaning or degreaser composition according to Claim 1, comprising on a weight basis:
 - (1) about 0.15% 5% of at least one alcohol alkoxylate with a fatty alcohol moiety selected from the group of compounds having the formula:

$$R[OCHCH_2)_m/(OCH_2CH_2)_n][(OCH_2CH_2)_o/(OCH_2CH_2)_p]R'''$$

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, m is within the range of about 0 to 14, n is within the range of about 0 to 14, o is within the range of about 0 to 14, p is within the range of about 0 to 14, and R' is $-CH_3$, $-CH_2CH_3$, and mixtures thereof, R" is $-CH_3$, $-CH_2CH_3$, and mixtures thereof, and R" is $-CH_3$, $-CH_3$, and mixtures thereof, and R" is $-CH_3$, $-CH_3$, and mixtures thereof, and R" is $-CH_3$, $-CH_3$, and mixtures thereof, and R" is $-CH_3$, $-CH_3$, and mixtures thereof.

(2) about 0.15 - 5.0% of one fatty alcohol moiety having the formula:

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$$R - (CH_2CHO)_x - (CH_2CH_2O)_y (CH_2CHO)_z - R'''$$

$$R''$$

wherein R is a C_8 to C_{18} branched or straight chain alkyl group, x is within the range of about 0 to 14; y is within the range of about 3 to 14; z is within the range of about 0 to 20; R' is -CH₃, -CH₂CH₃, and mixtures thereof, R" is -CH₃, -CH₂CH₃, and mixtures thereof, and R" is -OH, -CH₃, -O-C₃-C₁₈ hydroxyalkyl group and mixtures thereof;

(3) about 0.15 - 5% of at least one fatty alcohol having oxyethylate moieties of the following formula:

$$R(OCH_2CH_2)_xOH$$

wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and x is within the range of about 4 to 10; and water.

- 3. An aqueous based, solvent free cleaning or degreaser composition according to Claim 1, comprising on a weight basis:
- (1) about 0.15 5.0% of one alcohol alkoxylate with a fatty alcohol moiety selected from the group of compounds of the Formula:

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wherein R is a C_8 to C_{18} branched or straight chain alkyl group, m is within the range of about 0 to 14, n is within the range of about 0 to 14, o is within the range of about 0 to 14, p is within the range of about 0 to 14, and R' is $-CH_2$ CH₃, and mixtures thereof, R" is $-CH_3$, $-CH_2$ CH₃, and mixtures thereof, and R" is $-CH_3$, $-CH_3$, and mixtures thereof, and R" is $-CH_3$, $-CH_3$, and mixtures thereof;

(4/5/6) 0.15 - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 40°C selected from the group consisting of at least one of the polyoxyalkylenes having the Formulas:

$$Y[(EO/A)_{m}(A)_{n}H]_{x}$$
(I)

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$
(II)

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x}$$
(III)

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (ii) about 6 to about 18 atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound either alone in Formulas II and III or in admixture with ethylene oxide in Formula I and 75 percent by weight or more of A is subsequently reached to produce said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight is from about 1,000 to 20,000;

(3) 0.15 - 5% of one fatty alcohol containing oxyethylate moieties of the following Formula:

wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and y is within the range of about 4 to 10; and water.

4. An aqueous based, solvent free cleaning or degreaser composition according to Claim 1, comprising on a weight basis:

(4/5/6/) about 0. 15% - 5% of a polyoxyalkylene block copolymer selected from one of the following formulas:

$$Y[(EO/A)_{m}(A)_{n}H]_{x} \qquad (I)$$

$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x} \qquad (II)$$

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x} \qquad (III)$$

wherein, Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 3 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 1 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide, tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound either alone in Formulas II and III or in admixture with ethylene oxide in Formulas I and 75 percent by weight or more of A is subsequently reached to produce

said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26, wherein further, the molecular weight is from about 1000 to 20,000;

(7) about 0.15 - 5.0% of one alkyl phenol alkoxylates of the following formula:

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wherein R is a C_8 or C_9 branched or straight chain alkyl group, m is within the range of about 3 to 12, and n is within the range of about 0 to 12;

(3) about 0.15 - 5% of at least one fatty alcohol having oxyethylate moieties of the following formula:

wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and y is within the range of about 4 to 10; and water.

- 5. An aqueous based, solvent free cleaning or degreaser composition according to Claim 1, comprising on a weight basis:
 - (5a) about 0.15% to 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene polymer having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 10°C and a molecular weight ranging from about 1,000 to 12,000 having the Formula IIa

$$Y[A)_{o}(EO)_{m}(A)_{n}H]_{x}$$
 IIa

wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms; A represents propylene oxide (i.e. oxypropylene), wherein up to 25 percent by weight of A is reacted directly with said organic compound in Formula I and 75 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26;

(6) about 0.15% to 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging from about 1,500 to 15,000 having the Formula III:

$$Y[(A)_{o}(EO/A)_{m}(A)_{n}H]_{x}$$
 III

wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide (oxypropylene), butylene oxide (oxybutylene) or tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in admixture with ethylene oxide in Formula II and 75 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26;

(5b) about 0,15% to 5% of a surfactant charakterized as a block or heteric/block polyoxyakylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging from about 1,000 to 10,000 having the Formula IIb

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$$Y[(A)_{o}(EO)_{m}(A)_{n}H]_{x}$$
 IIb

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wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms; A represents butylene oxide (i.e. oxybutylene) wherein up to 25 percent by weight of A is reacted directly with said organic compound in Formula I and 75 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26; and water.

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6. An aqueous based, solvent free cleaning or degreaser composition, according to Claim 1, comprising on a weight

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(5) about 0.15% - 5% of a nonionic surfactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molcular weight ranging from about 1,000 to 12,000 having the Formula II:

 $Y[(A)_o(EO)_m(A)_nH]_x$

ΙI

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wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionality of x and (i) about 2 about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hydrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide or tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in Formula I 75 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26, m is within the range of about 0 to 110, and n is within the range of about 0 to 26;

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(6) about 0.15% - 5% of a nonionic sufactant characterized as a block or heteric/block polyoxyalkylene having a cloud point in a 1 weight percent aqueous solution of about 10°C to about 100°C and a molecular weight ranging from about 1,500 to 15,000 having the Formula III:

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$$Y[(A)_{O}(EO/A)_{m}(A)_{D}H]_{X}$$
 III

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wherein Y represents the nucleus of an active hydrogen-containing organic compound having a functionsality of x and (i) about 2 to about 6 carbon atoms and 2 to 4 reactive hydrogen atoms or (ii) about 6 to about 18 carbon atoms and 2 to 3 reactive hadrogen atoms; A represents a lower alkylene oxide selected from the group consisting of propylene oxide, butylene oxide or tetrahydrofuran or mixtures thereof wherein up to 25 percent by weight of A is reacted directly with said organic compound in admixture with ethylene oxide in Formula II and 75 percent by weight or more of A is subsequently reacted to produce the said polymer; o is within the range of about 0 to 26;

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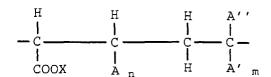
(3) about 0.15% - 5% at a least on fatty alcohol having oxyethylate moieties of the following formula:

$$R(O CH_2 CH_2)_x OH$$

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wherein R is a C_{10} to C_{13} branched or straight chain alkyl group and x is within the range of about 4 to 10, and; water.

- 7. An aqueous based solvent-free cleaning or degreaser composition according to Claims 1 to 6, additionally comprising
 - (8) 0.005 1% of a polycarboxylate polymer of the formula:



wherein X=H or alkali or alkaline earth metal, A=H, COOH or its alkali or alkaline earth metal salts, A' is COOH or its alkali or alkaline earth metal salts, or --OCH₃ or an alkyl group having a chain length of about 4 to 20 carbon atoms, A"=H or CH₃, and m and n are numbers such that the monomer ratio is within the range of about 10:1 to 1:10 and the total molcular weight of the polymer is within the range of about 1,000 to 70,000.



EUROPEAN SEARCH REPORT

Application Number

C-4		IDERED TO BE RELEVA indication, where appropriate,	Relevant	EP 98113620 CLASSIFICATION OF THI	
Category	of relevant pa		to claim	APPLICATION (Int. Cl. 6)	
A	WO 95/02668 A1 (HENKEL KGAA) 26 January 1995 (26.01.95), page 7, claims.		1-7	C 11 D 1/82 C 11 D 1/72	
A	EP 0161537 A2 (BASF AG) 21 November 1985 (21.11.85), claims 1-3.		1	`	
A	(08.11.89),	November 1989	1-7		
A	(02.04.92),	02 April 1992 ., claims.	1-7		
A	EP 0634476 A1 (THE PROCTER COMPANY) 18 J (18.01.95), examples	& GAMBLE	1	TECHNICAL FIELDS SEARCHED (Int. Ct.6) C 11 D	
٦	The present search report has t	peen drawn up for all claims			
Place of search		Date of completion of the search		Examiner	
VIENNA 22-10 CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		22-10-1998	T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons		
		E : earlier paten after the fili other D : document ci L : document ci			
		& : member of t	&: member of the same patent family, corresponding document		

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