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(54) **Stable aqueous emulsions of nonionic surfactants.**

(57) Stable aqueous emulsions are disclosed which comprise hydrophobic and hydrophilic nonionic surfactants and silicones to reduce viscosity and eliminate air bubbles.

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Technical field

The present invention relates to cleaning compositions. More particularly, the cleaning compositions according to the present invention are stable aqueous emulsions of nonionic surfactants particularly suitable for the pretreatment of laundry or the cleaning of hard surfaces.

Background

A great variety of cleaning compositions have been described in the art. For instance, in co-pending European Patent Application EP 92870188.7, a particular type of cleaning compositions is described which are aqueous emulsions of a nonionic surfactant system. Such emulsions find a preferred application in the formulation of bleaching compositions comprising hydrogen peroxide or water soluble source thereof and a liquid hydrophobic bleach activator, or any other hydrophobic ingredient which needs to be separated from hydrogen peroxide. Alternatively, such emulsions can be used to formulate products which do not contain hydrogen peroxide. In the latter case, such emulsions can be useful because they allow to keep a given hydrophobic ingredient separate from the aqueous phase, with which said hydrophobic ingredient could react, e.g., by hydrolysis. Another advantage of such emulsions is that they provide a means to formulate ingredients with very low water solubility, without the need for using alcoholic or solvent mixtures, which are usually undesirable for aesthetic (odour) and toxicity reasons.

A problem with such emulsions, especially with emulsions containing relatively high concentrations of surfactants, e.g, about 8 %, is that important viscosity tends to build up, which makes said emulsions difficult to dispense, and thus unacceptable from a consumer viewpoint.

It is thus an object of the present invention to formulate aqueous emulsions of nonionic surfactants wherein the viscosity can be conveniently controlled.

Various viscosity agents such as sodium cumene sulphonate and polyacrylates have been tried in this context, which resulted in a decreased viscosity but also reduced phase stability.

It is thus another object of the present invention to provide aqueous emulsions of nonionic surfactants wherein the viscosity can be conveniently controlled while maintaining adequate physical stability.

In order to manufacture such aqueous emulsions of nonionic surfactants, it is necessary to vigorously mix the ingredients together. During this vigorous mixing, lots of air bubbles are generated which are detrimental both to the composition's aesthetics and stability. Indeed, surfactants tend to concentrate at the air/liquid interfaces generated by said air bubbles. Thus the more air bubbles a composition contains, the less surfactants will be available for the stabilisation of the droplets of the dispersed phase. This problem of air bubbles is aggravated in that aqueous emulsions of nonionic surfactants are pseudoplastic fluids, i.e. they have a higher viscosity at low shear rates. Consequently, the air bubbles generated upon mixing, i.e. at low viscosity become entrapped in the compositions when mixing stops and viscosity consequently raises. For the same reasons, air bubbles tend to become entrapped in the compositions also when the product is pulled from the bottle into another container, i.e. a dosing device, or when the bottle is shaken.

It is thus another object of the present invention to provide aqueous emulsions of nonionic surfactants which are substantially free of air bubbles and thus acceptable for aesthetics and stability.

It has now been found that these objects can be efficiently met by formulating aqueous emulsions of nonionic surfactants which comprise silicone compounds. In other words, it has now been found that silicone compounds reduce the viscosity of aqueous emulsions comprising a nonionic surfactant system whatever the viscosity was before their addition and allow to substantially eliminate the air bubbles. Additionally, it has unexpectedly been found that emulsions comprising silicone compounds are physically more stable than emulsions without said silicone compounds.

The present invention allows for greater flexibility in formulating and provides stable aqueous emulsions suitable to be used in the most efficient manner by the consumer.

The viscosity-reducing effect and the air bubbles removal properties of the silicone compounds are unexpected and beneficial as said silicone compounds are only known in the context of laundry compositions as sud-suppressing agents, see for instance US 4 076 648, US 4 021 365, US 4 749 740, US 4 983 316, EP 150 872, EP 217 501 and EP 499 364.

As an additional advantage it has been found that the present invention finds a preferred application in formulating aqueous activated bleaching emulsions and bleaching emulsions which comprise any hydrophobic liquid ingredient which needs to be kept separate from the hydrogen peroxide. Indeed, the addition of silicone compounds according to the present invention to the nonionic surfactant system used to emulsify hydrophobic liquid ingredients as for instance bleach activators improves the storage stability of hydrogen peroxide.

Summary of the invention

The present invention is a stable aqueous emulsion having a pH of from 0.5 to 6, comprising a hydrophilic nonionic surfactant and a hydrophobic nonionic surfactant, said stable aqueous emulsion further comprises an effective amount of silicone compounds.

Detailed description of the invention

The compositions according to the present invention are stable aqueous emulsions of nonionic surfactants. By stable emulsion it is meant an emulsion which does not substantially separate into distinct layers, upon standing for at least 2 weeks at 50 °C.

The compositions according to the present invention are aqueous. Accordingly, the compositions according to the present invention comprise from 10% to 95% by weight of the total composition of water, preferably from 30% to 90%, most preferably from 60% to 80%. Deionized water is preferably used.

The compositions according to the present invention are emulsions of nonionic surfactants. Said emulsions of nonionic surfactants comprise at least two nonionic surfactants. Said two nonionic surfactants in order to form emulsions which are stable must have different HLB values (hydrophilic lipophilic balance), and preferably the difference in value of the HLBs of said two surfactants is at least 1, preferably at least 3. By appropriately combining at least two of said nonionic surfactants with different HLBs in water, emulsions according to the present invention will be formed.

One of said nonionic surfactants used herein is a nonionic surfactant with an HLB above 11 (herein referred to as hydrophilic nonionic surfactant), whereas the other one is a nonionic surfactant with an HLB below 10 (herein referred to as hydrophobic nonionic surfactant).

Suitable nonionic surfactants for use herein include alkoxylated fatty alcohols. Indeed, a great variety of such alkoxylated fatty alcohols are commercially available which have very different HLB values. The HLB values of such alkoxylated nonionic surfactants depend essentially on the chain length of the fatty alcohol, the nature of the alkoxylation and the degree of alkoxylation. Hydrophilic nonionic surfactants tend to have a high degree of alkoxylation and a short chain fatty alcohol, while hydrophobic surfactants tend to have a low degree of alkoxylation and a long chain fatty alcohol. Surfactants catalogues are available which list a number of surfactants including nonionics, together with their respective HLB values.

The compositions according to the present invention comprise from 2 % to 50 % by weight of the total composition of said hydrophilic and hydrophobic nonionic surfactants, preferably from 5 % to 40 %, most preferably from 8 % to 30%.

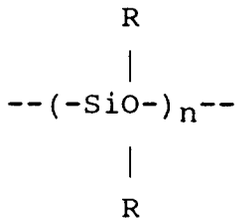
The compositions according to the present invention may further comprise other nonionic surfactants which should however not significantly alter the weighted average HLB value of the overall composition.

The compositions according to the present invention further comprise as an essential element an effective amount of silicone compounds. By "effective amount" it is meant an amount of silicone compounds which is sufficient to reduce and substantially eliminate the air bubbles generated in the aqueous emulsions according to the present invention. By "effective amount" it is also meant an amount of silicone compounds which is sufficient to provide physically stable aqueous emulsions wherein the viscosity can be conveniently controlled. Preferably the compositions according to the present invention comprise from 0.01 % to 5 % by weight of the total composition of said silicone compounds, more preferably from 0.1 % to 2 %.

Said silicone compounds reduce the viscosity of the aqueous emulsions herein whatever the viscosity was before the addition of said silicone compounds while increasing also physical stability. Preferred compositions obtained according to the present invention have a viscosity of from 100 cps to 3000 cps at 50 rpm shear rate at 25 °C, more preferably from 300 cps to 1500 cps, measured by a Brookfield DV II rotational viscosimeter.

Additionally, said silicone compounds substantially reduce and preferably substantially eliminate the air bubbles generated either during the manufacture of said emulsions or when pouring or shaking said emulsions, thereby providing aqueous emulsions which are acceptable for aesthetics and stability.

In industrial practice, the term "silicone" has become a generic term which encompasses a variety of relatively high-molecular-weight polymers containing siloxane units and hydrocarbyl groups of various types. Indeed, silicone compounds have been extensively described in the art, see for instance US 4 076 648, US 4 021 365, US 4 749 740, US 4 983 316, EP 150 872, EP 217 501 and EP 499 364. The silicone compounds disclosed therein are suitable in the context of the present invention. Generally, the silicone compounds can be described as siloxanes having the general structure :



wherein n is from 20 to 2.000, and where each R independently can be an alkyl or an aryl radical. Examples of such substituents are methyl, ethyl, propyl, isobutyl, and phenyl. Preferred polydiorganosiloxanes are polydimethylsiloxanes having trimethylsilyl endblocking units and having a viscosity at 25 °C of from 5 x 10^{-5} m^2/s to 0.1 m^2/s i.e. a value of n in the range 40 to 1500. These are preferred because of their ready availability and their relatively low cost.

A preferred type of silicone compounds useful in the compositions herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica.

The solid silica can be a fumed silica, a precipitated silica or a silica made by the gelformation technique. The silica particles can be rendered hydrophobic by treating them with diaklylsilyl groups and/or trialkylsilane groups either bonded directly onto the silica or by means of silicone resin. A preferred silicone compound comprises a hydrophobic silanated, most preferably trimethylsilanated silica having a particle size in the range from 10 mm to 20 mm and a specific surface area above 50 m^2/g. Silicone compounds employed in the compositions according to the present invention suitably have an amount of silica in the range of 1 to 30% (more preferably 2.0 to 15%) by weight of the total weight of the silicone compounds resulting in silicone compounds having an average viscosity in the range of from 2 x 10^{-4} m^2/s to 1m^2/s. Preferred silicone compounds may have a viscosity in the range of from 5 x $10^{-3}$$m^2/s$ to 0.1m^2/s. Particularly suitable are silicone compounds with a viscosity of 2 x $10^{-2}$$m^2/s$ or 4.5 x $10^{-2}$$m^2/s$.

Suitable silicone compounds for use herein are commercially available from various companies including Rhone Poulenc, Fueller and Dow Corning. An example of silicone compounds for use herein is Silicone DB ^{R} 100 commercially available from Dow Corning.

Formulating the compositions according to the present invention in an acidic pH range contributes to the stability of the composition. The compositions of the present invention have a pH as is of from 0.5 to 6, preferably of from 1 to 5. The pH of the composition can be trimmed by all means available to the man skilled in the art.

Preferred compositions according to the present invention comprise hydrogen peroxide or a water-soluble source thereof. Suitable water-soluble sources of hydrogen peroxide include perborate, percarbonate, persilicate and persulphate salts. Hydrogen peroxide is most preferred to be used in the compositions according to the present invention. Typically, the compositions according to the present invention comprise from 0.5% to 20% by weight of the total composition of hydrogen peroxide, preferably from 2% to 15%, most preferably from 3% to 10%.

Preferred compositions according to the present invention further comprise a bleach activator. By bleach activator, it is meant herein any compound which reacts with hydrogen peroxide to form a peracid. In the case of bleach activators, such hydrophobic bleach activators typically belong to the class of esters, amides, imides, or anhydrides. A particular family of bleach activators of interest in the present invention were disclosed in applicant's co-pending European patent application No 91870207.7. Particularly preferred in that family is acetyl triethyl citrate which was also disclosed in the context of bar soaps in FR 2 362 210. Acetyl triethyl citrate has the advantages that it is environmentally friendly as it eventually degrades into citric acid and alcohol. Furthermore, acetyl triethyl citrate has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator. As used herein and unless otherwise specified, the term bleach activator includes mixtures of bleach activators.

In a preferred embodiment of the present invention, wherein the compositions comprise a bleach activator which is a hydrophobic liquid ingredient, the nonionic surfactant system to be chosen to emulsify said bleach activator depends on the HLB value of said bleach activator. Accordingly, a suitable way to proceed is to determine the HLB value of the hydrophobic liquid ingredient (bleach activator), then select both the hydrophobic nonionic surfactants which have HLB values below said HLB value of said hydrophobic liquid ingredient and the hydrophilic nonionic surfactants which have HLB values above said HLB value of said hydrophobic liquid ingredient, wherein the difference in the HLB values of said hydrophobic and hydrophilic nonionic surfactants is preferably at least 3.

In a preferred embodiment comprising said bleach activator which is a hydrophobic ingredient, the emulsifying system meets the equation:

$$HLB(X) = \frac{\%A}{100} \times HLB(A) + \frac{\%B}{100} \times HLB(B) \text{ and } \%A+\%B = 100\%;$$

where X refers to the hydrophobic liquid ingredient to emulsify, A refers to one of said nonionic surfactants (hydrophilic or hydrophobic), and B refers to the other said nonionic surfactant (hydrophilic or hydrophobic).

In a particularly preferred embodiment of the present invention, wherein the compositions comprise Acetyl triethyl citrate with an HLB of about 10 as the bleach activator, an adequate nonionic surfactant system would comprise a hydrophobic nonionic surfactant with an HLB from 1 to 10, and a hydrophilic nonionic surfactant with an HLB of above 11. A particularly suitable system comprises a hydrophobic nonionic surfactant with an HLB of 6, for instance a Dobanol ^{R} 23-2 and a hydrophilic nonionic surfactant with an HLB of 15, for instance a Dobanol ^{R} 91-10. Another suitable nonionic surfactant system comprises a Dobanol ^{R} 23-6.5 (HLB about 12) and a Dobanol ^{R} 23 (HLB below 6). All these Dobanol ^{R} surfactants are commercially available from Shell.

Preferably, the compositions according to the present invention are free of other surfactant types, especially anionic surfactants.

Depending on the end use envisioned, the compositions according to the present invention may further comprise a variety of other ingredients such as perfumes, dyes, optical brighteners, builders and chelants, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents and the like.

The compositions according to the present invention are particularly useful as laundry pretreaters, i.e compositions which are dispensed and left to act onto fabrics before they are washed, or as laundry additives to be used together with detergents to boost their performance, or as dishwashing compositions to be used either in the dishwashing machines or by hand, or as hard surface cleaners, or as carpet cleaners to be used either by direct application onto the carpets or as detergent for carpet cleaning machines or also alone without detergents. The compositions according to the present invention are also particularly adapted to be used for delicate items.

The present invention further encompasses a process for the manufacture of the composition described herein. The process according to the present invention comprises at least three steps:

In the first step, a hydrophobic mixture is prepared which comprises said hydrophobic nonionic surfactant and silicone compounds together with other hydrophobic ingredients which are to be formulated in the composition, such as perfumes, solvents, enzymes, bleach activators and polymers.

In the second step, a hydrophilic mixture is prepared which comprises at least said water, and said hydrophilic nonionic surfactant. Said hydrophilic mixture preferably further comprises other hydrophilic ingredients which are to be formulated in the composition such as dyes, optical brighteners, builders, chelants, hydrogen peroxide and buffering agents. In this second step hydrogen peroxide is preferably added last, after said buffering agent has been added.

Naturally, said first and said second steps can be performed in any order, i.e second step first is also suitable.

In the third step of the process according to the present invention, said hydrophobic mixture and said hydrophilic mixture are mixed together.

The present invention is further illustrated by the following examples.

Examples

Compositions are made which comprise the listed ingredients in the listed proportions (weight %).

	I	II	III
Dobanol ^{R} 45-7	6	6	6
Dobanol ^{R} 91-10	3	3	3
Dobanol ^{R} 23-2	6	6	6
Hydrogen peroxide	7.5	7.5	7.5
Acetyl triethyl citrate	7.0	7.0	7.0
Brightener 49^{R}	0.20	0.20	0.20
S,S-ethylene diamino disuccinic acid	0.10	0.10	0.10
Poly(4-vinylpyridine -N-oxide)	0.10	0.10	0.10
Silicone DB ^{R} 100	-	0.10	0.50
Deionized water	---------balance-------		

Density at 30 °C measured with a floating viscosimeter:

Composition I	ρ = 0.97
Composition II	ρ = 1.00
Composition III	ρ = 1.01

Viscosity measured with a Brookfield DV II viscosimeter with spindle RV/6.4 at 30 °C:

Composition I	600 cps at 50 rpm
Composition II	580 cps at 50 rpm
Composition III	530 cps at 50 rpm

Compositions I to III are each made by preparing two mixtures. A hydrophilic mixture is prepared which comprises the water, the brightener, S,S-EDDS, poly(4-vinylpyridine-N-oxide), the Dobanol ^{R} 91-10 and the Dobanol ^{R} 45-7. Hydrogen peroxide is added in said hydrophilic mixture as last step. A hydrophobic mixture is prepared which comprises the acetyl triethyl citrate, Silicone DB ^{R} 100 and the Dobanol ^{R} 23-2.

Then said hydrophobic mixture is poured into said hydrophilic mixture, while mixing.

According to the present invention, the compositions II and III which comprise Silicone DB ^{R} 100 have a density which is higher than the density of the composition I which is free of any silicone compounds. In other words, the compositions II and III contain less air bubbles than the composition I. Furthermore, by visual inspection it is also established that the compositions II and III contain less air bubbles than the composition I and are therefore more acceptable from a consumer viewpoint for aesthetic reasons.

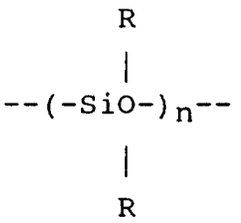
Additionally, the compositions II and III (with silicone compounds) have a lower viscosity than the composition I which is free of any silicone compounds.

The above results surprisingly show that the use of silicone compounds in compositions according to the present invention reduces and substantially eliminates the air bubbles and also reduces the viscosity of said compositions. Additionally, the compositions according to the present invention which comprise silicone compounds are physical stable emulsions, even more stable than analogous compositions without silicone compounds.

Claims

1. A stable aqueous emulsion having a pH of from 0.5 to 6, comprising at least a hydrophilic nonionic surfactant and at least a hydrophobic nonionic surfactant, **characterized in** that said aqueous emulsion further comprises an effective amount of silicone compounds.

2. An emulsion according to claim 1 wherein said silicone compounds are selected from siloxanes having the general structure:



wherein n is from 20 to 2.000, and where each R independently can be an alkyl or an aryl radical.

3. An emulsion according to claim 2 wherein said silicone compounds are a mixture of said siloxanes and solid silica.

4. An emulsion according to any of the preceding claims wherein the level of the silicone compounds is from 0.01 % to 5 % by total weight of the emulsion, preferably from 0.1 % to 2 %.

5. An emulsion according to any of the preceding claims wherein the nonionic surfactant amount is from 2 % to 50 % by weight of the total emulsion, preferably from 5 % to 40 %, most preferably from 8 % to 30 %.

6. An emulsion according to any of the preceding claims wherein the hydrophilic nonionic surfactant has an HLB above 11 and wherein the hydrophobic nonionic surfactant has an HLB below 10.

7. An emulsion according to claim 6 wherein the difference between the HLB values of the hydrophilic nonionic compounds and the hydrophobic compounds is of at least 1, preferably of at least 3.

8. An emulsion according to any of the preceding claims which further comprises hydrogen peroxide or a source thereof and a bleach activator wherein said bleach activator is emulsified by the nonionic surfactants.

9. An emulsion according to claim 8 which comprises from 0.5% to 20% by weight of the total emulsion of said hydrogen peroxide.

10. An emulsion according to claims 8 and 9 wherein said bleach activator is acetyl triethyl citrate.

11. An emulsion according to any of the preceding claims which has a viscosity in the range of from 100 cps to 3000 cps at 50 rpm shear rate at 25 °C, preferably from 300 cps to 1500 cps.

12. A detergent composition comprising an emulsion according to any of the preceding claims.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 87 0103

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	DATABASE WPI Section Ch, Week 9216, Derwent Publications Ltd., London, GB; Class A26, AN 88-252628 & JP-A-63 182 008 (SHINETSU CHEM. IND.) 27 July 1988 * abstract *	1-7	C11D3/37 C11D1/825 C11D3/39
A	EP-A-0 091 802 (THE PROCTER & GAMBLE COMPANY) * claim 1 *	1-3,12	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 November 1993	VAN BELLINGEN, I

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

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

& : member of the same patent family, corresponding document

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