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(54) **Stable aqueous emulsions of nonionic surfactants with a viscosity controlling agent.**

(57) Stable aqueous emulsions are disclosed which comprise hydrophobic and hydrophilic nonionic surfactants and a ethylenediamine-N,N'-disuccinic acid. Ethylenediamine-N,N'-disuccinic acid builds viscosity in said emulsions.

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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 which comprise a viscosity control system.

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.

It is also generally desirable that cleaning compositions be more or less viscous. Indeed, viscous compositions do not run like thin liquids, and their pouring, dispensing, i.e. their overall handling is therefore easier to control. This aspect is particularly important when cleaning compositions are used to clean hard surfaces, especially on inclined or vertical surfaces such as toilet bowls, or in the context of laundry. In those instances, the cleaning compositions must be thick enough for a controlled application onto fabrics, and for a good cling onto surfaces.

It is thus an object of the present invention to formulate thickened aqueous emulsions of nonionic surfactants.

A variety of thickening compounds are available for this purpose. By thickening compounds, it is meant herein compounds whose sole function is to thicken the compositions. Such compounds, typically polymers, are however rather undesirable for a variety of reasons. Indeed, they can significantly increase formula cost without participating to the overall cleaning performance, they may involve processing issues, they may affect product stability, particularly in extreme acidic conditions, and they may affect the cleaning performance of the compositions.

It is thus an object of the present invention to formulate such a thickened composition without having to use a thickening compound.

It has now been found that this object could be met by formulating ethylenediamine-N,N'-disuccinic acid in an aqueous emulsion of nonionic surfactant will significantly increase the formulation's viscosity.

Another advantage of the present invention is that it is only required to use a very small amount of ethylenediamine-N,N'-disuccinic acid in order to obtain the desired effect, which makes the present invention particularly cost-efficient.

Another advantage of the present invention is that ethylenediamine-N,N'-disuccinic acid also acts as a builder in the compositions of the present invention. Thus ethylenediamine-N,N'-disuccinic plays has a dual function in the compositions of the present invention.

Another advantage of the present invention is that it allows for the formulation of compositions which are thick and pseudoplastic, i.e. which are less viscous at higher shear stresses. Pseudoplasticity compositions achieve the multiple and somewhat contradictory objects of being easy to dispense, i.e. rather less viscous, and providing good cling onto surfaces, i.e. rather more viscous.

Yet another advantage of the present invention is that ethylenediamine-N,N'-disuccinic acid has been found to provide additional stability to the preferred compositions herein which may comprise hydrogen peroxide as an optional but preferred compound.

Yet another advantage of the present invention is that it allows to achieve a given viscosity target with a lower surfactant level, compared to a composition without ethylenediamine-N,N'-disuccinic acid.

Summary of the invention

The present invention is a stable aqueous emulsion comprising a hydrophilic nonionic surfactant and a hydrophobic nonionic surfactant, said stable aqueous emulsion further comprising a viscosity-building amount of ethylenediamine-N,N'-disuccinic acid.

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 two weeks at 20 °C, preferably at least six months.

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 85%. 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. In order to form emulsions which are stable, said two nonionic surfactants 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 (hydrophilic lipophilic balance). The HLB values of such alkoxylated nonionic surfactants depend essentially on the alkoxylation and the degree of alkoxylation. Hydrophilic nonionic surfactants tend to have a higher degree of alkoxylation, while hydrophobic surfactants tend to have a lower degree of alkoxylation. Surfactants catalogs 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 70 % by weight of the total composition of said hydrophilic and hydrophobic nonionic surfactants, preferably from 3 % to 40 %, most preferably from 4 % to 30 %.

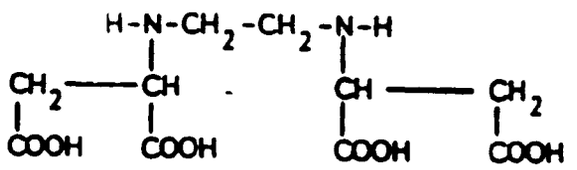
The compositions according to the present invention may further comprise other nonionic surfactants which should however not significantly alter the weighted average HLB value of the overall composition.

The compositions according to the present invention further comprise as an essential element a viscosity-building amount of ethylenediamine-N,N'-disuccinic acid. By viscosity-building, it is meant herein any amount of ethylenediamine-N,N'-disuccinic acid in a given composition which will provide an increase in viscosity compared to the same composition without ethylenediamine-N,N'-disuccinic acid, while maintaining acceptable stability.

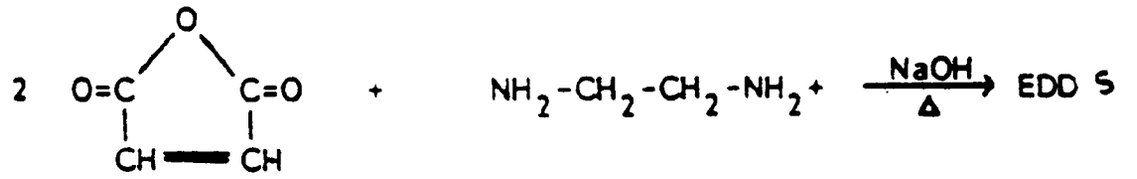
The compositions herein are not limited to any specific viscosity, and depending on the exact use envisioned, various viscosities may be achieved. In any case, the addition of the dipicolinic acid or derivatives thereof to a given composition may produce a viscosity increase or decrease of from 5 cps to 2000 cps, preferably from 50 cps to 1000 cps, at a given shear rate, compared to the same composition without dipicolinic acid or derivatives thereof. The decrease or increase is greater when measured at low shear rates (e.g. 12 rpm).

Typically the compositions according to the present invention may comprise from 0.01 % to 10 % by weight of the total composition of ethylenediamine-N,N'-disuccinic acid, preferably from 0.01 % to 1 %.

The structure of the acid form of ethylenediamine-N,N'-disuccinic acid is as follows:



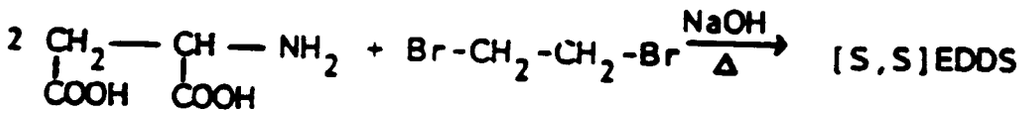
Ethylenediamine-N,N'-disuccinic acid can be synthesised, for example, from readily available, inexpensive starting materials such as maleic anhydride and ethylenediamine as follows.



A more complete disclosure of methods for synthesising ethylenediamine-N,N'-disuccinic acid from commercially available starting materials can be found in US Patent 3,158,635, Kezerian and Ramsay, issued November 24, 1964.

The synthesis of ethylenediamine-N,N'-disuccinic acid from maleic anhydride and ethylene diamine yields a mixture of three optical isomers, [R,R], [S,S], and [S,R], due to the two asymmetric carbon atoms. The biodegradation of ethylenediamine-N,N'-disuccinic acid is optical isomer-specific, with the [S,S] isomer degrading most rapidly and extensively, and for this reason the [S,S] isomer is most preferred for inclusion in the compositions of the invention.

The [S,S] isomer of ethylenediamine-N,N'-disuccinic acidcan be synthesised from L-aspartic acid and 1,2-dibromoethane, as follows.



A more complete disclosure of the reaction of L-aspartic acid with 1,2-dibromoethane to form the [S,S] isomer of ethylenediamine-N,N'-disuccinic acid can be found in Neal and Rose, Stereospecific Ligands and Their Complexes of Ethylenediamine-discuccinic Acid, Inorganic Chemistry, Vol. 7 (1968), pp. 2405-2412.

Ethylenediamine-N,N'-disuccinic acid can be used in the compositions of the present invention in its acid form or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred ethylenediamine-N,N'-disuccinic acid compounds for inclusion in the present compositions are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of ethylenediamine-N,N'-disuccinic acid include Mg ethylenediamine-N,N'-disuccinic acid and Mg_2 ethylenediamine-N,N'-disuccinic acid.

The magnesium complexes are the most preferred for inclusion in compositions according to the invention. These complexes may be added to the compositions as such, or they may be formed during the process for making the composition by the reaction of an inert magnesium salt such as $MgCl_2$ or Mg SO_4 with an ethylenediamine-N,N'-disuccinic acid compound added as either the acid, or as a salt or complex. Where the ethylenediamine-N,N'-disuccinic acid compound is added in the making process, together with the inert magnesium salt, it is preferred that the molar ratio of magnesium to ethylenediamine-N,N'-disuccinic acid should be greater than 1:1, preferably greater than 3:1, to ensure formation of the desired magnesium complexes.

It has been also found that the pH of the formulation influences its stability. Other than this, there are no other limitations in the pH of the composition. However, bleaching ingredients being optional but preferred ingredients of the compositions herein, it is of course necessary, for chemical stability purposes to formulate the compositions herein with bleaches at a pH as is of from 0 to 6, preferably of from 0.5 to 5. The pH of the can be trimmed by all means available to the man skilled in the art.

Accordingly, preferred compositions according to the present invention comprise bleaches, i.e. hydrogen peroxide or water-soluble sources thereof. Suitable water-soluble sources of hydrogen peroxide include perborate, percarbonate and persilicate 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%.

The compositions according to the present invention may further comprise a bleach activator as an optional ingredient. By bleach activator, it is meant herein any compound which reacts with hydrogen peroxide to form a peracid. Suitable bleach activators for use herein 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 the 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 said 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 an 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@ 23-2 and a hydrophilic nonionic surfactant with an HLB of 15, for instance a Dobanol@ 91-10. Another suitable nonionic surfactant system comprises a Dobanol@ 23-6.5 (HLB about 12) and a Dobanol@ 23 (HLB below 6). All these Dobanol@ surfactants are commercially available from Shell.

The compositions according to the present invention may further comprise the usual optional 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 toilet bowl cleaners, or as carpet cleaners to be used either by direct application onto the carpets or in carpet cleaning machines.

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, ethylenediamine-N,N'-disuccinic acid, together with other, optional, 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.

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 (weigh %).

Example 1:

Dobanol@ 91-10	1.2
Dobanol@ 91-2.5	4.8
Citric acid	6
Hydrogen peroxide	6
S,S-EDDS	0.1
Perfume	0.5
Water and minors	up to 100%

pH=1
Viscosity (12 rpm, 20°c, after 1 day): 630 cps (reference without S,S-EDDS: 470 cps).

Example 2:

Dobanol@ 91-10	1.2
Dobanol@ 91-2.5	4.8
Citric acid	6
S,S-EDDS	0.1
Perfume	0.5
Water and minors	up to 100%

pH=1
Viscosity (12 rpm, 20°c, after 1 day): 630 cps

Example 3:

Dobanol@ 91-10	1.2
Dobanol@ 91-2.5	4.8
Citric acid	6
Hydrogen peroxide	12
S,S-EDDS	0.1
Perfume	0.5
Water and minors	up to 100%

pH=1
Viscosity (12 rpm, 20°c, after 1 day): 650 cps

Example 4:

Dobanol@ 91-10	1.2
Dobanol@ 91-2.5	4.8
Citric acid	6
Hydrogen peroxide	6
S,S-EDDS	0.5
Perfume	0.5
Water and minors	up to 100%

pH=1
Viscosity (12 rpm, 20°c, after 1 day): 700 cps

Example 5:

Dobanol@ 23-3	4.8
C8EO4	1.2
Citric acid	6
Hydrogen Peroxide	6
S,S-EDDS	0.1
Perfume	0.5
Water and minors	up to 100%

pH=1
Viscosity (12 rpm, 20°c, after 1 day): 570 cps.

Claims

1. A stable aqueous emulsion comprising a hydrophilic nonionic surfactant and a hydrophobic nonionic surfactant, **characterized in** that said emulsion further comprises a viscosity-building amount of ethylenediamine-N,N'-disuccinic acid.

2. An emulsion according to claim 1 which comprises 0.01% to 10% by weight of the total composition of ethylenediamine-N,N'-disuccinic acid, preferably from 0.01 % to 1 %.

3. An emulsion according to any of the preceding claims wherein the nonionic surfactant amount is from 2 % to 70 % by weight of the total emulsion, preferably from 3 % to 40 %, most preferably from 4 % to 30 %.

4. 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.

5. An emulsion according to claim 5 wherein the difference between the HLB values of the hydrophilic nonionic surfactants and the hydrophobic nonionic surfactants is of at least 1, preferably of 3.

6. An emulsion according to any of the preceding claims which further comprises from 0.5% to 20% hydrogen peroxide.

7. An emulsion according to claim 6 which further comprises a bleach activator.

8. An emulsion according to claim 7 wherein said bleach activator is acetyl triethyl citrate.

9. A process for the manufacture of a composition according to any of the preceding claims which comprises the steps of:
   - Preparing a hydrophobic mixture comprising said hydrophobic nonionic surfactant, ethylenediamine-N,N'-disuccinic acid, together with other, optional, hydrophobic ingredients which are to be formulated in the composition, such as perfumes, solvents, enzymes, bleach activators and polymers;
   - Preparing a hydrophilic mixture comprising at least said water, and said hydrophilic nonionic surfactant, and possibly other, optional, hydrophilic ingredients which are to be formulated in the composition such as dyes, optical brighteners, builders, chelants, hydrogen peroxide and buffering agents;
   - Subsequently mixing said hydrophobic mixture and said hydrophilic mixture together.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 87 0134

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)
A	US-A-4 704 233 (F. A. HARTMAN ET AL.) * column 14, line 11 - line 22; claims 1,8 *	1-3,6,7	C11D3/33 C11D3/39 C11D1/825
			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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