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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 a terephthalate-based polymer as a viscosity decreasing agent.

**EP 0 629 690 A1**

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.

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.

However, a problem with such emulsions especially with emulsions containing relatively high concentration 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.

It has now been found that this object can be efficiently met by formulating aqueous emulsions of nonionic surfactants which comprise terephthalate-based polymers. In other words, it has now been found that terephthalate-based polymers reduce the viscosity of aqueous emulsions comprising a nonionic surfactant system whatever the viscosity was before the addition of said terephthalate-based polymers.

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 of terephthalate-based polymers is unexpected and beneficial as said terephthalate-based polymers are only known in the context of laundry compositions as soil release components, see for instance US- 4 116 885, US- 4 132 680, EP- 185 427, EP 220 156, EP 241 984, EP 241 985, EP 518 401 and European Patent Application EP 92870095.4

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 terephthalate-based polymers 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 a viscosity-reducing amount of terephthalate-based polymers.

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 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.

5 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).

10 Suitable nonionic surfactants for use herein include alkoxyated fatty alcohols. Indeed, a great variety of such alkoxyated fatty alcohols are commercially available which have very different HLB values (hydrophilic lipophilic balance). The HLB values of such alkoxyated 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

15 surfactants tend to have a low degree of alkoxylation and a long chain fatty alcohol. 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 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 %.

20 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 reducing amount of terephthalate-based polymers. By "viscosity reducing amount" it is meant an amount of terephthalate-based polymers which is sufficient to provide physically stable aqueous emulsions

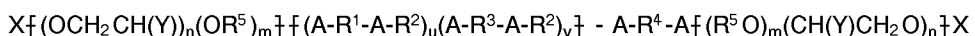
25 wherein the viscosity can be conveniently controlled. Typically the compositions according to the present invention comprise from 0.05 % to 5 % by weight of the total composition of said terephthalate-based polymers, preferably from 0.1 % to 2 %.

Said terephthalate-based polymers reduce the viscosity of aqueous emulsions herein whatever the viscosity was before the addition of said terephthalate-based polymers, while maintaining also physical

30 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 with a Brookfield DV II rotational viscosimeter.

Terephthalate-based polymers have been extensively described in the art as soil release agents, see for instance US- 4 116 885, US- 4 132 680, EP- 185 427, EP 220 156, EP 241 984, EP 241 985, EP 518 401

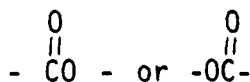
35 and European Patent Application EP 92870095.4. All polymers disclosed therein are suitable in the context of the present invention. More specifically, suitable polymers for use herein are according to the formula



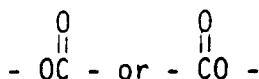
40 In this formula, the moiety  $\{(\text{A-R}^1\text{-A-R}^2)_u(\text{A-R}^3\text{-A-R}^2)_v\}$  A-R<sup>4</sup>-A-forms the oligomer or polymer backbone of the compounds.

It is believed that the backbone structure is important to the adsorption of the polymers on the fabrics while the end groups confer the soil release properties.

The linking A moieties are essentially



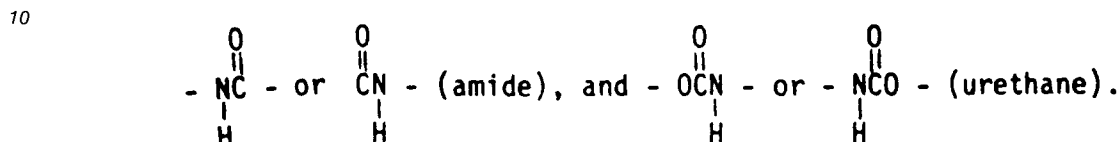
50 moieties, i.e. the compounds of the present invention are polyesters. As used herein, the term "the A moieties are essentially



moieties" refers to compounds where the A moieties consist entirely of moieties



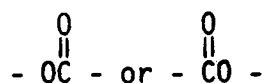
or are partially substituted with linking moieties such as



15 The degree of partial substitution with these other linking moieties should be such that the soil release properties are not adversely affected to any great extent. Preferably, linking moieties A consist entirely of (i.e., comprise 100%) moieties



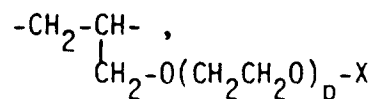
25 i.e., each A is either



30 The R<sup>1</sup> moieties are essentially 1,4-phenylene moieties. As used herein, the term "the R<sup>1</sup> moieties are essentially 1,4-phenylene moieties" refers to compounds where the R<sup>1</sup> moieties consist entirely of 1,4-phenylene moieties, or are partially substituted with other arylene or alkarylene moieties, alkylene moieties, alkenylene moieties, or mixtures thereof. Arylene and alkarylene moieties which can be partially substituted for 1,4-phenylene include 1,3-phenylene, 1,2-phenylene, 1,8-naphthylene, 1,4-naphthylene, 2,2-biphenylene, 4,4'-biphenylene and mixtures thereof. Alkylene and alkenylene moieties which can be partially substituted include ethylene, 1,2-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexamethylene, 1,7-heptamethylene, 1,8-octamethylene, 1,4-cyclohexylene, and mixtures thereof.

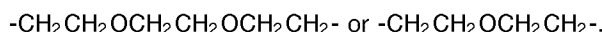
40 For the R<sup>1</sup> moieties, the degree of partial substitution with moieties other than 1,4-phenylene should be such that the soil release properties of the compound are not adversely affected to any great extent. Generally, the degree of partial substitution which can be tolerated will depend upon the backbone length of the compound, i.e., longer backbones can have greater partial substitution for 1,4-phenylene moieties. Usually, compounds where the R<sup>1</sup> comprise from about 50 to 100% 1,4-phenylene moieties (from 0 to about 50% moieties other than 1,4-phenylene) have adequate soil release activity. For example, polyesters made according to the present invention with a 40:60 mole ratio of isophthalic (1,3-phenylene) to terephthalic (1,4-phenylene) acid have adequate soil release activity. However, because most polyesters used in fiber making comprise ethylene terephthalate units, it is usually desirable to minimize the degree of partial substitution with moieties other than 1,4-phenylene for best soil release activity. Preferably, the R<sup>1</sup> moieties consist entirely of (i.e., comprise 100%) 1,4-phenylene moieties, i.e. each R<sup>1</sup> moiety is 1,4-phenylene.

50 The R<sup>2</sup> moieties are essentially ethylene moieties, or substituted ethylene moieties having C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy substituents. As used herein, the term "the R<sup>2</sup> moieties are essentially ethylene moieties, or substituted ethylene moieties having C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy substituents" refers to compounds of the present invention where the R<sup>2</sup> moieties consist entirely of ethylene, or substituted ethylene moieties, or are partially substituted with other compatible moieties. Examples of these other moieties include linear C<sub>3</sub>-C<sub>6</sub> alkylene moieties such as 1,3-propylene, 1,4-butylene, 1,5-pentylene or 1,6-hexamethylene, 1,2-cycloalkylene moieties such as 1,2-cyclohexylene, 1,4-cycloalkylene moieties such as 1,4-cyclohexylene and 1,4-dimethylene-cyclohexylene, polyoxyalkylated 1,2-hydroxyalkylenes such as



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and oxyalkylene moieties such as



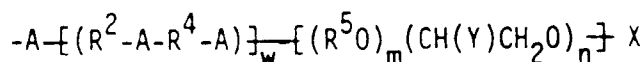
10 For the R<sup>2</sup> moieties, the degree of partial substitution with these other moieties should be such that the soil release properties of the compounds are not adversely affected to any great extent. Generally, the degree of partial substitution which can be tolerated will depend upon the backbone length of the compound, i.e., longer backbones can have greater partial substitution. Usually, compounds where the R<sup>2</sup> comprise from about 20 to 100% ethylene, or substituted ethylene moieties (from 0 to about 80% other  
15 compatible moieties) have adequate soil release activity. For example, polyesters made according to the present invention with a 75:25 mole ratio of diethylene glycol (-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-) to ethylene glycol (ethylene) have adequate soil release activity. However, it is desirable to minimize such partial substitution, especially with oxyalkylene moieties, for best soil release activity. (During the making of polyesters according to the present invention, small amounts of these oxyalkylene moieties (as dialkylene glycols) are  
20 typically formed from glycols in side reactions and are then incorporated into the polyester). Preferably, R<sup>2</sup> comprises from about 80 to 100% ethylene, or substituted ethylene moieties, and from 0 to about 20% other compatible moieties.

For the R<sup>2</sup> moieties, suitable ethylene or substituted ethylene moieties include ethylene, 1,2-propylene, 1,2-butylene, 1,2-hexylene, 3-methoxy-1,2-propylene and mixtures thereof. Preferably, the R<sup>2</sup> moieties are  
25 essentially ethylene moieties, 1,2-propylene moieties or mixtures thereof. Inclusion of a greater percentage of ethylene moieties tends to improve the soil release activity of the compounds. Surprisingly, inclusion of a greater percentage of 1,2-propylene moieties tends to improve the water solubility of the compounds.

For the R<sup>3</sup> moieties, suitable substituted C<sub>2</sub>-C<sub>18</sub> hydrocarbylene moieties can include substituted C<sub>2</sub>-C<sub>12</sub> alkylene, alkenylene, arylene, alkarylene and like moieties. The substituted alkylene or alkenylene  
30 moieties can be linear, branched, or cyclic. Also, the R<sup>3</sup> moieties can be all the same (e.g. all substituted arylene) or a mixture (e.g. a mixture of substituted arylenes and substituted alkylenes). Preferred R<sup>3</sup> moieties are those which are substituted 1,3-phenylene moieties.

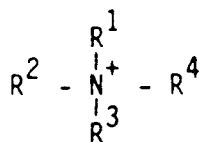
The substituted R<sup>3</sup> moieties preferably have only one -SO<sub>3</sub>M, -COOM, -O[(R<sup>5</sup>O)<sub>m</sub>(CH(Y)CH<sub>2</sub>O)<sub>n</sub>]<sub>3</sub>X or

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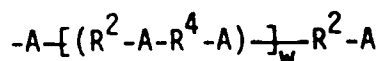
substituent. M can be H or any compatible water-soluble cation. Suitable water soluble cations include the  
40 water soluble alkali metals such as potassium (K<sup>+</sup>) and especially sodium (Na<sup>+</sup>), as well as ammonium (NH<sub>4</sub><sup>+</sup>). Also suitable are substituted ammonium cations having the formula:

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where R<sup>1</sup> and R<sup>2</sup> are each a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl group (e.g. alkyl, hydroxyalkyl) or together form a cyclic or  
50 heterocyclic ring of from 4 to 6 carbon atoms (e.g. piperidine, morpholine); R<sup>3</sup> is a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl group; and R<sup>4</sup> is H (ammonium) or a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl group (quat amine). Typical substituted ammonium cationic groups are those where R<sup>4</sup> is H (ammonium) or C<sub>1</sub>-C<sub>4</sub> alkyl, especially methyl (quat amine); R<sup>1</sup> is C<sub>10</sub>-C<sub>18</sub> alkyl, especially C<sub>12</sub>-C<sub>14</sub> alkyl; and R<sup>2</sup> and R<sup>3</sup> are each C<sub>1</sub>-C<sub>4</sub> alkyl, especially methyl.

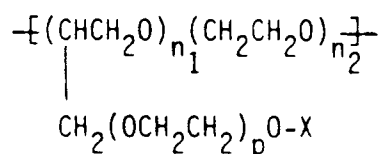
55 The R<sup>3</sup> moieties having -A[(R<sup>2</sup>-A-R<sup>4</sup>A)]<sub>w</sub> [(R<sup>5</sup>O)<sub>m</sub>(CH(Y)CH<sub>2</sub>O)<sub>n</sub>]<sub>3</sub>X substituents provide branched backbone compounds. R<sup>3</sup> moieties having



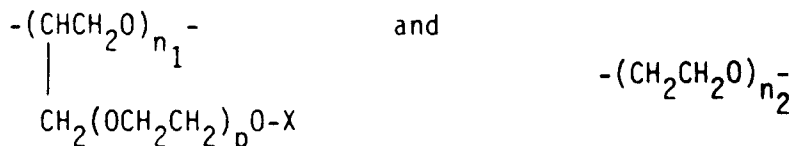
moieties provide crosslinked backbone compounds. Indeed, syntheses used to make the branched backbone compounds typically provide at least some crosslinked backbone compounds.

The moieties  $-(R^5O)-$  and  $-(CH(Y)CH_2O)-$  of the moieties  $\{(R^5O)_m(CH(Y)CH_2O)_n\}$  and  $\{(OCH(Y)CH_2)_n(OR^5)_m\}$  can be mixed together or preferably form blocks of  $-(R^5O)-$  and  $-(CH(Y)CH_2O)-$  moieties. Preferably, the blocks of  $-(R^5O)-$  moieties are located next to the backbone of the compound. When  $R^5$  is the moiety  $-R^2-A-R^6-$ ,  $m$  is 1; also, the moiety  $-R^2-A-R^6-$  is preferably located next to the backbone of the compound. For  $R^5$ , the preferred  $C_3-C_4$  alkylene is  $C_3H_6$  (propylene); when  $R^5$  is  $C_3-C_4$  alkylene,  $m$  is preferably from 0 to about 5 and is most preferably 0.  $R^6$  is preferably methylene or 1,4-phenylene. The moiety  $-(CH(Y)CH_2O)-$  preferably comprises at least about 75% by weight of the moiety  $\{(R^5O)_m(CH(Y)CH_2O)_n\}$  and most preferably 100% by weight ( $m$  is 0).

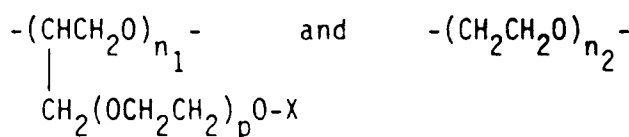
The  $Y$  substituents of each moiety  $\{(R^5O)_m(CH(Y)CH_2O)_n\}$  are the ether moiety  $-CH_2(OCH_2CH_2)_pO-X$ , or are, more typically, a mixture of this ether moiety and  $H$ ;  $p$  can range from 0 to 100, but is typically 0. When the  $Y$  substituents are a mixture, moiety  $-(CH(Y)CH_2O)_n-$  can be represented by the following moiety:



wherein  $n_1$  is at least 1 and the sum of  $n_1 + n_2$  is the value for  $n$ . Typically,  $n_1$  has an average value of from about 1 to about 10. The moieties



can be mixed together, but typically form blocks of



moieties.  $X$  can be  $H$ ,  $C_1-C_4$  alkyl or

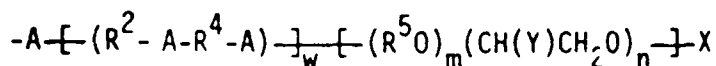


wherein  $R^7$  is  $C_1-C_4$  alkyl.  $X$  is preferably methyl or ethyl, and most preferably methyl. The value for each  $n$  is at least about 6, but is preferably at least about 10. The value for each  $n$  usually ranges from about 12 to about 113. Typically, the value for each  $n$  is in the range of from about 12 to about 43.

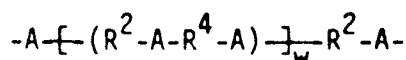
The backbone moieties  $\{A-R^1-A-R^2\}$  and  $\{A-R^3-A-R^2\}$  can be mixed together or can form blocks of  $\{A-R^1-A-R^2\}$  and  $\{A-R^3-A-R^2\}$  moieties. It has been found that the value of  $u + v$  needs to be at least about 3 in order for the compounds of the present invention to have significant soil release activity. The maximum value for  $u + v$  is generally determined by the process by which the compound is made, but can range up to about 25, i.e. the compounds of the present invention are oligomers or low molecular weight polymers. By comparison, polyesters used in fiber making typically have a much higher molecular weight,

e.g. have from about 50 to about 250 ethylene terephthalate units. Typically, the sum of  $u + v$  ranges from about 3 to about 10 for the compounds of the present invention.

Generally, the larger the  $u + v$  value, the less soluble is the compound, especially when the  $R^3$  moieties do not have the substituents  $-COOM$  or  $-SO_3M$ . Also, as the value for  $n$  increases, the value for  $u + v$  should be increased so that the compound will deposit better on the fabric during laundering. When the  $R^3$  moieties have the substituent

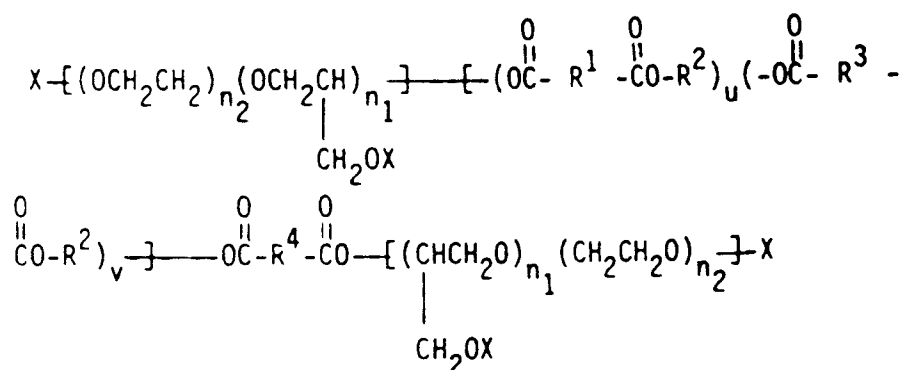


(branched backbone compounds) or

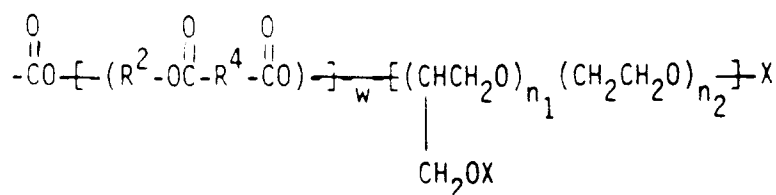


(crosslinked backbone compounds), the value for  $w$  is typically at least 1 and is determined by the process by which the compound is made. For these branched and crosslinked backbone compounds the value for  $u + v + w$  is from about 3 to about 25.

Preferred compounds in this class of polymers are block polyesters having the formula:



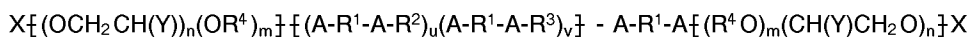
wherein the  $R^1$  moieties are all 1,4-phenylene moieties; the  $R^2$  moieties are essentially ethylene moieties, 1,2-propylene moieties or mixtures thereof; the  $R^3$  moieties are all potassium or preferably sodium 5-sulfo-1,3-phenylene moieties or substituted 1,3-phenylene moieties having the substituent



at the 5 position; the  $R^4$  moieties are  $R^1$  or  $R^3$  moieties, or mixtures thereof; each  $X$  is ethyl or preferably methyl; each  $n_1$  is from 1 to about 5; the sum of each  $n_1 + n_2$  is from about 12 to about 43; when  $w$  is 0,  $u + v$  is from about 3 to about 10; when  $w$  is at least 1,  $u + v + w$  is from about 3 to about 10.

Particularly preferred block polyesters are those where  $v$  is 0, i.e. the linear block polyesters. For these most preferred linear block polyesters,  $u$  typically ranges from about 3 to about 8. The most water soluble of these linear block polyesters are those where  $u$  is from about 3 to about 5.

Other suitable polymers for use herein include polymers of the formula :

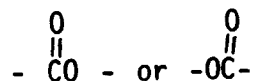


In this formula, the moiety  $\{[(A-R^1-A-R^2)_u(A-R^1-A-R^3)_v]\}_v$   $A-R^1-A$ -forms the oligomer or polymer backbone of

the compounds. Groups  $X\{(\text{OCH}_2\text{CH}(\text{Y})_n(\text{OR}^4)_m)\}$  and  $\{(\text{R}^4\text{O})_m(\text{CH}(\text{Y})\text{CH}_2\text{O})_n\}X$  are generally connected at the ends of the oligomer/polymer backbone.

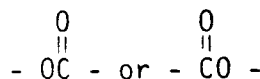
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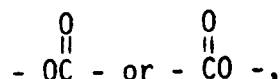
10 moieties, i.e. the compounds of the present invention are polyesters. As used herein, the term "the A moieties are essentially

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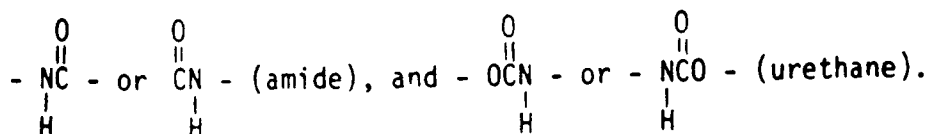
moieties" refers to compounds where the A moieties consist entirely of moieties

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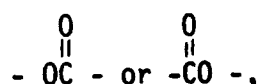
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The degree of partial substitution with these other linking moieties should be such that the soil release properties are not adversely affected to any great extent. Preferably, linking moieties A consist entirely of (i.e., comprise 100%) moieties

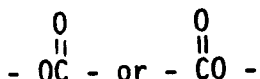
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i.e., each A is either

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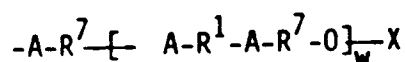


The  $\text{R}^1$  moieties are essentially 1,4-phenylene moieties. As used herein, the term "the  $\text{R}^1$  moieties are essentially 1,4-phenylene moieties" refers to compounds where the  $\text{R}^1$  moieties consist entirely of 1,4-phenylene moieties, or are partially substituted with other arylene or alkarylene moieties, alkylene moieties, alkenylene moieties, or mixtures thereof. Arylene and alkarylene moieties which can be partially substituted for 1,4-phenylene include 1,3-phenylene, 1,2-phenylene, 1,8-naphthylene, 1,4-naphthylene, 2,2-biphenylene, 4,4'-biphenylene and mixtures thereof. Alkylene and alkenylene moieties which can be partially substituted include ethylene- 1,2-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexamethylene, 1,7-heptamethylene, 1,8-octamethylene, 1,4-cyclohexylene, and mixtures thereof.

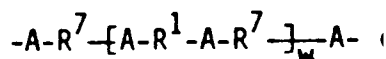
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These other arylene, alkarylene, alkylene and alkenylene moieties can be unsubstituted or can have at least one  $-\text{SO}_3\text{M}$ ,  $-\text{COOM}$  or



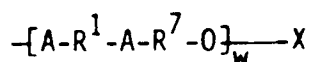


5 substituent or at least one moiety



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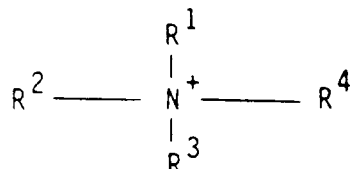
cross-linked to another R<sup>1</sup> moiety, wherein R<sup>7</sup> is the moiety R<sup>2</sup> or R<sup>3</sup>; and w is 0 or at least 1. Preferably, these substituted R<sup>1</sup> moieties have only one -SO<sub>3</sub>M, -COOM or -A-R<sup>7</sup>



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substituent. M can be H or any compatible water-soluble cation. Suitable water-soluble cations include the water-soluble alkali metals such as potassium (K<sup>+</sup>) and especially sodium (Na<sup>+</sup>), as well as ammonium (NH<sub>4</sub><sup>+</sup>). Also suitable are substituted ammonium cations having the formula:

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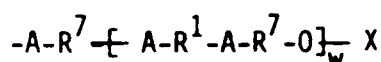
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where R<sup>1</sup> and R<sup>2</sup> are each a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl group (e.g. alkyl, hydroxyalkyl) or together form a cyclic or heterocyclic ring of from 4 to 6 carbon atoms (e.g. piperidine, morpholine); R<sup>3</sup> is a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl group; and R<sup>4</sup> is H (ammonium) or a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl group (quat amine). Typical substituted ammonium cationic groups are those where R<sup>4</sup> is H (ammonium) or C<sub>1</sub>-C<sub>4</sub> alkyl, especially methyl (quat amine); R<sup>1</sup> is C<sub>10</sub>-C<sub>18</sub> alkyl, especially C<sub>12</sub>-C<sub>14</sub> alkyl; and R<sup>2</sup> and R<sup>3</sup> are each C<sub>1</sub>-C<sub>4</sub> alkyl, especially methyl.

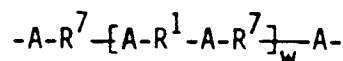
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The R<sup>1</sup> moieties having

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40 substituents provide branched backbone compounds. The R<sup>1</sup> moieties having



45 moieties provide cross-linked backbone compounds. Indeed, syntheses used to make the branched backbone compounds typically provide at least some cross-linked backbone compounds.

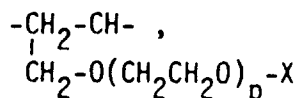
For the R<sup>1</sup> moieties, the degree of partial substitution with moieties other than 1,4-phenylene should be such that the soil release properties of the compound are not adversely affected to any great extent. Generally, the degree of partial substitution which can be tolerated will depend upon the backbone length of the compound, i.e., longer backbones can have greater partial substitution for 1,4-phenylene moieties. Usually, compounds where the R<sup>1</sup> comprise from about 50 to 100% 1,4-phenylene moieties (from 0 to about 50% moieties other than 1,4-phenylene) have adequate soil release activity. However, because most polyesters used in fiber making comprise ethylene terephthalate units, it is usually desirable to minimize the degree of partial substitution with moieties other than 1,4-phenylene for best soil release activity. Preferably, the R<sup>1</sup> moieties consist entirely of (i.e., comprise 100%) 1,4-phenylene moieties, i.e. each R<sup>1</sup> moiety is 1,4-phenylene.

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The R<sup>2</sup> moieties are essentially substituted ethylene moieties having C<sub>1</sub>-C<sub>4</sub> alkyl or alkoxy substituents. As used herein, the term "the R<sup>2</sup> moieties are essentially substituted ethylene moieties having C<sub>1</sub>-C<sub>4</sub> alkyl

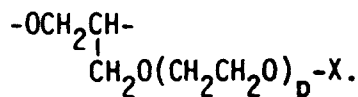
or alkoxy substituents" refers to compounds of the present invention where the R<sup>2</sup> moieties consist entirely of substituted ethylene moieties, or are partially replaced with other compatible moieties. Examples of these other moieties include linear C<sub>2</sub>-C<sub>6</sub> alkylene moieties such as ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene or 1,6-hexamethylene, 1,2-cycloalkylene moieties such as 1,2-cyclohexylene, 1,4-cycloalkylene moieties such as 1,4-cyclohexylene and 1,4-dimethylene-cyclohexylene, polyoxyalkylated 1,2-hydroxyalkylenes such as



and oxyalkylene moieties such as -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-.

For the R<sup>2</sup> moieties, the degree of partial replacement with these other moieties should be such that the soil release and solubility properties of the compounds are not adversely affected to any great extent. Generally, the degree of partial replacement which can be tolerated will depend upon the soil release and solubility properties desired, the backbone length of the compound, (i.e., longer backbones generally can have greater partial replacement), and the type of moiety involved (e.g., greater partial substitution with ethylene moieties generally decreases solubility). Usually, compounds where the R<sup>2</sup> comprise from about 20 to 100% substituted ethylene moieties (from 0 to about 80% other compatible moieties) have adequate soil release activity. However, it is generally desirable to minimize such partial replacement for best soil release activity and solubility properties. (During the making of polyesters according to the present invention, small amounts of oxyalkylene moieties (as dialkylene glycols) can be formed from glycols in side reactions and then incorporated into the polyester). Preferably, R<sup>2</sup> comprises from about 80 to 100% substituted ethylene moieties, and from 0 to about 20% other compatible moieties. For the R<sup>2</sup> moieties, suitable substituted ethylene moieties include 1,2-propylene, 1,2-butylene, 3-methoxy-1,2-propylene and mixtures thereof. Preferably, the R<sup>2</sup> moieties are essentially 1,2-propylene moieties.

The R<sup>3</sup> moieties are essentially the polyoxyethylene moiety -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>-CH<sub>2</sub>CH<sub>2</sub>-. As used herein, the term "the R<sup>3</sup> moieties are essentially the polyoxyethylene moiety -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>-H<sub>2</sub>CH<sub>2</sub>-" refers to compounds of the present invention in which the R<sup>3</sup> moieties consist entirely of this polyoxyethylene moiety, or further include other compatible moieties. Examples of these other moieties include C<sub>3</sub>-C<sub>6</sub> oxyalkylene moieties such as oxypropylene and oxybutylene, polyoxyalkylene moieties such as polyoxypropylene and polyoxybutylene, and polyoxyalkylated 1,2-hydroxyalkylene oxides such as



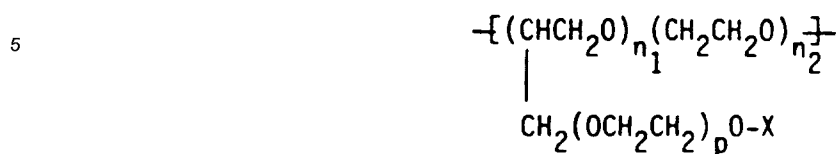
The degree of inclusion of these other moieties should be such that the soil release properties of the compounds are not adversely affected to any great extent. Usually, in compounds of the present invention, the polyoxyethylene moiety comprises from about 50 to 100% of each R<sup>3</sup> moiety. Preferably, the polyoxyethylene moiety comprises from about 90 to 100% of each R<sup>3</sup> moiety. (During the making of polyesters according to the present invention, very small amounts of oxyalkylene moieties may be attached to the polyoxyethylene moiety in side reactions and thus incorporated into the R<sup>3</sup> moieties).

For the polyoxyethylene moiety, the value for q is at least about 9, and is preferably at least about 12. The value for q usually ranges from about 12 to about 180. Typically, the value for q is in the range of from about 12 to about 90.

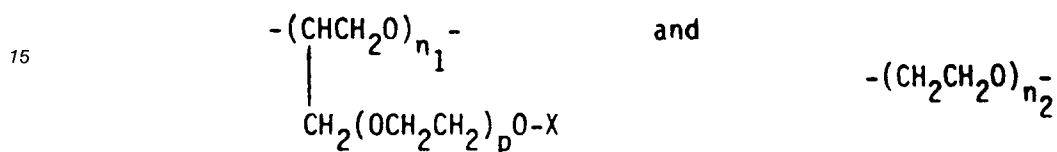
The moieties -(R<sup>4</sup>O)- and -(CH(Y)CH<sub>2</sub>O)- of the moieties {(R<sup>4</sup>O)<sub>m</sub>(CH(Y)CH<sub>2</sub>O)<sub>n</sub>} and {(OCH(Y)CH<sub>2</sub>)<sub>n</sub>-(OR<sup>4</sup>)<sub>m</sub>} can be mixed together or preferably form blocks of -(R<sup>4</sup>O)- and -(CH(Y)CH<sub>2</sub>O)-moieties. Preferably, the blocks of -(R<sup>4</sup>O)- moieties are located next to the backbone of the compound. When R<sup>4</sup> is the moiety -R<sup>2</sup>-A-R<sup>5</sup>-, m is 1; also, the moiety -R<sup>2</sup>-A-R<sup>5</sup>- is preferably located next to the backbone of the compound. For R<sup>4</sup>, the preferred C<sub>3</sub>-C<sub>4</sub> alkylene is C<sub>3</sub>H<sub>6</sub> (propylene); when R<sup>4</sup> is C<sub>3</sub>-C<sub>4</sub> alkylene, m is preferably from 0 to about 10 and is most preferably 0. R<sup>5</sup> is preferably methylene or 1,4-phenylene. The moiety -(CH(Y)CH<sub>2</sub>O)- preferably comprises at least about 75% by weight of the moiety {(R<sup>4</sup>O)<sub>m</sub>(CH(Y)CH<sub>2</sub>O)<sub>n</sub>} and most preferably 100% by weight (m is 0).

The Y substituents of each moiety [(R<sup>5</sup>O)<sub>m</sub>(CH(Y)CH<sub>2</sub>O)<sub>n</sub>] are H, the ether moiety -CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>p</sub>O-X, or a mixture of this ether moiety and H; p can range from 0 to 100, but is typically 0. Typically, the Y

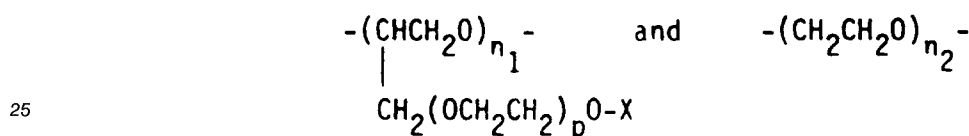
substituents are all H. When the Y substituents are a mixture of the ether moiety and H, the moiety  $-(CH(Y)-CH_2O)_n-$  can be represented by the following moiety:



wherein  $n_1$  is at least 1 and the sum of  $n_1 + n_2$  is the value for  $n$ . Typically,  $n_1$  has an average value of from about 1 to about 10. The moieties



can be mixed together, but typically form blocks of



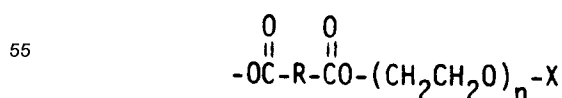
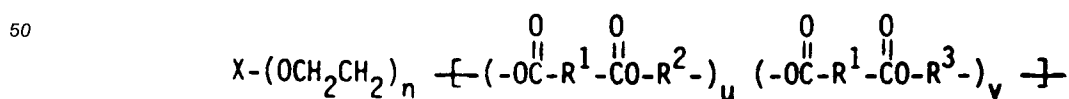
moieties. X can be H,  $C_1$ - $C_4$  alkyl or



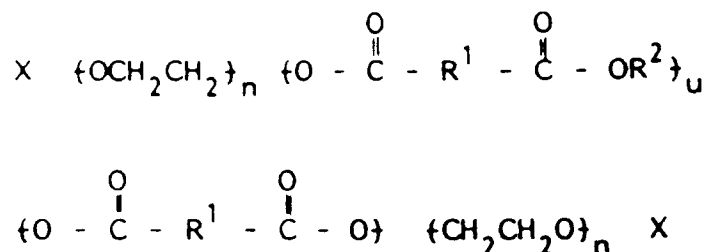
wherein  $R^7$  is  $C_1$ - $C_4$  alkyl. X is preferably methyl or ethyl, and most preferably methyl. The value for each  $n$  is at least about 6, but is preferably at least about 10. The value for each  $n$  usually ranges from about 12 to about 113. Typically, the value for each  $n$  is in the range of from about 12 to about 45.

The backbone moieties  $\{A-R^1-A-R^2\}$  and  $\{A-R^1-A-R^3\}$  can form blocks of  $\{A-R^1-A-R^2\}$  and  $\{A-R^1-A-R^3\}$  moieties but are more typically randomly mixed together. For these backbone moieties, the average value of  $u$  can range from about 2 to about 50; the average value of  $v$  can range from about 1 to about 20; and the average value of  $u + v$  can range from about 3 to about 70. The average values for  $u$ ,  $v$  and  $u + v$  are generally determined by the process by which the compound is made. Generally, the larger the average value for  $v$  or the smaller the average value for  $u + v$ , the more soluble is the compound. Typically, the average value for  $u$  is from about 5 to about 20; the average value for  $v$  is from about 1 to about 10; and the average value for  $u + v$  is from about 6 to about 30. Generally, the ratio of  $u$  to  $v$  is at least about 1 and is typically from about 1 to about 6.

Preferred compounds in this class of polymers are polyesters having the formula:



wherein each R<sup>1</sup> is a 1,4-phenylene moiety; the R<sup>2</sup> are essentially 1,2-propylene moieties; the R<sup>3</sup> are essentially the polyoxyethylene moiety -(CH<sub>2</sub>H<sub>2</sub>O)<sub>q</sub>-CH<sub>2</sub>CH<sub>2</sub>-; each X is ethyl or preferably methyl; each n is from about 12 to about 45; q is from about 12 to about 90; the average value of u is from about 5 to about 20; the average value of v is from about 1 to about 10; the average value of u + v is from about 6 to about 30; the ratio u to v is from about 1 to about 6. Highly preferred polymers for use herein are polymers of the formula :



in which X can be any suitable capping group, with each X being selected from the group consisting of H, and alkyl or acyl groups containing from 1 to about 4 carbon atoms, preferably 1 to 2 carbon atoms most preferably alkyl. n is selected for water solubility and is a range of values which generally averages from about 10 to about 50, preferably from about 10 to about 25. The selection of u is critical to formulation in a liquid detergent having a relatively high ionic strength. There should be very little material, preferably less than about 10 mol %, more preferably less than 5 mol %, most preferably less than 1 mol %, in which u is greater than 5. Furthermore there should be at least 20 mol %, preferably at least 40 mol %, of material in which u ranges from 3 to 5.

The R<sup>1</sup> moieties are essentially 1,4-phenylene moieties. As used herein, the term "the R<sup>1</sup> moieties are essentially 1,4-phenylene moieties" refers to compounds where the R<sup>1</sup> moieties consist entirely of 1,4-phenylene moieties, or are partially substituted with other arylene or alkarylene moieties, alkylene moieties, alkenylene moieties, or mixtures thereof. Arylene and alkarylene moieties which can be partially substituted for 1,4-phenylene include 1,3-phenylene, 1,2-phenylene, 1,8-naphthylene, 1,4-naphthylene, 2,2-biphenylene, 4,4'-biphenylene and mixtures thereof. Alkylene and alkenylene moieties which can be partially substituted include ethylene, 1,2-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexamethylene, 1,7-heptamethylene, 1,8-octamethylene, 1,4-cyclohexylene, and mixtures thereof.

For the R<sup>1</sup> moieties, the degree of partial substitution with moieties other than 1,4-phenylene should be such that the soil release properties of the compound are not adversely affected to any great extent. Generally, the degree of partial substitution which can be tolerated will depend upon the backbone length of the compound, i.e., longer backbones can have greater partial substitution for 1,4-phenylene moieties. Usually, compounds where the R<sup>1</sup> comprise from about 50% to 100% 1,4-phenylene moieties (from 0 to about 50% moieties other than 1,4-phenylene) have adequate soil release activity. For example, polyesters made according to the present invention with a 40:60 mole ratio of isophthalic (1,3-phenylene) to terephthalic (1,4-phenylene) acid have adequate soil release activity. However, because most polyesters used in fiber making comprise ethylene terephthalate units, it is usually desirable to minimize the degree of partial substitution with moieties other than 1,4-phenylene for best soil release activity. Preferably, the R<sup>1</sup> moieties consist entirely of (i.e., comprise 100%) 1,4-phenylene moieties, i.e. each R<sup>1</sup> moiety is 1,4-phenylene.

For the R<sup>2</sup> moieties, suitable ethylene or substituted ethylene moieties include ethylene, 1,2-propylene, 1,2-butylene, 1,2-hexylene, 3-methoxy-1,2-propylene and mixtures thereof. Preferably, the R<sup>2</sup> moieties are essentially ethylene moieties, or, preferably, 1,2-propylene moieties or mixtures thereof. Although inclusion of a greater percentage of ethylene moieties tends to improve the soil release activity of the compounds, the percentage included is limited by water solubility. Surprisingly, inclusion of a greater percentage of 1,2-propylene moieties tends to improve the water solubility of the compounds and consequently the ability to formulate isotropic aqueous detergent compositions without significantly harming soil release activity.

For this invention, the use of 1,2-propylene moieties or a similar branched equivalent is extremely important for maximizing incorporation of a substantial percentage of the soil release component in the heavy duty liquid detergent compositions. Preferably, from about 75% to about 100%, more preferably from about 90% to about 100% of the R<sup>2</sup> moieties are 1,2-propylene moieties.

In general, soil release components which are soluble in cool (15°C) ethanol are also useful in compositions of the invention.

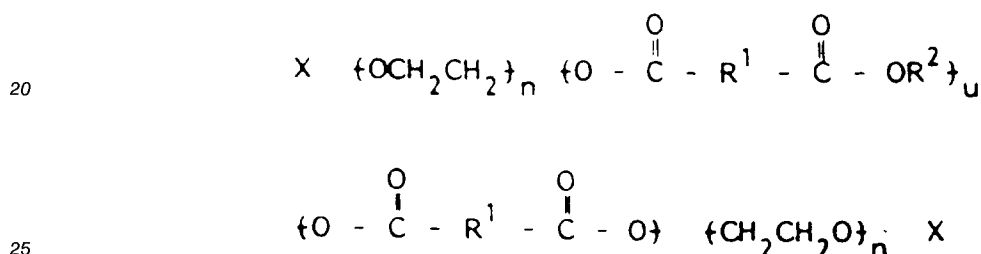
The value for n averages at least about 10, but a distribution of n values is present. The value for each n usually ranges from about 10 to about 50. Preferably, the value for each n averages in the range of from about 10 to about 25.

A preferred process for making the soil release component comprises the step of extracting a polymer having a typical distribution in which a substantial portion comprises a material in which u is equal to or greater than 6 with essentially anhydrous ethanol at low temperatures, e.g. from about 10 °C to about 15 °C, preferably less than about 13 °C. The ethanol soluble fraction is substantially free of the longer polymers and is much easier to incorporate into isotropic heavy duty liquids, especially those with higher builder levels. Although the polymers wherein u is less than about 3 are essentially of no value in providing soil release effects, they can be more easily incorporated than higher u values.

A more preferred process for making the soil release component is by direct synthesis.

A more comprehensive disclosure of the soil release component and methods for making it can be found in copending U.S. Patent Application, Serial No. 684, 511, filed December 21, 1984 by Eugene P. Gosselink, incorporated herein by reference.

The most preferred polymers for use herein are polymers according to the formula:



wherein X is methyl, n is 16, R<sup>1</sup> is 1,4-phenylene moiety, R<sup>2</sup> is 1,2-propylene moiety and u is essentially between 3 and 5.

Suitable terephthalate-based polymers for use herein are commercially available from various companies including for instance Hoechst. An example of said terephthalate-based polymers for use herein is HOES<sup>®</sup> 3639 (Hoechst).

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:

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

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<sup>®</sup> 23-2 and a hydrophilic nonionic surfactant with an HLB of 15, for instance a Dobanol<sup>®</sup> 91-10. Another suitable nonionic surfactant system comprises a Dobanol<sup>®</sup> 23-6.5 (HLB about 12) and a Dobanol<sup>®</sup> 23 (HLB below 6). All these Dobanol<sup>®</sup> surfactants are commercially available from Shell.

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

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 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 suited 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 the terephthalate-based polymers 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 when present 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 %).

5		I	II	III	IV	V
	Dobanol <sup>®</sup> 45-7	6	6	6	6	6
	Dobanol <sup>®</sup> 91-10	3	3	3	3	3
	Dobanol <sup>®</sup> 23-2	6	6	6	6	6
10	Hydrogen peroxide	7.5	7.5	7.5	7.5	7.5
	Acetyl triethyl citrate	7.0	7.0	7.0	7.0	7.0
	Brightener <sup>®</sup> 49	0.12	0.12	0.12	0.12	0.12
	S,S-ethylene diamino disuccinic acid	0.10	0.10	0.10	0.10	0.10
	Poly(4-vinylpyridine -N-oxyde)	0.10	0.10	0.10	0.10	0.10
15	HOES <sup>®</sup> 3639	0.20	0.30	0.40	0.50	----
	Deionized water	-----balance-----				

The compositions obtained have a viscosity after one week storage at 50 °C as specified.

20 Measurements with a Brookfield DV II viscosimeter with spindle RD/0.4 at 25 °C :

Composition V	664 cps at 50 rpm
Composition I	360 cps at 50 rpm

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Measurements with a Brookfield Din II viscosimeter with spindle RV/6.4 at 30 °C :

Composition V	580 cps at 60 rpm
Composition II	450 cps at 60 rpm
Composition III	380 cps at 60 rpm
Composition IV	280 cps at 60 rpm

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Compositions I to V 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<sup>®</sup> 45-7 and the Dobanol<sup>®</sup> 91-10. Hydrogen peroxide is added in said hydrophilic mixture as last step. A hydrophobic mixture is prepared which comprises the acetyl triethyl citrate, the Dobanol<sup>®</sup> 23-2 and Hoes<sup>®</sup> 3639.

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

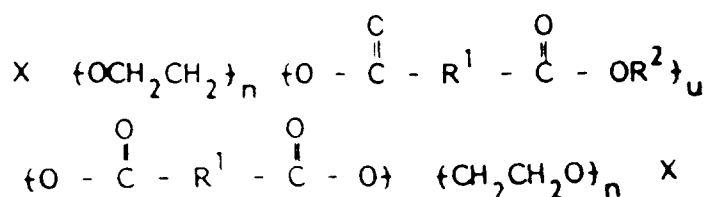
According to the present invention, the compositions I to IV which comprise a terephthalate-based polymer (Hoes<sup>®</sup> 3639) have lower viscosities than the composition V which is free of any terephthalate-based polymers. The above results surprisingly show that the use of terephthalate-based polymers in compositions according to the present invention reduces the viscosity of said compositions while maintaining physical stability.

## 45 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 a viscosity-reducing amount of a terephthalate-based polymer.
2. An emulsion according to claim 1 wherein said terephthalate-based polymer is a polymer according to the formula:

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wherein X is methyl, n is 16, R<sup>1</sup> is 1,4-phenylene moiety, R<sup>2</sup> is 1,2-propylene moiety and u is essentially between 3 and 5.

3. An emulsion according to any of the preceding claims wherein the level of said terephthalate-based polymer is from 0.05 % to 5 % by total weight of the emulsion, preferably from 0.1 % to 2 %.
4. 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 %.
5. 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.
6. 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.
7. An emulsion according to any of the preceding claims which further comprises hydrogen peroxide or a water soluble source thereof and a bleach activator wherein said bleach activator is emulsified by the nonionic surfactants.
8. An emulsion according to claim 7 which comprises from 0.5% to 20% by weight of the total emulsion of said hydrogen peroxide.
9. An emulsion according to claims 7 and 8 wherein said bleach activator is acetyl triethyl citrate.
10. 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.
11. A detergent composition comprising an emulsion according to any of the preceding claims.





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 87 0104

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	EP-A-0 199 403 (THE PROCTER & GAMBLE COMPANY) * claim 1 * ---	1,2	C11D1/825 C11D3/37 C11D3/39
D,A	EP-A-0 241 984 (THE PROCTER & GAMBLE COMPANY) * claims 1,7 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 November 1993	Examiner VAN BELLINGEN, I
<b>CATEGORY OF CITED DOCUMENTS</b> 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			