

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 576 777 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

04.02.1998 Bulletin 1998/06

(51) Int Cl.⁶: **C11D 3/37**

(21) Application number: **92870095.4**

(22) Date of filing: **29.06.1992**

(54) **Concentrated aqueous liquid detergent compositions comprising polyvinylpyrrolidone and a terephthalate-based soil release polymer**

Polyvinylpyrrolidon und schmutzabweisendes Polymer auf Basis von Polyterephthalate enthaltende konzentrierte wässrig-flüssige Waschmittelzusammensetzungen

Compositions détergentes liquides aqueuses concentrées contenant polyvinylpyrrolidone et un polymère antisalissure à base de polytéraphtate

(84) Designated Contracting States:
DE ES FR GB IT

(43) Date of publication of application:
05.01.1994 Bulletin 1994/01

(73) Proprietor: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(72) Inventors:
• **Cauwberghs, Serge Gabriel Pierre Roger**
B-9100 Nieuwkerken (BE)

• **Depoot, Karel Jozef Maria**
B-8790 Waregem (BE)

(74) Representative: **Canonici, Jean-Jacques et al**
Procter & Gamble European Technical Center
N.V.
Temselaan 100
1853 Strombeek-Bever (BE)

(56) References cited:
EP-A- 0 199 403 **EP-A- 0 262 897**
EP-A- 0 359 491 **GB-A- 2 137 221**

EP 0 576 777 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

DescriptionTechnical field

5 The present invention relates to concentrated aqueous liquid detergent compositions. The compositions according to the present invention comprise polyvinylpyrrolidone and a terephthalate-based soil release polymer.

Background of the invention

10 It is widely known in the art to use various polymers in liquid detergent compositions. The use of polyvinyl pyrrolidone in detergent compositions, mainly for fabric care properties, has been described for instance in EP-A-262 897, EP-A-327 927 and EP-A-203 486. These documents encompass the use of polyvinylpyrrolidone in liquid detergent compositions.

15 Terephthalate-based soil release polymers have also been described in the art, for instance in US-A-4,116,885, US-A-4,132,680, EP-A-185 427, EP-A-199 403, EP-A-241 985 and EP-A-241 984. These documents also encompass liquid detergent compositions.

A new trend in the field of detergent compositions is the formulation of so-called concentrated detergents. In the context of liquid aqueous detergents, this refers to products comprising less water and a higher total amount of active ingredients. The formulation of such concentrated detergent compositions raises specific problems.

20 In particular, formulating concentrated aqueous liquid detergent compositions comprising polyvinylpyrrolidone raises a problem in that polyvinylpyrrolidone becomes less soluble in such concentrated detergent matrixes as their water content drops. The same problem occurs with terephthalate-based soil release polymers. These problems result in products which have a hazy appearance and present physical stability issues.

25 It has now surprisingly been found that both polyvinylpyrrolidone and terephthalate-based soil release polymers can improve each others' solubility in said concentrated aqueous liquid detergent matrix. Thus, physically stable aqueous liquid detergent compositions can be formulated which comprise both said polymers whereas they would be less stable if they only contained either one.

30 Combinations of polyvinylpyrrolidone and terephthalate-based soil release polymers have been disclosed in GB-A-2 137 221 in the context of granular detergent compositions. In this context, the polyvinylpyrrolidone is said to protect the terephthalate soil release polymer against attack by alkaline builders.

Summary of the invention

35 The compositions according to the present invention are concentrated liquid detergent compositions comprising conventional detergency ingredients selected from surfactants and builders and mixtures thereof, from 2 % to 35 % by weight of the total composition of water, from 0.05 % to 5 % by weight of the total composition of polyvinylpyrrolidone and from 0.05 % to 2 % by weight of the total composition of a terephthalate-based polymer.

Detailed description of the invention

40 The present invention comprises polyvinylpyrrolidone (A), a terephthalate-based soil release polymer (B) and conventional detergency ingredients (C).

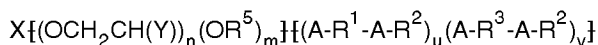
(A) Polyvinylpyrrolidone

45 The composition according to the invention comprises from 0.05 % to 5 % by weight of polyvinylpyrrolidone, preferably from 0.25 % to 2 %. Preferred polyvinylpyrrolidone for use herein have a molecular weight of from 1000 to 100 000, preferably from 1500 to 20000, most preferably from 2500 to 15000.

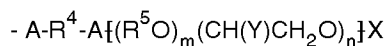
(B) Terephthalate-based soil release polymer

50 The compositions according to the present invention comprise from 0.05 % to 2 % by weight of the total composition, preferably from 0.1 % to 0.5 % of a terephthalate-based soil release polymer. Such soil release polymers have been extensively described in the art, for instance in US-A-4,116,885, US-A-4,132,680, EP-A-185 427, EP-A-199 403, EP-A-241 985 and EP-A-241 984.

55 Suitable polymers for use herein include polymers of the formula:



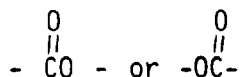
5



In this formula, the moiety $\{(A-R^1-A-R^2)_u(A-R^3-A-R^2)_v\}A-R^4-A-$ 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.

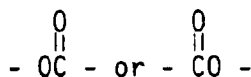
10 The linking A moieties are essentially

15



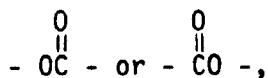
moieties, i.e. the compounds of the present invention are polyesters. As used herein, the term "the A moieties are essentially

20



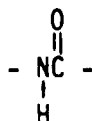
moieties" refers to compounds where the A moieties consist entirely of moieties

25



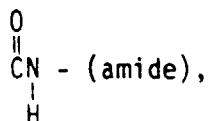
30 or are partially substituted with linking moieties such as

35



or

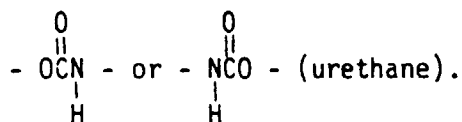
40



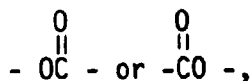
45

and

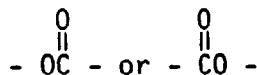
50



55 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



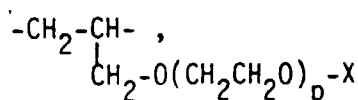
i.e., each A is either



The R¹ moieties are essentially 1,4-phenylene moieties. As used herein, the term "the R¹ moieties are essentially 1,4-phenylene moieties" refers to compounds where the R¹ moieties consist entirely of 1,4-phenylene moieties, or are partially substituted with other arylene or alkarylene moieties, alkenylene 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. Alkenylene 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 R¹ 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 R¹ comprise from 50 to 100% 1,4-phenylene moieties (from 0 to 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 R¹ moieties consist entirely of (i.e., comprise 100%) 1,4-phenylene moieties, i.e. each R¹ moiety is 1,4-phenylene.

The R² moieties are essentially ethylene moieties, or substituted ethylene moieties having C₁-C₄ alkyl or alkoxy substituents. As used herein, the term "the R² moieties are essentially ethylene moieties, or substituted ethylene moieties having C₁-C₄ alkyl or alkoxy substituents" refers to compounds of the present invention where the R² moieties consist entirely of ethylene, or substituted ethylene moieties, or are partially substituted with other compatible moieties. Examples of these other moieties include linear C₃-C₆ 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-dimethylenecyclohexylene, polyoxyalkylated 1,2-hydroxyalkylenes such as



and oxyalkylene moieties such as -CH₂CH₂OCH₂CH₂OCH₂CH₂- or -CH₂CH₂OCH₂CH₂-.

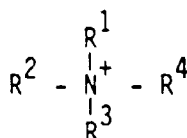
For the R² moieties, the degree of partial substitution with these other moieties should be such that the soil release properties of the compounds are not adversely affected to any great extent. Generally, the degree of partial substitution which can be tolerated will depend upon the backbone length of the compound, i.e., longer backbones can have greater partial substitution. Usually, compounds where the R² comprise from 20 to 100% ethylene, or substituted ethylene moieties (from 0 to 80% other 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 (-CH₂CH₂OCH₂CH₂-) 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 typically formed from glycols in side reactions and are then incorporated into the polyester). Preferably, R² comprises from 80 to 100% ethylene, or substituted ethylene moieties, and from 0 to 20% other compatible moieties.

For the R² 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 R² moieties are 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^3 moieties, suitable substituted C_2 - C_{18} hydrocarbylene moieties can include substituted C_2 - C_{12} alkylene, alkenylene, arylene, alkarylene and like moieties. The substituted alkylene or alkenylene moieties can be linear, branched, or cyclic. Also, the R^3 moieties can be all the same (e.g. all substituted arylene) or a mixture (e.g. a mixture of substituted arylenes and substituted alkyls). Preferred R^3 moieties are those which are substituted 1,3-phenylene moieties.

The substituted R^3 moieties preferably have only one $-SO_3M$, $-COOM$, $-O\{(R^5O)_m(CH(Y)CH_2O)_n\}X$ or $-A\{(R^2-A-R^4-A)\}_w\{(R^5O)_m(CH(Y)CH_2O)_n\}X$ 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^+) and especially sodium (Na^+), as well as ammonium (NH_4^+). Also suitable are substituted ammonium cations having the formula:

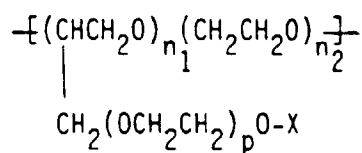


where R^1 and R^2 are each a C_1 - C_{20} hydrocarbyl group (e.g. alkyl, hydroxyalkyl) or together form a cyclic or heterocyclic ring of from 4 to 6 carbon atoms (e.g. piperidine, morpholine); R^3 is a C_1 - C_{20} hydrocarbyl group; and R^4 is H (ammonium) or a C_1 - C_{20} hydrocarbyl group (quat amine). Typical substituted ammonium cationic groups are those where R^4 is H (ammonium) or C_1 - C_4 alkyl, especially methyl (quat amine); R^1 is C_{10} - C_{18} alkyl, especially C_{12} - C_{14} alkyl; and R^2 and R^3 are each C_1 - C_4 alkyl, especially methyl.

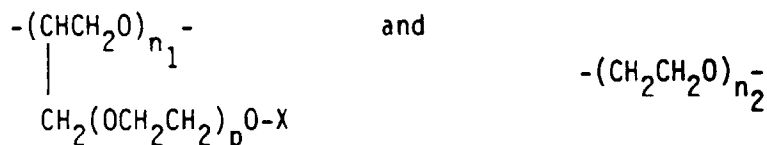
The R^3 moieties having $-A\{(R^2-A-R^4-A)\}_w\{(R^5O)_m(CH(Y)CH_2O)_n\}X$ substituents provide branched backbone compounds. R^3 moieties having $-A\{(R^2-A-R^4-A)\}_w-R^2-A$ moieties provide crosslinked backbone compounds. Indeed, syntheses used to make the branched backbone compounds typically provide 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 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 75% by weight of the moiety $\{(R^5O)_m(CH(Y)CH_2O)_n\}$ and most preferably 100% by weight (m is 0).

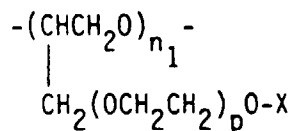
The Y substituents of each moiety $\{(R^5O)_m(CH(Y)CH_2O)_n\}$ are the ether moiety $-CH_2(OCH_2CH_2)_pO-X$, or are, more typically, a mixture of this ether moiety and H; p can range from 0 to 100, but is typically 0. When the Y substituents are a mixture, moiety $-(CH(Y)CH_2O)_n$ can be represented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



and $\text{-(CH}_2\text{CH}_2\text{O)}_{n_2}\text{-}$ moieties.

X can be H, C₁-C₄ alkyl or

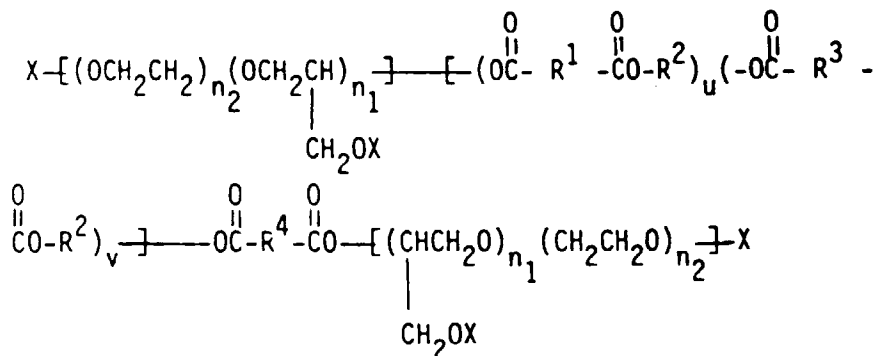


wherein R⁷ is C₁-C₄ alkyl. X is preferably methyl or ethyl, and most preferably methyl. The value for each n is at least 6, but is preferably at least 10. The value for each n usually ranges from 12 to 113. Typically, the value for each n is in the range of from 12 to 43.

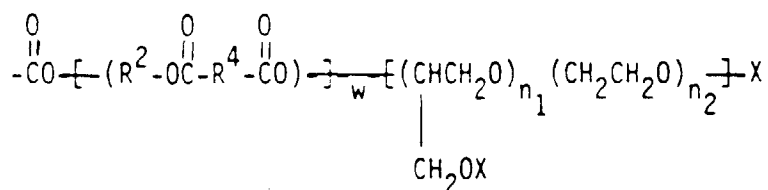
The backbone moieties $\{\text{A-R}^1\text{-A-R}^2\}$ and $\{\text{-A-R}^3\text{-A-R}^2\}$ can be mixed together or can form blocks of $\{\text{A-R}^1\text{-A-R}^2\}$ and $\{\text{A-R}^3\text{-A-R}^2\}$ moieties. It has been found that the value of u + v needs to be at least 3 in order for the compounds 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 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 50 to 250 ethylene terephthalate units. Typically, the sum of u + v ranges from 3 to 10 for the compounds of the present invention.

Generally, the larger the u + v value, the less soluble is the compound, especially when the R³ moieties do not have the substituents -COOM or -SO₃M. 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 R³ moieties have the substituent -A[(R²-A-R⁴-A) $\frac{1}{w}$ (R⁵O)_m(CH(Y)CH₂O)_n]X (branched backbone compounds) or -A[(R²-A-R⁴-A) $\frac{1}{w}$ R²-A- (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 3 to 25.

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



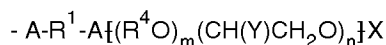
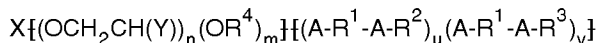
wherein the R¹ moieties are all 1,4-phenylene moieties; the R² moieties are essentially ethylene moieties, 1,2-propylene moieties or mixtures thereof; the R³ moieties are all potassium or preferably sodium 5-sulfo-1,3-phenylene moieties or substituted 1,3-phenylene moieties having the substituent



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 12 to 43; when w is 0, $u + v$ is from 3 to 10; when w is at least 1, $u + v + w$ is from 3 to 10.

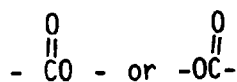
Particularly preferred block polyesters are those where v is 0, i.e. the linear block polyesters. For these most preferred linear block polyesters, u typically ranges from 3 to 8. The most water soluble of these linear block polyesters are those where u is from 3 to 5.

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

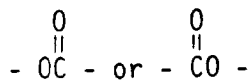


In this formula, the moiety $\{(\text{A-R}^1-\text{A-R}^2)_u(\text{A-R}^1-\text{A-R}^3)_v\}$ forms the oligomer or polymer backbone of the compounds. Groups $X\{(\text{OCH}_2\text{CH}(\text{Y}))_n(\text{OR}^4)_m\}$ and $\{(\text{R}^4\text{O})_m(\text{CH}(\text{Y})\text{CH}_2\text{O})_n\}\text{X}$ are generally connected at the ends of the oligomer/polymer backbone.

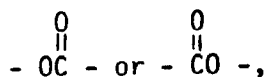
The linking A moieties are essentially or



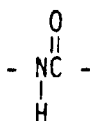
moieties, i.e. the compounds of the present invention are polyesters. As used herein, the term "the A moieties are essentially or



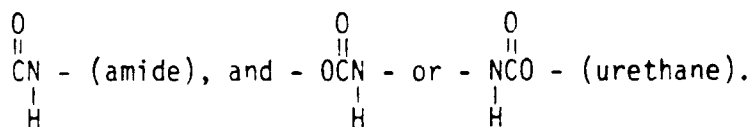
moieties" refers to compounds where the A moieties consist entirely of moieties



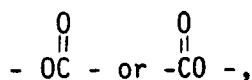
or are partially substituted with linking moieties such as



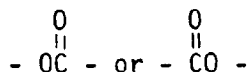
or



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



5 i.e., each A is either

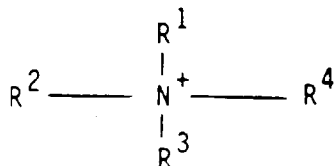


10

The R¹ moieties are essentially 1,4-phenylene moieties. As used herein, the term "the R¹ moieties are essentially 1,4-phenylene moieties" refers to compounds where the R¹ 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.

15 These other arylene, alkarylene, alkylene and alkenylene moieties can be unsubstituted or can have at least one -SO₃M, -COOM or -A-R⁷[A-R¹-A-R⁷-O]_w X substituent or at least one moiety -A-R⁷[A-R¹-A-R⁷-O]_w A- cross-linked to another R¹ moiety, wherein R⁷ is the moiety R² or R³; and w is 0 or at least 1. Preferably, these substituted R¹ moieties have only one -SO₃M, -COOM or -A-R⁷[A-R¹-A-R⁷-O]_w X 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⁺) and especially sodium (Na⁺), as well as ammonium (NH₄⁺). Also suitable are substituted ammonium cations having the formula:

25



30

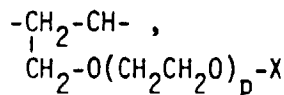
where R¹ and R² are each a C₁-C₂₀ hydrocarbyl group (e.g. alkyl, hydroxyalkyl) or together form a cyclic or heterocyclic ring of from 4 to 6 carbon atoms (e.g. piperidine, morpholine); R³ is a C₁-C₂₀ hydrocarbyl group; and R⁴ is H (ammonium) or a C₁-C₂₀ hydrocarbyl group (quat amine). Typical substituted ammonium cationic groups are those where R⁴ is H (ammonium) or C₁-C₄ alkyl, especially methyl (quat amine); R¹ is C₁₀-C₁₈ alkyl, especially C₁₂-C₁₄ alkyl; and R² and R³ are each C₁-C₄ alkyl, especially methyl.

35 The R¹ moieties having -A-R⁷[A-R¹-A-R⁷-O]_w X substituents provide branched backbone compounds. The R¹ moieties having -A-R⁷[A-R¹-A-R⁷-O]_w A- moieties provide cross-linked backbone compounds. Indeed, syntheses used to make the branched backbone compounds typically provide at least some cross-linked backbone compounds.

40 For the R¹ 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 R¹ comprise from 50 to 100% 1,4-phenylene moieties (from 0 to 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 R¹ moieties consist entirely of (i.e., comprise 100%) 1,4-phenylene moieties, i.e. each R¹ moiety is 1,4-phenylene.

50 The R² moieties are essentially substituted ethylene moieties having C₁-C₄ alkyl or alkoxy substituents. As used herein, the term "the R² moieties are essentially substituted ethylene moieties having C₁-C₄ alkyl or alkoxy substituents" refers to compounds of the present invention where the R² moieties consist entirely of substituted ethylene moieties, or are partially replaced with other compatible moieties. Examples of these other moieties include linear C₂-C₆ 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

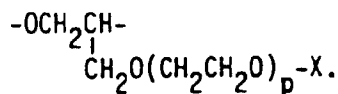
55



and oxyalkylene moieties such as $\text{-CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{-}$.

For the R^2 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^2 comprise from 20 to 100% substituted ethylene moieties (from 0 to 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^2 comprises from 80 to 100% substituted ethylene moieties, and from 0 to 20% other compatible moieties. For the R^2 moieties, suitable substituted ethylene moieties include 1,2-propylene, 1,2-butylene, 3-methoxy-1,2-propylene and mixtures thereof. Preferably, the R^2 moieties are essentially 1,2-propylene moieties.

The R^3 moieties are essentially the polyoxyethylene moiety $\text{-(CH}_2\text{CH}_2\text{O)}_q\text{-CH}_2\text{CH}_2\text{-}$. As used herein, the term "the R^3 moieties are essentially the polyoxyethylene moiety $\text{-(CH}_2\text{CH}_2\text{O)}_q\text{-H}_2\text{CH}_2\text{-}$ " refers to compounds of the present invention in which the R^3 moieties consist entirely of this polyoxyethylene moiety, or further include other compatible moieties. Examples of these other moieties include $C_3\text{-C}_6$ oxyalkylene moieties such as oxypropylene and oxybutylene, polyoxyalkylene moieties such as polyoxypropylene and polyoxybutylene, and polyoxyalkylated 1,2-hydroxyalkylene oxides such as

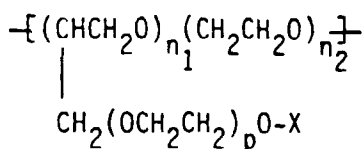


The degree of inclusion of these other moieties should be such that the soil release properties of the compounds are not adversely affected to any great extent. Usually, in compounds of the present invention, the polyoxyethylene moiety comprises from 50 to 100% of each R^3 moiety. Preferably, the polyoxyethylene moiety comprises from 90 to 100% of each R^3 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^3 moieties).

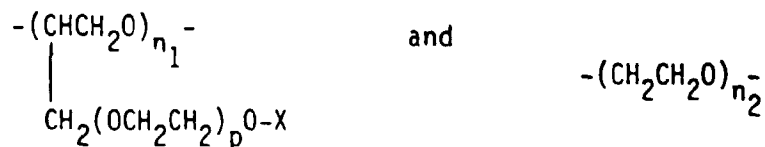
For the polyoxyethylene moiety, the value for q is at least 9, and is preferably at least 12. The value for q usually ranges from 12 to 180. Typically, the value for q is in the range of from 12 to 90.

The moieties $\text{-(R}^4\text{O)-}$ and $\text{-(CH(Y)CH}_2\text{O)-}$ of the moieties $\{(\text{R}^4\text{O})_m(\text{CH(Y)CH}_2\text{O})_n\}$ and $\{(\text{OCH(Y)CH}_2)_n(\text{OR}^4)_m\}$ can be mixed together or preferably form blocks of $\text{-(R}^4\text{O)-}$ and $\text{-(CH(Y)CH}_2\text{O)-}$ moieties. Preferably, the blocks of $\text{-(R}^4\text{O)-}$ moieties are located next to the backbone of the compound. When R^4 is the moiety $\text{-R}^2\text{-A-R}^5\text{-}$, m is 1; also, the moiety $\text{-R}^2\text{-A-R}^5\text{-}$ is preferably located next to the backbone of the compound. For R^4 , the preferred $C_3\text{-C}_4$ alkylene is C_3H_6 (propylene); when R^4 is $C_3\text{-C}_4$ alkylene, m is preferably from 0 to 10 and is most preferably 0. R^5 is preferably methylene or 1,4-phenylene. The moiety $\text{-(CH(Y)CH}_2\text{O)-}$ preferably comprises at least 75% by weight of the moiety $\{(\text{R}^4\text{O})_m(\text{CH(Y)CH}_2\text{O})_n\}$ and most preferably 100% by weight (m is 0).

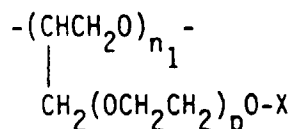
The Y substituents of each moiety $\{(\text{R}^5\text{O})_m(\text{CH(Y)CH}_2\text{O})_n\}$ are H, the ether moiety $\text{-CH}_2(\text{OCH}_2\text{CH}_2)_p\text{O-X}$, or a mixture of this ether moiety and H; p can range from 0 to 100, but is typically 0. Typically, the Y substituents are all H. When the Y substituents are a mixture of the ether moiety and H, the moiety $\text{-(CH(Y)CH}_2\text{O)-}$ 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 1 to 10. The moieties



can be mixed together, but typically form blocks of



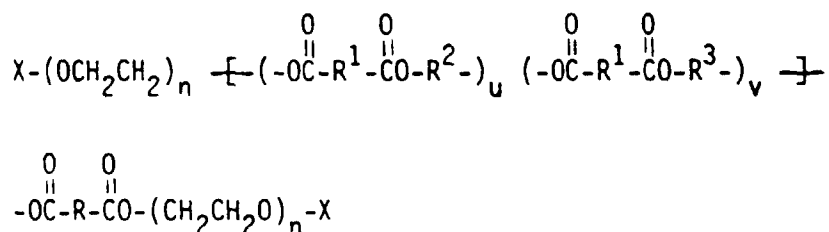
and $\text{-(CH}_2\text{CH}_2\text{O)}_{n_2}\text{-}$ moieties.
X can be H, $\text{C}_1\text{-C}_4$ alkyl or



wherein R^7 is $\text{C}_1\text{-C}_4$ alkyl. X is preferably methyl or ethyl, and most preferably methyl. The value for each n is at least 6, but is preferably at least 10. The value for each n usually ranges from 12 to 113. Typically, the value for each n is in the range of from 12 to 45.

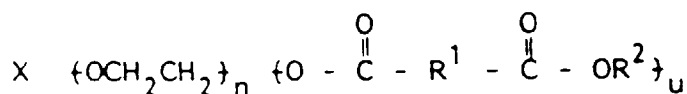
The backbone moieties $\{\text{A-R}^1\text{-A-R}^2\}$ and $\{\text{A-R}^1\text{-A-R}^3\}$ can form blocks of $\{\text{A-R}^1\text{-A-R}^2\}$ and $\{\text{A-R}^1\text{-A-R}^3\}$ moieties but are more typically randomly mixed together. For these backbone moieties, the average value of u can range from 2 to 50; the average value of v can range from 1 to 20; and the average value of $u + v$ can range from 3 to 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 5 to 20; the average value for v is from 1 to 10; and the average value for $u + v$ is from 6 to 30. Generally, the ratio of u to v is at least 1 and is typically from 1 to 6.

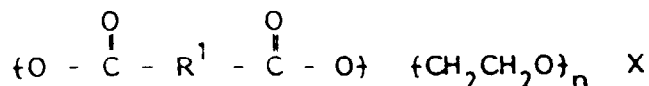
Preferred compounds in this class of polymers are polyesters having the formula:



wherein each R^1 is a 1,4-phenylene moiety; the R^2 are essentially 1,2-propylene moieties; the R^3 are essentially the polyoxyethylene moiety $(\text{CH}_2\text{H}_2\text{O})_q\text{-CH}_2\text{CH}_2\text{-}$; each X is ethyl or preferably methyl; each n is from 12 to 45; q is from 12 to 90; the average value of u is from 5 to 20; the average value of v is from 1 to 10; the average value of $u + v$ is from 6 to 30; the ratio u to v is from 1 to 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 10 to 50, preferably from 10 to 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 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 R¹ moieties are essentially 1,4-phenylene moieties. As used herein, the term "the R¹ moieties are essentially 1,4-phenylene moieties" refers to compounds where the R¹ 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 R¹ 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 R¹ comprise from 50% to 100% 1,4-phenylene moieties (from 0 to 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 R¹ moieties consist entirely of (i.e., comprise 100%) 1,4-phenylene moieties, i.e. each R¹ moiety is 1,4-phenylene.

For the R² 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 R² 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 75% to 100%, more preferably from 90% to 100% of the R² moieties are 1,2-propylene moieties.

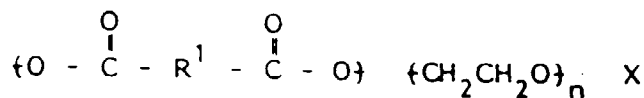
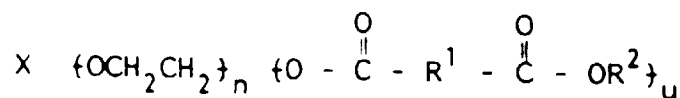
In general, soil release components which are soluble in cool (15°C) ethanol are also useful in compositions of the invention.

The value for n averages at least 10, but a distribution of n values is present. The value for each n usually ranges from 10 to 50. Preferably, the value for each n averages in the range of from 10 to 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 10°C to 15°C, preferably less than 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 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 EP-A-0 185 427. The most preferred polymers for use herein are polymers according to the formula:



wherein X is methyl, n is 16, R¹ is 1,4-phenylene moiety, R² is 1,2-propylene moiety and u is essentially between 3 and 5.

(C) Common detergency ingredients

The compositions according to the present invention are concentrated liquid detergents which comprise from 2 % to 35 % by weight of the total composition of water. Preferred compositions according to the present invention comprise from 5 % to 25 % by weight of the total composition of water.

The compositions according to the present invention further comprise conventional detergency ingredients. Such ingredients are selected from surfactants and builder and mixtures thereof.

Suitable surfactant materials for use herein include organic surface-active agent selected from nonionic, anionic, cationic and zwitterionic surface-active agents and mixtures thereof.

Suitable anionic surface-active salts are selected from the group of sulfonates and sulfates. The like anionic surfactants are well-known in the detergent art and have found wide application in commercial detergents.

Preferred anionic water-soluble sulfonate or sulfate salts have in their molecular structure an alkyl radical containing from 8 to 22 carbon atoms. Examples of such preferred anionic surfactant salts are the reaction products obtained by sulfating C₈-C₁₈ fatty alcohols derived from e.g. tallow oil, palm oil, palm kernel oil and coconut oil; alkylbenzene sulfonates wherein the alkyl group contains from about 9 to about 15 carbon atoms; sodium alkylglyceryl ether sulfonates; ether sulfates of fatty alcohols derived from tallow and coconut oils; coconut fatty acid monoglyceride sulfates and sulfonates; and water-soluble salts of paraffin sulfonates having from about 8 to about 22 carbon atoms in the alkyl chain. Sulfonated olefin surfactants as more fully described in e.g. U.S. Patent Specification 3,332,880 can also be used. The neutralizing cation for the anionic synthetic sulfonates and/or sulfates is represented by conventional cations which are widely used in detergent technology such as sodium, potassium or alkanolammonium.

A suitable anionic synthetic surfactant component herein is represented by the water-soluble salts of an alkylbenzene sulfonic acid, preferably sodium alkylbenzene sulfonates, preferably sodium alkylbenzene sulfonates having from 10 to 13 carbon atoms in the alkyl group. Another preferred anionic surfactant component herein is sodium alkyl sulfates having from 10 to 15 carbon atoms in the alkyl group.

The nonionic surfactants suitable for use herein include those produced by condensing ethylene oxide with a hydrocarbon having a reactive hydrogen atom, e.g., a hydroxyl, carboxyl, or amido group, in the presence of an acidic or basic catalyst, and include compounds having the general formula RA(CH₂CH₂O)_nH wherein R represents the hydrophobic moiety, A represents the group carrying the reactive hydrogen atom and n represents the average number of ethylene oxide moieties. R typically contains from 8 to 22 carbon atoms. They can also be formed by the condensation of propylene oxide with a lower molecular weight compound. n usually varies from 2 to 24.

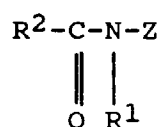
A preferred class of nonionic ethoxylates is represented by the condensation product of a fatty alcohol having from 12 to 15 carbon atoms and from 4 to 10 moles of ethylene oxide per mole of fatty alcohol. Suitable species of this class of ethoxylates include: the condensation product of C₁₂-C₁₅ oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of alcohol; the condensation product or narrow cut C₁₄-C₁₅ oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of fatty(oxo)alcohol; the condensation product of a narrow cut C₁₂-C₁₃ fatty(oxo)alcohol and 6,5 moles of ethylene oxide per mole of fatty alcohol; and the condensation products of a C₁₀-C₁₄ coconut fatty alcohol with a degree of ethoxylation (moles EO/mole fatty alcohol) in the range from 4 to 8. The fatty oxo alcohols while mainly linear can have, depending upon the processing conditions and raw material olefins, a certain degree of branching, particularly short chain such as methyl branching. A degree of branching in the range from 15% to 50% (weight%) is frequently found in commercial oxo alcohols.

Suitable cationic surfactants include quaternary ammonium compounds of the formula R₁R₂R₃R₄N⁺ where R₁, R₂ and R₃ are methyl groups, and R₄ is a C₁₂₋₁₅ alkyl group, or where R₁ is an ethyl or hydroxy ethyl group, R₂ and R₃ are methyl groups and R₄ is a C₁₂₋₁₅ alkyl group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds in which the aliphatic moiety can be straight or branched chain and wherein one of the aliphatic substituents contains from 8 to 24 carbon atoms and another substituent contains, at least, an anionic water-solubilizing group. Particularly preferred zwitterionic materials are the ethoxylated ammonium sulfonates and sulfates disclosed in U.S. Patents 3,925,262, Laughlin et al., issued December 9, 1975 and 3,929,678, Laughlin et al., issued December 30, 1975.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl or hydroxy alkyl moiety of from 8 to 28 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxy alkyl groups, containing from 1 to 3 carbon atoms which can optionally be joined into ring structures.

Also suitable are polyhydroxy fatty acid amide surfactants of the formula



wherein R¹ is H, C₁₋₄hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R₂ is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R₁ is methyl, R₂ is a straight C₁₁₋₁₅ alkyl or alkenyl chain or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula R-CH(COOH)CH₂(COOH) wherein R is C₁₀₋₂₀ alkyl or alkenyl, preferably C₁₂₋₁₆, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US-A-4,663,071

Suitable fatty acid builders for use herein are saturated or unsaturated C₁₀₋₁₈ fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

A preferred builder system for use herein consists of a mixture of citric acid, fatty acids and succinic acid derivatives described herein above. The builder system according to the present invention preferably represents from 5% to 35% by weight of the total composition.

The compositions according to the invention preferably comprise enzymes. Suitable enzymes for use herein are protease, lipases, cellulases and amylases and mixtures thereof. The compositions according to the present invention may also comprise an enzyme stabilizing system. Any conventional enzyme stabilizing system is suitable for use herein, and preferred enzyme stabilizing systems are based on boric acid or derivatives thereof, 1,2-propanediol, carboxylic acids, and mixtures thereof.

The compositions herein can contain a series of further, optional ingredients. Examples of the like additives include solvents, alkanolamines, pH adjusting agents, suds regulants, opacifiers, agents to improve the machine compatibility in relation to enamel-coated surfaces, perfumes, dyes, bactericides, brighteners and softening agents.

The present invention is further illustrated in the following examples.

Examples

	Weight %	
	I	II
Alkyl benzene sulfonate	18	6

(continued)

		Weight %	
		I	II
5	C13-15 Alkyl 3 ethoxylate sulfate	-	12
	C13-15 alcohol 7 ethoxylate	13	5
	C12-14 N-methyl glucosamide	-	9
10	Topped palm kernel fatty acid	11	11
	Dodecyl succinic acid anhydride	4.2	-
	Citric acid	1.8	5
	Di-ethylene triamine pentamethylene phosphonic acid	1	1
15	Ethanol	1	2
	Propane diol	11	9.8
	Sodium hydroxide	0.6	-
	Potassium hydroxide	2.2	-
20	Monoethanolamine	9	12.6
	Enzymes	0.7	1.5
25	Boric acid	1.2	2
	Calcium chloride	0.02	-
	Ethoxylated tetraethylene pentamine	0.5	0.5
	Perfume	0.6	0.5
30	PVP	0.5	1.0
	Terephthalate-based polymer	0.46	0.46
	Water	23	19
35	Minors	up to 100 %	

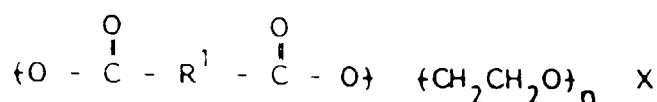
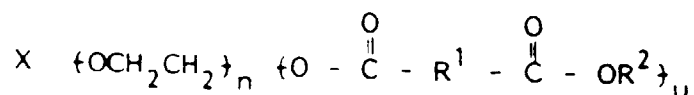
The PVP used in both examples is Luviskol[®] K12, from BASF (MW 2500). The terephthalate polymer used in both examples is the preferred polymer described in page 17 hereinbefore, where X is Me, n is 16, R¹ is 1,4-phenylene, R² is 1,2-propylene, and u is essentially between 3 and 5.

Similar compositions were also made, comprising either no terephthalate-based soil release polymer, or neither PVP nor terephthalate-based soil release polymer. All the compositions were then put on storage at room temperature (about 20°C). Compositions freshly made all had the same appearance. After 2 weeks storage, it was observed that compositions comprising neither polymers were clear, compositions comprising no terephthalate-based soil release polymer were hazy, and compositions I and II were clear.

Claims

1. A concentrated liquid detergent composition comprising conventional detergency ingredients selected from surfactants and builders and mixtures thereof and from 2 % to 35 % by weight of the total composition of water, characterized in that it comprises from 0.05 % to 5 % by weight of the total composition of polyvinylpyrrolidone and from 0.05 % to 2 % by weight of the total composition of a terephthalate-based polymer.
2. A liquid detergent composition according to claim 1 which comprises from 5 % to 25 % by weight of the total composition of water.
3. A composition according to claims 1 or 2, which comprises from 0.25 % to 2 % by weight of the total composition of said polyvinylpyrrolidone.

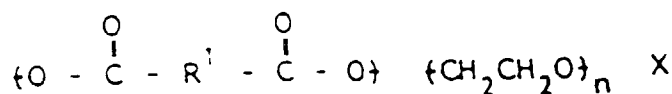
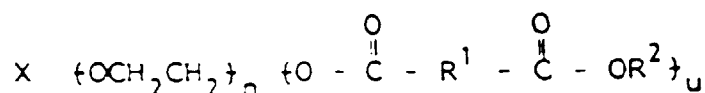
4. A composition according to any of the preceding claims wherein said polyvinylpyrrolidone has a molecular weight of 2500 to 15000.
5. A composition according to any of the preceding claims which comprises from 0.1 % to 0.5 % by weight of said terephthalate-based polymer.
6. A composition according to any of the preceding claims wherein said terephthalate-based polymer is a polymer according to the formula:



wherein X is methyl, n is 16, R¹ is 1,4-phenylene moiety, R² is 1,2-propylene moiety and u is essentially between 3 and 5.

Patentansprüche

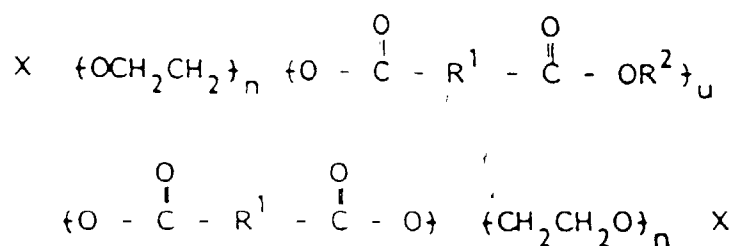
1. Konzentrierte, flüssige Waschmittelzusammensetzung, umfassend herkömmliche Waschmittelbestandteile, gewählt aus Tensiden und Buildern sowie Mischungen hiervon, und 2 bis 35 Gew. -% der gesamten Zusammensetzung an Wasser, dadurch gekennzeichnet, daß sie 0.05 bis 5 Gew.-% der gesamten Zusammensetzung an Polyvinylpyrrolidon und 0.05 bis 2 Gew.-% der gesamten Zusammensetzung eines Polymeren auf Terephthalatbasis umfaßt.
2. Flüssige Waschmittelzusammensetzung nach Anspruch 1, umfassend 5 bis 25 Gew.-% der gesamten Zusammensetzung an Wasser.
3. Zusammensetzung nach den Ansprüchen 1 oder 2, umfassend 0,25 bis 2 Gew.% der gesamten Zusammensetzung an dem Polyvinylpyrrolidon.
4. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei das Polyvinylpyrrolidon ein Molekulargewicht von 2500 bis 15000 aufweist.
5. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend 0.1 bis 0.5 Gew.-% des Polymeren auf Terephthalatbasis.
6. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei das Polymer auf Terephthalatbasis ein Polymer gemäß der Formel



ist, worin X Methyl ist, n 16 ist, R¹ eine 1,4-Phenylengruppe ist, R² eine 1,2-Propylengruppe ist und u im wesentlichen zwischen 3 und 5 liegt.

Revendications

1. Composition détergente liquide concentrée comprenant des ingrédients de détergence classiques sélectionnés parmi les agents tensioactifs, les adjuvants et leurs mélanges et 2 à 35% en poids de la composition totale d'eau, caractérisée en ce qu'elle comprend 0,05 à 5% en poids de la composition totale de polyvinylpyrrolidone et 0,05 à 2% en poids de la composition totale d'un polymère à base de téréphtalate.
2. Composition détergente liquide selon la revendication 1, qui comprend 5 à 25% en poids de la composition totale d'eau.
3. Composition selon la revendication 1 ou 2, qui comprend 0,25 à 2% en poids de la composition totale de ladite polyvinylpyrrolidone.
4. Composition selon l'une quelconque des revendications précédentes, dans laquelle ladite polyvinylpyrrolidone a un poids moléculaire de 2500 à 15000.
5. Composition selon l'une quelconque des revendications précédentes, qui comprend 0,1 à 0,5% en poids dudit polymère à base de téréphtalate.
6. Composition selon l'une quelconque des revendications précédentes, dans laquelle ledit polymère à base de téréphtalate est un polymère répondant à la formule :



dans laquelle X est un groupe méthyle, n est égal à 16, R¹ est un radical 1,4phénylène, R² est un radical 1,2-propylène et u est essentiellement compris entre 3 et 5.