

(19)



Europäisches Patentamt

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(11)

EP 0 693 116 B1

(12)

EUROPEAN PATENT SPECIFICATION

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

07.01.1998 Bulletin 1998/02

(21) Application number: **94912957.1**

(22) Date of filing: **05.04.1994**

(51) Int Cl.⁶: **C11D 3/00, C11D 3/39**

(86) International application number:
PCT/US94/03727

(87) International publication number:
WO 94/24250 (27.10.1994 Gazette 1994/24)

(54) **COMPOSITION AND PROCESS FOR INHIBITING DYE TRANSFER**

**ZUSAMMENSETZUNG UND VERFAHREN ZUR VERBINDERUNG DER
FARBSTOFFÜBERTRAGUNG**

COMPOSITION ET PROCEDE D'INHIBITION DU TRANSFERT DE COULEUR

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

(30) Priority: **08.04.1993 US 45742**

(43) Date of publication of application:
24.01.1996 Bulletin 1996/04

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(56) References cited:
EP-A- 0 306 089 **EP-A- 0 384 503**
US-A- 4 077 768

EP 0 693 116 B1

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DescriptionFIELD OF THE INVENTION

5 The invention pertains to prevention of dye transfer among fabrics when said fabrics are treated in an aqueous medium, such as in laundering.

BACKGROUND OF THE INVENTION

10 This invention relates to a process for prevention of dye transfer among fabrics in an aqueous bath (particularly a washing solution) by decolorizing dyes which bleed from fabrics into the solution, and to compositions for use in carrying out the process.

15 One of the more annoying problems in domestic washing procedures is the staining of fabrics by fugitive dyes from other fabrics in the same wash. This is the problem known as "dye transfer." It will be convenient, herein, to include within the meaning of this term the transfer of coloring matter in the "dirt" on fabrics which may likewise be transferred to other articles in the wash.

20 One way of overcoming this problem is to bleach the fugitive dyes washed out of dyed fabrics while in the wash liquor, and before they have an appreciable opportunity to become attached to other articles in the wash. Clearly it is important at the same time not to bleach the dyes actually remaining on the fabrics, that is, not to cause color damage.

25 For many years detergent compositions have contained bleaching agents to decolorize stains such as tea, coffee, wine and fruit stains on household laundry. Most commonly sodium perborate or like compounds (salts) which release hydrogen peroxide in the wash liquor have been used. These compounds are effective bleaches mainly at high washing temperatures near the boil. Persulfates, e.g., Oxone (Trade Name), although sometimes deemed low temperature bleaches, in fact have little effect at low temperatures in washing conditions and may be included in this class.

30 As most colored articles are not washed at such temperatures, these bleaches in practice seldom harm dyed fabrics, but they are not effective dye-transfer-inhibitors at temperatures at which colored fabrics are washed.

35 Hydrogen-peroxide-releasing bleaching agents can be made more effective at lower temperatures by adding "activators," which are usually organic acid anhydrides, esters or imides. These activators have to be present in about the same molar proportion as the perhydrate bleaching agent and are not regenerated in use. Thus they are not catalysts. Furthermore the activated bleaching agents attack intentional colors (dyes) as well as unintentional colors (stains) on fabrics, and yet, perhaps because their action upon dispersed or dissolved dyes is too slow, they are not very effective as dye transfer inhibitors.

40 Again, low-temperature bleaching can be effected using more aggressive oxidizing agents, such as percarboxylic acid bleaches. These may cause color damage and even damage to some fibers, and yet are not very effective dye transfer inhibitors. Chlorine bleaches are reasonably effective dye transfer inhibitors, but are generally very harmful to colored fabrics.

45 U.S. Pat. 4,077,768, Johnston et al., issued March 7, 1978 discloses a process for washing or bleaching fabrics wherein dye transfer among fabrics is inhibited by use of an oxidizing agent, preferably hydrogen peroxide, and a bleaching agent selected from iron porphins, haemin chlorides and iron phthalocyanines. This patent teaches that in order to maintain effectiveness of the catalyst in the dye bleaching process, the hydrogen peroxide should be released into the solution at a rate not substantially greater than it is used up by reaction with substances in the solution. It is postulated by Johnston et al. that excess hydrogen peroxide will react with an intermediate substance formed by the catalyst, thereby forming molecular oxygen which is ineffective as a bleaching agent, and which destroys unchanged catalyst. This phenomenon is illustrated in Example 1(b) of Johnston et al. wherein all of the hydrogen peroxide was added to a dye solution in one aliquot, thereby achieving a molar ratio of hydrogen peroxide to catalyst of about 50:1. The result was that no oxidation of the dye occurred. On the other hand, when the hydrogen peroxide was added dropwise over a period of five minutes, effective dye bleaching occurred. Johnston et al. teach, therefore, that hydrogen peroxide should be added to the catalyst containing solution at substantially the same rate it is being used up in the bleaching process. Johnston et al. teach further that if one wishes to use a solid source of hydrogen peroxide and add all of it to the bleaching solution in one aliquot, the solid source should be coated with a material (e.g., tallow alcohol) to insure that the hydrogen peroxide will be released into the solution at a controlled rate so the hydrogen peroxide is used up in the bleaching process at substantially the same rate it is being released from the solid source.

50 It is the object of the present invention to provide a means to achieve dye transfer inhibition with hydrogen peroxide and a bleaching catalyst without the need to take measures for controlled release of hydrogen peroxide into the bleaching solution.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has now been found that if dye transfer inhibition is measured by actual transfer of dye from colored to white fabrics rather than by color measurement of the bleaching of dye in solution, some inhibition of dye transfer is found to occur at a 50:1 molar ratio of hydrogen peroxide to metalloporphin catalyst. It has been further discovered, however, that dye transfer inhibition performance can be improved by operating within a range of molar ratios of hydrogen peroxide to catalyst which is below 50:1 and within a specified pH range. Excellent dye transfer inhibition is achieved without controlling the rate of hydrogen peroxide addition. The pH should be in the range of from about 9 to about 10 (preferably about 9.3 to about 9.7) and the molar ratio of hydrogen peroxide to catalyst should be from about 20:1 to 40:1 (preferably 25:1 to 35:1).

Accordingly, in its process aspect, the present invention is a process for treating fabrics, which process comprises contacting said fabrics in an aqueous solution comprising:

- a) a bleaching catalyst selected from the group consisting of metalloporphin and metallo porphyrins and their water-soluble and water-dispersible derivatives, and b) hydrogen peroxide;

the concentration of a) being from about 0.02 to about 10 (preferably about 1 to about 10) micromoles (μM) per liter and the initial concentration of hydrogen peroxide in solution being such that the molar ratio of said hydrogen peroxide to said catalyst is from about 20:1 to about 40:1, the said solution having a pH of from about 9 to about 10.

The process herein is preferably carried out at 5°C to about 75°C, especially from about 20°C to 60°C, but the catalysts are effective at up to about 95°C. The process is typically carried out in the process of laundering fabrics. In addition to being soiled with materials which may contain color bodies, typically at least some of the fabrics in a load of laundry are colored, i.e., contain dyes which may bleed into the laundering solution and onto other fabrics.

The present invention also encompasses compositions suitable for use in carrying out the process. The said compositions comprise:

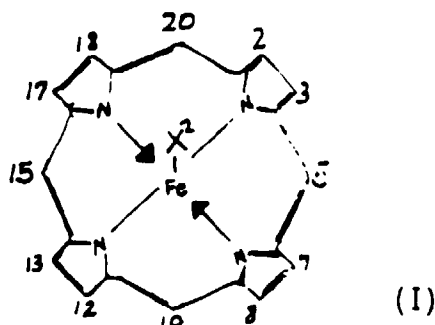
- a) a bleaching catalyst selected from the group consisting of metalloporphins and metallo porphyrins and their water-soluble and water-dispersible derivatives, and
b) a bleaching agent selected from the group consisting of hydrogen peroxide, and water-soluble sources of hydrogen peroxide wherein the water solubility of the said source is such that substantially all of the hydrogen peroxide in said source is released quickly into solution when the composition is added to water, the molar ratio of hydrogen peroxide to catalyst in said composition being from about 20:1 to about 40:1.

The said composition should have a pH of from about 9 to about 10 when dissolved in water at a concentration sufficient to provide from about 0.02 to about 10 μM per liter of said bleaching catalyst.

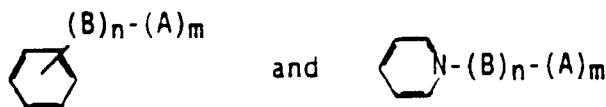
Bleaching Catalyst

The bleaching catalysts of the present invention are selected from metalloporphins, metalloporphyrins, and their water-soluble or water-dispersible derivatives.

The metalloporphin structure may be visualized as indicated in Formula I below. In Formula I the atom positions of the porphin structure are numbered conventionally and the double bonds are put in conventionally. In Formula II, the double bonds have been omitted in the drawing of the structure, but are actually present as in I.



Preferred metalloporphin structures are those substituted at one or more of the 5, 10, 15 and 20 carbon positions of Formula I (meso positions), with a phenyl or pyridyl substituent selected from the group consisting of

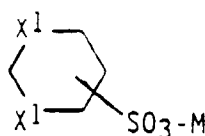


10 wherein n and m may be 0 or 1; A may be sulfate, sulfonate, phosphate or carboxylate groups; and B is C₁-C₁₀ alkyl, polyethoxy alkyl or hydroxy alkyl.

Preferred molecules are those in which the substituents on the phenyl or pyridyl groups are selected from the group consisting of

-CH₃, -C₂H₅, -CH₂CH₂CH₂SO₃⁻, -CH₂-⁻, and -CH₂CH(OH)CH₂SO₃⁻, -SO₃⁻

15 A particularly preferred metalloporphin is one in which the molecule is substituted at the 5, 10, 15, and 20 carbon positions with the substituent.

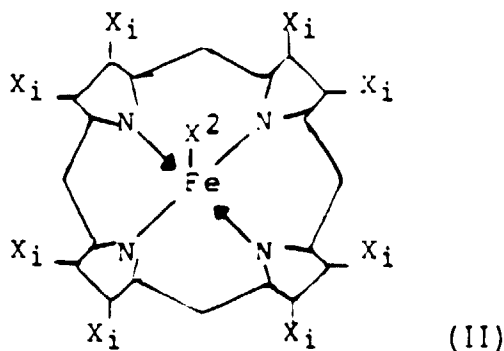


25 This preferred compound is known as metallo tetrasulfonated tetraphenylporphin. The symbol X¹ is (-CY-) wherein each Y, independently, is hydrogen, chlorine, bromine or meso substituted alkyl, cycloalkyl, aralkyl, aryl, alkaryl or heteroaryl. M is hydrogen or a neutralizing metal ion, preferably sodium.

The symbol X² of Formula I represents an anion, preferably OH⁻ or Cl⁻. The compound of Formula I may be substituted at one or more of the remaining carbon positions with C₁-C₁₀ alkyl, hydroxyalkyl or oxyalkyl groups.

30 Porphin derivatives also include chlorophylls, chlorines, i.e., isobacterio chlorines and bacteriochlorines.

Metalloporphyrin and water-soluble or water-dispersible derivatives thereof have a structure given in Formula II.



where the symbol X_i can be alkyl, alkylcarboxy, alkylhydroxyl, vinyl, alkenyl, alkylsulfate, alkylsulfonate, sulfate, sulfonate.

40 The symbol X² of Formula II represents an anion, preferably OH⁻ or Cl⁻.

50 Bleaching Agents

The bleaching agents for the method and compositions of the invention are hydrogen peroxide itself (when practicable) or solid sources of hydrogen peroxide, e.g., persalts such as sodium or potassium perborate, percarbonate and perpolyphosphates, or addition products such as the addition product of hydrogen peroxide and urea. The lithium, calcium or magnesium persalts can also be used. When catalyzed, hydrogen peroxide becomes a very effective dye transfer inhibitor, and yet causes practically no attack on dyes actually on fabrics.

Detergent Compositions

The fabric treatment process of the invention is conveniently carried out in the course of a washing process, and the treatment bath as well as the compositions of the invention can contain the usual components of detergent compositions in the usual amounts. In addition to the essential bleaching agent and bleaching catalyst, detergent compositions of the invention typically contain from 1% to 60% (preferably 5 to 30%) of a detergent surfactant. The detergent compositions herein are in the form of granules or solids, and the source of hydrogen peroxide is an addition compound of hydrogen peroxide. In such compositions, the bleaching catalyst is usually present in an amount of from about 0.01% to about 1%, preferably from about 0.05% to about 0.5%. The source of hydrogen peroxide is present in an amount so as to provide a molar ratio of hydrogen peroxide to catalyst of from about 20:1 to about 40:1. In a detergent composition intended for use at 0.10% concentration, using sodium perborate monohydrate as the source of hydrogen peroxide and iron tetrasulfonated tetraphenyl porphyrin (FeTPPS) as the catalyst the amount of sodium perborate monohydrate will be present in the composition at from about 0.1% to about 2% and the FeTPPS will be present at about 0.05 to about 0.5%.

When the granular composition is dissolved in water to form a wash solution, it is important that the hydrogen peroxide source dissolve quickly to achieve the desired solution ratio of hydrogen peroxide to catalyst. The product should therefore be formulated so the hydrogen peroxide source will be completely dissolved, i.e., will release all of its hydrogen peroxide into the solution, within two minutes at the intended wash temperature. This can be achieved by choice of a hydrogen peroxide source having inherently quick dissolving properties at the desired fabric treatment temperature, and/or using small particle size to enhance rate of solution. Particularly preferred hydrogen peroxide sources because of their high solubility over a wide temperature range are sodium perborate monohydrate and sodium percarbonate.

The surfactant can be selected from anionics, nonionics, zwitterionics, amphoterics, cationics and mixtures thereof.

Water-soluble salts of the higher fatty acids, i.e., "soaps," are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₁₂-C₁₈ carbon atoms) such as those produced by reducing the glycerides to tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 10 to about 16 carbon atoms, in straight chain or branched chain configuration, i.e., see U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14, abbreviated C₁₁₋₁₄ LAS.

Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

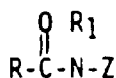
Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Water-soluble nonionic surfactants are also useful in the instant compositions. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 80 moles of ethylene oxide per mole of alkyl phenol.

Included are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol.

Other types of nonionic surfactants useful herein are polyhydroxy fatty acid amides of the formula



wherein R is C₉-C₁₇ alkyl or alkenyl, R₁ is methyl and Z is glyceryl derived from a reduced sugar or alkoxyated derivative thereof. Examples are N-Methyl N-1-deoxyglucityl cocoamide and N-Methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known, e.g., see U.S. Pat. 2,965,576, Wilson, issued December 20, 1960 and U.S. Pat. 2,703,798, Schwartz, issued March 8, 1955.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred nonionic surfactants are of the formula R¹(OC₂H₄)_nOH, wherein R₁ is a C₁₀-C₁₆ alkyl group or a C₈-C₁₂ alkyl phenyl group, and n is from 3 to about 80.

Particularly preferred are condensation products of C₁₂-C₁₅ alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C₁₂-C₁₃ alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Amphoteric surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms. See U.S. Pat. 3,929,678, Laughlin et al., issued December 30, 1975. Zwitterionic surfactants are sometimes classified as a type of amphoteric surfactants.

Cationic surfactants can also be included in the present detergent compositions. Cationic surfactants comprise a wide variety of compounds characterized by one or more organic hydrophobic groups in the cation and generally by a quaternary nitrogen associated with an acid radical. Pentavalent nitrogen ring compounds are also considered quaternary nitrogen compounds. Halides, methyl sulfate and hydroxide are suitable balancing anions for such compounds. Tertiary amines can have characteristics similar to cationic surfactants at washing solution pH values less than about 8.5. A more complete disclosure of these and other cationic surfactants useful herein can be found in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Cationic surfactants are often used in detergent compositions to provide fabric softening and/or antistatic benefits. Antistatic agents which provide some softening benefit and which are preferred herein are the quaternary ammonium salts described in U.S. Patent 3,936,537, Baskerville, Jr., et al., issued February 3, 1976, which is incorporated herein by reference.

Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both incorporated herein by reference.

Further disclosures of surfactants are set forth in U.S. Pat. 3,644,961, Norris, issued May 23, 1972; U.S. Pat. 3,929,678, Laughlin et al., issued December 30, 1975; and U.S. 4,379,080, Murphy, issued April 5, 1983, all incorporated in their entirety herein by reference.

Compositions herein can also contain a variety of other components which are useful in the employment of said compositions.

Inorganic detergency builders useful in the compositions herein include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates (i.e., zeolites). Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions (hereinafter, collectively "borate builders"), can also be used. Preferably, non-borate builders are used in the compositions of the invention intended for use at wash conditions less than about 50°C, especially less than about 40°C.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range

1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck, incorporated herein by reference.

Organic detergency builders preferred for the purposes of the present invention include a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least two carboxylates. For example, citric acid is a useful organic builder.

Polycarboxylate builders can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates. A number of ether polycarboxylates have been disclosed for use as detergent builders. Examples of useful ether polycarboxylates include oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1965 and Lamberti et al., U.S. Patent 3,635,830, issued January 18, 1972, both of which are incorporated herein by reference.

Organic polycarboxylate builders also include the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples include the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, and nitrilotriacetic acid.

Detergency builders are useful for precipitating or chelating hardness ions (i.e., Ca^{2+} and Mg^{2+}) in water used in formulating the compositions herein and in wash solutions made with the compositions. Typically, builders are used at levels of from about 1% to about 40%, preferably from about 5% to about 30% in the compositions herein.

pH adjustment agents such as alkali metal hydroxides and organic and inorganic acids can be used to adjust the compositions to the pH desired. The composition should be formulated so as to produce a pH of from about 9 to about 11 when diluted for use in laundering.

Enzymes which attack soils and stains such as lipases, alkaline proteases and cellulases can be used, and enzyme stabilizers such as diethylaminoethanol can be used.

Soil release polymers such as block copolymers of ethylene terephthalate with polyethylene oxide or polypropylene oxide (see U.S. Pat. 3,959,230, Hayes, issued May 25, 1976 and incorporated by reference herein) can be used in the present compositions at levels of from about 0.1% to about 2%.

Materials which stabilize the bleaching catalyst, e.g., imidazole can be included in the compositions at levels of from about 0.005 to about 5%.

Various "non-bleach" types of dye transfer inhibition agents, e.g., polyvinylpyrrolidone and polyvinylpyridine-N-oxide can be used in combination with the dye transfer inhibition agents of the present invention.

Phenolic compounds such as sodium salt of phenol sulfonate can be used to accelerate the rate of dye bleaching by the compositions herein.

Other optional ingredients which can be present in the compositions herein include soil dispersing agents such as polyacrylic acid and polyaspartic acid and their salts (e.g., sodium or potassium salts) and tetraethylene-pentaamine ethoxylate (15-18 EO units). Optical brighteners, perfumes, and suds suppressants (e.g., fatty acids or silicones) can also be used.

Unless expressed otherwise, all percentages and ratios set forth herein are by weight.

The invention will be illustrated by the following non-limiting examples:

EXAMPLE I

This example illustrates the dye bleaching performance of tetrasulfonated tetraphenyl porphyrin (FeTPPS) at various pH's and ratios of hydrogen peroxide to catalyst.

Experimental Procedure:

10 grams of a non-bleach granular detergent is added to 1 liter of city water at 35°C (95°F) in a Tergotometer and agitated for 1 minute (75 RPM). Wash water pH is adjusted to desired value with HCl or NaOH and sodium perborate monohydrate and FeTPPS catalyst in the desired amount are added before the fabrics are added to the washing pot. 40 g of a variety fabrics, two 4x4 inch bleeding fabrics (Acid Red 151 dyed on to nylon fabric supplied by Textile Innovators, York, PA) and a 2x4 inch multi-fibre pickup swatch (obtained from Test Fabrics, Middlesex, NJ) are added to the pot and agitated (75 RPM) for 12 minutes at 35°C (95°F). All the fabrics are then hand squeezed to remove most of the water and rinsed twice with 1 liter of water at 21,1°C (70°F). The multifibre pickup swatches are dried at room temperature overnight and measured for the amount of dye transferred on to the cotton portion of the swatches from the bleeding fabric during the wash process. Amount of the dye transferred on to the pickup swatches is measured in L, a, b units using a Hunter Color Meter and the results are expressed in delta C units vs. the original unwashed cotton. The granular detergent used-in these experiments is substantially the same formula as that shown in Example

EP 0 693 116 B1

II, except that it does not contain perborate and FeTPPS.

Experimental Results:

Experiments are conducted with and without FeTPPS and the corresponding levels of perborate. The results are expressed in delta C units (ΔC). The lower the ΔC number, the better the dye transfer inhibition performance.

a) Variation in pH

Catalyst:	FeTPPS	1 ppm (1 μ M/liter)
Bleach:	sodium perborate	3.5 ppm (35 μ M/liter H_2O_2)
	ΔC	
pH	Control (no bleach/no catalyst)	H_2O_2 + Catalyst
7.5	12.04	7.43
8.5	12.56	5.01
9.5	12.61	1.04
10.5	12.37	4.17

b) Variation in H_2O_2 /catalyst ratio at pH 9.5 and 1 μ M/liter catalyst

Catalyst:	FeTPPS	1 ppm (1 μ M/liter)
Bleach:	Sodium perborate	1-5 ppm (10-50 μ M H_2O_2 / liter)
	Control	Molar Ratio H_2O_2 /FeTPPS
	(no bleach/no catalyst)	10:1 20:1 35:1 50:1
ΔC	12.61	5.32 2.66 1.04 2.84

EXAMPLE II

A granular laundry detergent of the present invention has the following formula:

Na linear $C_{12,3}$ alkylbenzene sulfonate	12.71
Na C_{14-15} alkyl sulfate	5.45
Na alumino silicate (zeolite)	25.40
Na carbonate	5.70
Na silicate	2.19
Citric acid	6.00
Protease (Alcalase)	0.90
Ammonium sulfate	2.00
Polyacrylic acid	3.27
Polyethylene glycol 8000	1.40
Optical brightener	0.27
Sodium sulfate	25.60
Iron tetrasulfonated tetraphenylporphin	0.10
Sodium perborate monohydrate	0.35
Moisture and misc.	to 100

When used at 0.10% concentration for laundering fabrics, excellent dye transfer inhibition performance is achieved.

Claims

1. A process for treating fabrics comprising the step of contacting said fabrics with an aqueous solution comprising

- a) a bleaching catalyst selected from the group consisting of iron porphins and iron porphyrins and their water-soluble and water-dispersible derivatives, and
- b) hydrogen peroxide;

characterised in that

the concentration of a) is from 0.02 to 10 μ Moles per liter and the concentration of hydrogen peroxide in solution is such that the molar ratio of said hydrogen peroxide to said catalyst is from 20:1 to 40:1, the said solution having a pH of from 9 to 10.

2. The process of Claim 1 wherein the concentration of bleaching catalyst is from 1 to 10 μ M per liter.

3. The process of Claim 2 wherein the pH is from 9.3 to 9.7.

4. The process of Claim 2 wherein the molar ratio of hydrogen peroxide to catalyst is from 25:1 to 35:1.

5. The process of any of Claims 1 to 4 wherein the catalyst is iron tetrasulfonated tetraphenyl porphin.

6. A bleaching composition suitable for preventing dye transfer among fabrics in an aqueous solution of said composition, the said composition comprising:

- a) a bleaching catalyst selected from the group consisting of iron porphins and iron porphyrins and their water-soluble and water-dispersible derivatives, and
- b) a bleaching agent selected from the group consisting of hydrogen peroxide, and water-soluble sources of hydrogen peroxide wherein the water solubility of the hydrogen peroxide source is such that substantially all of the hydrogen peroxide in said source is released quickly into solution when the composition is added to water, the molar ratio of hydrogen peroxide to catalyst in said composition being from 20:1 to 40:1

wherein the said composition has a pH of from 9 to 10 when dissolved in water at a concentration sufficient to provide from 0.02 to 10 μ Moles per liter of said bleaching catalyst.

7. The composition of Claim 6 wherein the molar ratio of hydrogen peroxide to catalyst is from 25:1 to 35:1.

8. The composition of Claim 6 wherein the composition has a pH of from 9.3 to 9.7 when dissolved in water.

9. The composition of any of Claims 6 to 8 wherein the catalyst is iron tetrasulfonated tetraphenyl porphin.

10. The composition of Claim 9 in the form of a granular laundry detergent additionally comprising from 1 to 60% of a surfactant and from 1% to 40% of a detergency builder.

Patentansprüche

1. Verfahren zur Behandlung von Textilien, umfassend den Schritt des Kontaktierens der Textilien mit einer wäßrigen Lösung, welche

- a) einen Bleichkatalysator, gewählt aus der Eisenporphine und Eisenporphyrine und deren wasserlösliche und wasserdispergierbare Derivate umfassenden Gruppe, und
- b) Wasserstoffperoxid umfaßt,

dadurch gekennzeichnet, daß die Konzentration von a) 0.02 bis 10 μ mol pro Liter beträgt und die Konzentration von Wasserstoffperoxid in Lösung derart ist, daß das Molverhältnis von Wasserstoffperoxid zu dem Katalysator 20:1 bis 40:1 beträgt, wobei die Lösung einen pH von 9 bis 10 aufweist.

2. Verfahren Anspruch 1, wobei die Konzentration des Bleichkatalysators 1 bis 10 μ M pro Liter beträgt.

3. Verfahren Anspruch 2, wobei der pH 9,3 bis 9,7 beträgt.
4. Verfahren Anspruch 2, wobei das Molverhältnis von Wasserstoffperoxid zu Katalysator 25:1 zu 35:1 beträgt.
5. Verfahren nach mindestens einem der Ansprüche 1 bis 4, wobei der Katalysator tetrasulfoniertes Eisentetraphenylporphin ist.
6. Bleichzusammensetzung, welche zur Verhinderung der Farbstoffübertragung unter Textilien in einer wäßrigen Lösung der Zusammensetzung geeignet ist, wobei die Zusammensetzung
 - a) einen Bleichkatalysator, gewählt aus der Eisenporphine und Eisenporphyrine und deren wasserlösliche und wasserdispergierbare Derivate umfassenden Gruppe gewählt ist, und
 - b) ein Bleichmittel, gewählt aus der Wasserstoffperoxid und wasserlösliche Quellen von Wasserstoffperoxid umfassenden Gruppe, umfaßt, wobei die Wasserlöslichkeit der Wasserstoffperoxid-Quelle so ist, daß im wesentlichen das gesamte Wasserstoffperoxid in der Quelle rasch in die Lösung freigesetzt wird, wenn die Zusammensetzung zu Wasser gegeben wird, wobei das Molverhältnis von Wasserstoffperoxid zu Katalysator in der Zusammensetzung 20:1 bis 40:1 beträgt,wobei die Zusammensetzung einen pH von 9 bis 10 bei Auflösung in Wasser bei einer ausreichenden Konzentration, um 0,02 bis 10 µMol pro Liter des Bleichkatalysators vorzusehen, aufweist.
7. Zusammensetzung Anspruch 6, wobei das Molverhältnis von Wasserstoffperoxid zu Katalysator 25:1 bis 35:1 beträgt.
8. Zusammensetzung Anspruch 6, wobei die Zusammensetzung einen pH von 9,3 bis 9,7 bei Auflösung in Wasser aufweist.
9. Zusammensetzung nach mindestens einem der Ansprüche 6 bis 8, wobei der Katalysator tetrasulfoniertes Eisentetraphenylporphin ist.
10. Zusammensetzung Anspruch 9 in Form eines granulatförmigen Wäschewaschmittels, welches weiterhin 1 bis 60 % eines Tensids und 1 bis 40 % eines Waschmittelbuilders umfaßt.

Revendications

1. Procédé pour traiter des tissus comprenant les étapes consistant à mettre en contact lesdits tissus avec une solution aqueuse comprenant:
 - a) un catalyseur de blanchiment choisi dans le groupe constitué par les porphines de fer et les porphyrines de fer et leurs dérivés solubles dans l'eau ou dispersibles dans l'eau; et
 - b) du peroxyde d'hydrogène;caractérisé en ce que la concentration de a) est de 0,02 à 10 µmol par litre et la concentration du peroxyde d'hydrogène dans la solution est telle que le rapport molaire dudit peroxyde d'hydrogène audit catalyseur est de 20:1 à 40:1, ladite solution ayant un pH de 9 à 10.
2. Procédé selon la revendication 1, dans lequel la concentration de catalyseur de blanchiment est de 1 à 10 µmol par litre.
3. Procédé selon la revendication 2, dans lequel le pH est de 9,3 à 9,7.
4. Procédé selon la revendication 2, dans lequel le rapport molaire du peroxyde d'hydrogène au catalyseur est de 25:1 à 35:1.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le catalyseur est de la tétraphénylporphine de fer tétrasulfonée.

6. Composition de blanchiment convenable pour empêcher le transfert de teinture d'un tissu à un autre dans une solution aqueuse de ladite composition, ladite composition comprenant:

a) un catalyseur de blanchiment choisi dans le groupe constitué par les porphines de fer et les porphyrines de fer et leurs dérivés solubles dans l'eau ou dispersibles dans l'eau; et
b) un agent de blanchiment choisi dans le groupe constitué par le peroxyde d'hydrogène et les sources solubles dans l'eau de peroxyde d'hydrogène, la solubilité dans l'eau de la source de peroxyde d'hydrogène étant elle que la quasi-totalité du peroxyde d'hydrogène présent dans ladite source soit rapidement libérée en solution lorsque la composition est ajoutée à de l'eau, le rapport molaire du peroxyde d'hydrogène au catalyseur dans ladite composition étant de 20:1 à 40:1,

dans laquelle ladite composition possède un pH de 9 à 10 lorsqu'elle est dissoute dans de l'eau en concentration suffisante pour donner 0,02 à 10 μmol par litre dudit catalyseur de blanchiment.

7. Composition selon la revendication 6, dans laquelle le rapport molaire du peroxyde d'hydrogène au catalyseur est de 25:1 à 35:1.

8. Composition selon la revendication 6, dans laquelle la composition possède un pH de 9,3 à 9,7 lorsqu'elle est dissoute dans l'eau.

9. Composition selon l'une quelconque des revendications 6 à 8, dans laquelle le catalyseur est de la tétraphénylporphine de fer tétrasulfonée.

10. Composition selon la revendication 9, sous forme d'un détergent granulaire pour la lessive, comprenant en outre de 1 à 60% d'un tensioactif et de 1% à 40% d'un adjuvant de détergence.