Detergent compositions inhibiting dye transfer in washing.

A. a non-iron metallo catalyst selected from
   a) non-iron metallo porphin and water-soluble or water-dispersable derivatives thereof;
   b) non-iron metallo porphyrin and water-soluble or water-dispersable derivatives thereof;
   c) non-iron metallo phthalocyanine and water-soluble or water-dispersable derivatives thereof;

B. an efficient amount of a quick releasing bleaching agent, the bleaching agent being in such form that it is released into the wash solution within the first five minutes after the composition has been dissolved or dispersed in water.
Field of the Invention

The present invention relates to a composition and a process for inhibiting dye transfer between fabrics during washing.

Background of the Invention

One of the most persistent and troublesome problems arising during modern fabric laundering operations is the tendency of some colored fabrics to release dye into the laundering solutions. The dye is then transferred onto other fabrics being washed therewith.

One way of overcoming this problem would be to bleach the fugitive dyes washed out of dyed fabrics before they have the opportunity to become attached to other articles in the wash. Suspended or solubilized dyes can to some degree be oxidized in solution by employing known bleaching agents.

However it is important at the same time not to bleach the dyes actually remaining on the fabrics, that is, not to cause color damage.

U.S. Patent 4,077,768 describes a process for inhibiting dye transfer by the use of an oxidizing bleaching agent together with a catalytic compound such as iron porphins. Copending EP Patent Application 91202655.6 filed October 9, 1991, relates to dye transfer inhibiting compositions comprising an enzymatic system capable of generating hydrogen peroxide and porphin catalysts.

It has now been found that non-iron metallo catalysts in the presence of an efficient amount of a quick releasing bleaching agent are very efficient in preventing dye transfer. Accordingly, a dye transfer inhibiting composition is provided which exhibits optimum dye transfer inhibiting properties.

According to another embodiment, the invention provides an efficient process for laundering operations involving colored fabrics.

Summary of the Invention

The present invention relates to inhibiting dye transfer compositions comprising:

A. a non-iron metallo catalyst selected from
   a) non-iron metallo porphin and water-soluble or water-dispersable derivatives thereof;
   b) non-iron metallo porphyrin and water-soluble or water-dispersable derivatives thereof;
   c) non-iron metallo phthalocyanine and water-soluble or water-dispersable derivatives thereof;

B. an efficient amount of a quick releasing bleaching agent, the bleaching agent being in such form that it is released into the wash solution within the first five minutes after the composition has been dissolved or dispersed in water.

According to another embodiment of this invention a process is also provided for laundering operations involving colored fabrics.

Detailed description of the invention

The present invention provides a dye transfer inhibiting composition comprising:

A. a non-iron metallo catalyst selected from
   a) non-iron metallo porphin and water-soluble or water-dispersable derivatives thereof;
   b) non-iron metallo porphyrin and water-soluble or water-dispersable derivatives thereof;
   c) non-iron metallo phthalocyanine and water-soluble or water-dispersable derivatives thereof;

B. an efficient amount of a quick releasing bleaching agent, the bleaching agent being in such form that it is released into the wash solution within the first five minutes after the composition has been dissolved or dispersed in water.

A) Non-iron Metallo catalyst

The preferred usage range of the catalyst in the wash is 10^-8 molar to 10^-3 molar, more preferred 10^-6 - 10^-4 molar.

The essential metallo porphin structure may be visualized as indicated in Formula I in the accompanying drawings. In Formula I the atom positions of the porphin structure are numbered conventionally and the
double bonds are put in conventionally. In other formulas, the double bonds have been omitted in the drawings, but are actually present as in I.

Preferred metallo porphin 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

\[
\text{wherein } n \text{ and } m \text{ may be } 0 \text{ or } 1; \ A \text{ is selected from water-solubilizing group, e.g., sulfate, sulfonate, phosphate, and carboxylate groups; and } B \text{ is selected from the group consisting of } C_1-C_{10} \text{ alkyl, } C_1-C_{10} \text{ polyethoxy alkyl or } C_1-C_{10} \text{ hydroxy alkyl.}
\]

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

- \(-CH_3, -C_2H_5, -CH_2CH_2CH_2SO_3-, -CH_2CH(OH)CH_2SO_3-, -SO_3^-
\]

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

\[
\text{This preferred compound is known as metallo tetrasulfonated tetraphenylporphin. The symbol } X^1 \text{ is } (=CY-) \text{ wherein each } Y, \text{ independently, is hydrogen, chlorine, bromine, fluorine or meso substituted alkyl, cycloalkyl, aralkyl, aryl, alkaryl or heteroaryl. The symbol } X^2 \text{ of Formula I represents an anion, preferably OH}^- \text{ or Cl}^- \text{. The compound of Formula I may be substituted at one or more of the remaining carbon positions with } C_1-C_{10} \text{ alkyl, hydroxyalkyl or oxyalkyl groups.}
\]

Porphin derivatives also include chlorophyls, chlorines, i.e. isobacterio chlorines and bacteriochlorines. Metallo porphyrin and water-soluble or water-dispersable derivatives thereof have a structure given in formula II.
where X can be alkyl, alkyl carboxy, alkyl hydroxyl, vinyl, alkenyl, alkyl sulfate, alkylsulfonate, sulfate, sulfonate, aryl.

The symbol \( X^2 \) of Formula II represents an anion, preferably OH\(^-\) or Cl\(^-\).

The symbol X can be alkyl, alkylcarboxy, alkylhydroxyl, vinyl, alkenyl, alkylsulfate, alkylsulfonate, sulfate, sulfonate.

Metallo phthalocyanine and derivatives have the structure indicated in Formula III, wherein the atom positions of the phthalocyanine structure are numbered conventionally. The anionic groups in the above structures contain cations selected from the group consisting of sodium and potassium cations or other non-interfering cations which leave the structures water-soluble. Preferred phthalocyanine derivatives are metallo phthalocyanine trisulfonate and metallo phthalocyanine tetrasulfonate.

Another form of substitution possible for the present invention is substitution of the central metal by Mn, Co Rh, Cr, Ru, Mo or other transition metals.

Still a number of considerations are significant in selecting variants of or substituents in the basic porphin or azaporphin structure. In the first place, one would choose compounds which are available or can be readily synthesized.

Beyond this, the choice of the substituent groups can be used to control the solubility of the catalyst in water or in detergent solutions. Yet again, especially where it is desired to avoid attacking dyes attached to solid surfaces, the substituents can control the affinity of the catalyst compound for the surface. Thus, strongly negatively charged substituted compounds, for instance the tetrasulfonated porphin, may be repelled by negatively charged stained surfaces and are therefore most likely not to cause attack on fixed dyes, whereas the cationic or zwitterionic compounds may be attracted to, or at least not repelled by such stained surfaces.

B. An efficient amount of a quick releasing bleaching agent, the bleaching agent being in such form that it is released into the wash solution within the first five minutes after the composition has been dissolved or dispersed in water.

The bleach used in the different examples should be such that at least 70%, preferably all of the oxygen active species is available after 5 min at 40 °C. The available oxygen species can be determined very easily.
by titration by the man skilled in the art.

A 1% solution of detergent is prepared in 40 °C water. 5 min later, the solution is centrifuged to precipitate all non-dissolving substances. From the supernatant the available oxygen is measured as follows: a known weight of the supernatant solution to be measured is sampled and the reaction is stopped using glacial acetic acid. Excess potassium iodide (KI) is added to the solution:

\[ \text{H}_2\text{O}_2 + 2\text{KI} + 2\text{ CH}_3\text{COOH} \rightarrow \text{I}_2 + 2 \text{ CH}_3\text{COOK} + 2\text{ H}_2\text{O} \quad (\text{eq 1}) \]

The liberated iodine (according to eq 1) is then titrated with sodium thiosulfate (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}). Starch which gives a purple/blue complex with I\textsuperscript{-} is used as an indicator.

\[ \text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 + (\text{CH}_3\text{COOH}) \rightarrow 2 \text{NaN}_2\text{S}_4\text{O}_6 + (\text{CH}_3\text{COOH}) \quad (\text{eq 2}) \]

A quick releasing bleach should have at least 70%, preferably all the available oxygen in solution after 5 minutes at 40 °C.

The quick releasing bleaches suitable for the present invention include peroxygen bleaches. Examples of suitable water-soluble solid peroxygen bleaches include hydrogen peroxide releasing agents such as hydrogen peroxide, perborates, e.g. perborate monohydrate, perborate tetrahydrate, persulfates, percarbonates, peroxydisulfates, perphosphates and peroxyhydrates. Preferred bleaches are percarbonates and perborates.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylene-diamine (TAED), nonanoxybenzene sulfonate (NOBS, described in US 4,412,934), 3,5,5-trimethylhexanoxylbenzene sulfonate (ISONOBS, described in EP 120,591), or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect.

Other peroxygen bleaches suitable for the present invention include organic peroxyacids such as percarbonic acids.

According to the present invention, an efficient amount of bleach is by definition the necessary amount of bleach which combined with a bleach catalyst leads to a level of dye oxidation which is between 40% to 100%, preferably 40% to 60%, more preferred 60% to 80%, most preferred 80%-100% of the maximum (Z) per cent of dye oxidation that can be achieved under the most optimal conditions determined by those skilled in the art.

**Test Methods:**

For a given catalyst concentration, temperature and pH, the following two test methods can be used to estimate the optimum bleach level that gives the maximum level of dye oxidation, i.e. Z.

(a) In solution dye bleaching:

In a detergent solution, fix the initial concentration of dye (e.g. 40 ppm) and catalyst. Record the absorbance spectrum of this solution using a UV-Vis spectrophotometer according to procedures known to those skilled in the art. Add a given concentration of bleach (H\textsubscript{2}O\textsubscript{2}, oxone, percarbonate, perborate, activated bleach, etc.) and stir the solution containing the dye and catalyst. After stirring for 30 min, record again the absorbance spectrum of the solution. The amount of dye oxidation can then be determined from the change in the absorbance maximum for the dye. Keeping the experimental conditions the same, vary the amount of bleach so as to achieve the maximum dye oxidation.

(b) Reduction of dye transfer from fabric to another fabric

In either a washing machine or launderometer, add a known bleeding fabric and a known uncolored pick-up tracer (e.g. cotton) to the wash load. After simulating a wash cycle, determine the amount of dye that has been pick-up by the tracer according to methods known to those skilled in the art. Now to separate washing machines, add the same amount of bleeding fabric and pick-up tracer, a fixed amount of catalyst and vary the bleach level. Determine the level of dye transfer onto the pick tracers and vary the amount of bleach as to minimize dye transfer. In this way the most optimal bleach concentration can be determined.

The present compositions are conveniently used as additives to conventional detergent compositions for use in laundry operations.
The present invention also encompasses dye transfer inhibiting compositions which will contain detergent ingredients and thus serve as detergent compositions.

**DETERGENT INGREDIENTS**

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C_{12-18} fatty source preferably from a C_{15-18} fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants are alkyl sulphates having from 12 to 18 carbon atoms in the alkyl radical, optionally in admixture with ethoxy sulphates having from 10 to 20, preferably from 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. Examples of preferred alkyl sulphates herein are tallow alkyl sulphate, coconut alkyl sulphate, and C_{14-15} alkyl sulphates. The cation in each instance is again an alkali metal cation, preferably sodium.

One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene 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.

Especially preferred nonionic surfactants of this type are the C_{9-15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{14-15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C_{12-14} primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula

\[
RO\left(C_{n}H_{2n}O\right)_{t}Z_{x}
\]

wherein \(Z\) is a moiety derived from glucose; \(R\) is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; \(t\) is from 0 to 10 and \(n\) is 2 or 3; \(x\) is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

Also suitable as nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula

\[
R^{2} - C - N - Z,
\]

wherein \(R^{1}\) is H, or \(R^{1}\) is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, \(R^{2}\) is C_{9-31} hydrocarbyl, and \(Z\) is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, \(R^{1}\) is methyl, \(R^{2}\) is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl 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 aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyposphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylenetriamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B or HS.
Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate (Na₂Si₂O₅). 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-dodecenyl succinate, 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 4,663,071. Especially for the liquid execution herein, 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. Another preferred builder system for liquid compositions is based on dodecenyl succinic acid.

Preferred builder systems for use in granular compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions for the purposes of this invention include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Other components used in detergent compositions may be employed, such as suds boosting or depressing agents, enzymes and stabilizers or activators therefore, soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and perfumes. Also particularly suitable are amine base catalyst stabilizers disclosed in EP 92870019.4 filed January 31, 1992.

The detergent compositions according to the invention can be in liquid, paste or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 90 °C, especially 20 to 60, but the catalysts are effective at up to 95 °C. The pH of the treatment solution is preferably from 7 to 11, especially from 7.0 to 9.0.

The process and compositions of the invention can also be used as additive during laundry operations. The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.
EXAMPLE 1:

The extent of dye oxidation was measured by two different methods: (i) in solution dye bleaching and (2) measurement of the reduction of dye transfer from textile to textile.

In solution dye bleaching experiments

A detergent solution (100 mL) containing dyes (40 ppm final concentration) and the catalyst (1 x 10-5 M) was prepared and its pH value adjusted to 8.0 or 10.

Experimental conditions:

The absorbance spectrum was recorded from 350-800 nm. This region should encompasses the wavelength maximum of the dyes (as noted for some example in the table below) and the maximum absorbance of the catalyst (Soret band and Q band for porphyrins and phthalocyanines, respectively). The oxidant (H2O2, perborate, percarbonate, activated bleach or oxone) was then added to the stirred solution to initiate the reaction. The level of oxidant should be optimum as defined in described test method. After 30 min the absorbance spectrum was recorded and the decrease in absorbance of the dyes noted.

Blank experiments indicated that no oxidation of the dyes occurred over the same period in the absence of catalyst or oxidant.

<table>
<thead>
<tr>
<th>pH 8</th>
<th>CI</th>
<th>No catalyst</th>
<th>MnPPS</th>
<th>MnTDPP8S</th>
<th>CrTPPS</th>
<th>MnPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Blue I</td>
<td>24410</td>
<td>0</td>
<td>80</td>
<td>85</td>
<td>75</td>
<td>95</td>
</tr>
<tr>
<td>Acid Blue 9</td>
<td>42000</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Direct Blue 98</td>
<td>23155</td>
<td>0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>55</td>
</tr>
<tr>
<td>Acid Red 1</td>
<td>10850</td>
<td>0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH 10</th>
<th>CI</th>
<th>No catalyst</th>
<th>MnPPS</th>
<th>MnTDPP8S</th>
<th>CrTPPS</th>
<th>MnPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Blue I</td>
<td>24410</td>
<td>0</td>
<td>100</td>
<td>85</td>
<td>80</td>
<td>95</td>
</tr>
<tr>
<td>Acid Blue 9</td>
<td>42000</td>
<td>0</td>
<td>25</td>
<td>10</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Direct Blue 98</td>
<td>23155</td>
<td>0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>65</td>
</tr>
<tr>
<td>Acid Red 1</td>
<td>10850</td>
<td>0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>40</td>
</tr>
</tbody>
</table>

MnTPPS: Mangano tetrasulfonated phenylporphyrin
MnTDPP8S: Mangano octasulfonated dichlorophenylporphyrin
Cr-TPPS: Chromium-tetrasulfonated phenylporphyrin
MnPC: Mangano-tetrasulfonated phenylporphyrin

Reduction of Dye transfer from textile to textile

Fabric dyed with Direct Blue I or Direct Blue 90 on cotton and Acid Red 151 on nylon were used in these experiments. In the present experiment, washing was carried out in a Launder-o-meter. The extent of dye transfer was evaluated with a multifibre (Testfabrics, Inc.) that was added in each launder-o-meter beaker. Each swatch consisted of 6 strips of textile (1.5 cm x 5 cm, sewn together; the 6 textile types were Polyacetate, cotton, polyamide, polyester, orlon, and wool. The model wash liquor was made of a detergent solution (200ml with a concentration of detergent as will be used under full washing machine conditions) which pH value was adjusted to 8.0 or pH 10.

Experimental conditions:

One piece of dyed fabric (10 x 10 cm) and one multifibre were placed in the launder-o-meter beakers. In beaker 1, the detergent solution as described above was added and in beaker 2 the detergent solution contained the catalyst (10 ppm final concentration) and the optimum level of bleach as defined in described
Test Method. A wash of 30 min at 30-40 °C with 60 rotations/min was performed, after which the swatches were rinsed in tap water and dried. The Hunter color difference readings (L, a, b) were obtained for the multifibres using a Colorimeter (Spectraflash manufactured by ICS). The change in the color of the fabric can be characterized by a parameter DC defined as \( \Delta C = (\Delta a^2 + \Delta b^2)^{1/2} \) where \( \Delta a \) and \( \Delta b \) represents the difference in the intensity of reflected light between the test multifibres and a multifibre reference that was not in contact with the dyed fabrics. \( b \) represents the intensity of reflected yellow light (positive \( b \) value) or the intensity of reflected blue light (negative \( b \) value), and \( a \) is the measure of the intensity of the reflected red light (positive \( a \) value) or the reflected green light (negative \( a \) value). The higher \( \Delta C \), the more dye has transferred onto the multifibre.

<table>
<thead>
<tr>
<th></th>
<th>No Catalyst ( \Delta C )</th>
<th>MnPC ( \Delta C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Blue 90 on cotton</td>
<td>8.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Acid Red 114 on cotton</td>
<td>20.1</td>
<td>13.8</td>
</tr>
</tbody>
</table>

**EXAMPLE II (A/B/C)**

A liquid dye transfer inhibiting composition according to the present invention is prepared, having the following compositions:

- Linear alkyl benzene sulfonate 10
- Sodium C\(_{12-15}\) alkyl sulfate 3
- C\(_{14-15}\) alkyl 2.5 times ethoxylated sulfate 0
- C\(_{12}\) glucose amide 0
- C\(_{12-15}\) alcohol 7 times ethoxylated 11.6
- Oleic acid 2.5
- Citric acid 1
- C\(_{12-14}\) alkenyl substituted succinic acid 0
- Sodium Hydroxide 3.5
- Ethanol 6
- Monoethanolamine 0
- Triethanolamine 6.4
- 1,2-propane diol 1.5
- Glycerol 0
- Boric acid 0
- Diethylene triamine penta (methylene phosphonic acid) 0.8
- CaCl\(_2\) 0
- Soil release polymers 0.5
- Fatty acids 12
- Enzymes 0.65
- Water and minors

The above composition was supplemented with the catalyst and bleach according to table I

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst 1: Mn-tetrasulfonated tetraphenylporphine</td>
<td>0.05</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>Catalyst 2: Cr-tetrasulfonated tetraphenylporphine</td>
<td>0</td>
<td>0</td>
<td>0.100</td>
</tr>
<tr>
<td>Catalyst 3: Mn-Phthalocyanine tetrasulfonated</td>
<td>0</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>0.3-0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Perborate</td>
<td>0</td>
<td>0</td>
<td>1-5</td>
</tr>
<tr>
<td>Percarbonate</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
</tr>
</tbody>
</table>
Example III (A/B/C):

A compact granular dye transfer inhibiting composition according to the present invention is prepared, having the following formulation:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear alkyl benzene sulphonate</td>
<td>11.40</td>
</tr>
<tr>
<td>Tallow alkyl sulphate</td>
<td>1.80</td>
</tr>
<tr>
<td>C_{15} alkyl sulphate</td>
<td>3.00</td>
</tr>
<tr>
<td>C_{15} alcohol 7 times ethoxylated</td>
<td>4.00</td>
</tr>
<tr>
<td>Tallow alcohol 11 times ethoxylated</td>
<td>1.80</td>
</tr>
<tr>
<td>Dispersant</td>
<td>0.07</td>
</tr>
<tr>
<td>Silicone fluid</td>
<td>0.80</td>
</tr>
<tr>
<td>Trisodium citrate</td>
<td>14.00</td>
</tr>
<tr>
<td>Citric acid</td>
<td>3.00</td>
</tr>
<tr>
<td>Zeolite</td>
<td>32.50</td>
</tr>
<tr>
<td>Maleic acid acetylic acid copolymer</td>
<td>5.00</td>
</tr>
<tr>
<td>DETMPA</td>
<td>1.00</td>
</tr>
<tr>
<td>Cellulase (active protein)</td>
<td>0.03</td>
</tr>
<tr>
<td>Alkalase/BAN</td>
<td>0.60</td>
</tr>
<tr>
<td>Lipase</td>
<td>0.36</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>2.00</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>3.50</td>
</tr>
<tr>
<td>Minors</td>
<td>up to 100</td>
</tr>
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</table>

The above composition was supplemented with the catalyst and bleach according to table II

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A</th>
<th>B</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>Catalyst 1: Mn-tetrasulfonated tetraphenylporphine</td>
<td>0.1</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>Catalyst 2: Cr-tetrasulfonated tetraphenylporphine</td>
<td>0</td>
<td>0</td>
<td>0.100</td>
</tr>
<tr>
<td>Catalyst 3: Mn-Phthalocyanine tetrasulfonated</td>
<td>0</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>H_{2}O_{2}</td>
<td>0.3-0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Perborate</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>Percarbonate</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>TAED</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Claims

1. A dye transfer inhibiting composition comprising:
   A. an non-iron metallo catalyst selected from
      a) non-iron metallo porphin and water-soluble or water-dispersable derivatives thereof;
      b) non-iron metallo porphyrin and water-soluble or water-dispersable derivatives thereof;
      c) non-iron metallo phthalocyanine and water-soluble or water-dispersable derivatives thereof;
   B. an efficient amount of a quick releasing bleaching agent, the bleaching agent being in such form
      that it is released into the wash solution within the first five minutes after the composition has been
      dissolved or dispersed in water.

2. A dye transfer inhibiting composition according to claim 1 containing a non-iron metallo porphin
   derivative, wherein said porphin is substituted on at least one of its meso positions with a phenyl or
   pyridyl substituent selected from the group consisting of
wherein \( n \) and \( m \) may be 0 or 1, \( A \) is selected from water-solubilizing group, e.g., sulfate, sulfonate, phosphate, and carboxylate groups, and \( B \) is selected from the group consisting of \( C_1-C_{10} \) alkyl, \( C_1-C_{10} \) polyethoxyalkyl and \( C_1-C_{10} \) hydroxyalkyl.

3. A dye transfer inhibiting composition according to claim 2 wherein the substituents on the phenyl or pyridyl groups are selected from the group consisting of -\( \text{CH}_3 \), -\( \text{C}_2\text{H}_5 \), -\( \text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^- \), -\( \text{CH}_2\text{COO}^- \), -\( \text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{SO}_3^- \), and -\( \text{SO}_3^- \).

4. A dye transfer inhibiting composition according to claims 1-3, containing a metallo porphin derivative, wherein said non-iron metallo porphin is substituted on at least one of its meso positions with a phenyl substituent selected from the group consisting of

\[
\begin{align*}
\text{X}_1 \equiv \text{CY}^+ \quad \text{wherein each Y, independently, is hydrogen, chlorine, bromine, fluorine or meso substituted alkyl, cycloalkyl, aralkyl, aryl, alkaryl or heteroaryl.}
\end{align*}
\]

5. A dye transfer inhibiting composition according to claim 1 wherein the central atom is selected from Mn, Co, Rh, Cr, Ru, Mo or other transition metals.

6. A dye transfer inhibiting composition according to claim 1 wherein the wash concentration of metallo catalyst is from \( 10^{-8} \) to \( 10^{-3} \) molar, preferably from \( 10^{-6} \) to \( 10^{-4} \) molar.

7. A dye transfer inhibiting composition according to claim 1 wherein the bleaching agent is a peroxyn bleaching agent.

8. A dye transfer inhibiting composition according to claims 1-7 which is a detergent additive, in the form of a non-dusting granule or a liquid.

9. A detergent composition which comprises a dye transfer inhibiting composition according to any of the preceding claims further comprising enzymes, surfactants, builders, and other conventional detergent ingredients.

10. A detergent composition which comprises a dye transfer inhibiting composition according to any of the preceding claims further comprising a cellulase.
## DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cl.5)</th>
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<td>EP-A-0 003 861 (PROCTER &amp; GAMBLE CO.) * the whole document *</td>
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**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**

- C11D

The present search report has been drawn up for all claims.

**PLACE OF SEARCH**

BERLIN

**DATE OF COMPLETION OF THE SEARCH**

10 JUNE 1993

**EXAMINER**

PELLI-WABLAT B.

**CATEGORY OF CITED DOCUMENTS**

- X: particularly relevant if taken alone
- Y: particularly relevant if combined with another document of the same category
- A: technological background
- O: non-written disclosure
- P: intermediate document
- T: theory or principle underlying the invention
- E: earlier patent document, but published on, or after the filing date
- D: document cited in the application
- L: document cited for other reasons
- N: member of the same patent family, corresponding document