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Office européen des brevets



(11)

EP 0 579 295 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
28.10.1998 Bulletin 1998/44

(51) Int Cl.⁶: **C11D 3/00, C11D 3/37**

(21) Application number: **93201198.4**

(22) Date of filing: **26.04.1993**

(54) **Detergent compositions inhibiting dye transfer**

Waschmittelzusammensetzungen zur Verhinderung der Farbstoffübertragung

Détergents avec additifs pour éviter le transfert de colorant

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT
SE**

(30) Priority: **15.07.1992 EP 92202168**

(43) Date of publication of application:
19.01.1994 Bulletin 1994/03

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EP-A- 135 217 **EP-A- 265 257**
EP-A- 327 927

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DescriptionField of the Invention

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

Background of the Invention

10 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 complex or adsorb the fugitive dyes washed out of dyed fabrics before they have the opportunity to become attached to other articles in the wash.

15 Polymers have been used within detergent compositions to inhibit dye transfer.

EP-A-0 102 923 describes the use of carboxyl containing polymers within an aqueous compositions.

DE-A-2 814 329 discloses the use of N-vinyl-oxazolidone polymers and FR-A-2 144 721 discloses the use of 15-35% of a copolymer of polyvinylpyrrolidone and acrylic acid nitrile or maleic anhydride within a washing powder.

20 EP-265 257 describes detergent compositions comprising an alkali-metal carboxy-metal carboxymethylcellulose, a vinylpyrrolidone polymer and a polycarboxylate polymer.

EP-A- 135 217 discloses water-soluble ethoxylated amine oxides selected from ethoxylated monoamine oxides, ethoxylated diamine oxides, ethoxylated polyamine oxides, ethoxylated amine oxide polymers, having clay soil removal/anti-redeposition properties useful in detergent compositions.

25 It is now surprisingly found that certain polyamine N-oxide polymers are very efficient in eliminating transfer of solubilized or suspended dyes. This finding allows to formulate compositions which exhibit excellent dye transfer inhibiting properties.

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

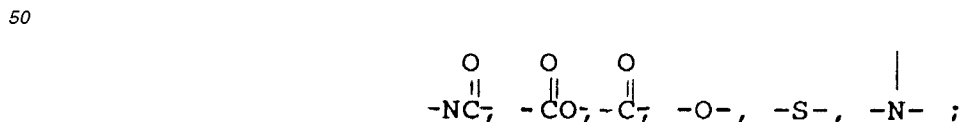
30 Summary of the Invention

The present invention relates to detergent compositions which comprise conventional detergent ingredients and an inhibiting dye transfer composition comprising polyamine N-oxide polymers which contain units having the following structure formula :



45 wherein P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit or a combination of both.

A is



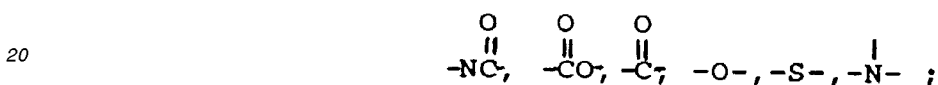
55 x is 0 or 1; R are aliphatic, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group form part of these groups, with the proviso that R is not an ethoxylated group.

In another embodiment, the present invention relates to the use of polyamine N-oxide polymers which contain units having the following structure formula :



wherein P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit.

A is



x is 0 or 1; R are aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic groups whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups for inhibiting dye transfer between fabrics during washing.

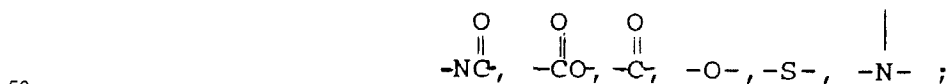
Detailed description of the invention

The polyamine N-oxide polymers used in the present invention contain units having the following structure formula :



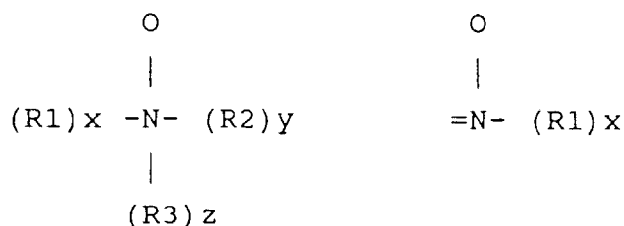
wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

A is



x is 0 or 1; R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein

R1, R2, R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/ and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

The polyamine N-oxides of the present invention are typically present from 0.001 to 10% , more preferably from 0.01 to 2%, most preferred from 0.05 to 1% by weight of the dye transfer inhibiting composition.

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.

Methods for making polyamine N-oxides :

The production of the polyamine-N-oxides may be accomplished by polymerizing the amine monomer and oxidizing the resultant polymer with a suitable oxidizing agent, or the amine oxide monomer may itself be polymerized to obtain the polyamine N-oxide.

The synthesis of polyamine N-oxide can be exemplified by the synthesis of polyvinyl-pyridine N-oxide.

Poly-4-vinylpyridine ex Polysciences (mw. 50 000, 5.0 g., 0.0475 mole) was predissolved in 50 ml acetic acid and treated with a peracetic acid solution (25 g of glacial acetic acid, 6.4 g of a 30% vol. solution of H_2O_2 , and a few drops of H_2SO_4 give 0.0523 mols of peracetic acid) via a pipette. The mixture was stirred over 30 minutes at ambient temperature (32°C). The mixture was then heated to 80-85°C using an oil bath for 3 hours before allowing to stand overnight.

The polymer solution then obtained is mixed with 1l of acetone under agitation. The resulting yellow brown viscous syrup formed on the bottom is washed again with 1l of acetone to yield a pale crystalline solid.

The solid was filtered off by gravity, washed with acetone and then dried over P_2O_5 .

The amine : amine N-oxide ratio of this polymer is 1:4.

DETERGENT ADJUNCTS

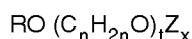
A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, amphotytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

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} - C_{18} fatty source preferably from a C_{16} - C_{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 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.

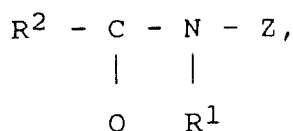
Especially preferred nonionic surfactants of this type are the C_9 - C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{14} - C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C_{12} - C_{14} primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

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



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 poly hydroxy fatty acid amide surfactants of the formula



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_{5-31} 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, 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 aminopolymers, 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 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 ($\text{Na}_2\text{Si}_2\text{O}_5$).

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 $\text{R-CH}(\text{COOH})\text{CH}_2(\text{COOH})$ 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.

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.

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

Other builder materials that can form part of the builder system for use in granular compositions the purposes of the 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 copolymeric 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 bleaches, bleach stabilizers or activators therefor, soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and perfumes.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m^2/g intimately admixed with dimethyl silicone fluid having a molecular weight in the range from 500 to 200 000 at a weight ratio of silicone to silanated silica of from 1:1 to 1:2.

A preferred silicone suds controlling agent is disclosed in Bartolotta et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°0 573 699. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil®.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight. The incorporation of the suds modifiers is preferably made as separate particulates, and this permits the inclusion therein of other suds controlling materials such as C20-C24 fatty acids, microcrystalline waxes and high MW copolymers of ethylene oxide and propylene oxide which would otherwise

adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al U.S. Patent No. 3 933 672.

Other detergent ingredients that can be included are deterative enzymes which can be included in the detergent formulations for a wide variety of purposes including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to 5 mg by weight, more typically 0.05 mg to 3 mg, of active enzyme per gram of the composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames Alcalase, Savinase and Esperase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands) and FN-base by Genencor, Optimase and opticlean by MKC.

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A and methods for its preparation are described in European Patent Application 130,756, published January 9, 1985. Protease B is a proteolytic enzyme which differs from Protease A in that it has a leucine substituted for tyrosine in position 217 in its amino acid sequence. Protease B is described in European Patent Application No. 0 251 446, filed April 28, 1987. Methods for preparation of Protease B are also disclosed in European Patent Application 130,756, Bott et al, published January 9, 1985, incorporated herein by reference.

Amylases include, for example, amylases obtained from a special strain of *B. licheniformis*, described in more detail in British Patent Specification No. 1,296,839 (Novo). Amylolytic proteins include, for example, Rapidase, Maxamyl (International Bio-Synthetics, Inc.) and Termamyl (Novo Industries).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-A-2,247,832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800, and cellulases produced by a fungus of *Bacillus N* or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula Solander*).

Especially suitable cellulase are the cellulase having color care benefits. Examples of such cellulases are cellulase described in European patent application No. 0 495 257, filed November 6, 1991 Carezyme (Novo).

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase and a method for its purification have been described in Japanese Patent Application 53-20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Such lipases of the present invention should show a positive immunological cross reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Ouchterlony (Acta. Med. Scan., 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-reaction with Amano-P, are also described in U.S. Patent 4,707,291, Thom et al, issued November 17, 1987. Typical examples thereof are the Amano-P lipase, the lipase ex *Pseudomonas fragi* FERM P 1339 (available under the trade name Amano-B), lipase ex *Pseudomonas nitroreducens* var. *lipolyticum* FERM P 1338 (available under the trade name Amano-CES), lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*.

Especially suitable Lipase are lipase such as M1 Lipase (Ibis) and Lipolase (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes of pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase.

Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO

89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S, and in European Patent application EP No. 0 540 784, filed on November 6, 1991.

A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al (incorporated herein by reference). Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. patent 4,507,219, Hughes, issued March 26, 1985, both incorporated herein by reference. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981.

For granular detergents, the enzymes are preferably coated or prilled with additives inert toward the enzymes to minimize dust formation and improve storage stability. Techniques for accomplishing this are well-known in the art. In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. patent 4,318,818, Letton, et al, issued March 9, 1982. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., diethanolamine, triethanolamine, di-isopropanolamine), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. patent 4,261,868, issued April 14, 1981 to Horn, et al, U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, both incorporated herein by reference, and European Patent Application Publication No. 0 199 405. Non-boric acid and borate stabilizers are preferred. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319 and 3,519,570.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Co-pending European Patent application N 0 553 607 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

Especially preferred detergent ingredients are combinations with technologies which also provide a type of color care benefit. Examples of these technologies are cellulase and/or peroxidases and/or metallo catalysts for color maintenance rejuvenation.

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 liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

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 75 °C, especially 20 to 60°C, but the polymers are effective at up to 95 °C. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

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.

A liquid detergent composition according to the present invention is prepared, having the following compositions :

Table I

% by weight of the total detergent composition	
Linear alkylbenzene sulfonate	10
Alkyl sulphate	4
Fatty alcohol (C ₁₂ -C ₁₅) ethoxylate	12
Fatty acid	10
Oleic acid	4
Citric acid	1
NaOH	3.4

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Table I (continued)

% by weight of the total detergent composition	
Propanediol	1.5
Ethanol	10

The extent of dye transfer is assessed by a Hunter Colour measurement. The Hunter Colour system evaluates the colour of a fabric sample in terms of the Δc value which represents the change in the Hunter a, b values which are determined by reflecting spectrometrie. The Δc value is defined by the following equation:

$$\Delta c = \{(a_f - a_i)^2 + (b_f - b_i)^2\}^{1/2}$$

where the subscripts i and f refer to the Hunter value before and after washing in the presence of the bleeding fabric, respectively. The least significant difference is 1 at 95% confidence level.

Example I :

The extent of dye transfer from different colored fabrics was studied using a launder-o-meter test that simulates a 30 min wash cycle. The launder-o-meter beaker contains 200 ml of a detergent solution, a 10cmx10cm piece of the colored fabric and a multifiber swatch which is used as a pick-up tracer for the bleeding dye. The multifiber swatch consists of 6 pieces (1.5cmx5cm each) of different material (polyacetate, cotton, polyamide, polyester, wool and orlon) which are sewn together.

Experimental conditions:

pH = 7.8

A: A detergent composition according to Table I which does not contain any dye transfer inhibition system.

B: A detergent composition according to Table I containing 10 ppm of PVNO (poly(4-vinylpyridine-N-oxide)) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of 1:4.

Results: Δc values for the cotton pick-up tracer.

Bleeding fabric composition	Bleeding fabric color	A	B
55% Linen/45% Polyester	Green	4.2	1.7
Jeans	Blue	15.7	3.3
60% Polyester/40% Flax	Blue	4.3	1.9
100% cotton	Brown	7.6	0.8
100% Flax	Brown	3.6	1.1

Example II

The test of Example I was carried out using the following experimental conditions:
pH = 7.8

A: A detergent composition according to Table I without any dye transfer inhibition system

B: A detergent composition according to Table I containing 100 ppm of poly(2-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of 1:4.

Results: Δc values for the cotton pick-up tracer.

Bleeding fabric composition	Bleeding fabric color	A	B
33% Viscose/67% Polyester	Green	10.0	4.9
35% Viscose/65% Polyester	Blue	4.9	0.8
100% cotton	Black	3.5	2.2
Jeans	Blue	15.7	14
60% Polyester/40% Flax	Blue	4.3	2.3
100% cotton	Brown	7.6	5.9
60% Wool/40% Polyamide	Mauve	2.2	1.1

Example III

The extent of dye transfer from brown cotton fabric was studied using a launder-o-meter test which simulates a 30 min wash cycle. The launder-o-meter beaker contains 400 ml of a detergent solution, a 20cm piece of the colored fabric and two multifiber swatches which are used as a pick-up tracer for the bleeding dye.
pH= 10.5

A: A detergent composition according to Table I without any dye transfer inhibition system

B: A detergent composition according to Table I containing 70 ppm of poly 2-(dimethylamino)-ethylmethacrylate-N-oxide which has an average molecular weight of about 100,000.

Results: Δc values for the cotton pick-up tracer.

Bleeding fabric composition	Bleeding fabric color	A	B
100% Cotton	Brown	4.0	2.5

Example IV

The extent of dye transfer from brown cotton fabric was studied using a launder-o-meter test which simulates a 30 min wash cycle. The launder-o-meter beaker contains 200 ml of a detergent solution, a 4cmx10cm piece of the colored fabric and two multifiber swatches which are used as a pick-up tracer for the bleeding dye.
pH= 10.5

A: A detergent composition according to Table I without any dye transfer inhibition system

B: A detergent composition according to Table I containing 7ppm (B1), 35ppm (B2) and 70 ppm (B3) of poly-1-vinylimidazole-N-oxide which has an average molecular weight of about 150,000.

Results: Δc values for the cotton pick-up tracer.

Bleeding fabric composition	Bleeding fabric color	A	B1	B2	B3
100% cotton	Brown	16.9	5.5	3.6	2.1
100% cotton	Blue	11.1	8.5	6.2	3.9

Example V

The dye transfer inhibition performance of poly(dimethylamino)-ethylmethacrylate-N-oxide was tested in a domestic washing machine using a 40° C cycle. The washing machine loads consisted of ballast laundry and 1000 cm² of a known bleeding fabric. A 26cm by 31cm terry towel was used as the pick-up tracer for the bleeding dye.
pH= 10.5

A: detergent solution without any dye transfer inhibition system

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B: detergent solution which delivers 7ppm of polydialkylmethylamine-N-oxide in the wash solution(average molecular weight range of about 150,000).

Results: Δc values for the cotton pick-up tracer.

Bleeding fabric composition	Bleeding fabric color	A	B
100% cotton	Brown	15.9	11.9
100% cotton	Blue	8.08	2.8

Example VI

The dye transfer inhibition performance of poly(4-vinylpyridine)-N-oxide was tested in a domestic washing machine using a 40° C cycle. The washing machine loads consisted of ballast laundry and 1000 cm² of a known bleeding fabric. A 26cm by 31cm terry towel was used as the pick-up tracer for the bleeding dye.

Test conditions:

A: detergent without any dye transfer inhibition system

B: detergent composition which delivers 7 ppm of poly(4-vinylpyridine-N-oxide) in the wash solution (average molecular weight is about 50,000).

Table 1:

Δc values at wash pH of 7.8			
Dye	C.I. #	A	B
Direct Blue 90	n/a	8.1	0.7
Direct Red 80	35780	24.8	3.4
Direct Brown 90	31785	14.2	0.6
Acid Red 151	26900	5.1	4.6

Table 1:

Δc values at wash pH of 9.8			
Dye	C.I. #	A	B
Direct Blue 90	n/a	4.7	3.9
Direct Red 80	35780	33.0	17
Direct Brown 90	31785	13.4	2.0

Example VII

The effect of degree of oxidation of polyvinylpyridine-N-oxide (PVNO) on the DTI performance was evaluated in a launder-o-meter test which simulates a 30 min wash cycle. The dye transfer inhibition capacity of the different PVNO samples was tested using the same amount of a cotton bleeding fabric dyed with Direct Blue 90. The pick-up tracer for dye transfer is a multifiber swatch.

The extent of dye transfer is reported in terms of the Hunter ΔE value which is calculated versus a reference washed in the absence of the bleeding fabric.

Experimental conditions:

10 ppm of PVNO (Average MW ~ 60,000) in a detergent solution according to Table I.
The oxidation degree was determined by Nuclear Magnetic resonance (NMR).

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Results: ΔE values as a function of PVNO degree of oxidation (lower ΔE means better performance)

Reference ΔE in the absence of PVNO is 17.0

5		
	Oxidation degree (%)	ΔE
	35	16.4
	40	15.9
	58	11.3
10	73	10.6
	83	8.3
	92	6.7

Conclusion: The dye transfer inhibition properties of PVNO improve with higher degree of oxidation.

Example VIII

A liquid detergent composition according to the present invention is prepared, having the following compositions :

20	Linear alkylbenzene sulfonate	10
	Alkyl sulphate	4
	Fatty alcohol (C ₁₂ -C ₁₅) ethoxylate	12
	Fatty acid	10
25	Oleic acid	4
	Citric acid	1
	Diethylenetriaminepentamethylene Phosphonic acid	1.5
	NaOH	3.4
	Propanediol	1.5
30	Ethanol	10
	Ethoxylated tetraethylene pentamine	0.7
	Poly(4-vinylpyridine)-N-oxide	0.3
	Thermamyl	0.13
35	Carezyme	0.014
	FN-Base	1.8
	Lipolase	0.14
	Endoglucanase A	0.53
	Suds supressor (ISO FOL)	2.5
40	Minors	up to 100

Example IX

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

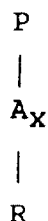
50	Linear alkyl benzene sulphonate	11.40
	Tallow alkyl sulphate	1.80
	C ₄₅ alkyl sulphate	3.00
	C ₄₅ alcohol 7 times ethoxylated	4.00
	Tallow alcohol 11 times ethoxylated	1.80
	Dispersant	0.07
55	Silicone fluid	0.80
	Trisodium citrate	14.00
	Citric acid	3.00
	Zeolite	32.50

(continued)

Maleic acid actylic acid copolymer	5.00
DETPA	1.00
Cellulase (active protein)	0.03
Alkalase/BAN	0.60
Lipase	0.36
Sodium silicate	2.00
Sodium sulphate	3.50
Glucose	10.00
Poly(4-vinylpyridine)-N-oxide	0.3
Minors	up to 100

Claims

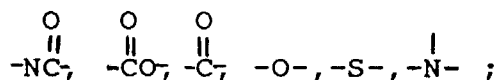
1. A detergent composition which comprises conventional detergent ingredients and a dye transfer inhibiting composition comprising polyamine N-oxide polymers which contain units having the following structure formula :



wherein

P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit.

A is



x is 0 or 1; R are aliphatic, aromatic, heterocyclic or alicyclic groups whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups, with the proviso that R is not an ethoxylated group.

2. A detergent composition according to claim 1 wherein P is a polymerisable unit wherein the N-O group is attached to and wherein R is selected from an aromatic or heterocyclic group.
3. A detergent composition according to claim 2 wherein the nitrogen of the N-O group forms part of the R-group.
4. A detergent composition according to claim 3 wherein the R-group is selected from pyridine, pyrrole, quinoline, acridine, imidazole and derivatives thereof.
5. A detergent composition according to claim 1 or 2 wherein the nitrogen of the N-O group is attached to the R-group.
6. A detergent composition according to claim 5 wherein R is a phenyl group.
7. A detergent composition according to claim 1 wherein P is a polymerisable unit, whereto the N-O group forms part

of the polymerisable unit and wherein R is selected from an aromatic or heterocyclic group.

8. A detergent composition according to claim 7 wherein the nitrogen of the N-O group forms part of the R-group.

9. A detergent composition according to claim 8 wherein the R-group is selected from pyridine, pyrrole, quinoline, acridine, imidazole and derivatives thereof.

10. A detergent composition according to claims 1-9 wherein the polymeric backbone is derived from the group of the polyvinyl polymers.

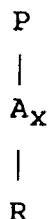
11. A detergent composition according to claims 1-10 wherein the ratio of amine to amine N-oxide in the polyamine N-oxide polymers is from 2:3 to 1:1000000, preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000.

12. A detergent composition according to claims 1-11 wherein the polyamine N-oxide has an average molecular weight within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

13. A detergent composition according to claims 1-12 wherein the polyamine N-oxide is present at levels from 0.001 to 10 % by weight of the composition.

14. A detergent composition according to claims 1-13 which is a detergent additive, in the form of a non-dusting granule or a liquid.

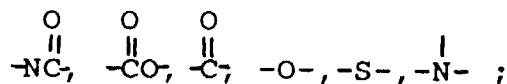
15. Use of polyamine N-oxide polymers which contain units having the following structure formula :



wherein

P is a polymerisable unit, where to the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit.

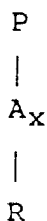
A is



x is 0 or 1; R are aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic groups where to the nitrogen of the N-O group can be attached to or wherein the nitrogen of the N-O group is part of these groups for inhibiting dye transfer, between fabrics during washing.

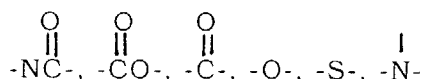
Patentansprüche

1. Waschmittelzusammensetzung, umfassend herkömmliche Waschmittelbestandteile und eine die Farbstoffübertragung inhibierende Zusammensetzung, umfassend Polyamin-N-oxid-Polymere, welche Einheiten der folgenden Strukturformel enthalten:



worin P eine polymerisierbare Einheit ist, an welche die N-O-Gruppe gebunden werden kann oder worin die N-O-Gruppe einen Teil der polymerisierbaren Einheit bildet;

A



bedeutet; x 0 oder 1 ist; R aliphatische, aromatische, heterocyclische oder alicyclische Gruppen sind, an welche der Stickstoff der N-O-Gruppe gebunden werden kann, oder worin der Stickstoff der N-O-Gruppe Teil dieser Gruppen ist, mit der Maßgabe, daß R keine ethoxylierte Gruppe ist.

2. Waschmittelzusammensetzung nach Anspruch 1, wobei P eine polymerisierbare Einheit ist, an welche die N-O-Gruppe gebunden ist und wobei R aus einer aromatischen oder heterocyclischen Gruppe gewählt ist.

3. Farbstoffzusammensetzung nach Anspruch 2, wobei der Stickstoff der N-O-Gruppe einen Teil der R-Gruppe bildet.

4. Waschmittelzusammensetzung nach Anspruch 3, wobei die R-Gruppe aus Pyridin, Pyrrol, Chinolin, Acridin, Imidazol und Derivaten hiervon gewählt ist.

5. Waschmittelzusammensetzung nach Anspruch 1 oder 2, wobei der Stickstoff der N-O-Gruppe an die R-Gruppe gebunden ist.

6. Waschmittelzusammensetzung nach Anspruch 5, wobei R eine Phenylgruppe ist.

7. Waschmittelzusammensetzung nach Anspruch 1, wobei P eine polymerisierbare Einheit ist, worin die N-O-Gruppe einen Teil der polymerisierbaren Einheit bildet und wobei R aus einer aromatischen oder heterocyclischen Gruppe gewählt ist.

8. Waschmittelzusammensetzung nach Anspruch 7, wobei der Stickstoff der N-O-Gruppe einen Teil der R-Gruppe bildet.

9. Waschmittelzusammensetzung nach Anspruch 8, wobei die R-Gruppe aus Pyridin, Pyrrol, Chinolin, Acridin, Imidazol und Derivaten hiervon gewählt ist.

10. Waschmittelzusammensetzung nach den Ansprüchen 1-9, wobei das polymere Grundgerüst aus der Gruppe der Polyvinylpolymeren abgeleitet ist.

11. Waschmittelzusammensetzung nach den Ansprüchen 1-10, wobei das Verhältnis von Amin zu Amin-N-oxid in den Polyamin-N-oxid-Polymeren 2:3 bis 1: 1.000.000, vorzugsweise 1:4 bis 1:1.000.000, am meisten bevorzugt 1:7 bis 1: 1.000.000 beträgt.

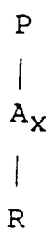
12. Waschmittelzusammensetzung nach den Ansprüchen 1-11, wobei das Polyamin-N-oxid ein Durchschnittsmolekulargewicht innerhalb des Bereichs von 500 bis 1.000.000; vorzugsweise von 1.000 bis 50.000, weiter vorzugsweise von 2.000 bis 30.000, am meisten bevorzugt von 3.000 bis 20.000, aufweist.

13. Waschmittelzusammensetzung nach den Ansprüchen 1-12, wobei das Polyamin-N-oxid in Anteilen von 0,001 bis

10 Gew.-% der Zusammensetzung vorliegt.

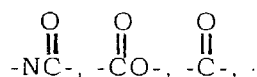
14. Waschmittelzusammensetzung nach den Ansprüchen 1-13, welche ein Waschmitteladditiv in Form eines nicht staubenden Granulats oder einer Flüssigkeit ist.

15. Verwendung von Polyamin-N-oxid-Polymeren, welche Einheiten der folgenden Strukturformel enthalten:



worin P eine polymerisierbare Einheit ist, an welche die N-O-Gruppe gebunden werden kann oder worin die N-O-Gruppe einen Teil der polymerisierbaren Einheit bildet:

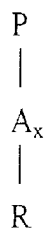
A



-O-, -S-, -N-bedeutet; x 0 oder 1 ist; R aliphatische, ethoxylierte aliphatische, aromatische, heterocyclische oder alicyclische Gruppen sind, an welche der Stickstoff der N-O-Gruppe gebunden werden kann, oder wobei der Stickstoff der N-O-Gruppe Teil dieser Gruppen ist, zur Inhibierung der Farbstoffübertragung zwischen Textilien während dem Waschen.

Revendications

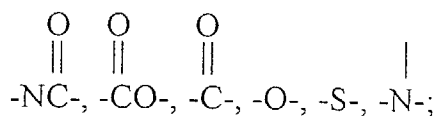
1. Composition détergente qui comprend des ingrédients détergents classiques et une composition inhibitrice de transfert de colorants comprenant des polymères de N-oxydes de polyamines qui contiennent des motifs ayant la formule développée suivante :



dans laquelle :

P est un motif polymérisable, auquel le groupe N-O peut être fixé ou dont le groupe N-O fait partie;

A est



x est 0 ou 1;

R représente des groupes aliphatiques, aromatiques, hétérocycliques ou alicycliques auxquels l'atome d'azote du groupe N-O peut être fixé ou dont l'atome d'azote du groupe N-O fait partie, à condition que R ne soit pas un groupe éthoxylé.

2. Composition détergente selon la revendication 1, dans laquelle P est un motif polymérisable auquel le groupe N-O est fixé et dans lequel R est sélectionné parmi un groupe aromatique ou hétérocyclique.

3. Composition détergente selon la revendication 2, dans laquelle l'atome d'azote du groupe N-O fait partie du groupe R.

4. Composition détergente selon la revendication 3, dans laquelle le groupe R est sélectionné parmi la pyridine, le pyrrole, la quinoléine, l'acridine, l'imidazole et leurs dérivés.

5. Composition détergente selon la revendication 1 ou 2, dans laquelle l'atome d'azote du groupe N-O est fixé au groupe R.

6. Composition détergente selon la revendication 5, dans laquelle R est un groupe phényle.

7. Composition détergente selon la revendication 1, dans laquelle P est un motif polymérisable dont le groupe N-O fait partie et dans laquelle R est sélectionné parmi un groupe aromatique ou hétérocyclique.

8. Composition détergente selon la revendication 7, dans laquelle l'atome d'azote du groupe N-O fait partie du groupe R.

9. Composition détergente selon la revendication 8, dans laquelle le groupe R est sélectionné parmi la pyridine, le pyrrole, la quinoléine, l'acridine, l'imidazole et leurs dérivés.

10. Composition détergente selon les revendications 1 à 9, dans laquelle l'ossature polymère est dérivée du groupe des polymères polyvinyliques.

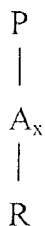
11. Composition détergente selon les revendications 1 à 10, dans laquelle le rapport de l'amine au N-oxyde d'amine dans les polymères de N-oxydes de polyamines se situe dans une plage de 2:3 à 1:1 000 000, de préférence de 1:4 à 1:1 000 000, mieux encore de 1:7 à 1:1 000 000.

12. Composition détergente selon les revendications 1 à 11, dans laquelle le N-oxyde de polyamine a un poids moléculaire moyen dans la plage de 500 à 1 000 000, de préférence de 1000 à 50 000, mieux encore de 2000 à 30 000, bien mieux encore de 3000 à 20 000.

13. Composition détergente selon les revendications 1 à 12, dans laquelle le N-oxyde de polyamine est présente à des niveaux de 0,001 à 10% en poids de la composition.

14. Composition détergente selon les revendications 1 à 13, qui est un additif détergent sous la forme d'un granulé sans poussière ou d'un liquide.

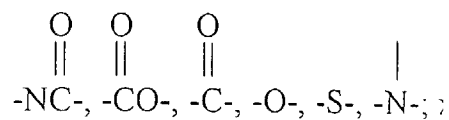
15. Utilisation de polymères de N-oxydes de polyamines qui contiennent des motifs ayant la formule développée suivante :



dans laquelle :

P est un motif polymérisable, auquel le groupe N-O peut être fixé ou dont le groupe N-O fait partie;

A est



x est 0 ou 1;

R représente des groupes aliphatiques, aliphatiques éthoxylés, aromatiques, hétérocycliques ou alicycliques auxquels l'atome d'azote du groupe N-O peut être fixé ou dont l'atome d'azote du groupe N-O fait partie, pour empêcher le transfert de colorants entre des tissus au cours du lavage.