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(54) Title: LONG ALKYL CHAIN AZO-DYE AND LAUNDRY DETERGENT COMPOSITION

(57) Abstract: The present invention provides a blue or violet azo-dye having improved performance, a laundry detergent composition comprising said dye and a domestic method of treating a textile with said dye.

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LONG ALKYL CHAIN AZO-DYE AND LAUNDRY DETERGENT COMPOSITION

Field of Invention

The present invention concerns the use of dyes in laundry compositions.

Background of Invention

To enhance the whiteness of textiles during domestic laundering, blue or violet shading dyes are used to counteract yellowing of textiles.

WO2006/045375 (Unilever) discloses azo dyes for the shading of textiles during domestic laundering.

WO2012/166768 (Procter & Gamble) and WO2013/006871 (Milliken) discloses azo dyes modified with long alkyl chains to improve performance.

There is a need to improve the performance of azo dyes modified with long alkyl chains.

Summary of the Invention

In one aspect the present invention provides laundry detergent composition comprising between 0.0001 to 1.0 wt% of a blue or violet azo dye, 2 to 70 wt% of a surfactant, and from 0.005 to 2 wt % of a fluorescent agent, wherein the blue or violet dye azo is of the form:

$$\text{Dye-NR}_1\text{R}_2,$$

wherein,

R_1 is a $-(L)_n-(X)_p-CH_2-CH(OH)CH_2(O)_qR_3$ group, wherein n = p = 0 or 1, q = 0 or 1, and L is selected from C1 to C2-alkyl, and ether group having from 1 to 15 ether linkages;
when n = 1, X is selected from S, N and O;

R_3 is a branched, linear or cyclic C_4 to C_{24} alkyl chain; and,

R_2 is selected from: H; C_1 to C_3-alkyl; phenyl; benzyl; and a $–(L)_n$-$(X)_p$-CH_2-$CH(OH)CH_2(O)_qR_3$ group, wherein n = p = 0 or 1, q = 0 or 1, and L is selected from C1 to C2-alkyl, and an ether group having from 1 to 15 ether linkages.

The groups R_1 and R_2 may both take R_3 and when this is the case R_1 and R_2 do not have to be the same.

The phenyl and benzyl groups of R_2 may be further substituted by organic groups, such as methyl and ethyl, however this not preferred.

In another aspect the present invention provides a domestic method of treating a textile, the method comprising the steps of:

(i) treating a textile with an aqueous solution of the blue or violet azo dye, the aqueous solution comprising from 1 ppb to 5000 ppm, preferably 10ppb to 1ppm, most preferably 50ppb to 300ppb, most preferably blue or violet azo-dye; and, from 0.0 g/L to 5 g/L, preferably from 0.2 to 4 g/L, of a surfactant, most preferably from 0.4 to 0.8g/L; and,

(ii) optionally rinsing and drying the textile.

Preferably, the aqueous solution comprises a fluorescer in the range from 0.0001 g/l to 0.1 g/l.

In a further aspect the present invention provides the blue or violet azo-dye per se.

Detailed Description of the Invention

Preferably, R3 is substituted by a group selected from: F; Cl; Br; ester; acid amide; and, phenyl. R_3 is also preferably a C5 to C11-n-alkyl chain. Preferably q = 0.
Preferably, the azo dye is either a mono-azo dye or di-azo dye.

X is preferably a N or O and most preferably an O.

When L is an ether group, the ether group has preferably from 1 to 10 ether linkages, more preferably from 1 to 3 ether linkages.

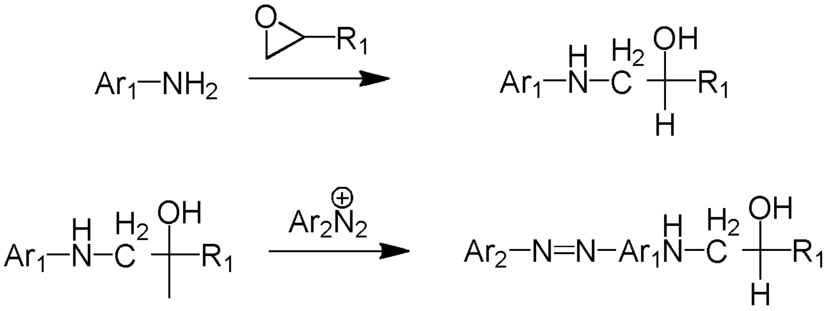
In one aspect of preference R_3 is substituted by groups selected from: SO_3H and COOH. In another aspect of preference the blue or violet azo dye is not substituted by a group selected from: quaternary ammonium groups, SO_3H and COOH.

Azo dyes and azo dye synthesis is discussed in Color Chemistry (H. Zollinger, Wiley VCH 2003) and Industrial Dyes (K.Hunger Wiley VCH 2003).

The azo chromophore of the present invention may be selected from a wide class of azo chromophores of the direct blue and violet, acid blue and violet, and disperse bleu and violet dyes as listed in the colour Index (Society of Dyers and Colourists/American Association of Textile Chemists and Colorists).

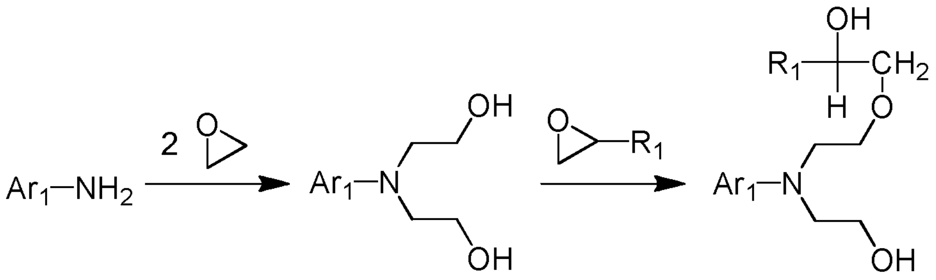
The blue or violet azo dye may carry, for example, sulphonate, carboxylic acid groups and quaternary ammonium groups.

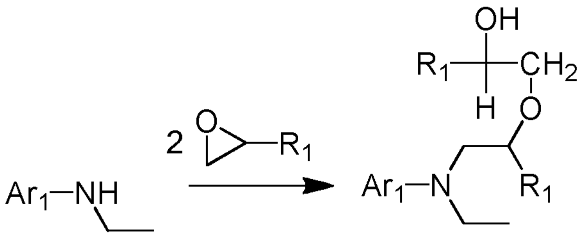
The blue or violet azo dye may be synthesised via the reaction of a 1,2 epoxy alkyl compound with a primary aromatic amine, following by azo coupling to form the azo dye. For example:



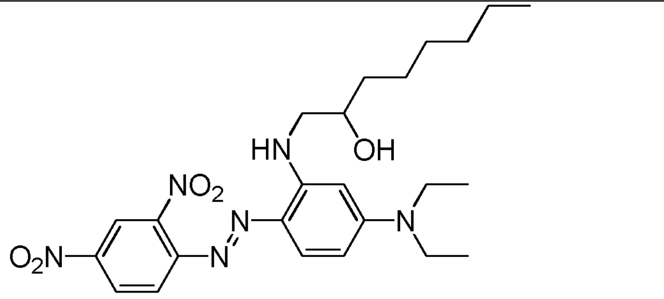
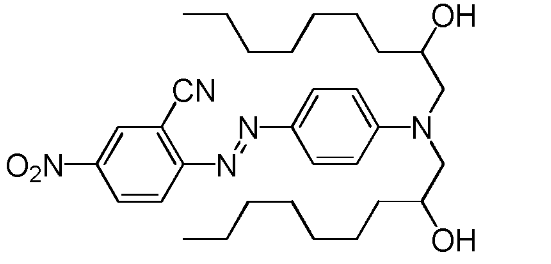
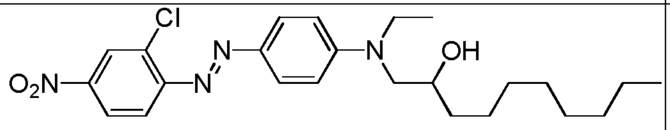
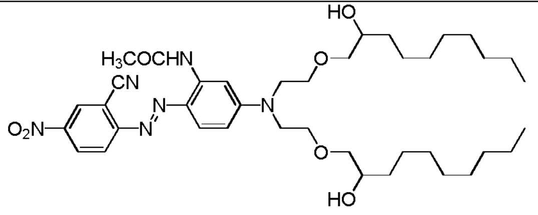
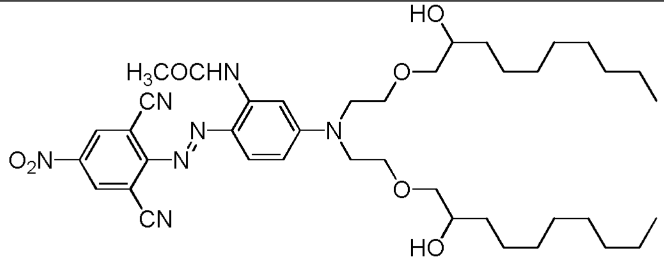
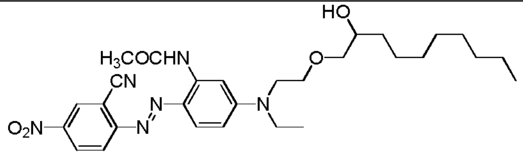
Where Ar_1 and Ar_2 are aromatic rings.

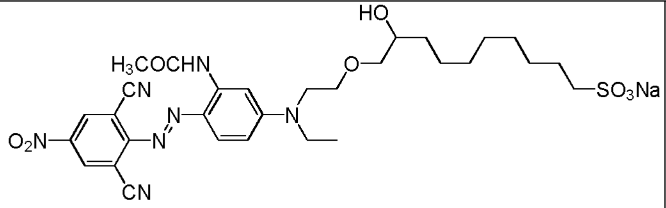
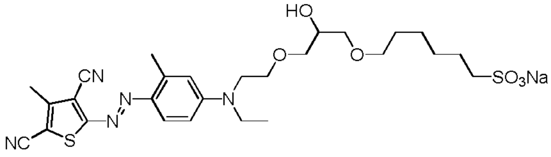
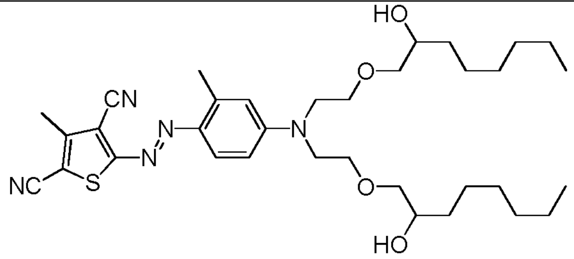
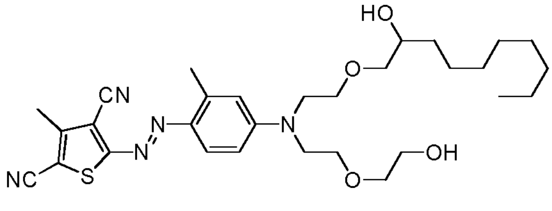
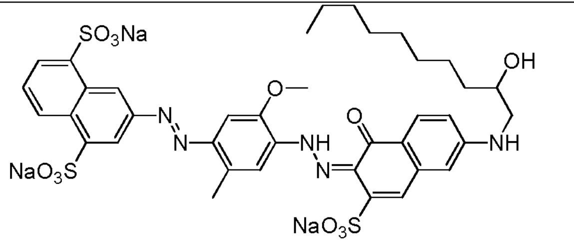
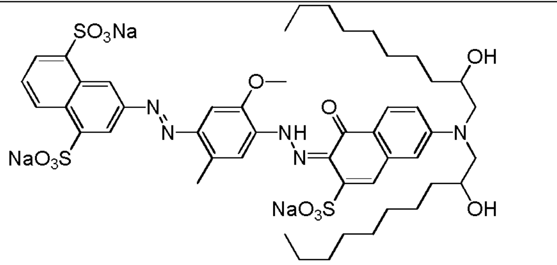
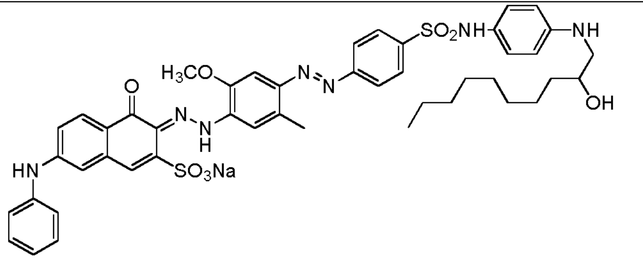
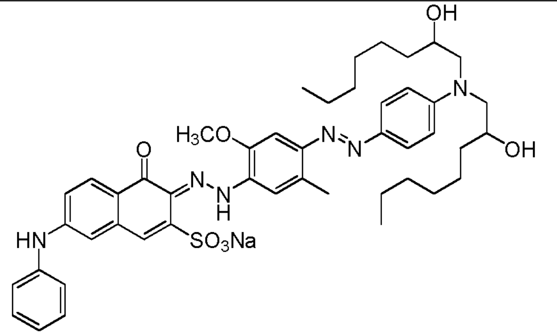
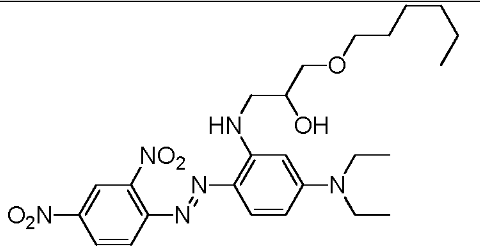
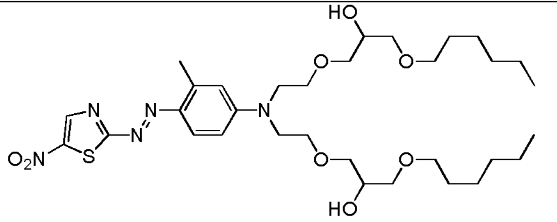
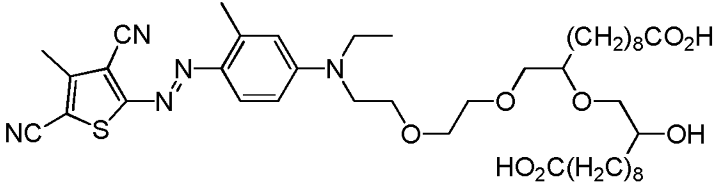
Further examples of the first step in the synthesis are:





Example of dyes of the invention:

Other Dyes

In a preferred embodiment of the invention, other shading colourants may be present. They are preferably selected from hydrophobic dyes more preferably solvent and disperse dyes such as solvent violet 13, disperse violet 27, disperse violet 28 and alkoxylated thiophene dyes.

A hydrophobic dye is uncharged pH = 7.

Even more preferred is the presence of acid azine dyes as described in WO 2008/017570; the level of the acid azine dyes should be in the range from 0.0001 to 0.1 wt%. Preferred acid azine dyes are acid violet 50, acid blue 59, dye with CAS-No 72749-80-5, and acid blue 98. Blue and Violet cationic phenazine dyes may also be present as discussed in WO2009/141172 and WO2009/141173.

Photobleaches such as sulphonated Zn/Al phthalocyanins may be present.

Surfactant

The laundry composition comprises between 2 to 70 wt percent of a surfactant, most preferably 10 to 30 wt %. In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. Preferably the surfactants used are saturated.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C_6 to C_{22} alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C_8 to C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10} to C_{15} benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C_{11} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C_{16} to C_{18} primary alcohol sulphate together with a C_{12} to C_{15} primary alcohol 3 to 7 EO ethoxylate.

The nonionic detergent is preferably present in amounts less than 50wt%, most preferably less than 20wt% of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 50% to 100 wt % of the surfactant system.

In another aspect which is also preferred the surfactant may be a cationic such that the formulation is a fabric conditioner.

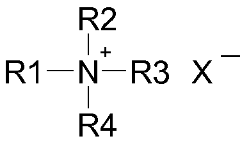
Cationic Compound

When the present invention is used as a fabric conditioner it needs to contain a cationic compound.

Most preferred are quaternary ammonium compounds.

It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C_{12} to C_{22} alkyl chain.

It is preferred if the quaternary ammonium compound has the following formula:



$$R1-\overset{\overset{\displaystyle R2}{|}}{\underset{\underset{\displaystyle R4}{|}}{N^+}}-R3 \quad X^-$$

in which R^1 is a C_{12} to C_{22} alkyl or alkenyl chain; R^2, R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion. A preferred compound of this type is the quaternary ammonium compound cetyl trimethyl quaternary ammonium bromide.

A second class of materials for use with the present invention are the quaternary ammonium of the above structure in which R^1 and R^2 are independently selected from C_{12} to C_{22} alkyl or alkenyl chain; R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion.

A detergent composition according to claim 1 in which the ratio of (ii) cationic material to (iv) anionic surfactant is at least 2:1.

Other suitable quaternary ammonium compounds are disclosed in EP 0 239 910 (Procter and Gamble).

It is preferred if the ratio of cationic to nonionic surfactant is from 1:100 to 50:50, more preferably 1:50 to 20:50.

The cationic compound may be present from 1.5 wt % to 50 wt % of the total weight of the composition. Preferably the cationic compound may be present from 2 wt % to 25 wt %, a more preferred composition range is from 5 wt % to 20 wt %.

The softening material is preferably present in an amount of from 2 to 60% by weight of the total composition, more preferably from 2 to 40%, most preferably from 3 to 30% by weight.

The composition optionally comprises a silicone.

Builders or Complexing Agents

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

The composition may also contain 0-65 % of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate) are preferred builders.

The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15%w. Aluminosilicates are materials having the general formula:

$$0.8\text{-}1.5\ M_2O.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$$

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to alumuminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term ‘phosphate’ embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt% of phosphate. Preferably the laundry detergent formulation is carbonate built.

Fluorescent Agent

The composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %. Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium

4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl.

It is preferred that the aqueous solution used in the method has a fluorescer present. When a fluorescer is present in the aqueous solution used in the method it is preferably in the range from 0.0001 g/l to 0.1 g/l, preferably 0.001 to 0.02 g/l.

Perfume

Preferably the composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, most preferably 0.1 to 1 wt %. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

Perfume and top note may be used to cue the whiteness benefit of the invention.

It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

Polymers

The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

Polymers present to prevent dye deposition, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole), are preferably absent from the formulation.

Enzymes

One or more enzymes are preferred present in a composition of the invention and when practicing a method of the invention.

Preferably the level of each enzyme is from 0.0001 wt% to 0.1 wt% protein.

Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202, WO 00/60063.

Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ (Novozymes A/S).

The method of the invention may be carried out in the presence of phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids.

Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A_1 and A_2 which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

The enzyme and the shading dye may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme or shading dye and/or other segregation within the product.

Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

The method of the invention may be carried out in the presence of cutinase, classified in EC 3.1.1.74. The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g. a special strain of *B. licheniformis*, described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g. the fungal cellulases produced from *Humicola insolens*, *Thielavia terrestris*, *Myceliophthora thermophila,* and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™, Celluclean™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus*, e.g. from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

Further enzymes suitable for use are discussed in WO2009/087524, WO2009/090576, WO2009/107091, WO2009/111258 and WO2009/148983.

Enzyme Stabilizers

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Where alkyl groups are sufficiently long to form branched or cyclic chains, the alkyl groups encompass branched, cyclic and linear alkyl chains. The alkyl groups are preferably linear or branched, most preferably linear.

The indefinite article “a” or “an” and its corresponding definite article “the” as used herein means at least one, or one or more, unless specified otherwise.

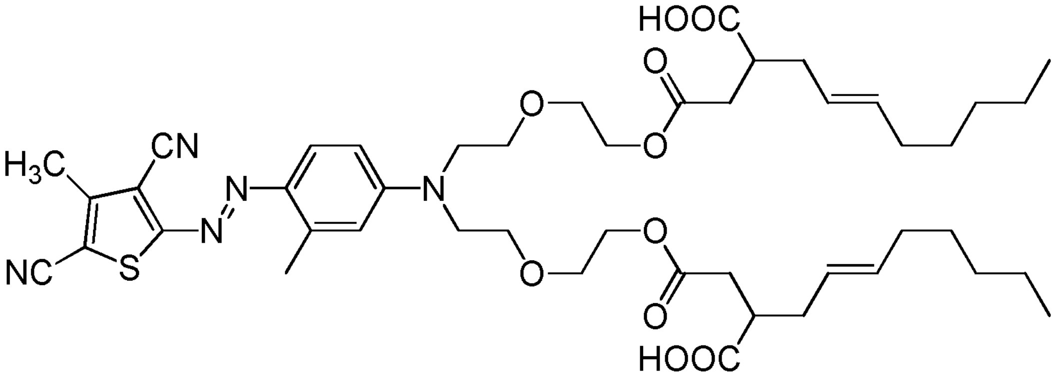
Dye weights refer to the sodium or chloride salts unless otherwise stated.

Preferably the laundry treatment composition is in a plastic bag, plastic box or a cardboard box.

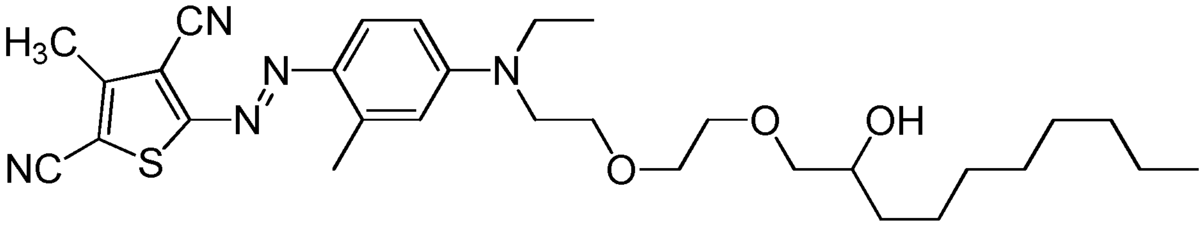
For ease of use it is preferred that the laundry treatment composition is present in 0.5 to 5kg packs.

Examples

Reference dye A may be synthesised according to the methods described in WO2013/006871.

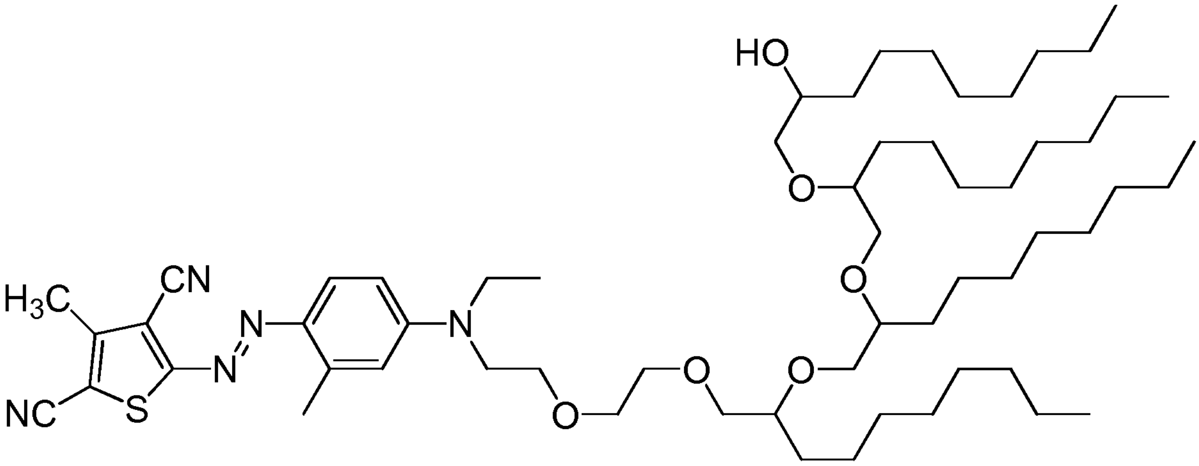


Reference Dye A
Molecular weight = 878



Inventive Dye 1

Molecular weight = 554



Inventive Dye 2

Molecular weight = 1023

The inventive dyes were synthesised by the reaction of N-Ethyl-N-hydroxyethoxyethyl-m-toluidine with 1,2-epoxydecane, followed by azo coupling.

To synthesise Inventive Dye 1: the reaction was performed with 1.1 mol equivalent of 1,2-epoxydecane in acetic acid at 363K. The initial product was the acetate ester, which was then hydrolysed using LiOH. Reaction products were confirmed by MS.

To synthesise Inventive Dye 2: the reaction was performed 1,2-epoxydecane in refluxing tetrahydrofuran and KO*t*Bu. Reaction products were confirmed by MS.

0.02wt% of the pure dye was dissolved in an aqueous liquid detergent contains 10wt% linear alkyl benzene sulfonate and 10wt% non-ionic surfactant (Neodol 25-9 (Shell chemicals) a primary alcohol ethoxylate with an average of approximately 9 moles of ethylene oxide per mole of alcohol. The alcohol is a blend of C12, C13, C14 and C15 primary alcohols.). The remainder of the liquid detergent was water. 4g/L of the liquid detergent was added to a plastic bottle containing demineralised water and a piece of woven cotton a fabric and a piece of knitted polyester fabric at 293K. The Liquor to cloth ratio was 100:1 and the pH of the wash liquor was buffered to pH=7. The bottle was agitated on an orbital shaker at 150 rpm for 30 minutes, the clothes removed, rinsed in water and dried. The colour of the cloth was measured using a reflectometer and expressed as the CIE L*a*b* values. The colour deposition of the blue-violet dyes to the cloth was quantified as Δb, where:

Δb = b (control, wash without dye) – b(wash with dye)

The experiment was repeated at pH=8, 9 and 10. The results are given in the table below.

pH	**Δb (colour deposition)**					
	cotton			**polyester**		
	Reference A	**Dye 1**	**Dye 2**	**Reference A**	**Dye 1**	**Dye 2**
7	0.26	1.74	0.58	1.97	4.18	3.50
8	0.23	1.84	0.48	1.13	4.17	3.62
9	0.20	1.57	0.46	1.03	3.85	3.77
10	0.33	1.73	0.27	0.97	4.00	3.81

Dye 1 and Dye 2 of the invention give much higher colour deposition (Δb) to both cotton and polyester than the reference dye, reference A. On polyester a strong pH dependence is observed for Reference A, this is not observed for Dye 1 and Dye 2.

CLAIMS

1. A laundry detergent composition comprising between 0.0001 to 1.0 wt% of a blue or violet azo dye, 2 to 70 wt% of a surfactant, and from 0.005 to 2 wt % of a fluorescent agent, wherein the blue or violet dye azo is of the form:

$$\text{Dye-NR}_1\text{R}_2,$$

wherein,

R_1 is a $–(L)_n-(X)_p-CH_2-CH(OH)CH_2(O)_qR_3$ group, wherein n = p = 0 or 1, q = 0 or 1, and L is selected from C1 to C2-alkyl, and ether group having from 1 to 15 ether linkages;

when n = 1, X is selected from S, N and O;

R_3 is a branched, linear or cyclic C_4 to C_{24} alkyl chain; and,

R_2 is selected from: H; C_1 to C_3-alkyl; phenyl; benzyl; and a $–(L)_n-(X)_p-CH_2-CH(OH)CH_2(O)_qR_3$ group, wherein n = p = 0 or 1, q = 0 or 1, and L is selected from C1 to C2-alkyl, and an ether group having from 1 to 15 ether linkages.

2. A laundry detergent composition according to claim 1, wherein R_3 is substituted by a group selected from: F; Cl; Br; ester; acid amide; and, phenyl.

3. A laundry detergent composition according to claim 1 or 2, wherein R_3 is a C5 to C11-n-alkyl chain.

4. A laundry detergent composition according to any preceding claim, wherein q = 0.

5. A laundry detergent composition according to any preceding claim, wherein the azo dye is a mono-azo dye.

6. A laundry detergent composition according to any one of claims 1 to 4, wherein the azo dye is a di-azo dye.

7. A laundry detergent composition according to any preceding claim, wherein X is selected from N and O.

8. A laundry detergent composition according to claim 7, wherein X is O.

9. A laundry detergent composition according to any preceding claim, wherein the ether group has from 1 to 10 ether linkages.

10. A laundry detergent composition according to claim 9, wherein the ether group has from 1 to 3 ether linkages.

11. A laundry detergent composition according to any preceding claim, wherein R_3 is substituted by groups selected from: SO_3H and COOH.

12. A laundry detergent composition according to any one of claims 1 to 10, wherein the blue or violet azo dye is not substituted by a group selected from: quaternary ammonium groups, SO_3H and COOH.

13. A laundry detergent composition according to any preceding claim, wherein the blue or violet azo dye is an azothiophene.

14. The azo-dye as defined in any one of claims 1 to 13.

15. A domestic method of treating a textile, the method comprising the steps of:

    (i) treating a textile with an aqueous solution of the blue or violet azo dye as defined in any one of claims 1 to 12, the aqueous solution comprising from 1 ppb to 5000 ppm, blue or violet azo-dye; and, from 0.0 g/L to 5 g/L of a surfactant; and,

    (ii) optionally rinsing and drying the textile.

16. A domestic method of treating a textile according to claim 15, wherein the aqueous solution comprises from 0.2 to 4 g/L of a surfactant.

17. A domestic method of treating a textile according to claim 15 or 16, wherein the aqueous solution comprises a fluorescer in the range from 0.0001 g/l to 0.1 g/l.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/053277

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/40 C09B29/08 C09B31/047 C09B31/08 C09B33/02
C11D3/42
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 321 055 A (HANSEN GUENTER ET AL) 23 March 1982 (1982-03-23) examples 1, 2, 5, 7, 8, 11, 14, 15, 17, 19, 20, 22, 26 -----	14
X	GB 2 099 009 A (BASF AG) 1 December 1982 (1982-12-01) examples 1, 2 -----	14
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 11 May 2015	Date of mailing of the international search report 20/05/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bertran Nadal, Josep

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 2010/151906 A2 (MILLIKEN & CO [US]) 29 December 2010 (2010-12-29) page 2, paragraphs 2, 3 compounds BA1-BA81 examples -----	1-17
A	WO 2007/087252 A1 (MILLIKEN & CO [US]) 2 August 2007 (2007-08-02) page 3, lines 13-20 table 1; compounds 1-80 examples -----	1-17
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Information on patent family members

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