(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 894 890 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.02.1999 Bulletin 1999/05

(21) Application number: **98202592.6**

(22) Date of filing: **31.07.1998**

(51) Int. Cl.[6]: **D06P 5/02**, C11D 11/00, D06P 3/66, D06P 1/673, D06P 5/08

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **31.07.1997 NL 1006703**

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(54) Process for washing off dyed tectile

(57) The invention relates to a process for washing off textile, on the basis of cellulose fibres, which is dyed with a reactive dye, which comprises using a combination of at least one alkali metal silicate and at least one metal aluminosilicate to remove non-covalently bonded dye. It has been found that the combination of an alkali metal silicate and a metal aluminosilicate gives a synergistic effect as regards the removal of non-covalently bonded dye.

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Description

[0001] The invention relates to a process for washing off textile dyed with a reactive dye.

[0002] Reactive dyes belong to the most important dyes for dyeing and printing textile on the basis of cellulose fibres. Examples of such dyes are described in the "Colour Index", Volume 2, third edition, 1971, pages 3391-3562, "Reactive Dyes" and in U.S. patent 5,490,866.

[0003] When applying the dye to the textile, e.g. by dyeing or printing, a reaction takes place between the reactive part of the dye and the textile fibres. This reaction, which takes place under alkaline conditions, effects a covalent bond, thus stably bonding the dye to the textile.

[0004] Besides this desired reaction, an undesirable reaction occurs in nearly all cases. Owing to the presence of hydroxide ions in the reaction mixture, part of the reactive dye hydrolyses, thus forming a product which is no longer capable of forming a covalent bond with the textile. In practice, the amount of hydrolysed dye is about 5-40% of the total amount of dye employed.

[0005] Apart from an amount of hydrolysed dye, under less favourable fixation conditions an amount of non-hydrolysed dye may be present which is also non-covalently bonded to the textile. The total amount of non-covalently bonded dye, consisting of hydrolysed dye and optionally non-hydrolysed dye, more or less adsorptively bonds to the textile. Because the non-covalently bonded dye may result in poor wetfastness and/or rub fastness properties of the dyed textile, this non-covalently bonded dye must be removed after the operation of applying the reactive dye to the textile. In this connection the term wetfastness properties is understood to mean both water-fastness and wash- and sweat-fastness.

[0006] A treatment for removing dye which is non-covalently bonded to textile must be carried out before the textile is subjected to a further treatment or reaches the consumer. Within the context of the invention such a treatment is referred to as "washing-off treatment" or "soaping-off treatment".

[0007] In the literature different washing-off treatments or soaping-off treatments have already been proposed. These known washing-off treatments comprise, inter alia, treatments with surfactants, polyphosphates, polyvinyl pyrrolidone or polymeric acrylates.

[0008] Furthermore, U.S. patent 4,500,320 describes a washing-off treatment in which only a zeolite is used as active substance.

[0009] European patent application 0 382 183 proposes a washing-off treatment with an alkali metal salt of a polyphosphate or a silicate in combination with a salt of a hydroxycarboxylic acid or an aliphatic carboxylic acid polymer. For the silicate preference is given to sodium metasilicate, which is the only silicate for which results are mentioned.

[0010] U.S. patent 5,490,866 describes a washing-off treatment in which a polyvinyl pyrrolidone homopolymer or copolymer is used to remove a non-covalently bonded dye from textile. In this treatment a water softener may be present. This water softener is an alkali metal silicate, a zeolite, a carboxylic acid group-containing polymer, a polyphosphate, a polyphosphonate or mixtures thereof.

[0011] The international patent application WO-A-88/07603 describes the use of lamellar silicates charged with quaternary ammonium compounds for the use as soaping-off agent. These are natural bentonite-type swelling lamellar silicates and synthetic lamellar silicates with a smectite-like crystalline phase and large contents of bonded alkali metal.

[0012] U.S. patent 5,378,242 describes an aqueous solution containing an alkali metal hydroxide and an alkali metal silicate as agent for carrying out a soaping-off treatment of cotton. Alternatively, the solution may further contain a small amount of a borate.

[0013] In view of the amount and the highly bonded character of the hydrolysed dyes the known washing-off treatments in practice do not always prove to be suitable for the effective removal of the hydrolysed dyes. It is therefore an object of the invention to provide an improved washing-off treatment.

[0014] Surprisingly, it has been found that the use of a combination of at least one alkali metal silicate and at least one metal aluminosilicate in a washing-off treatment of textile results in a drastic removal of non-covalently bonded reactive dye present.

[0015] The invention therefore relates to a process for washing off textile, on the basis of cellulose fibres, which is dyed with a reactive dye, which comprises using a combination of at least one alkali metal silicate and at least one metal aluminosilicate to remove non-covalently bonded dye.

[0016] It has been found that a process according to the invention gives better results than when a known washing-off agent is used. The washed-off textile has excellent wetfastness and rub fastness properties.

[0017] It has further been found that the combination of alkali metal silicate and metal aluminosilicate gives a synergistic effect. With the above combination better results are obtained than when one of both substances is used separately.

[0018] Types of textile suitable for being washed off in a process according to the invention are dyed with a reactive dye and based on cellulose fibres. The term cellulose fibres is understood to mean fibres containing an amount of natural or synthetic cellulose. Both materials which only contain cellulose fibres and materials based on mixtures of cellu-

lose and other materials are suitable. These mixtures may contain both mixed fibres and mixtures of fibres. Typical examples of materials that may be present in such a mixture are synthetic organic materials, such as linear polyesters or modified cellulose (cellulose esters). When a mixture of cellulose fibres and other material is used, this mixture must contain sufficient free hydroxyl groups to enable covalent bonding to a reactive dye. The knowledge of an average skilled worker is sufficient to know what minimum amount of cellulose is necessary for what mixtures.

[0019] Preferably, a textile dyed with a reactive dye selected from the group consisting of hemp, linen, jute, viscose and cotton is washed off.

[0020] The textile may be in any form conventional in the art when it is washed off according to the invention. Examples of such forms comprise fibres, yarns, strands, knit or woven cloths and the like. Preferably, strands or cloths of textile based on cellulose fibres are subjected to a soaping-off treatment.

[0021] The textile based on cellulose fibres which is washed off is dyed with one or more reactive dyes. This dye may be applied in any known manner, such as by dyeing or printing. Depending on the desired intensity of the colour, a larger amount of dye will be applied to the textile. For an extensive description of examples of suitable reactive dyes and how to apply them to textile, reference is made to the above-mentioned "Colour Index", Volume 2, third edition, 1971, pages 3391-3562, "Reactive Dyes" or to U.S. patent 5,490,866. In itself, any known reactive dye may be used to dye the textile.

[0022] In general, textile dyed with a reactive dye will first be rinsed with water after applying the reactive dye. This is done to remove non-bonded dye as much as possible. Only then will a washing-off treatment according to the invention be carried out to remove non-covalently but adsorptively bonded dye.

[0023] According to the invention dyed textile of the above-discussed type is washed off using a combination of at least one alkali metal silicate and at least one metal aluminosilicate.

[0024] According to the invention an alkali metal silicate is understood to mean a compound comprising one or more metals, all of which are selected from the group of alkali metals, and a silicate group. The alkali metal of the alkali metal silicate employed is preferably sodium.

[0025] An alkali metal silicate eligible for use in a process according to the invention is preferably a lamellar silicate. More preferably, a disilicate is used. Especially preferred is a δ-disilicate. With such a silicate it has been found that optimum removal of non-covalently bonded dye is obtained.

[0026] Other alkali metal silicates with which good results are obtained are selected from the group of aqueous silicate solutions, such as solutions of water glass. These silicate solutions are also referred to as liquid silicates. For a general description of silicate solutions reference may be made to Winnacker, Kuchler, Chemische Technologie, Band 3, Anorganische Technologie II, 4th edition, 1983 and Ullmanns Encyklopedie der technischen Chemie, Band 21, 4th edition, 1982, pages 409-412.

[0027] A preferred silicate solution is a solution of sodium silicate (x Na_2O.y SiO_2, in which x/y is preferably between 30/70 and 70/30, by special preference between 40/60 and 60/40), which is prepared by a hydrothermal process, as described, inter alia, in European patent applications 0 456 655 and 0 380 997. It has been found that the combination of the above solutions of alkali metal silicates and a metal aluminosilicate gives good results when removing non-covalently bonded dye in a washing-off treatment of textile.

[0028] Metal aluminosilicates suitable for use in a washing-off treatment according to the invention are synthetic and natural minerals. Examples are zeolites, talc and clays, such as bentonite, montmorrilonite, saponite and the like.

[0029] Excellent results are obtained when using a metal aluminosilicate satisfying the formula

$$M_m(AlO_2)_n(SiO_2)_p.xH_2O,$$

in which

- M represents one or more metals selected from the group of alkali metals and alkaline-earth metals,
- m is a number selected between 0.3 and 3, preferably between 0.8 and 1.2,
- n is a number selected between 0.5 and 3, preferably between 0.8 and 1.2,
- p is a number selected between 0.5 and 8, preferably between 0.6 and 1.5, and
- x is an integer selected between 0 and 10.

[0030] These materials prove to possess properties that are eminently suitable in a washing-off treatment of textile, on the basis of cellulose fibres, which is dyed with a reactive dye. Of the compounds having the above-mentioned formula, zeolites, such as zeolite A or zeolite P, are preferred.

[0031] A very important property that renders a metal aluminosilicate suitable for use in a process according to the invention is the particle size. This particle size must be small enough to provide a sufficiently large active surface. A metal aluminosilicate preferably has a particle size of up to 25 μm, more preferably up to 10 μm and most preferably up to 1 μm.

[0032] According to the invention an alkali metal silicate and a metal aluminosilicate will normally be used in a mutual weight ratio between 1:9 and 9:1. It has been found that when the mutual weight ratio is between 1:4 and 4:1, preferably between 2:3 and 3:2, the resulting synergistic effect is most favourable. In these mutual ratios the two substances considerably enhance each other's effects when removing non-covalently bonded reactive dye from textile based on cellulose fibres.

[0033] Besides the above-described combination of at least one alkali metal silicate and at least one metal aluminosilicate, a washing-off agent for a washing-off treatment according to the invention may contain any conventional additive. Examples of such additives are binders, fillers, emulsifiers, water softeners, perfumes and the like.

[0034] Polyvinyl pyrrolidone (PVP) has proved to be a very suitable additive which significantly improves the activity of a washing-off agent for a washing-off treatment according to the invention. Preferably, the washing-off agent therefore comprises from 0.5 to 2% by weight, based on the weight of the washing-off agent, PVP having a weight-average molecular weight between 10,000 and 360,000.

[0035] The presence of specific additives depends on the form in which a washing-off agent containing the above combination of substances is used. In a soaping-off treatment according to the invention a washing-off agent may be used in solid or liquid form. Preferably, a washing-off agent is used in the form of an aqueous suspension. When using the washing-off agent in liquid form, it will also contain water. Suitable amounts of water are from 40 to 80% by weight, based on the weight of the washing-off agent. In liquid form the washing-off agent will usually also contain a binder, such as xanthane gum, a cellulose thickener or an acrylate thickener. The common amounts of additives, apart from water, will usually not exceed 10-15% by weight, based on the weight of the washing-off agent.

[0036] A washing-off treatment according to the invention is carried out in sufficient water, usually in a liquor ratio of 3-20 l water to 1 kg textile. To this water is added a washing-off agent containing the constituents required by the invention. The common concentration of the combination of alkali metal silicate and metal aluminosilicate depends on the hardness of the water employed, but will usually range between 0.1 and 10 g/l. It has been found that at higher concentrations a progressive removal of non-covalently bonded dye is obtained. Mostly, however, the above concentration will not exceed 1 g/l, because above this concentration the effect of the progressive removal of non-covalently bonded dye is outweighed by the higher costs of using more washing-off agent.

[0037] The washing-off treatment itself may then be carried out in any known manner. Usually, during washing off the temperature will range between 80°C and 98°C. It is preferred, however, to work at a higher temperature, e.g. between 90°C and 110°C. It will be clear that higher temperatures and longer washing-off times give better results. In each individual case a skilled worker will be capable of determining what temperatures and times are most favourable, both from a standpoint of costs and from a standpoint of quality.

[0038] After the washing-off treatment the textile will be rinsed a number of times to remove all the remnants of dye and washing-off agent. Finally, the textile may be dried.

[0039] The invention will now be explained in more detail by means of the following examples.

Example I

[0040] A phthalocyanide dye, namely C.I. Reactive Blue 41, was completely reacted with caustic soda in the hydrolysed form. To this end, 2.5 g of the dye were dissolved together with 2 ml NaOH 38° Baumé in 1 l water. The resulting solution was stirred for 1 hour at 98°C.

[0041] Then three cloths of bleached cotton ready for dyeing were soaked in the aqueous solution of the hydrolysed Reactive Blue 41 (2.5 g/l) and uniformly pressed out (bath absorption about 100%). Then the cloths were dried, after which they each contained 0.25% by weight, based on the weight of the dyed cloth, of the hydrolysed dye.

[0042] The dyed cloths were each individually washed for 20 minutes at 98°C with an undyed but otherwise identical cloth. 10 parts by weight of water were used per 1 part by weight of cotton.

[0043] For each of the three cloths the water contained another washing-off agent:

cloth A: 0.5 g/l zeolite A (particle size ± 1 μm);
cloth B: 0.5 g/l δ-sodium disilicate;
cloth C: 0.25 g/l δ-sodium disilicate and 0.25 g/l zeolite A (particle size ± 1 μm).

[0044] After washing the cloths were examined. Considered were the degree of removal of the hydrolysed dye from the dyed cloths, on the one hand, and the bleeding of the undyed cloths, on the other hand. The results are listed in Table I.

Table I

	degree of removal of hydrolysed dye	degree of bleeding
cloth A	+	-
cloth B	+	--
cloth C	+++	---

[0045] The amount of plus or minus signs indicates respectively a larger or a smaller degree. According as more plus signs are mentioned for the degree of removal of hydrolysed dye, a larger part of the hydrolysed dye has been removed. According as more minus signs are mentioned for the degree of bleeding, the co-washed undyed cloth has changed its colour less after the washing treatment.

Example II

[0046] The same procedure as in Example I was repeated, with the difference that the dye employed was C.I. Reactive Red 141 and that the cloths were soaked in a solution having a concentration of 10 g/l hydrolysed dye. After dyeing the cloths each contained 1.0% by weight, based on the weight of the dyed cloth, of the hydrolysed dye.

[0047] The results obtained after the washing treatment are given in Table II.

Table II

	degree of removal of hydrolysed dye	degree of bleeding
cloth A	++	-
cloth B	+	-
cloth C	+++	--

[0048] The amount of plus or minus signs indicates respectively a larger or a smaller degree. According as more plus signs are mentioned for the degree of removal of hydrolysed dye, a larger part of the hydrolysed dye has been removed. According as more minus signs are mentioned for the degree of bleeding, the co-washed undyed cloth has changed its colour less after the washing treatment.

Claims

1. A process for washing off textile, on the basis of cellulose fibres, which is dyed with a reactive dye, which comprises using a combination of at least one alkali metal silicate and at least one metal aluminosilicate to remove non-covalently bonded dye.

2. A process according to claim 1, wherein the alkali metal silicate is a lamellar alkali metal silicate.

3. A process according to claim 2, wherein the lamellar alkali metal silicate is an alkali metal disilicate.

4. A process according to claim 1, wherein the alkali metal silicate is an aqueous alkali metal silicate solution.

5. A process according to claims 1-4, wherein the alkali metal silicate is a sodium silicate.

6. A process according to claims 1-5, wherein the metal aluminosilicate satisfies the formula

$$M_m(AlO_2)_n(SiO_2)_p.xH_2O,$$

in which

M represents one or more metals selected from the group of alkali metals and alkaline-earth metals,
m is a number selected between 0.3 and 3,
n is a number selected between 0.5 and 3,
p is a number selected between 0.5 and 8, and
x is an integer selected between 0 and 10.

7. A process according to claims 1-6, wherein the metal aluminosilicate has a particle size of up to 25 μm, preferably up to 1 μm.

8. A process according to claims 1-7, wherein the weight ratio between the metal aluminosilicate and the alkali metal disilicate is between 1:9 and 9:1.

9. A process according to claims 1-8, wherein the textile is selected from the group consisting of hemp, linen, jute, viscose and cotton.

10. A washing-off agent for use in a process according to claims 1-9, comprising an alkali metal silicate and a metal aluminosilicate in a mutual weight ratio between 1:9 and 9:1.

11. A washing-off agent according to claim 10, which also comprises polyvinyl pyrrolidone.

12. A washing-off agent according to claim 10 or 11 in the form of an aqueous suspension in which the alkali metal silicate and the metal aluminosilicate are present in an amount of 20 to 60% by weight, based on the weight of the washing-off agent, and in which conventional additives are optionally included.

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EUROPEAN SEARCH REPORT

Application Number
EP 98 20 2592

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 287 514 A (CIBA GEIGY AG) 19 October 1988 * the whole document * ---	1,6,7,9, 10,12	D06P5/02 C11D11/00 D06P3/66 D06P1/673
A	GB 2 246 146 A (COURTAULDS PLC) 22 January 1992 * claims * ---	1-5,9, 10,12	D06P5/08
A	DE 195 16 957 A (STOCKHAUSEN CHEM FAB GMBH) 14 November 1996 * page 8, line 35 - line 46; claims; examples * ---	1-12	
A D	EP 0 631 008 A (CIBA GEIGY AG) 28 December 1994 * page 3, line 5 - line 13; claims * & US 5 490 866 A (GUTH CHRISTIAN) 13 February 1996 ---	1,4,5,9, 11	
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D,A	US 5 378 242 A (CHRISTIE NICK J ET AL) 3 January 1995 * the whole document * ---	1-5,9, 10,12	D06P C11D
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 September 1998	Blas, V

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 98 20 2592

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 260 971 A (UNILEVER PLC ;UNILEVER NV (NL)) 23 March 1988 * the whole document * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

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THE HAGUE	30 September 1998	Blas, V

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