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- (73) Patenthaver: **Sanko Tekstil Isletmeleri San. Ve Tic. A.S., Organize Sanayi Bölgesi 3. Cadde, 16400 Inegol - Bursa, Tyrkiet**
- (72) Opfinder: **KAPLAN, Gökhan, c/o Sanko Tekstil Isletmeleri San. Ve Tic. A.S., Organize Sanayi Bölgesi 3. Cadde, 16400 Inegol - Bursa, Tyrkiet**
Zengi, Leyla, c/o SANKO Tekstil Isletmeleri San. ve Tic. A.S., Organize Sanayi Bölgesi 3. Cadde, 16400 Inegol - Bursa, Tyrkiet
ZEYREK, Mustafa, c/o Sanko Tekstil Isletmeleri San. Ve Tic. A.S., Organize Sanayi Bölgesi 3. Cadde, 16400 Inegol - Bursa, Tyrkiet
KAZANÇ, Semih, c/o Sanko Tekstil Isletmeleri San. Ve Tic. A.S., Organize Sanayi Bölgesi 3. Cadde, 16400 Inegol - Bursa, Tyrkiet
- (74) Fuldmægtig i Danmark: **Marks & Clerk (Luxembourg) LLP, 44 rue de la Vallée, B.P. 1775, L-1017 Luxembourg, Luxembourg**
- (54) Benævnelse: **ANVENDELSE AF COPOLYMERER TIL TILVEJEBRINGELSE AF ANTIMIKROBIEL OG ANTIPILLING-EFFEKT OG TIL FORBEDRING AF TEKSTILERS FARVEOPTAGELSE**
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KAZANÇ ET AL.: "Multi-Functional Textile Coatings Based on Polymeric Mate", MARMARA UNIVERSITY JOURNAL OF SCIENCE, vol. 27, no. 3, 2015, XP055525400, ISSN: 2146-5150, DOI: 10.7240/mufbed.91838

DESCRIPTION

ABSTRACT OF THE INVENTION

[0001] The present invention relates to an aqueous composition for providing an anti-microbial and an anti-pilling effect to textiles and for improving dye uptake to textiles. The invention also relates to novel co-polymers to be used according to the invention and to novel textiles.

TECHNICAL BACKGROUND

[0002] Antimicrobial, especially antibacterial textiles are known in the art, which are usually prepared by applying antimicrobial substances to said textiles or to yarns. Said antimicrobial substances must of course be non-toxic and non-allergenic to human skin.

[0003] Currently antimicrobial substances are generally selected from quaternary ammonium compounds (QACs), triclosan, metal ions, oxides, some inorganic compounds and salts (such as Ag, TiO₂, Cu, Ni, Pd, Ag(I), Pd(II) complexes) and natural polymers (such as chitosan, chitin).

[0004] Among above mentioned compounds QACs are widely used, for instance on cotton, polyester, nylon and wool. The antimicrobial effect of QAC's highly depends on length of alkyl chain and the number of cationic ammonium groups.

[0005] It is easy to understand that the applied antimicrobial substance must show a strong attachment to textiles especially because for some industrial textiles manufacturing process, such as denim, washing is an inevitable stage of garment production.

[0006] At present, the available antimicrobial substances do not meet the essential stability requirement and easily leach from textile surfaces and/or show hydrolytic instability and/or decrease their antimicrobial activity over time and/or make the tensile strength of the textiles decrease.

[0007] Kazanc et al. (Marmara Journal of Pure and Applied Sciences, 2015, Special issue-I:49-52) disclose polyurethanes obtained by co-polymerization of monomers bearing hydroxy functions and monomers bearing quaternized tertiary amine moieties, and the subsequent cross-linking of the hydroxy functions present in the co-polymer with isocyanates to form polyurethane films. Said films are applied onto non-dyed indigo fabrics to the surface of which they adhere by positive-negative charge interaction between the quaternized ammonium functions and the negatively charged indigo molecules. Said interaction however is weak and the applied coating leaches away upon use and washing.

[0008] Pilling is a common flaw of textiles caused for instance by wear and washing, which provoke the loosing of the fibers over time. Pilling represents an important problem to be solved in the textile field.

[0009] EP1354935 describes a detergent composition having at least one surfactant and a copolymer having amine functionality. The copolymers are at least partially neutralized to present a balance between hydrophobicity and cationic character. The described detergent composition is aimed to provide color protection and anti-pill properties in laundry applications.

[0010] There is therefore a need for novel antimicrobial substances which overcome the shortcomings of the prior art, such as those disclosed above and, hopefully, provide the textiles with further interesting and useful properties, such as anti-pilling effect and others.

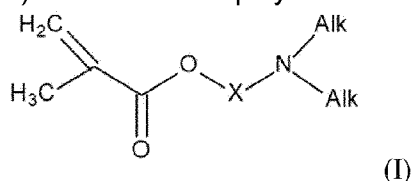
OBJECTS OF THE INVENTION

[0011] It is a first object of the invention to provide the use of an aqueous composition for providing an anti-microbial and an anti-pilling effect and for improving dye uptake to textiles, by means of a treatment with known and novel co-polymers and diisocyanates.

DESCRIPTION OF THE INVENTION

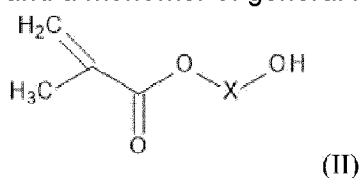
[0012] According to one of its aspects, the present invention relates to the use of an aqueous composition for providing an anti-microbial and an anti-pilling effect and for improving dye uptake to a textile, said use comprising:

1. (i) treating said textile with an aqueous solution comprising
 1. a) at least one co-polymer made of a monomer of general formula (I)



or mixture thereof,

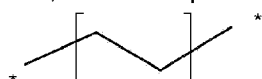
and a monomer of general formula (II)

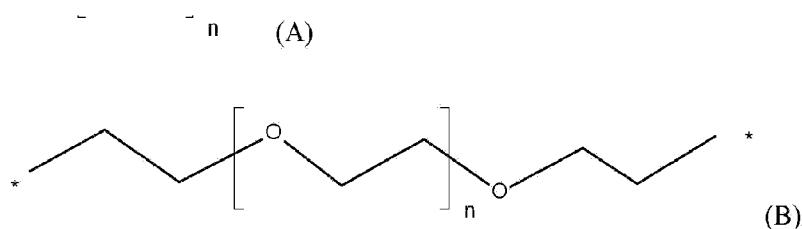


or mixture thereof,

wherein

- X is, each independently selected from the following (A) or (B) chains





- the stars indicate the bonds linked to the oxygen and nitrogen atoms in the monomers of formula (I) and formula (II);
- n is, each independently, an integer from 1 to 10; and
- Alk is a C₁-C₄ alkyl group;

and wherein the tertiary amino groups in formula (I) are optionally partially quaternized with halo-long chain alkyl groups;
and

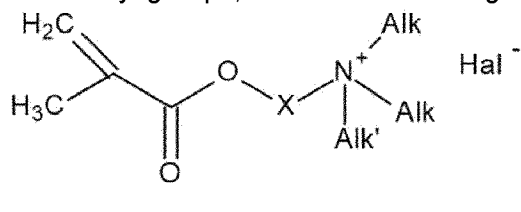
2. b) at least one aliphatic or cycloaliphatic diisocyanate;
and
2. (ii) optionally drying and/or fixing said textile.

[0013] According to the use of the invention, the treatment of a textile with the components (a) and (b) above forms an urethane bridge between the free hydroxy groups in the monomer of general formula (II) and the free hydroxy groups present in said textile, as shown in Figure 1.

[0014] The term "Alk" herein indicates a linear or branched, saturated C₁-C₄ alkyl group, preferably a linear alkyl group, more preferably a methyl or an ethyl group, methyl being particularly preferred.

[0015] According to a preferred embodiment, n is an integer from 1 to 8, for instance 1, 2, 3 or 4, more preferably n is 1 or 2, advantageously n is 1.

[0016] The expression "wherein tertiary amino groups in formula (I) are optionally partially quaternized with halo-long chain alkyl groups" means that quaternized ammonium groups may be present in the co-polymer which is achieved by reaction of the co-polymer with halo-long chain alkyl groups, so that the resulting monomer of formula (I) is a monomer of formula (I')



wherein X and Alk are as above defined, Alk⁻ is a C₆ to C₂₂ alkyl group, preferably a C₈ to C₂₀ alkyl group, such as for instance C₁₀, C₁₂, C₁₄, C₁₆ or C₁₈, and Hal⁻ indicates a halogen counter ion, such as a Br⁻ or a Cl⁻, preferably a Br⁻.

[0017] The expression "aliphatic or cycloaliphatic diisocyanate" is self evident for the skilled in

the art, and herein preferably includes hexamethylene diisocyanate, isophorone diisocyanate and methylene-bis(4-cyclohexylisocyanate), hexamethylene diisocyanate being particularly preferred. Other diisocyanates may however be used according to the invention, provided that they are able to create an urethane bridge reacting with the hydroxy groups of the co-polymer and the hydroxy groups of the textile.

[0018] According to the invention, the diisocyanate may be a blocked diisocyanate, such as a diisocyanate blocked with dimethyl pyrazole, caprolactame, butanone oxime, 1,2-pyrazole, 1,2,4-triazole, diisopropylamine, 3,5-dimethylpyrazole and diethyl malonate. Blocked diisocyanate are known in the art and the skilled man is perfectly able to select the appropriate one to carry out the invention.

[0019] The above mentioned monomers and compounds are known to the art, or they can be prepared according to known and conventional processes.

[0020] The term "textile" herein indicates any material suitable to prepare fabrics and garments, and includes fibers, filaments, yarns, fabrics, ready for dyeing fabrics and any textile articles, such as for instance garments, clothes and fabric based articles. The expression "ready for dyeing fabrics" means a fabric which has undergone the desizing, mercerization (or bleaching) and washing steps.

[0021] According to a preferred embodiment, the textile of the invention are indigo textiles, such as denim.

[0022] According to a preferred embodiment, the monomer of formula (I)/monomer of formula (II) molar ratio is about 95-85/5-15, preferably about 90/10.

[0023] According to a preferred embodiment, 20-40% of the tertiary amino groups are quaternized in the co-polymer, most preferably about 30%.

[0024] Preferably only one type of monomer of formula (I) and only one type of monomer of formula (II) are present in the co-polymer.

[0025] Preferably only one type of diisocyanate is used according to the invention.

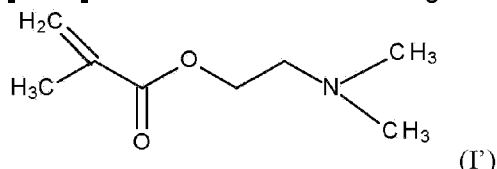
[0026] According to a preferred embodiment, the invention relates to the use of an aqueous composition for providing an anti-microbial and an anti-pilling effect to a textile, such as above defined, said use comprising coating said textile with an aqueous solution comprising

a') at least a co-polymer of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 2-hydroxyethyl methacrylate (HEMA) said co-polymer, optionally being quaternized with halo-long chain alkyl groups; and

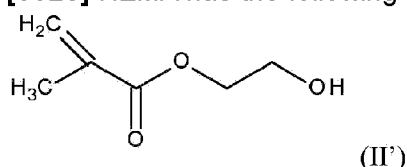
b') at least one aliphatic or cycloaliphatic diisocyanate;

to form a urethane bridge between the free hydroxy groups in HEMA and the free hydroxy groups present in said textile.

[0027] DMAEMA has the following chemical formula (I')



[0028] HEMA has the following chemical formula (II')



[0029] According to a preferred embodiment, the DMAEMA/HEMA molar ratio is about 95-85/5-15, preferably about 90/10.

[0030] According to a preferred embodiment, 20-40% of the tertiary amino groups are quaternized as disclosed above, most preferably about 30%.

[0031] The above preferred embodiments above disclosed also apply to DMAEMA and HEMA above.

[0032] Besides the co-polymers (a) and the diisocyanates (b) as above defined, the aqueous solution used according to the invention (herein also "coating composition") may further comprise other components, such as for instance, wetting agents and thickeners, such as for instance commercial wetting agents, i.a. those presently marketed under the commercial names Leonil KS, Mersitol 2334 AQ, Mercerol QWLF which are preferably used about 1%(vol) with respect to the total volume of the solution and/or commercial thickeners such as those presently marketed under the commercial names Pirusulan DCA 24 ST, Pirusulan DCA 130 which are used to adjust the viscosity preferably between 20-24 d.cP.

[0033] The term "coating" herein indicates any possible application of a solution on a textile and includes, but is not limited to, padding, dipping, printing and the like.

[0034] After the application of an aqueous solution above to the textile, the coated fabric is dried, for instance by heating, the temperature depending on the type of textile. For instance, for denim, the drying step may be made at 100-160°C, such as 150°C, for some minutes. The coated textile may also be fixed, for instance at higher temperatures, such as 170-190°C for one or more minutes.

[0035] According to a preferred embodiment, the co-polymer concentration in the aqueous solution is from about 2 to about 15 g/L.

[0036] With the use of the invention, it was surprisingly found that when the aqueous solution comprising the co-polymer (a) and the diisocyanate (b) (or (a') and (b')), as above defined, is applied to a textile, the diisocyanate molecule reacts either with the hydroxy groups present in the co-polymer and the hydroxy groups present on the textile surface, thus creating urethane bridges which covalently bind the co-polymer to the textile.

[0037] It results a stable co-polymer coating on the textile, which does not leach even after multiple washings (both industrial, such as stone wash and home laundry washings). This co-polymer coating provides for very interesting effects, such as an anti-microbial effect, thanks to the presence of quaternized ammonium groups, and also anti-pilling effect.

[0038] It has also been observed that the co-polymer coating of the invention allows to obtain darker shades which can be obtained thanks to an increased dye uptake activated by the co-polymer coating.

[0039] The reaction for the preparation of the co-polymer of the invention may be carried out according to Kazanc et al., Marmara Journal of Pure and Applied Sciences, 2015, Special issue-I:49-52.

[0040] A possible alternative process is disclosed in the Experimental Section which follows. According to another of its aspects, the invention relates to novel co-polymers made of DMAEMA and HEMA, characterized in that the molar DMAEMA/HEMA ratio is 95-85/5-15, preferably about 90/10, and 20-40% of the tertiary amino groups are quaternized with a substituent (C) as above defined, most preferably about 30%. According to another of its aspects, the invention relates to the use of an aqueous solution comprising at least one co-polymer as herein defined, including novel co-polymers of the invention and at least one aliphatic or cycloaliphatic diisocyanate as herein defined in the coating of textiles according to the invention.

[0041] According to another of its aspects, the invention relates to the use of an aqueous solution comprising at least one co-polymer as herein defined, including novel co-polymers of the invention and at least one aliphatic or cycloaliphatic diisocyanate as herein defined, (herein also "coating composition") for providing an anti-microbial and anti-pilling effect to textiles, as herein defined.

[0042] According to another of its aspects, the invention relates to the use of an aqueous solution comprising at least one co-polymer as herein defined, including novel co-polymers of the invention and at least one aliphatic or cycloaliphatic diisocyanate as herein defined, for improving dye uptake of a textile as herein defined, so that darker shades can be obtained. Preferably, the textile is a denim.

[0043] According to another of its aspects, the invention relates to textiles, preferably denim, fabrics and garments, yarns treated according to the invention.

[0044] Details are given in the Experimental Section which follows.

[0045] The anti-pilling effect has been evaluated by experts with a method for anti-pilling effect detection and measurement. In this method, the coating composition showed very interesting results.

[0046] The following Experimental Section illustrates representative embodiments of the invention, without limiting it.

BRIEF DESCRIPTION OF THE FIGURES

[0047]

Figure 1 shows a schematic representation of the reaction which occurs according to the invention, wherein n and m represent the number of monomers present in the co-polymer.

Figures 2A and 2B show the anti-microbial effect of a representative quaternized co-polymer of the invention.

EXPERIMENTAL SECTION

Example 1

Preparation of the co-polymer

[0048] A monomer solution containing 100 mmol HEMA and 900 mmol DMAEMA is prepared and 10% of (v/v) said solution is added the reactor that is set 70 °C. Then, 50 ml of distilled water is added in the reactor and stirred while monomer mixture, ammonium persulfate (22 g of ammonium persulfate is dissolved in 100 ml of water), and sodium metabisulfate (19 g sodium metabisulfate is dissolved in 100 ml of water) solutions are being fed with the 2 ml/min rate. The co-polymer is collected from the reactor and washed with hot water (70-80 °C) to remove unreacted monomer, ammonium persulfate and sodium metabisulfite.

Example 2

Quaternizing process

[0049] 25-30% of DMAEMA residues present in the co-polymer of Example 1 were quaternized with alkyl halides by following procedure: 50 g of the co-polymer is dissolved in 300 ml dry ethanol, and 75 mmol of an alkyl halide, preferably 1-bromodecane, is added, then the solution is stirred for 24 hour at room temperature. Ethanol is evaporated to collect the quaternized co-polymer by a conventional work-up step.

Example 3

Coating process

[0050] A coating solution is prepared with water, the quaternized co-polymer of Example 2, hexamethylene diisocyanate, a wetting agent and a thickener according to the following: 2.5 g of quaternized co-polymer (10% of HEMA in co-polymer) is dissolved in 1 L of water with 50-75 mg of the diisocyanate, 6-8 g of wetting agent, and an amount of thickener which allows a 20-24 d.cP viscosity. The solution is then applied onto the fabric. This can be made for instance by coating or impregnation. In coating method, it is useful to add a thickener to the solution in order to have desired viscosity, whereas in impregnation process a thickener is not necessary. A sanforizing machine can also be used for applying the solution to the fabric. The coated fabric is dried at 150 °C for about 3 minutes and subsequently fixed at 170°C for about 1 minute.

Example 4

Anti-microbial effect

[0051] The anti-bacterial effects of the co-polymer of Example 2 and the fabrics coated therewith were tested according to ASTM E2149-01 on:

- ATCC 35218 (Escherichia coli)
- ATCC 6538 (Staphylococcus aureus)

[0052] The results showed that, the quaternized co-polymer of Example 2 shows an

antimicrobial effect against *Staphylococcus aureus* and *Escherichia coli*, as reported in Figures 2A and 2B.

[0053] Figures 2A and 2B show two petri dishes, each one divided into eight portions. In both Figures 2A and 2B, each one of the eight portions of the petri dishes corresponds to a different concentration of co-polymer tested. As can be observed from Figures 2A and 2B, the tested concentrations of the quaternized co-polymer of Example 2 were: 0.0195 g/L, 0.039 g/L, 0.078 g/L, 0.156 g/L, 0.3125 g/L, 0.625 g/L, 1.25 g/L and 2.5 g/L.

[0054] As it can be seen from the Figures, the antimicrobial effect on *Staphylococcus aureus* is achieved even with very low concentrations of the co-polymer (starting from 0.0195 g/L) and the effect on *Escherichia coli* starts from 1.25 g/L and is very satisfying at 2.5 g/L.

REFERENCES CITED IN THE DESCRIPTION

Cited references

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Patent documents cited in the description

- [EP1354935A](#) **[0009]**

Non-patent literature cited in the description

- **KAZANC et al.** Marmara Journal of Pure and Applied Sciences, 2015, 149-52 **[0007]**
- **KAZANC et al.** Marmara Journal of Pure and Applied Sciences, 2015, vol. I, 49-52 **[0039]**

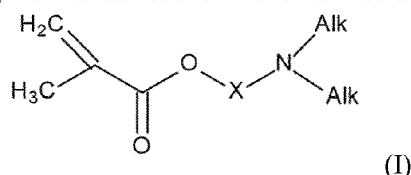
ANVENDELSE AF COPOLYMERER TIL TILVEJEBRINGELSE AF ANTIMIKROBIEL OG ANTIPILLING-EFFEKT OG TIL FORBEDRING AF TEKSTILERS FARVEOPTAGELSE

PATENTKRAV

1. Anvendelse af en vandig opløsning,

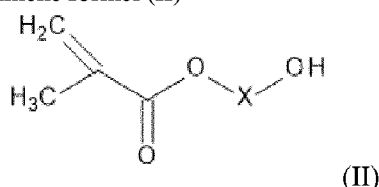
5 der omfatter

- a) mindst én copolymer fremstillet af en monomer med den almene formel (I)



eller blanding deraf,

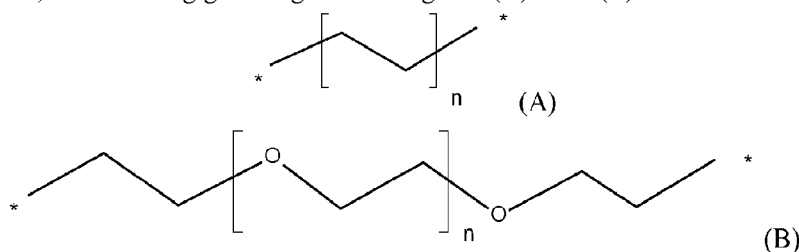
og en monomer med den almene formel (II)



eller blanding deraf,

hvor

- X, hver uafhængigt er valgt blandt følgende (A)- eller (B)-kæder



- stjernerne angiver bindinger forbundet med oxygen- og nitrogenatomer i monomerne med (I) og formelen (II);

- n , hver uafhængigt, er et heltal fra 1 til 10; og

- Alk er en C₁-C₄-alkylgruppe;

20 og hvor de tertiære aminogrupper i formen (I) er delvist kvaterniseret med halo-langkædede alkylgrupper;

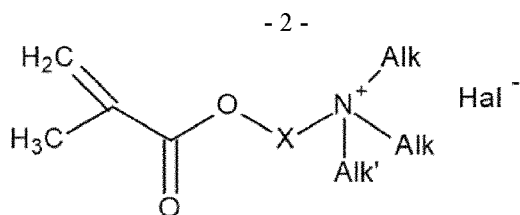
og

- b) mindst ét alifatisk eller cycloalifatisk diisocyanat; til at tilvejebringe en antimikrobiel, antipilling-effekt til et tekstil og til forbedring af et tekstils farveoptagelse.

- 25 2. Anvendelse ifølge krav 1, kendetegnet ved, at Alk er en lineær eller forgrenet, mættet C₁-C₄-alkylgruppe, fortrinsvis en methylgruppe.

3. Anvendelse ifølge krav 1 eller 2, kendetegnet ved, at n er et heltal fra 1 til 8, fortrinsvis 1.

4. Anvendelse ifølge et hvilket som helst af kravene 1 til 3, kendetegnet ved, at nitrogenatomet i formelen (I) er kvaterniseret for at tilvejebringe en monomer med formelen (I')



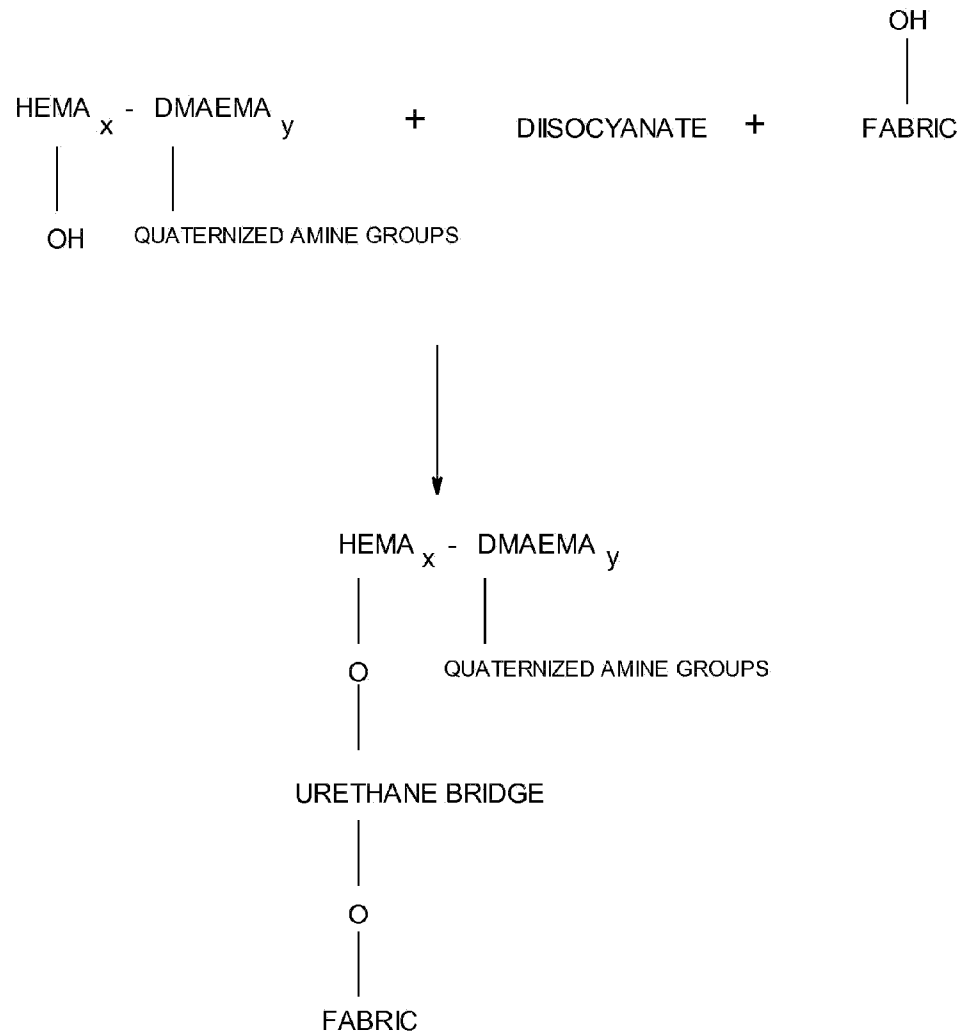
(I')

hvor X og Alk er som defineret ovenfor, Alk⁺ er en C₆- til C₂₂-alkylgruppe, fortrinsvis en C₈- til C₂₀-alkylgruppe, såsom for eksempel C₁₀, C₁₂, C₁₄, C₁₆ eller C₁₈, og Hal⁻ angiver en halogenanion, såsom en Br⁻ eller en Cl⁻.

5. Anvendelse ifølge et hvilket som helst af kravene 1 til 4, kendetegnet ved, at det alifatiske eller cykloalifatiske diisocyanat er valgt blandt hexamethyldiisocyanat, isophorondiisocyanat, methylen-bis(4-cyclohexylisocyanat) og blokerede, alifatiske eller cykloalifatiske diisocyanater.
6. Anvendelse ifølge et hvilket som helst af kravene 1 til 5, kendetegnet ved, at copolymeren er fremstillet af 2-(dimethylamino)ethylmethacrylat (DMAEMA) og 2-hydroxyethylmethacrylat (HEMA).
7. Anvendelse ifølge et hvilket som helst af kravene 1 til 6, kendetegnet ved, at molforholdet mellem monomeren med formlen (I)/monomer med formlen (II) er ca. 95-85/5-15, fortrinsvis ca. 90/10.
8. Anvendelse ifølge et hvilket som helst af kravene 1 til 7, kendetegnet ved, at 20-40 % af de tertiære aminogrupeer er kvaterniseret i copolymeren, mest fortrinsvis ca. 30 %.
9. Anvendelse ifølge et hvilket som helst af kravene 1 til 8, kendetegnet ved, at tekstilet er valgt blandt et hvilket som helst egnet materiale til fremstilling af stoffer og beklædningsgenstande, garner, stoffer klar til farvning, en hvilken som helst tekstilartikel og beklædningsgenstande.
10. Anvendelse ifølge krav 9, kendetegnet ved, at tekstilerne er denim.
11. Anvendelse af en copolymer af DMAEMA og HEMA, kendetegnet ved, at DMAEMA/HEMA-molforholdet er 95-85/5-15, fortrinsvis ca. 90/10, og 20-40 % af de tertiære aminogrupeer er kvaterniseret som defineret i krav 4, mest fortrinsvis ca. 30 %, til at tilvejebringe en antimikrobiel, antipilling-effekt til et tekstil og til forbedring af et tekstils farveoptagelse.
12. Anvendelse af mindst én copolymer som defineret i krav 1 til 8 til at tilvejebringe antimikrobiel, antipilling-effekt til et tekstil og til forbedring af et tekstils farveoptagelse.
13. Anvendelse ifølge krav 12, kendetegnet ved, at tekstilet er denim.

DRAWINGS

Figure 1



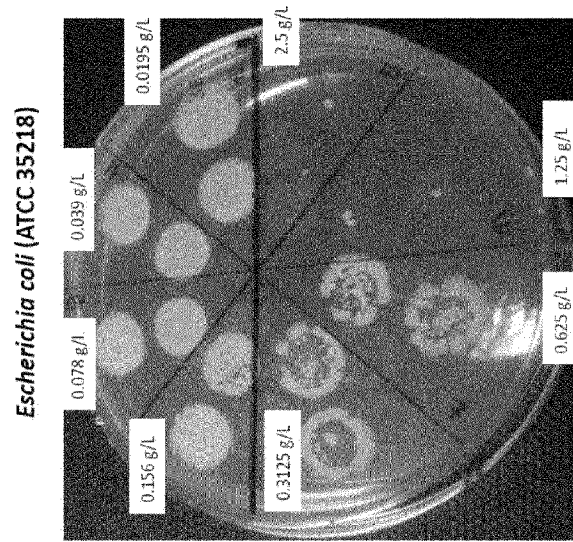


Fig. 2B

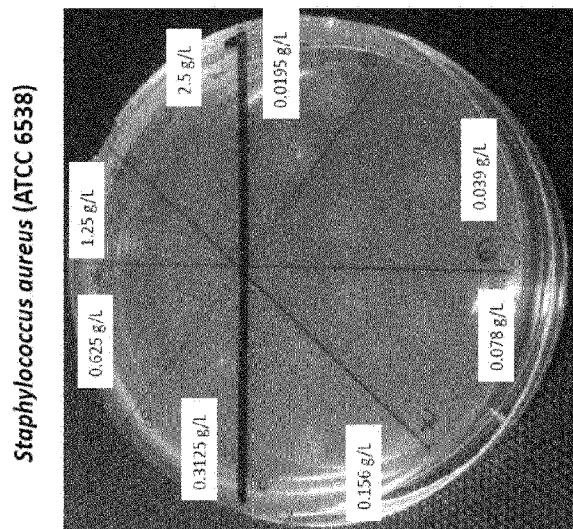


Fig. 2A