Abstract Title: Making anti-microbial lyocell fibres containing silver and phosphate

Anti-microbial lyocell fibres are made by a process in which a particulate anti-microbial agent of silver ions held in a matrix of a phosphate glass is mixed into an ingredient or precursor of the spinning solution. This gives improved distribution of the agent and allows the addition of the agent in dry powder form, so helping to limit premature loss of the soluble agent from the system. In a preferred system, the spinning solution is made by forming a pasty pre-mix of cellulose pulp and amine oxide solvent and the agent is mixed into the pre-mix or into an ingredient of the pre-mix.
PROCESS FOR MAKING ANTI-MICROBIAL FIBRES

Field of the Invention

The present invention relates to anti-microbial lyocell fibres which can impart qualities of freshness and hygiene to fabrics made from the fibres and, specifically, to a process for making such fibres.

Background

There is an increasing interest in fabrics offering qualities of improved hygiene and freshness, for example in use as clothing, and also having better protection from deterioration caused by microbes.

A way of achieving this is to apply anti-microbial agents to the fabric, for example as a finishing treatment. Another way, offering greater commercial flexibility, is to provide fibres which are already anti-microbial, by virtue of having an anti-microbial agent applied to or incorporated into the fibres.

Many organic anti-microbial agents have been used or proposed for use on fibres, including triclosan, biguanides, phenols and derivatives, isothiazolones, quaternary ammonium salts, tri-butyl tin oxide, haloamines and alcohols. The most widely-used of these is triclosan, which has been used as a fibre or fabric finish for both natural and man-made fibres and has also been incorporated into man-made fibres such as regenerated cellulose fibres and acrylic fibres by inclusion in the spinning dope.

Inorganic anti-microbial agents have also been used, and these are predominantly compounds in which a metal ion such as silver is supported on an inert matrix. An example of such an agent is silver zeolite.

The present invention is concerned with anti-microbial lyocell fibres. Lyocell fibres are produced by extrusion of a solution of cellulose through a spinning jet into a coagulation bath by a process known as solvent spinning, and they are therefore alternatively known as solvent-spun cellulose fibres. Such a process is described in US-A-4,246,221 and uses as the solvent an aqueous tertiary amine N-oxide, particularly N-methylmorpholine N-oxide, and an aqueous coagulation bath. Lyocell fibres are
distinguished from regenerated cellulose fibres, such as viscose fibres, which are produced by forming the cellulose into a soluble chemical derivative and then extruding a solution of this derivative into a bath which regenerates the extrudate as cellulose fibres.

Unfortunately, many of the anti-microbial agents which can be incorporated into other man-made fibres are incompatible with the amine oxide spinning system used to make lyocell fibres. For example, triclosan is too easily washed out of the fibres during processing. Also, some silver ion complexes are deactivated by amine oxide solvents and yield a brown or yellow colouration on the fibres that is not acceptable. A process using silver ion complexes in cellulose fibres, including viscose rayon fibres and organic solvent-spun cellulose fibres, is described in lapsed JP-A-6-235116. The process described has not become commercial, possibly because of compatibility and colour problems with the spinning systems. Another process of this type is described in EP-A-0,905,289 and involves adding to a solution of cellulose in an amine oxide solvent a slurry of a silver-based anti-bacterial agent and a magnetised mineral ore powder. The selected silver-based anti-bacterial agents include silver zeolites, silver zirconium phosphates and silver calcium phosphates. We have found that these silver compounds produce unacceptable colour staining on the fibres.

Ishizuka Garasu Kabushiki Kaisha (Ishizuka Glass Co. Ltd.) has developed an anti-microbial additive for use in fibres and other materials, which is a controlled-solubility phosphate glass incorporating silver ions. This material is provided in particulate form for incorporation into polymers. In use, the silver ions are slowly released from the phosphate glass matrix in which they are held, as that glass matrix gradually dissolves in an aqueous medium. These materials, which are marketed under the trademark “IonPure”, are described in the specification of US-A-6,593,260, the contents of which are incorporated herein by reference.

We have found that these phosphate glasses incorporating silver ions are effective anti-microbial agents which are resistant to deactivation and colour-release in the amine oxide system used to make lyocell fibres. However, it has been found necessary to make changes to the fibre spinning process in order to achieve their successful use.
Disclosure of the invention

The present invention provides a process for making anti-microbial lyocell fibres in which cellulose is dissolved in a solvent of aqueous amine oxide to form a spinning solution which is extruded through a spinning jet into a coagulation bath to produce lyocell fibres and in which an anti-microbial agent is incorporated into the fibres, characterised in that particles of the agent, which comprises silver ions held in a matrix of a phosphate glass, are mixed into an ingredient or a precursor of the spinning solution.

The addition of the anti-microbial agent to an ingredient or to a precursor of the spinning solution allows much more effective dispersion of the particles within the spun lyocell fibres. The agent is in particulate form and may be added as a dispersion or as a dry powder. The latter option allows the agent to be kept dry right up to the point of addition. This is important in order to minimise loss of agent during the manufacturing process, bearing in mind the solubility in water of the phosphate glass.

The anti-microbial agent may be added to an ingredient of the spinning solution, which may be the amine oxide solvent or the cellulose pulp. Alternatively, it may be added to a precursor of the cellulose solution comprising a pasty pre-mix of the cellulose pulp and the amine oxide solvent. One method of forming the solution of cellulose in an amine oxide solvent such as a tertiary amine N-oxide, for example N-methylmorpholine N-oxide, is to form a pre-mix of cellulose and aqueous amine oxide solvent incorporating an excess of water over the optimum required for solution to take place. The pre-mix, which is a paste or dough, is then subjected to an evaporation process, for example in a thin-film evaporator, to remove the excess water and form a solution of the cellulose. The anti-microbial agent, which has been mixed into the pre-mix (or into an ingredient of the pre-mix), is effectively dispersed throughout this resulting cellulose solution. In this preferred solution process, the anti-microbial agent may be added to the pre-mix itself or to an ingredient of the pre-mix.

The anti-microbial agent preferably is added in dry powder form and may be added, for example, to the vessel in which the pre-mix is made, using injection equipment such as is used to add pigments such as titanium dioxide.
The anti-microbial agent comprises particles of a phosphate glass matrix in which silver ions are held. The phosphate glass has a controlled solubility in aqueous media, so that the silver ions can be gradually released to provide continuing anti-microbial protection for a fabric made from the anti-microbial fibres of the invention.

The anti-microbial agent preferably is as described in US-A-6,593,260 already referred to. That is, it is a glass composition comprising 0.1 to 5% by weight of Ag$_2$O in a composition containing 45 to 67 mol.% of P$_2$O$_5$, 5 to 20 mol.% of Al$_2$O$_3$, 1 to 40 mol.% of one or more metal oxides from MgO, CaO and ZnO, and 20 mol.% or less of B$_2$O$_3$.

The anti-microbial particles may have a mean particle diameter in the range 0.1 to 5 microns, preferably in the range 0.1 to 3 microns, and more preferably in the range 0.1 to 1 micron.

The concentration of the anti-microbial particles in the product lyocell fibres may be in the range 0.1 to 10% by weight owc (on weight of cellulose), preferably in the range 0.1 to 1% by weight owc, and more preferably in the range 0.1 to 0.5% by weight owc.

The invention includes lyocell fibres made by the process of the invention. These fibres show effective anti-microbial properties, which continue in effect after normal textile processing and laundering.

The invention is illustrated by the following Example:

**Example**

The silver ion-containing phosphate glass particles used in this Example were IonPure ZAF particles provided by Ishizuka Glass Co. Ltd. (IonPure ZAF is a trademark of Ishizuka Glass Co. Ltd.). The particles were in the form of a dry powder of which 98% of the particles had a diameter of below 4.2 microns and 50% of the particles had a diameter of below 1.6 microns.

The fibre-making process was based on a commercial process for making lyocell fibres of 1.7 dtex by spinning a solution of cellulose in an aqueous solvent of N-methylmorpholine N-oxide through a spinning jet into an aqueous coagulating bath to form fibres.

The spinning solution was made by a process in which cellulose pulp and the aqueous solvent of N-methylmorpholine N-oxide were fed into a mixing vessel and mixed to
form a paste or dough, known as the pre-mix. The solvent contained excess water over the optimum required for the cellulose to go into solution, in order to promote efficient wetting and mixing of the cellulose with the solvent. This excess water was then evaporated from the pasty pre-mix by passing the pre-mix through a type of thin-film evaporator called a Filmtruder (trademark of Buss AG) to form the spinning solution. The IonPure ZAF particles were added dry to the pre-mix mixing vessel through a hopper at a concentration of 0.25% by weight owc. (An alternative method of addition would be to use the injection equipment normally used to add titanium dioxide pigment to the vessel.)

The IonPure ZAF particles were evenly distributed in the pre-mix and became evenly distributed in the spinning solution and hence in the spun lyocell fibres. The IonPure ZAF additive did not adversely affect the process of making the spinning solution or of spinning the fibres, and it was not itself adversely affected by these processes. The product lyocell fibres were of a normal appearance and colour.

The fibres were tested for physical properties and found to have properties generally in line with a Control, which was a standard Tencel lyocell fibre of 1.7 dtex. (Tencel is a registered trademark of Tencel Limited.)

The results of the physical property measurements are shown below in Table 1:

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Control Fibre</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Water imbibition</td>
<td>66.6</td>
<td>63.4</td>
</tr>
<tr>
<td>Dry breaking tenacity (cN/tex)</td>
<td>36.8</td>
<td>34.9</td>
</tr>
<tr>
<td>Dry breaking extension (%)</td>
<td>11.4</td>
<td>10.1</td>
</tr>
<tr>
<td>Dry initial modulus</td>
<td>1445</td>
<td>1588</td>
</tr>
<tr>
<td>Wet breaking tenacity (cN/tex)</td>
<td>28.7</td>
<td>27.3</td>
</tr>
<tr>
<td>Wet breaking extension (%)</td>
<td>14.9</td>
<td>13.3</td>
</tr>
<tr>
<td>Wet modulus at 2%</td>
<td>163</td>
<td>171</td>
</tr>
</tbody>
</table>
Samples of spun yarns of count 20 Tex were made respectively from the fibres of the Example and of the Control, the fibres having been cut to 38mm staple length. These yarns were used to weave greige fabrics in an interlock construction of basis weight 200 gms per square metre.

A portion of the fabric made from the fibres of the Example was given a 2-hour detergent wash in a washing machine at a water temperature of 60°C, using Persil Original Non-Biological Automatic washing powder and Comfort fabric conditioner, before being tumble-dried. (Persil and Comfort are trade marks of Lever Faberge Limited).

The fabric produced from the fibres of the Example was tested for colour whiteness against the Control fabric produced from the standard lyocell control fibres. Testing was carried out using a Minolta Spectrophotometer CM-3300d and produced a CIE (Commission Internationale d’Eclairage) whiteness index of 45.4 for the fabric of the Example against a CIE index of 46.6 for the Control fabric. This shows that the silver-based anti-microbial agent, IonPure ZAF, has no adverse effect on fibre colour. The fabrics were re-tested after controlled exposure to a xenon lamp, which mimicked 4 weeks of outdoor natural light exposure, and, again, there was little difference in colour between the fabrics.

Anti-microbial testing of the fabrics was carried out using two different tests:

**Qualitative Agar Plate test (Swiss SNV 195-920)**

This is a quick test to determine the anti-microbial activity of leaching anti-microbial agents on a sample. Evaluation is based upon the presence or absence of bacterial growth beneath and surrounding the sample (inhibition zone). Non-leaching anti-microbial agents show no zones of inhibition and weak bacterial growth beneath the samples.

This test was carried out using a *Staphylococcus aureus* bacterium. The results showed that the fabrics made from the fibres of the Example produced no zones of inhibition and weak bacterial growth beneath the samples, which confirmed the anti-microbial agent IonPure ZAF as of the non-leaching type. This is the preferred type of
agent for anti-microbial fibres because one is looking for a prolonged effect in which the agent acts at the fibre boundary but does not leach beyond it, for example onto skin adjacent to clothing.

**Quantitative Dynamic Shake Flask Test (ASTM E2149-01)**

This is a test of the American Society for Testing and Materials, which measures the anti-microbial activity of both leaching and non-leaching anti-microbial materials under dynamic contact conditions.

Evaluation is based upon the calculated percentage reduction in bacteria from counts taken at various times and expressed as calculated percentage reduction and also as log reduction versus a no-sample control.

The fabrics produced from the fibres of the Example were tested alongside the Control fabric and also against a control in which no fabric was used, i.e. a no-sample control. In the case of the test using the *Staphylococcus aureus* bacterium, a detergent-washed sample of the fabric of the Example was also tested. The results for the dynamic shake flask tests on these fabrics after 24 hours are shown in Table 2 for the *Staphylococcus aureus* bacterium and in Table 3 for the *Klebsiella pneumoniae* bacterium.
Table 2

**Calculated Percentage Reduction and Log Reduction for S. aureus**

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Redn. 24 hrs.</th>
<th>Log Redn. 24 hrs.</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No-sample control</td>
<td>8.0</td>
<td>-</td>
<td>Relatively little change in cell numbers.</td>
</tr>
<tr>
<td>Control fabric</td>
<td>54.8</td>
<td>0.16</td>
<td>Small but insignificant antibacterial activity.</td>
</tr>
<tr>
<td>Example</td>
<td>99.99</td>
<td>4.71</td>
<td>Total kill after 24 hrs</td>
</tr>
<tr>
<td>Example (washed)</td>
<td>99.99</td>
<td>3.53</td>
<td>Total kill after 24 hrs</td>
</tr>
</tbody>
</table>

Table 3

**Calculated Percentage Reduction and Log Reduction for K. pneumoniae**

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Redn. 24 hrs.</th>
<th>Log Redn. 24 hrs.</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No-sample control</td>
<td>23.0</td>
<td>-</td>
<td>Relatively little change in cell numbers.</td>
</tr>
<tr>
<td>Control fabric</td>
<td>73.5</td>
<td>0.60</td>
<td>Insignificant antibacterial activity</td>
</tr>
<tr>
<td>Example</td>
<td>&lt;99.9995</td>
<td>&gt;5.28</td>
<td>Total kill within 24 hrs.</td>
</tr>
</tbody>
</table>

The results of this dynamic shake flask test show significant anti-microbial activity for the fibres of the Example against both *Staphylococcus aureus* and *Klebsiella pneumoniae*. The detergent-washed fabric sample tested against *Staphylococcus aureus* showed equally strong anti-microbial activity.
Claims

1. A process for making anti-microbial lyocell fibres in which cellulose is dissolved in a solvent of aqueous amine oxide to form a spinning solution which is extruded through a spinning jet into a coagulation bath to produce lyocell fibres and in which an anti-microbial agent is incorporated into the fibres, characterised in that particles of the agent, which comprises silver ions held in a matrix of a phosphate glass, are mixed into an ingredient or precursor of the spinning solution.

2. A process according to claim 1, characterised in that the anti-microbial agent is in the form of a dry powder.

3. A process according to claim 1 or claim 2, characterised in that the anti-microbial agent is mixed into an ingredient of the spinning solution comprising the amine oxide solvent.

4. A process according to claim 1 or claim 2, characterised in that the anti-microbial agent is mixed into an ingredient of the spinning solution comprising the cellulose pulp.

5. A process according to claim 1 or claim 2, in which the spinning solution is made by forming a precursor comprising a pre-mix of cellulose pulp and aqueous amine oxide solvent having excess water over the optimum required for solution to take place, characterised in that the anti-microbial agent is mixed into the pre-mix or into an ingredient of the pre-mix, and water is then evaporated from the pre-mix to form the spinning solution having the anti-microbial agent dispersed therein.

6. A process according to any preceding claim, characterised in that the amine oxide solvent is a tertiary amine N-oxide and the coagulating bath is aqueous.
7. A process according to claim 6, characterised in that the amine oxide solvent is N-methylmorpholine N-oxide.

8. A process according to any preceding claim, characterised in that the antimicrobial agent comprising silver ions held in a matrix of a phosphate glass has a composition comprising 0.1 to 5% by weight of Ag₂O in a composition containing 45 to 67 mole% of P₂O₅, 5 to 20 mole% of Al₂O₃, 1 to 40 mole% of one or more metal oxides selected from MgO, CaO and ZnO, and 20 mole% or less of B₂O₃.

9. A process according to any preceding claim, characterised in that the antimicrobial agent is incorporated in the lyocell fibres in a concentration in the range of 0.1 to 10% by weight on weight of cellulose (owc).

10. A process according to claim 9, characterised in that the anti-microbial agent is incorporated in the lyocell fibres in a concentration in the range 0.1 to 1% by weight owc.

11. A process according to claim 10, characterised in that the anti-microbial agent is incorporated in the lyocell fibres in a concentration in the range 0.1 to 0.5% by weight owc.

12. A process according to any preceding claim, characterised in that the anti-microbial agent has a mean particle diameter in the range 0.1 to 5 microns.

13. A process according to claim 12, characterised in that the anti-microbial agent has a mean particle diameter in the range 0.1 to 3 microns.

14. A process according to claim 13, characterised in that the anti-microbial agent has a mean particle diameter in the range 0.1 to 1 micron.

15. Anti-microbial lyocell fibres made by a process as claimed in any of claims 1 to 14.
Application No: GB0406262.6  
Claims searched: 1-15

Examiner: Mr Robert Black  
Date of search: 8 June 2004

**Patents Act 1977: Search Report under Section 17**

**Documents considered to be relevant:**

<table>
<thead>
<tr>
<th>Category</th>
<th>Relevant to claims</th>
<th>Identity of document and passage or figure of particular reference</th>
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| X        | 1-6 and 9-15       | EP 0905289 A2  
(NAKAMURA) see especially the abstract, column 3 lines 10-58, example 2, and claims 4, 5, 7 and 8 |

**Categories:**

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<td>Document indicating lack of inventive step if combined with one or more other documents of same category.</td>
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<td>&amp;</td>
<td>Member of the same patent family</td>
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<th>Document indicating technological background and/or state of the art.</th>
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<tr>
<td>P</td>
<td>Document published on or after the declared priority date but before the filing date of this invention.</td>
</tr>
<tr>
<td>E</td>
<td>Patent document published on or after, but with priority date earlier than, the filing date of this application.</td>
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**Field of Search:**

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:

- B5B
- Worldwide search of patent documents classified in the following areas of the IPC:
- D01F

The following online and other databases have been used in the preparation of this search report:

- EPDOC; WPI; PAJ; Full text English language