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(71) Applicant:
Acordis Fibres (Holdings) Limited
Spondon, Derby DE21 7BP (GB)

(72) Inventors:
• **Barnes, Alan Jeffrey**
Botanical Gardens, Sheffield S11 8RJ (GB)
• **Thompson, Joseph**
Stivichall, Coventry CV3 8BW (GB)

(74) Representative:
Hallam, Arnold Vincent et al
Lewis & Taylor
5 The Quadrant
Coventry CV1 2EL Warwickshire (GB)

(54) **Flame retardant fibre**

(57) In a method for producing a flame retardant polymeric fibre which includes or is treated to include carboxylic acid groups or monovalent salts thereof, the fibre is immersed in water which is neutralised by the addition of acid to pH6-pH7 and the fibre is then subsequently reacted with an aqueous solution of an amphoteric metal salt. The treatment may also be applied to fabric or garments formed from polymeric fibre which includes or is treated to include carboxylic acid groups or monovalent salts thereof.

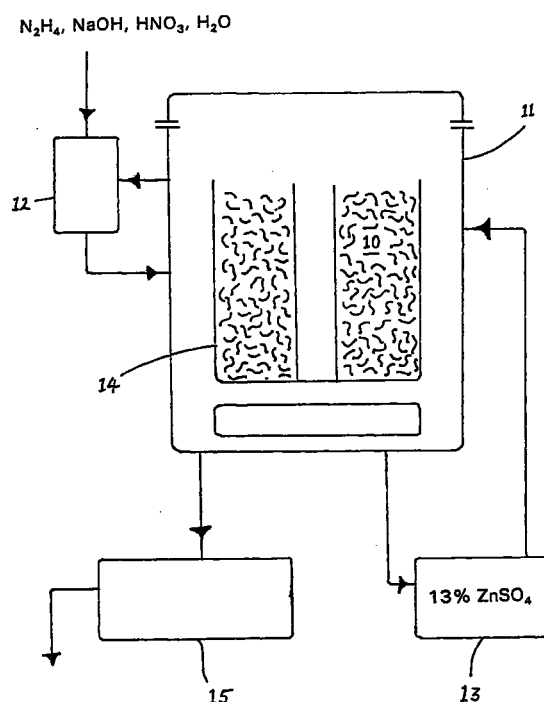


FIG. 1

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Description

[0001] This invention relates to flame retardant fibres, in particular acrylic based fibres which may be used for filling or padding in clothes, furnishing, transport or building.

[0002] The use of flame retardant polymeric fibre is well known and in particular it is known to treat acrylic fibres so that the polymer material takes up a metal ion which makes the fibre more flame retardant. Such a process is disclosed in GB 1459309.

[0003] In GB 1459309 there is described a process in which acrylic fibre is treated with hydrazine to crosslink the fibre through a proportion of the nitrile groups. The crosslinked product is then hydrolysed using sodium hydroxide to convert the residual nitrile groups into the sodium carboxylate form. After completion of this reaction the fibre is immersed in a large excess of hydrochloric acid and dried. After having been dried the fibre is immersed in and reacted with a 10% aqueous solution of a metal compound. After completion of this last reaction the finished fibre is washed and dried. The resultant fibre had increased flame retardancy due to the cross-linking and due to the presence of the metal ion.

[0004] It has now been found that the use of amphoteric metal salts produces an acrylic fibre having good to excellent fibre retardant property. Generally, it is possible to produce fibre having fire retardancy, measured using the limited oxygen ignition (LOI) method, in excess of 35%. The LOI value is dependent upon the percentage of metal content of the treated fibres, and it is an object of the present invention to produce an acrylic fibre having an increased amphoteric metal content and a higher value LOI.

[0005] According to the present invention there is provided a method of making a flame retardant acrylic based fibre in which the acrylic fibre is first crosslinked through at least some of its nitrile groups, and the residual nitrile groups are then hydrolysed using an hydroxide of an alkali metal to produce a fibre having carboxylate groups, the fibre then being neutralised to pH6-pH7 and treated with an amphoteric metal compound to convert carboxylate groups to the amphoteric metal carboxylate.

[0006] It has been found, somewhat surprisingly, that if after treatment with the hydroxide the hydrolysed fibre is acidified only to the point of neutrality i.e. pH6-pH7, it is possible in the subsequent reaction stage with the metal salt to produce a fibre having a higher metal content. It is surmised that this is because the carboxylate groups, instead of being hydrolysed to carboxylic acid by the addition of excess acid as in the prior art process, undergo an ion exchange with the amphoteric metal ions, to produce the flame retardant fibre. The amphoteric metal is preferably zinc and the preferred zinc compound is zinc sulphate.

[0007] In GB 1459309 there is disclosed in one

Example acrylic crosslinked fibre treated with a zinc salt (zinc acetate). The process consumes 0.9 kg of zinc per kg treated acrylic fibre to produce a fibre having a zinc content of 6.1% and an LOI of 36.5%. In contrast, the method of the present invention, in which the crosslinked fibre is neutralised before treatment with the zinc salt, uses 0.3 kg of zinc per kg of acrylic fibre and yet produces a fibre having a higher zinc content.

[0008] Preferably the hydroxide is sodium hydroxide, and the carboxylated fibre is then neutralised to pH6-7 by the addition of a mineral acid, preferably nitric acid.

[0009] In a particularly preferred embodiment, the hydrolysed crosslinked acrylic fibre is reacted with aqueous zinc sulphate containing 139% by weight of hydrated zinc sulphate, at a temperature of 120°C in an enclosed pressurised vessel.

[0010] Also according to the invention there is provided a flame retardant acrylic based fibre which has been treated with a compound of an amphoteric metal such that the fibre has a metal content of at least 7% based on weight of fibre.

[0011] The preferred acrylic fibre is staple fibre having a decitex of 1.7 decitex and a length of 100-110 mm before treatment, and 4.5 decitex after treatment with length of about 75 mm, and is impregnated with zinc. The fibre may be crimped if desired. The flame retardancy is measured using the limited oxygen ignition method (LOI) test based on ASTM-D-2863-87 flammability of plastics using the oxygen index method. However, the samples used for the test were three 1g samples of teased fibre, the first sample being used to obtain the approximate oxygen level, and samples two and three being used to obtain the more accurate LOI results. The preferred fibre has an LOI in excess of 35% and more typically 36-38%.

[0012] Also, according to another aspect of the invention, there is provided a method of producing a flame retardant polymeric fibre, said fibre including, or being treated to include, carboxylic acid groups or a monovalent salt thereof, wherein the fibre is mixed with water and neutralised to pH6-pH7, and subsequently reacted with an aqueous solution of an amphoteric metal salt. Preferably the carboxylic groups are present as alkali metal carboxylates.

[0013] The fibre may be spun into yarns or threads, before the start of the process to make the fibre fire retardant. Furthermore, the yarns may be woven or knitted into fabric or garments which are then subjected to said process to render the fabric or garment fire retardant.

[0014] The invention will hereafter be described by means of example only and with reference to the accompanying drawing in which there is shown a schematic diagram of a process for producing flame retardant acrylic fibre according to the present invention.

[0015] The fibre is first crosslinked by treatment with hydrazine. A quantity, preferably 155 kg of Cour-

telle (Reg TM) acrylic staple fibre 10 having a length of about 100 mm is placed in an open basket 14 in a reaction vessel 11, for example a Kier Dyer. The fibre is immersed in a 35% by weight aqueous solution of hydrazine hydrate and allowed to react for two hours at 120°C. About 70 litres of hydrazine hydrate solution is used for each 155 kg batch of fibre. The water and some of the reagents are added to the reaction vessel through an expansion tank 12 which is connected to the reaction vessel 11.

[0016] After the reaction, spent hydrazine solution is then run into an effluent tank 15, and the crosslinked staple fibre washed with water at 40°C for about 5-10 minutes, preferably 6 minutes. The wash is then also discharged into the effluent tank 15.

[0017] The crosslinked product is then hydrolysed using sodium hydroxide solution, made up using a 32% by weight aqueous solution of sodium hydroxide which is added to water in the ratio of about 1:9, at 120°C for thirty minutes.

[0018] The spent reaction fluid is then run off as before and the fibre washed with water at 40°C as previously described.

[0019] The fibre is then washed in situ in the reaction vessel in at least one weak nitric acid wash up to the point where the wash is maintained at pH6-pH7. The acid wash comprises 10 parts 59% aqueous nitric acid mixed in about 1000 parts of water. The fibre is washed at 65 °C for ten minutes, and the wash may be repeated as is required to achieve the correct pH measurement. The water wash is run off into the effluent tank.

[0020] Alternatively the fibre is immersed in a weak aqueous nitric acid solution, and then the nitric acid added to the reaction solution until the desired pH value is achieved.

[0021] The neutralised fibre is then washed in a 13% by weight aqueous solution of zinc sulphate which is delivered from a holding tank 13. The reaction lasts for 20 minutes at 120°C, and the reaction mixture is then recovered into the holding tank 13. The fibre is again washed several times as previously described.

[0022] Any fabric treatment may now be added in a last wash. For example, to obtain a soft finish, the fibre is washed in 0.3% by weight aqueous solution of a softening treatment fluid at 40°C for ten minutes.

[0023] The fibre produced by the above process has a decitex of 4.5 decitex after treatment and an average fibre length of 75 mm. The zinc content of the fibre is at least 7% and typically is between 7-14%, more typically 8-11%, and has a LOI value of at least 35% and more typically between 36-38%.

[0024] The tensile properties of the single fibres were measured at room temperature in an Instron 6021 with a load cell "A" and a cross head speed of 20 mm/minute.

[0025] The treated fibres had a breaking load of about 6 cN, a tenacity of about 11 cN/tex and an extension to break of about 20%.

[0026] A similar treatment may be used on polymeric fibres which include a carboxylic acid group, or carboxylate group. Such fibres may include carboxymethyl cellulose or a polyacrylic acid, for example the fibre sold under the trade name OASIS, which includes acrylic acid groups, or the sodium salt thereof. The fibre may be neutralised with nitric acid as previously described and then treated with zinc sulphate solution.

10 Claims

1. A flame retardant acrylic based fibre which has been treated with a compound of an amphoteric metal such that the fibre has a metal content of at least 7% based on weight of fibre.
2. A fibre as claimed in claim 1 wherein the metal is zinc.
3. A fibre as claimed in claim 1 or claim 2 wherein the fibre, prior to treatment, has a decitex of 1.7 dtex and after treatment about 4.5 dtex.
4. A fibre as claimed in any one of claims 1 to 3, wherein the fibre has a LOI value of at least 35%.
5. A process for producing a flame retardant acrylic based fibre in which the acrylic fibre is first crosslinked through at least some of its nitrile groups, and the residual nitrile groups are then hydrolysed using the hydroxide of an alkali metal to produce fibre having a proportion of carboxylate groups, the mixture is then neutralised to pH 6-7 and treated with an amphoteric metal compound to convert the carboxylate group to the amphoteric metal carboxylate.
6. A process as claimed in claim 5 wherein the hydroxide of the alkali metal is sodium hydroxide.
7. A process as claimed in claim 5 or claim 6 wherein the hydrolysed fibre reaction mixture is neutralised to pH7 using nitric acid.
8. A process as claimed in any one of claims 5 to 7 wherein the amphoteric metal is zinc, and the zinc compound is zinc sulphate.
9. A process as claimed in claim 8 wherein the fibre is treated with an aqueous zinc solution of zinc sulphate containing 13% by weight of salt at 120°C for at least 20 minutes.
10. A process as claimed in any one of claims 5 to 8, wherein any fibre conditioners are added to the fibres after the zinc sulphate treatment.
11. An acrylic fibre treated by a process as claimed in

any one of claims 5 to 10.

12. A method for producing a flame retardant polymeric fibre, said fibre including or being treated to include carboxylic acid groups or monovalent salts thereof, wherein the fibre is immersed in water which is neutralised by the addition of acid to pH6-pH7 and the fibre is then subsequently reacted with an aqueous solution of an amphoteric metal salt. 5 10
13. A fire retardant fabric or garment formed from a polymeric yarn or filament which is treated with a compound of an amphoteric metal such that the fabric or garment has a metal content of at least 7% based on the weight of the fabric. 15
14. A process for producing a flame retardant polymeric fabric or garment made from a fibre or filament having, or being processed to have, carboxylic acid groups or monovalent salts thereof, wherein the fabric or garment is immersed in water which is neutralised by the addition of acid to pH 6-7, and the fabric/garment is then treated with an aqueous solution of an amphoteric metal salt. 20 25
15. A process as claimed in claim 14, wherein the fabric or garment is made from acrylic fibre or filament which is first crosslinked through at least some of its nitrile groups, and the residual nitrile groups are then hydrolysed using the hydroxide of an alkali metal to produce a fibre or filament having a proportion of carboxylate groups. 30 35 40 45 50 55

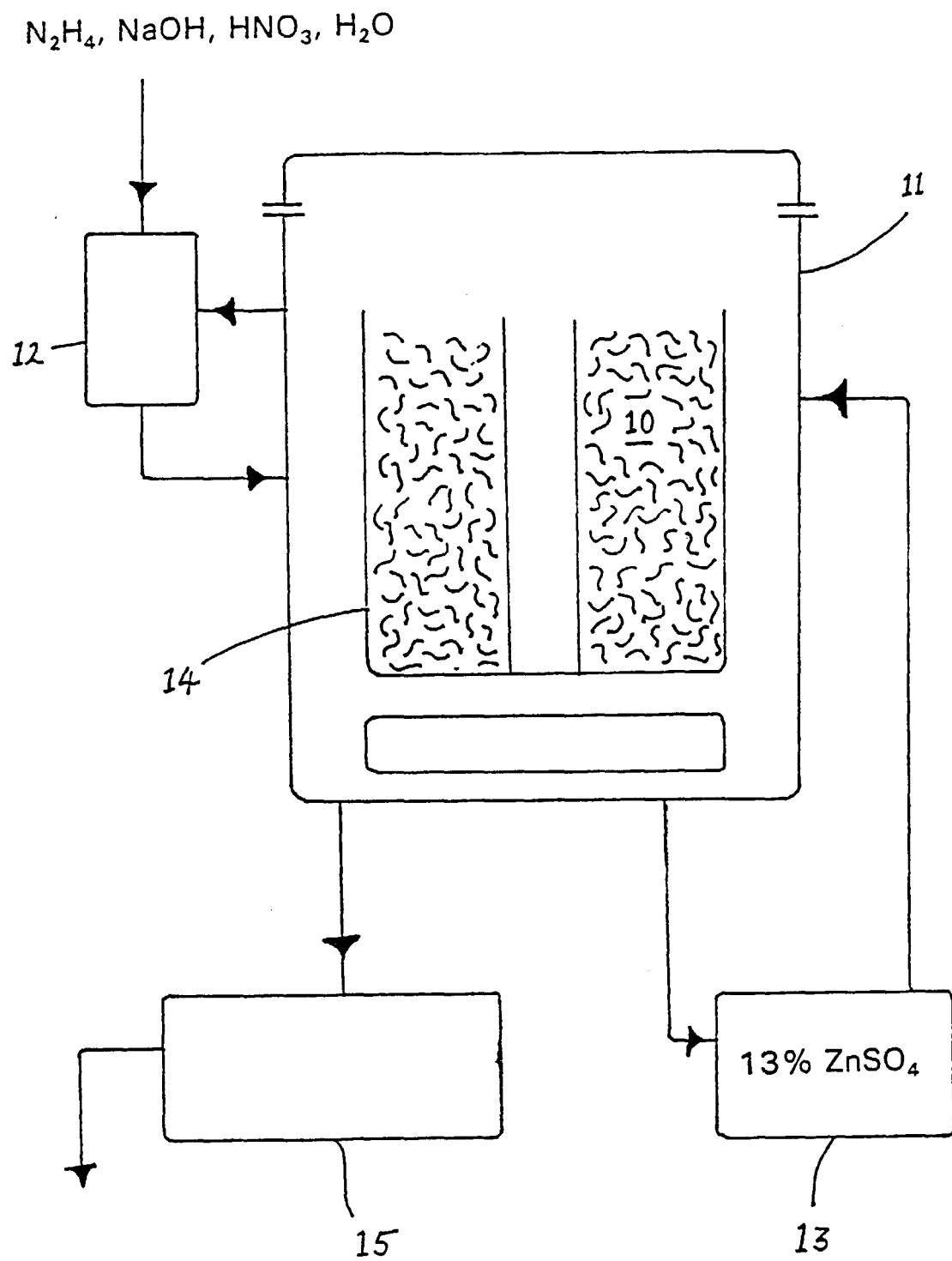


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