(12) PATENT (11) Application No. AU 199726378 B2 (10) Patent No. 711723 (19) AUSTRALIAN PATENT OFFICE (54)Composite fibres, wound dressings incorporating such fibres and a method for making same International Patent Classification(s) DO1F 009/04 DO1F 002/28 A61L 015/28 Application No: 199726378 (21)(22) Application Date: 1997 .04 .11 WIPO No: w097/39170 (87) (30)Priority Data (32) Date (33) Country (31)Number GB 9607600 1996 .04 .12 GB 9618658 1996 .09 .06 (43) Publication Date : 1997 .11 .07 Publication Journal Date: 1998 .01 .15 (43)(44) Accepted Journal Date: 1999 .10 .21 (71)Applicant(s) Bristol-Myers Squibb Company (72)David Kershaw; Peter M. J. Mahoney; Paul Hanmer; David Pritchard (74)Agent/Attorney PHILLIPS ORMONDE and FITZPATRICK, 367 Collins Street, MELBOURNE VIC 3000 (56)Related Art

WO 96/10106 JP 63-042917 JP 61-289886 OPI DATE 07/11/97 APPLN. ID 26378/97 AOJP DATE 15/01/98 PCT NUMBER PCT/EP97/01880



(51) International Patent Classification 6: D01F 9/04, 2/28, A61L 15/28

(11) International Publication Number:

WO 97/39170

A1

(43) International Publication Date:

23 October 1997 (23.10.97)

(21) International Application Number:

PCT/EP97/01880

(22) International Filing Date:

11 April 1997 (11.04.97)

12 April 1996 (12,04,96) GB (81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, Signated States. AL. AM, AT, AO, AZ, BB, BG, BG, BH, BT, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

(30) Priority Data: 9607600.5

INTE

9618658.0

6 September 1996 (06.09.96)

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of

(71) Applicant (for all designated States except US): BRISTOL-MYERS SQUIBB COMPANY [US/US]; 345 Park Avenue, New York, NY 10154 (US).

(72) Inventors; and

- (75) Inventors/Applicants (for US only): KERSHAW, David [GB/GB]; The Flat, Greyhound Vaults, Market Street, Abergavenny, Gwent NP7 5SD (GB). MAHONEY, Peter, M., J. [GB/GB]; Lletty Meirch Farm, Llanfihangel-Ng-Nhwynfa, Near Llanfyllin, Powys SY22 5JF (GB). HANMER, Paul [GB/GB]; Brackenwood, Alltami Road, Buckley, Flintshire CH7 3PD (GB). PRITCHARD, David [GB/GB]; 18 Parc-Y-Fro, Creigau, Cardiff, South Glamorgan CF4 8SA (GB).
- (74) Agent: MAYS, Julie; Bristol-Myers Company Limited, Patent Dept., Swakeleys House, Milton Road, Ickenham, Uxbridge UB10 8NS (GB).
- (54) Title: COMPOSITE FIBRES, WOUND DRESSINGS INCORPORATING SUCH FIBRES AND A METHOD FOR MAKING SAME

(57) Abstract

An absorbent, composite fibre comprising a matrix of from 10 % to less than 50 % of water insoluble alginate having dispersed therein at least 40 % of another polysaccharide.

WO 97/39170 PCT/EP97/01880

COMPOSITE FIBRES, WOUND DRESSINGS INCORPORATING SUCH FIBRES AND A METHOD FOR MAKING SAME

1.0

15

20

25

30

The invention relates to composite fibres, particularly absorbent composite fibres for use in wound treatment, wound dressings incorporating such fibres and a method for making same.

Absorbent fibres for use in wound treatment are well known in the art. Examples include cellulose fibres, chemically modified cellulose fibres, pectin fibres, alginate fibres, chitosan fibres, hyaluronic acid fibres or other polysaccharide fibres or fibres derived from gums. In the treatment of wounds it is desirable to use fibres made from pectin or carboxymethyl cellulose but the known processes for making such fibres are complex and expensive and the resulting fibres not always viable. For instance it is known to make carboxymethyl cellulose fibres by chemically converting preformed cellulose fibres. It is also known that both pectin fibres and carboxymethyl cellulose fibres are difficult to spin.

It has been proposed in GB 2062652 A to make cellulose fibres comprising anionically modified polysaccharides by adding the polysaccharide to preformed viscose. Similarly in US 4063558 there is described a method for making fibres of cellulose with alkali metal salts of alginic acid uniformly dispersed therein by adding a solution of sodium alginate to preformed viscose.

25

30

- In WO 96/10106 there are described fibres which preferably comprise from 70 to 95% by weight of an alginate co-spun with from 5 to 30% by weight of at least one water soluble organic polymeric species (other than alginate).
- We have now found that it is possible to make a composite, absorbent fibre comprising a matrix of water insoluble alginate having another polysaccharide dispersed therein where the fibre comprises less than 50% by weight of the alginate, the fibre mitigating the disadvantages of the prior art fibres.

Accordingly the invention provides an absorbent, composite fibre comprising a matrix of at least 10% and less than 50% by weight of water insoluble alginate having dispersed therein at least 40% of another polysaccharide. Unless otherwise stated all percentages herein are by weight based on the weight of the fibre.

Whilst not wishing to be bound by theory it is believed that the water insoluble alginate effectively provides, as a matrix, a molecular backbone to the fibre that enables the other polysaccharides to be incorporated and results in a fibre that may be spun and otherwise processed. The use of water insoluble alginate for this purpose enables the fibres to be made without the need for complex and expensive processing and without the need to use preformed cellulose as a starting material. Preferred polysaccharides for addition to the alginate backbone are carboxymethyl cellulose and/or pectin.

Since it is believed that the fibres of the invention rely on the water insoluble alginate to provide integrity to the fibres it is truly surprising that it is possible to make viable fibres processable into products that comprise a minor proportion of insoluble alginate. One of the advantages of such fibres is that they may comprise a major proportion of polysaccharide other than alginate which generally makes them more absorbent than fibres which have insoluble alginates in a major proportion.

Preferably the fibres comprise, in addition to insoluble alginate, from 40% to 90% of another polysaccharide, more preferably from 60% to 85% and most preferably from 70% to 80% of another polysaccharide which is most preferably carboxymethyl cellulose or pectin or a mixture thereof.

Polysaccharides suitable for use in fibres according the invention include carboxymethyl cellulose, carboxyethyl cellulose, other derivatives of cellulose, cellulose, pectin, hyaluronic acid and chitosan. Preferably the

pectin, hyaluronic acid and chitosan. insoluble alginate is calcium alginate.

25

30

Preferably the fibres comprise from 10% to less than 50% by weight of the fibre of insoluble alginate, more preferably 10% to 49%, more preferably 15% to 40% and most preferably from 20% to 30% by weight of the fibre of water insoluble alginate. Preferably the insoluble alginate is calcium alginate.

A particularly preferred embodiment of the absorbent, composite fibres of the invention comprise a matrix of 20%

to 30% of calcium alginate based on the weight of the fibre having dispersed therein from 55% to 60% of carboxymethyl cellulose and 15% to 20% of pectin based on the weight of the fibre.

10

15

25

Accordingly in another aspect the invention provides a method for making a composite, absorbent fibre comprising the following steps:

- (i) adding sodium alginate and another polysaccharide to water to form a dope;
 - (ii) forcing the dope through a spinneret to form fibres;(iii) treating the resulting fibres with a source of calcium ions to convert the alginate to calcium alginate and cross-link the alginate to the other polysaccharide;
- 20 (iv) drying the fibres.

The process enables composite fibres to be prepared which comprise large quantities of other polysaccharides and in particular, carboxymethyl cellulose, pectin or both. The fibres so produced are capable of being spun or otherwise mechanically processed. In addition the resulting fibres have a high tensile strength compared to alginate, carboxymethyl cellulose or pectin alone.

As used herein the term fibre means both relatively short, discrete, randomly oriented material (sometimes known as staple fibre) and yarns made therefrom (sometimes known as staple yarn) and relatively long, structured, continuous filament yarn. The fibres may have a staple length of 5mm

to 70 mm, more usually 20mm to 50 mm, favourably 25mm to 40 mm.

The fibres prepared according to the above described process may be dried using conventional methods, for example, using acetone or hot air drying.

Alginates are produced by a variety of micro-organisms and marine algae which are the normal commercial source. The alginates being natural materials show considerable variety but are characterised in being block copolymers, the individual monosaccharide units being arranged into groups as blocks of mannuronic (M) and guluronic (G) residues. In addition to the repeating blocks each polymer chain can contain a proportion of alternating M and G monosaccharide units. The alginate may be obtained from any convenient source, for example L. Hyperborea or Ascophyllum Nodosum or those described in EP-A-0721355 to Bristol-Myers Squibb Company which are particularly preferred.

25

30

20

10

15

In a further embodiment of the invention the absorbent, composite fibres are employed in the manufacture of wound dressings. Accordingly the invention provides a wound dressing comprising an absorbent, composite fibre comprising a matrix of between at least 10% and less than 50% of water insoluble alginate having dispersed therein at least 40% of another polysaccharide.

The wound dressings may be in the form of swabs, wound

WO 97/39170 PCT/EP97/01880

6

pads, wadding ribbons, sponges, nets and bandages and may be used as a primary or secondary dressing especially in the treatment of leg ulcers. The wound dressings according to the invention may benefit from an improved integrity over that of dressings made from alginate, pectin or carboxymethyl cellulose alone.

According to a further aspect of the invention there is provided a wound dressing comprising a mixture of discrete textile fibres and discrete absorbent, composite fibres said absorbent, composite fibres comprising a matrix of at least 10% of water insoluble alginate having dispersed therein at least 40% of another polysaccharide. Such a dressing may have the advantage that it is non-adherent to wound tissue while being absorbent and relatively inexpensive and the added advantage that it may be retained on the wound for longer than conventional cotton gauze. The absorbent, composite fibres according to the invention incorporated in the wound dressing become moist and slippery or gelatinous upon the uptake of wound exudate. This reduces the tendency for the textile fibres to adhere to the wound.

15

20

25

30

In general textile fibres absorb liquids by capillary action and are not hygroscopic. This means that their absorbencies as measured by the free swell absobancy test are low such as less than 1 gram of liquid per gram of fibre. Suitable textile fibres can be natural or synthetic depending on the end use of the dressing and method of manufacture. Suitable textile fibres are for instance

WO 97/39170 PCT/EP97/01880

7

described in PCT/GB95/00114. For example where the dressing is made from a non-woven mixture of discrete fibres the textile fibre is preferably one that can be fused at relatively low temperatures, for example polypropylene. The entire dressing can be heat fused to give a dressing with sufficient tensile strength that it may be removed intact from the wound even though saturated with exudate. This avoids the need for the painstaking removal from the wound of parts of a dressing that has lost its integrity on exposure to exudate.

15

20

25

30

Where the dressing is made from a woven mixture of discrete fibres the textile yarn can be polyester, polypropylene or polyamide or any other suitable support yarn. surprisingly found that it is possible to knit fibres of the invention in a knitting process where it is preferable for the textile yarn to form the pillar or chain stitches of the knit (the warp) and the composite fibre to form or be included in the the in-laid yarn of the knit. A particularly suitable knit of this type is a Raschel knit as described in Textile Science by Kathryn Hatch, West Publishing Company 1993. If composite fibres are included in both the pillar and the in-laid yarn then the pillar yarn tends to break and shed fibres. If composite fibres are included only in the in-laid yarn then this tendancy is overcome and quite high machine knitting speeds can be achieved and a dressing of better integrity is produced.

According to a further aspect the invention provides a wound dressing as claimed in claims 11 to 14 wherein the

dressing is in the form of a warp knitted fabric comprising pillar yarn and in-laid yarn, the pillar yarn being substantially free of composite fibres.

Various optional ingredients can be included in the final composition of the fibres such as preservatives and small amounts of pharmacologically active ingredients. For example an antibiotic or antimicrobial agent such s metronidazole, silver sulphadiazine, neomycin or penicillin and antiseptic agent such as povidone iodine, iodine and antiinflammatory agent such as hydrocortisone or triamcinolone acteonide or a skin protective agent such as a zinc oxide can be included.

The invention is illustrated by the following examples:-

20

10

15

Example 1

Fibres according to the invention in the form of a continuous yarn were prepared as follows:

800ml of a 6% w/w dope was made by adding 28g of carboxymethyl cellulose (ex Hercules), 12g of alginate (ex Kelco), and 8g of pectin (ex Aldrich Ltd) to 752g of deionised water. The mixture was stirred with a high speed mixer until the ingredients had dissolved and the dope allowed to stand overnight to degas.

30

25

The degassed dope was then poured into a pressure vessel connected to the dope pumping/filtering system of a spinning rig. The pressure vessel was pressurised to 2 to 3 atmospheres with compressed air and the pump, $60\mu m$ pore

size filter and associated pipe work purged to remove any A 400 jet spinneret, air bubbles. previously ultrasonically cleaned for 20 minutes, was connected to the rig and the rig started. On exit from the spinneret, the dope was fed into a spin bath of 2m length containing 30L 10 of 0.4 mol/dm3 of calcium chloride. The fibres so produced were threaded over three sets of rollers of a first godet and then over the rollers of a second godet. Propan-2-ol was dripped onto the fibres at a rate sufficient to wet the resulting yarn. The yarn was then passed into two baths, 15 the first contained 4L of propan-2-ol and the second contained 2.5L of propan-2-ol. The propan-2-ol was maintained at a concentration to dry the yarn. was then passed through a set of pinch rollers that serve to apply tension to yarn. The yarn was then wound onto 20 The dope was supplied to the system at 6ml per minute and a speed differential maintained between the first and second godets resulted in a stretch of 60%. The resulting yarn had a denier of 300 to 400.

25 Example 2

30

A knitted wound dressing according to the invention was prepared comprising the yarn of example 1 and a crimped polyester yarn. The dressing was knitted on a crochet knitting machine (Model STP7 ex KOHLER) each needle of which creates a chain of interlocked loops (pillar or clain stitches). These form the warp threads of the dressing. The warp threads are held together by weft threads. 45 warp threads of stiches were knitted from 150 denier crimped polyester yarn. These were held together by 44 threads of

15

20

25

30

the yarn of example 1 (in-laid yarn) to form a dressing.

Example 3

A non-woven wound dressing according to the invention was made by mixing 200g of the aborbent, composite fibres of example 1 cut into 5cm lengths and 200g of polypropylene staple fibre cut to 5cm lengths in a rag roller to randomise the fibre. The mixture of fibres was then carded and cross-lapped into a web of 100gsm basis weight. The web was then passed through heated callender rollers at 65°C and pressure. The resultant product was slit into discrete dressings 10cm by 10cm square.

Example 4

A staple yarn was made from the composite fibres of the invention in the following way. A mixture of the composite fibre (20kg) and polypropylene (20kg) (all 3 denier) was cut to a staple length of 40mm and converted into a lap of approximately 100gsm on a conventional short staple scutching line - a Truteschler Opening line. The line comprised a feed table, coarse fibre opener, volumetric feeder, fine opener and lap former.

The lap once formed was fed into a worsted type carding machine - a Thibeau CA6 comprising a weigh pan hopper, fibre opening section and a main carding cylinder. The web of fibres formed was condensed into the form of a sliver with an average weight of 5 grammes per metre length.

The slivers were then attenuated on a conventional short-

5 staple draw frame - a Platts Globe Draw Frame - in which rollers operated at differential surface speeds to attenuate the multiple feed of slivers (6-8) into a uniform single sliver of uniform weight and thickness (approximately 3g per metre length).

The drawn sliver was converted into roving on a roving frame which further attenuates the sliver. Twist was inserted to add cohesion to the strand. The roving was then spun on a ring spinning machine in which further drafting took place and twist was inserted to form the final yarn.

Throughout the description and claims of the specification the word "comprise" and variations of the word, such as "comprising" and "comprises" is not intended to exclude other additives, components, integers or steps.



5 THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

- 1. An absorbent, composite fibre comprising a matrix of from at least 10% to less than 50% by weight of water insoluble alginate having dispersed therein at least 40% by weight of another polysaccharide.
- An absorbent composite fibre as claimed in claim 1 wherein the water insoluble alginate is calcium alginate.

(-

3. An absorbent composite fibre as claimed in claim 1 or claim 2 wherein the other polysaccharide is selected from the group comprising carboxymethyl cellulose, carboxyethyl cellulose, other derivatives of cellulose, cellulose, pectin, hyaluronic acid and chitosan.

20

30

- 4. An absorbent composite fibre as claimed any preceding claim wherein the fibres comprise from 40% to 90% by weight of another polysaccharide, preferably 60% to 85% by weight.
- 5. An absorbent composite fibre as claimed in any preceding claim wherein the fibres comprise from 70% to 80% by weight of another polysaccharide.
 - 6. An absorbent, composite fibre as claimed in any preceding claim wherein the other polysaccharide is carboxymethylcellulose or pectin or a mixture thereof.
 - 7. An absorbent, composite fibre as claimed in any preceding claim wherein the fibres comprise from 10% to 49%



by weight of the fibre of calcium alginate, preferably 30% to 40%.

- 8. An absorbent, composite fibre as claimed in any preceding claim wherein the fibres comprise from 20% to 30% by weight of the fibre of calcium alginate.
 - 9. A method for making a composite, absorbent fibre comprising the following steps:
- (i) adding sodium alginate and another polysaccharide towater to form a dope;
 - (ii) forcing the dope through a spinneret to form fibres;(iii) treating the resulting fibres with a source of ions to convert the alginate to water insoluble alginate and cross-link the alginate to the other polysaccharide;
- 20 (iv) drying the fibres.

- 10. A method as claimed in claim 8 wherein the source of ions in step (iii) is calcium ions.
- 25 11. A wound dressing comprising an absorbent, composite fibre comprising a matrix of from 10% to less than 50% of water insoluble alginate having dispersed therein at least 40% of another polysaccharide.
- 12. A wound dressing comprising a mixture of discrete textile fibres and discrete absorbent, composite fibres said absorbent, composite fibres comprising a matrix of from 10% to less than 50% of water insoluble alginate having dispersed therein at least 40% of another

15

25

- 5 polysaccharide.
 - 13. A wound dressing as claimed in claim 12 comprising from 50% by weight to 95% by weight of textile fibres and 5% by weight to 50% by weight of absorbent, composite fibres.
 - 14. A wound dressing as claimed in any claim 11 or claim 12 comprising from 75% to 90% by weight of textile fibres and 10% to 25% by weight of absorbent, composite fibres.
 - 15. A wound dressing as claimed in claims 11 to 14 wherein the fibres are in the form of a woven fabric.
- 16. A wound dressing as claimed in claims 11 to 15 wherein the fibres are in the form of a carded web.
 - 17. Use of a wound dressing as claimed in claims 11 to 16 for the treatment of a wound by placing the dressing in direct contact with the wound.
 - 18. A wound dressing as claimed in claims 12 to 15 wherein the dressing is in the form of a knitted fabric comprising support yarn and in-laid yarn, the support yarn being substantially free of composite fibres.
 - 19. A wound dressing as claimed in claim 18 wherein the fabric is a warp knitted fabric.

- 20. An absorbent, composite fibre substantially as hereinbefore described with reference to any one of the examples.
- 5 21. A method for making a composite, absorbent fibre substantially as hereinbefore described with reference to any one of the examples.
 - 22. A wound dressing substantially as hereinbefore described with reference to any one of the examples.

DATED: 19 May, 1999

PHILLIPS ORMONDE & FITZPATRICK

15 Attorneys for:

BRISTOL-MYERS SQUIBB COMPANY

