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(54) **SPUNDYED CELLULOSIC FIBER**

(57) This invention relates to cellulosic fibers, containing incorporated indigo pigments in the oxidized form, wherein the fibers are made according to a modal process, show a tenacity (conditioned) of at least 29cN/tex and a wet modulus according to BISFA of at least 5cN/tex/%. Furthermore the invention relates to the manufacture and the use of such fibers in fabrics.

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Description

[0001] This invention relates to cellulosic fibers, containing incorporated indigo pigments in the oxidized form, wherein the fibers are made according to a modal process, show a tenacity (conditioned) measured according to BISFA of at least 29cN/tex and a wet modulus measured according to BISFA of at least 5cN/tex/% at 5% elongation. Furthermore the invention relates to the manufacture and the use of such fibers in fabrics and garments (footwear, etc).

Prior Art

[0002] Natural or manmade cellulosic fibres and articles made from them such as yarns or fabrics can be dyed using a number of dye classes. The most common dye types used are reactive, where the dyes chemically react with the hydroxyl groups on the cellulose molecules which make up the fibre. This creates a covalent linkage which gives this type of dye high fastness properties. Reactive dyes are the most common because they give a high degree of fastness and a full shade range. As well as with reactive dyes, cellulosic fibres can be coloured with other dye types such as direct, vat or sulphur dyes.

[0003] One of the most important vat dyes is indigo (CI Vat Blue 1).
Indigo is used to colour yarns that subsequently are used to produce indigo denim fabrics. Spun warp yarns are first prepared into beams and then dyed with indigo (CI Vat Blue 1) prior to weaving the fabric. Preparation of yarn is normally simple scouring to remove any impurities but can include such chemical treatments such as caustic soda treatments. Indigo can be applied by a number of methods but application to yarn via Rope or Slasher applications account for the vast majority.

[0004] Indigo dye is insoluble in water so is first converted into the soluble, so called "leuco" form using an alkaline reduction system using sodium hydroxide and sodium dithionite. This leuco indigo has low substantivity for cellulose, hence only pale depths are obtainable by exhaust dyeing procedures. Indigo is therefore applied in a series of dips, with intermediate squeezing and atmospheric oxidation. By repeating the process, dye is applied to the substrate layer by layer to give deep dyeings with relatively low rubbing fastness.

[0005] In rope dyeing the cellulosic warp yarns are extended along the range in the form of a rope. Yarn groups are typically 300-400 ends called ropes or cables. In slasher dyeing the warp yarns are extended flatly and separately and arranged parallel to each other. Indigo can also be dyed batchwise or in a fabric form, usually continuously. Batchwise dyeing of hanks of yarn can be carried out in becks with repeated short dips, followed by squeezing and atmospheric oxidation, although these applications are far less common.

[0006] The most common denim is derived from coloured warp while the weft thread is left white. As result of the warp faced twill weaving one side of the textile is dominated by the blue warp threads and the other side is dominated by the white weft threads. The indigo dyeing process, in which the core of the warp threads remains white, creates denim's signature fading characteristics.

[0007] Other vat dyes and sulphur dyes can also be used to colour yarns or fabrics.

[0008] The dyestuffs used to colour cellulosic fibres and articles made from them cannot normally be used to colour fibres (e.g. viscose, modal) during the fibre spinning process. The introduction of reactive dyes into the dope used to produce lyocell fibres have been found to adversely affect the stability of the process and is not acceptable for process safety reasons.

[0009] Indigo-dyed denim has some properties which are disadvantageous to some extent and to some requirements (while they are indeed highly welcome to others): Fastness to rubbing and washing is quite poor as the dyestuff is only at the outer surface of the cotton fibers. Denim articles show wash-down effect by losing indigo after washing and laundry treatments (bleaching, oxidizing, etc).

[0010] Denim laundries use various methods to give a variety of effects such as bleached, worn-down and faded look onto the denim fabrics. Historically bleaching chemicals such as hydrogen peroxide, hypochlorite and permanganate have been used mainly. Recent sustainable options for denim laundry are laser and ozone treatments. Laser light sublimates dye from the fabric surface to give faded and used look as well as to mark certain design patterns. Ozone gas is used to bleach the denim garments via its high oxidation potential.

[0011] Another very big disadvantage is the dyeing process for common denim products: The dyeing with the indigo is performed on the yarn. This process is not only very expensive but potentially heavily polluting the environment, in particular the waste water of the dyehouses.

[0012] A solution to this problem was the incorporation of Indigo pigment of natural or synthetic origin in the oxidized, i.e. blue, form or other dyestuff type imitating the colour and laundry wash-down of indigo into viscose fibers during spinning. Such fibers are marketed under the term "Viscose Indigo". However, Viscose Indigo has a relatively low mechanical strength, in particular in the wet state. Therefore Viscose Indigo fibers are usually blended with significant quantities of polyester fibers. Garments made using such blend yarns show some significant disadvantages: Due to the high content of synthetic fibers the wear comfort is reduced in comparison to garments consisting of 100% cellulosic

fibers. Furthermore there may be a need to dye the polyester fiber component as well; however this fiber type needs a different type of dyestuff which is unsuitable for cellulose.

Problem

[0013] In view of this prior art the problem to be solved consisted in providing a fiber which is suitable to create a denim appearance but shows improved rub fastness while providing a good wear comfort to the garments made of it.

Description

[0014] It is an object of the present invention to provide cellulosic fibers, containing incorporated indigo pigments in the oxidized form, wherein the fibers are made according to a modal process, show a tenacity (conditioned), also called "breaking force", measured according to BISFA of at least 29cN/tex, a wet modulus measured according to BISFA of at least 5cN/tex/% at 5% elongation. Both properties are measured according to the methods as described in the BISFA booklet "Testing methods viscose, modal, lyocell and acetate staple fibers and tows", 2004 edition. In a preferred embodiment of the invention the fibers according to the invention fulfill the requirements for a modal fiber according to BISFA (see BISFA Terminology, 2009 edition), which includes that these mechanical properties depend on the titer of the fibers. This means that a fiber of 1.3 dtex according to the invention will show a tenacity (conditioned) of at least 31.4 cN/tex and a wet modulus (wet) of at least 4.39 cN/tex/% at 5% elongation. A fiber of 1.5dtex according to the invention will show a tenacity (conditioned) of at least 30.61 cN/tex and a wet modulus (wet) of at least 4.8 cN/tex/% at 5% elongation.

[0015] Preferably the indigo pigment contains a very low content of aniline of less than 50ppm, preferably less than 25ppm and even more preferably less than 20ppm.

[0016] Preferably the fibers according to the invention contain between 0.5 and 4.0 % (w/w) of the indigo pigment, especially preferred between 1.8 and 3.0 % (w/w), related to the total weight of bone dry fiber. Lower indigo pigment content would not provide for sufficiently deep color of the fibers and higher indigo pigment contents would reduce the mechanical strength of the fiber.

[0017] The fibers can be made as follows by a process in analogy to the FR pigment incorporated cellulose fiber process as disclosed in AT 287905 B: A viscose with a content of 4 to 7% cellulose, 5 to 10% NaOH, 36 to 42% (in relation to cellulose) carbon disulphide and 1 to 5% (in relation to cellulose) of a modification agent was made. It showed a spinning gamma value of 50 to 68 and a spinning viscosity of 50 to 120 ballfall seconds; and an alkali ratio (=cellulose concentration/alkali content) of the viscose ready for spinning of between 0.7 and 1.5. An indigo pigment with very low aniline content in the oxidized form was incorporated during spinning in the form of a pigment masterbatch dispersion, in an amount suitable to obtain an final concentration in the fiber of between 0.5 and 4.0 % (w/w) of the indigo pigment, especially preferred between 1.8 and 3.0 % (w/w), related to the total weight of bone dry fiber. The indigo-containing viscose was extruded through spinning nozzles into a spinning bath showing a temperature of between 34 to 48°C and the following spinning bath concentrations: H_2S0_4=68-90g/l, Na_2S0_4=90-160g/l, $ZnS0_4$=30-65g/l. The coagulated threads were drawn off from the spinning bath at a speed between 15 and 60m/min. The coagulated, drawn threads were further washed thoroughly and cut into staple fibers, having a titer of 1.3dtex and a length of 38mm. For the purpose of the examples in this patent these fibers are hereinafter referred to as "Modal Indigo".

[0018] According to the invention the indigo pigment is incorporated inside the whole cross-section of the fiber. I.e. a microphoto of the cross-section of the fiber shows pigments distributed over the whole area for the cross-section, while conventionally dyed cellulosic fibers show indigo pigments only on the outer surface of the fibers. Surprisingly the bleeding rate of the indigo pigment in the fibers according to the invention is significantly lower than the bleeding rate of the indigo pigment in Viscose Indigo.

[0019] Another aspect of the invention is the use of the fiber according to the invention as described above for the manufacture of a fabric (knits, wovens, seamless, etc) with denim appearance, given by laundry effects such as laser and ozone. Preferably this colored fiber is used in the warp while ecru (i.e. undyed) fibers are used in the weft of the woven fabric to imitate the conventional denim fabrics.

[0020] In order to achieve different aesthetics and wear comfort for the consumer, this colored fiber can be used in the weft while warp yarn can contain conventional indigo-dyed cellulose fiber. In such product indigo-colored modal fiber is on the skin side by bringing the softness, i.e.comfort, of the modal fiber. Wash-down of the warp side would behave differently than using an ecru (i.e. undyed) fiber causing darker shades on the warp side.

[0021] Preferably this fabric is a textile fabric with denim appearance that contains between 40 and 100% (w/w) of the fibers according to the invention as described above.

[0022] In a preferred embodiment of the invention the fabric shows a rub fastness according to ISO 105-X12:2016 of between 4.0 and 5.0. A typically yarn-dyed denim shows a rub fastness of about 3.0.

[0023] In a preferred embodiment of the invention the fabric is a woven fabric. Preferably this fabric contains in the

warp between 80 and 100% (w/w), preferably between 95 and 100% (w/w), of the fibers according to the invention. This will result in the typical denim appearance, especially in twill weaving where one side of the textile is dominated by the blue warp threads and the other side is dominated by the white weft threads. This fabric may show a shrinkage at washing according to ISO 6330 and shrinkage test according to ONORM ISO 3759 of lower than 5.0%.

[0024] In another preferred embodiment of the invention is a knit fabric. Preferably this fabric shows a shrinkage at washing according to ISO 6330 and shrinkage test according to ONORM ISO 3759 of lower than 12.0%.

[0025] Yet another aspect of the invention is a method for manufacturing a fiber according to the invention as described above that includes the steps:

a. Preparation of a Modal spinning solution,
b. Preparation of indigo pigments in the oxidized form,
c. Adding the indigo pigments to the Modal spinning solution
d. Extruding the solution of step c. into a coagulation bath according to a Modal spinning process

[0026] The pigments used in the process of the invention can be made e.g. according to WO 2004/024826 A2. Common modal spinning conditions, as described e.g. in Patent AT287905B or WO 2011/026159 A1 may be applied.

[0027] Preferably the indigo pigment is added to the Modal spinning solution in the form of a masterbatch, with an indigo pigment content of e.g. 20% (w/w) in the masterbatch suspension. E.g. to obtain 0.5 to 4.0% (w/w) indigo pigment in the final fiber, 2.7 to 20.0% ((w/w), related to the dissolved cellulose) of masterbatch suspension has to be added to the Modal spinning solution, if using a masterbatch containing 20% (w/w) indigo pigment.

[0028] Surprisingly it was found that the fibers according to the invention further have a much lower bleeding rate than other spun-dyed modal fibers. The bleeding rate of Modal Indigo is also lower than that of Viscose Indigo while the mechanical textile properties are on the much higher level of modal fibers, compared to viscose fibers.

[0029] Further, surprisingly it was found that indigo pigments in the oxidized form keep their typical blue color very stable if they are incorporated in the cellulosic man-made fiber according to the invention, although the dye is very sensitive against oxidation if it is applied on e.g. cotton by conventional denim indigo dyeing.

DENIM LAUNDRY

[0030] With regular, in denim laundry commercially applied hypochlorite bleaching treatments (e.g. 2g/l soda, 3g/l sodium hypochlorite; 30min at 30°C, warm and cold rinse, dechlorination with 0.8g/l H_2O_2- 30 min at 40°C, warm and cold rinse) as well as with strong peroxide bleaching treatments (e.g. 4g/l peroxide, 4g/l NaOH, 90°C for 30min, followed by neutralization (1g/l acetic acid)) little effect was observed.

[0031] Enhancing the hypochlorite concentration (4g/l sodium hypochlorite, 40°C, 10min, followed by neutralization (3g/l sodium thiosulphate, 30°C, 10min)) could provide a slight effect. However, this treatment is not recommended considering the high amount of chemical used to obtain very small effect on the product.

[0032] However, denim laundry conditions using permanganates (e.g. 4g/l potassium permanganate, 40°C, 10min, followed by neutralization (2g/l metabisulphite, 40°C, 10min) were very effective to remove indigo from spun-dyed Modal Indigo product.

[0033] Also local bleach effects with potassium permanganate by spraying 20g/l potassium permanganate solution and drying in the air (or at 80°C in a stenter frame dryer), followed by washing the fabric in sodium dithionite solution (1 - 4g/l) for 20 minutes at 40°C, gave significantly visible results.

[0034] Significant visible results were also obtained on the fibers according to the invention by ozone treatment (50% G2 Lab machine, ozone gas conc: 45 gr/Nm3, 15min, 30min or 45min) as well as by laser marking (using machinery of Jeanologia) for example 40-150tpx (time per pixel).

HOME LAUNDRY

[0035] Home-laundry washing (water and detergent) of conventional denim articles cause indigo dyestuff to lose from the fabric in that faded look appears after each washing cycle. Therefore conventional denim products do not have color retention after home-laundry washes.

[0036] Indigo dyestuff trapped in the spun-dyed Modal-Indigo fiber is not lost during home-laundry washes. Our studies have shown that 30 home-laundry washes didn't cause color loss on spun-dyed Modal Indigo garments therefore color retention was proven. For home-laundry washing test, commercial home-laundry detergent (Fewa Color) was used and spun-dyed Modal Indigo garments (knits and woven) were washed at 40°C and flat or tumble dried.

[0037] Briefly faded, wash-down or similar looks on the spun-dyed Modal Indigo product can only be given by commercial denim laundries (laser, ozone, permanganate, etc). Such garment effect/look will be kept during the consumer life of garment as indigo is not removed with home-laundry washing. This property differentiates indigo spun-dyed modal

product from conventional dyed indigo dyed products in the market.

[0038] Preferred uses of the fibers according to the invention are:

- Denim-type woven fabric constructions, in particular denim fabrics with an area weight of more than 100 g/m^2.
- Woven-type fabric constructions, light-weight fabrics in particular shirting, dresses, etc with an area weight of more than 80 g/m2
- Knitwear including seamless, in particular tops, bottoms, underwear, but also other garments, shoes, bags made of or containing textile fabrics etc..

[0039] In all of these applications Modal Indigo shows a much better performance than Viscose Indigo owing to its lower shrinkage and higher strength. In all of these applications the low bleeding tendency of the fibers according to the invention may be an advantage.

[0040] The invention will now be illustrated by examples. These examples are not limiting the scope of the invention in any way. The invention includes also any other embodiments which are based on the same inventive concept

Examples

Example 1: Manufacture of an indigo-containing spun-dyed modal fiber:

[0041] The incorporated cellulose fiber was made as follows by a process in analogy to the FR pigment incorporated cellulose fiber process as disclosed in AT 287905 B:
A viscose with a content of 6% cellulose, 7% NaOH, 39% (in relation to cellulose) carbon disulphide and 3% (in relation to cellulose) of a modification agent was made. It showed a spinning gamma value of 57 and a spinning viscosity of 80 ballfall seconds. 2.3% (w/w), related to the cellulose content of the spinning solution, of indigo pigment with very low aniline content in the oxidized form was incorporated during spinning in the form of a pigment masterbatch, containing 20% (w/w) of pigment. The indigo-containing viscose was extruded through spinning nozzles into a spinning bath showing a temperature of 38°C and the following spinning bath concentrations:
H_2S0_4=72 g/l, Na_2S0_4=120 g/l, $ZnS0_4$=60 g/l. The coagulated threads were drawn off from the spinning bath at a speed between 45 m/min. The coagulated, drawn threads were further washed thoroughly and cutted into staple fibers, having a titer of 1.58 dtex and a length of 38 mm. The tenacity (conditioned) was 32.1 cN/tex and the wet modulus (wet) was 5.5 cN/tex/% at 5% elongation. Elongation at break was 15.5%. All mechanical properties were measured according to the methods as described in the BISFA booklet "Testing methods viscose, modal, lyocell and acetate staple fibers and tows", 2004 edition. For the purpose of the examples in this patent these fibers are hereinafter referred to as "Modal Indigo".

Example 2: Properties of fabrics containing the fibers according to the invention and their properties

[0042] Three fabrics were made as follows, using the fibers of Example 1; yarns of the fibers were spun by rotor yarn spinning machines:

2.a.: Jeans bottom-weight fabric

- Warp: Modal Indigo yarn, Ne 11
- Weft: Cotton/Elastane (98%/2%) yarn, Ne 15
- 3/1 RHT fabric construction; 7ends/cm, 20picks/cm

2.b.: Shirting weight fabric

- Warp: Modal Indigo yarn, Ne 24/1
- Weft: Cotton, Ne 15
- 2/1 RHT fabric construction; 185 gsm

2.c.: Knit top fabric

- Modal Indigo yarn Ne 24
- Single jersey fabric construction with 2% elastane; 185 gsm

[0043] These fabrics were tested for several properties as follows:
Rub fastness was measured according to ISO 105-X12:2016 (1 = worst; 5 = best); see Table 1:

Table 1:

Fabric	Dry	Wet
2.b	4-5	4-5
2.c	4-5	4

[0044] Both fabrics with the fibers according to the invention showed very good rub fastness properties.

[0045] Wash fastness was measured according to ISO 105-C10:2006 The fabric was washed together with a white cotton resp. white modal fabric and the staining was evaluated on a color scale (1 = worst fastness; 5 = best fastness)); see Table 2:

Table 2:

	Color of the fabric before washing	Staining on modal stripe	Staining on cotton stripe
Denim	45	4-5	5
Knit	4	5	5

[0046] Both fabrics with the fibers according to the invention showed very good wash fastness properties.

[0047] Shrinkage was measured according to ONORM ISO 3759:2011 after washing of the samples according to ISO 6330:2012. The tested woven fabric was the denim fabric of Example 2.a. with Modal Indigo and a denim fabric made in the same way, but containing Viscose Indigo instead of Modal Indigo. The tested knitted fabric was the fabric of Example 2.c. with Modal Indigo and a knitted fabric made in the same way, but containing Viscose Indigo instead of Modal Indigo. Table 3 shows that the fabrics containing the Modal Indigo fibers according to the invention show significantly lower shrinkage than comparable fabrics made using Viscose Indigo.

Table 3:

Shrinkage [%]	Viscose Indigo	Modal Indigo
Woven fabric	7.0	4.5
Knit fabric	17.5	11.5

Example 3: Yarn tenacity after denim bleaching processes, compared to Viscose Indigo

[0048] Modal Indigo fibers according to the invention were compared to commercially available Viscose Indigo fibers (obtained from Lenzing Aktiengesellschaft, Lenzing/Austria). Yarns were spun using a Quickspin machine, i.e. by a rotor spinning process. The yarn tenacities were measured before and after treatment with permanganate in aqueous solution according to the following conditons: Pottasium permanganate concentration 4g/l, 40°C, 10min, followed by neutralization with 2g/l disodium metabisulphite at 40°C for 10min.). Table 4 shows that while Viscose Indigo after Permanganate bleaching was so degraded that the yarn strength and yarn elongation were unmeasurable (the yarn teared when clamping), Modal Indigo even after Permanganate bleaching shows satisfying mechanical properties.

Table 4:

Fiber type	Viscose Indigo	Viscose Indigo	Modal Indigo	Modal Indigo
treatment	untreated	Permanganate bleach	untreated	Permanganate bleach
yarn count [dtex]	303	303	313	323
yarn strength [cN/tex]	9,5	not possible	12,4	5,4
yarn elongation [%]	12,5	not possible	9,6	5,6

Example 4: Test of fibers for bleeding

[0049] A Labomat device with 500mL-tubes operating at a rotation velocity of 20rpm was used. 200ml de-ionized water were measured in a graduated cylinder and heated in the Labomat device to 85°C. 5g fiber were added. The

Labomat temperature was raised to 98°C as quickly as possible. The samples were treated at 98°C for five minutes, then cooled down to 70°C as fast as possible. The liquor was transferred into a 100ml beaker and cooled down to room temperature (i.e. 20°C) while the fibers were removed manually.

[0050] Two methods were applied to the resulting liquor to assess the bleeding:

- Photometric assessment of absorption at a wave length of 480nm in the resulting liquor.
- Turbidity measurement using a Tubidimeter according to ISO 7027-1:2016; the result is given in [NTU] = Nephelometric Turbidity Units.

[0051] For each measurement, a test tube filled with pure water is necessary as blanc reference. The tested fibers were as follows:
Modal Indigo was obtained according to Example 1. Viscose Indigo, Viscose Black (spun dyed) and Modal Black (spun dyed) were obtained as commercially available products from Lenzing Aktiengesellschaft, Lenzing/Austria. All fibers used were staple fibers with a titer of between 1,3 and 1,7 dtex and a cut length of between 38 and 39mm.

Table 5:

	Abs [480nm]	Turbidity [NTU]
Viscose Black	0,0363	10,2
Viscose Indigo	0,0495	22,4
Modal Black	0,1168	29,9
Modal Indigo	0,0158	5,82

[0052] The results (Table 5) show that while in spun dyed viscose fibers the switch from a conventional pigment to indigo pigment leads to higher bleeding, in spun dyed modal fibers the switch from a conventional pigment to indigo pigment surprisingly results in significantly reduced bleeding. This is in particular surprising because the fundamental chemistry of both processes - formation of cellulose xanthogenate and subsequently coagulation and regeneration of the cellulose - is the same.

Example 5: Sustainability assessment based on a theoretical model

[0053] To assess the sustainability of the invention, it was compared to three conventional denim dyeing methods. The three conventional methods compared are hereinafter referred to as Methods A, B and C.

[0054] The comparisons were made by the sustainability expert consulting company GAVILAN AD using an expert software developed by Archroma, called 'One Way'. This expert system has a built-in database with all the information about resources (water, energy, CO2 generated, etc) required to run each part of equipment in the application process (padder, washing box, pre-dryer, drying cans, stenter, etc). This expert program also calculates indirect resource requirements (e.g. energy depending on type of fuel for the boiler, heating system for an application box - direct/indirect steam, electrical power required by engines, etc). "owf" means "on weight of fiber".

[0055] Assumptions made for the Methods A, B and C were as follows:
General assumptions for all four methods, i.e. including the Modal Indigo processing according to the invention:

- Length of warp yarn to the dyed: 10000m
- Weight: 2190 Kg
- Type of Denim article: light weight (7 Oz/Yd^2, i.e. approx. 235 g/m^2)
- 25°C for all process steps
- Methods A-B-C include yarn spinning before indigo dyeing while spun-dyed Modal Indigo fiber according to the invention covers yarn spinning after indigo spun-dyeing of the fiber.

[0056] Additional assumption for the Method A (conventional indigo yarn dyeing) was as follows:

- Concentration of indigo (the standard commercial form of granulated indigo granulated): 4% owf (dark tone)
- Indigo yarn dyeing process is pre-wetting, warm rinsing (2 boxes), cold rinsing (1 box), indigo dyeing (6 boxes), rinsing (3 boxes).

[0057] Additional assumption for the Method B (pre-reduced indigo yarn dyeing) was as follows:

- 4% owf (dark tone) for pre-reduced liquid indigo under nitrogen gas to prevent it from oxidation
- Indigo yarn dyeing process is pre-wetting, warm rinsing (2 boxes), cold rinsing (one box), indigo dyeing (3 boxes), rinsing (3 boxes)

[0058] Additional assumption for the Method C (low water consumption Sulphur dyeing) was as follows:

- Concentrations of non-indigo dyes adjusted according to both lab and bulk comparative dyeing: 12% pre-reduced Sulphur dyestuff
- Application of non-indigo dyes consider a pre-mercerization step instead of the conventional pre-wetting for indigo.
- Mercerizing, warm rinsing (2 boxes), sulfur dyeing (2 boxes), fixation bath (2 boxes), rinsing (3 boxes)

[0059] When the spun-dyed Modal Indigo fiber production method according to this invention is compared to the other dyeing methods A to C, the method according to the invention has a distinctive savings in water, chemicals, electricity, heat and wastewater (see Table 6: Savings achieved with indigo spun-dyed modal according to the invention compared to methods A, B and C). Heat energy needed to dry the conventionally dyed yarns are not needed for Modal Indigo fibers.

Table 6

Savings by the invention compared to	Method A	Method B	Method C
Water	99.5 %	99.5 %	99.1 %
Chemicals	87.4 %	81 %	83.7 %
Electricity	99.96 %	99.96 %	99.96 %
Wastewater	99.5 %	99.5 %	99.1 %
Heat	100%	100%	100%

Claims

1. Cellulosic fibers, containing incorporated indigo pigments in the oxidized form, **characterized in that** the fibers are made according to a modal process, show a tenacity (conditioned) of at least 29cN/tex, a wet modulus according to BISFA of at least 5cN/tex/%.

2. Fiber according to claim 1, wherein the indigo pigment is incorporated inside the whole cross-section of the fiber.

3. Use of the fiber according to claim 1 for the manufacture of a fabric with denim appearance.

4. Textile fabric with denim appearance, **characterized in that** it contains between 40 and 100% (w/w) of the fibers according to claim 1.

5. Fabric according to claim 4, which shows a rub fastness according to ISO 105-X12:2016 of between 4.0 and 5.0.

6. Fabric according to claim 4, which is a woven fabric.

7. Fabric according to claim 6, which contains in the warp between 80 and 100% (w/w), preferably between 95 and 100% (w/w), of the fibers according to claim 1.

8. Fabric according to claim 6, which shows a shrinkage at washing according to ISO 6330 and shrinkage test according to ONORM ISO 3759 of lower than 5.0%.

9. Fabric according to claim 4, which is a knit fabric.

10. Fabric according to claim 9, which shows a shrinkage at washing according to ISO 6330 and shrinkage test according to ONORM ISO 3759 of lower than 12.0%.

11. Method for manufacturing a fiber according to claim 1, **characterized in that** it includes the steps:

a. Preparation of a Modal spinning solution
b. Preparation of indigo pigments in the oxidized form
c. Adding the indigo pigments to the Modal spinning solution
d. Extruding the solution of step c. into a coagulation bath according to a Modal spinning process.

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EUROPEAN SEARCH REPORT

Application Number
EP 20 17 2742

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2015/154110 A1 (CHEMIEFASER LENZING AG [AT]) 15 October 2015 (2015-10-15) * page 1, line 7 - line 10 * * claims *	1-11	INV. D01F2/14
A	WO 2014/040098 A1 (CHEMIEFASER LENZING AG [AT]) 20 March 2014 (2014-03-20) * page 4, line 27 - page 5, line 14 * * page 11, line 29 - page 12, line 10 *	1-11	
A	CN 105 755 634 A (NANTONG JIANWEI YARN-DYED CLOTHING CO LTD) 13 July 2016 (2016-07-13) * abstract * * examples *	1-11	
			TECHNICAL FIELDS SEARCHED (IPC) D01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	2 October 2020	Fiocco, Marco

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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