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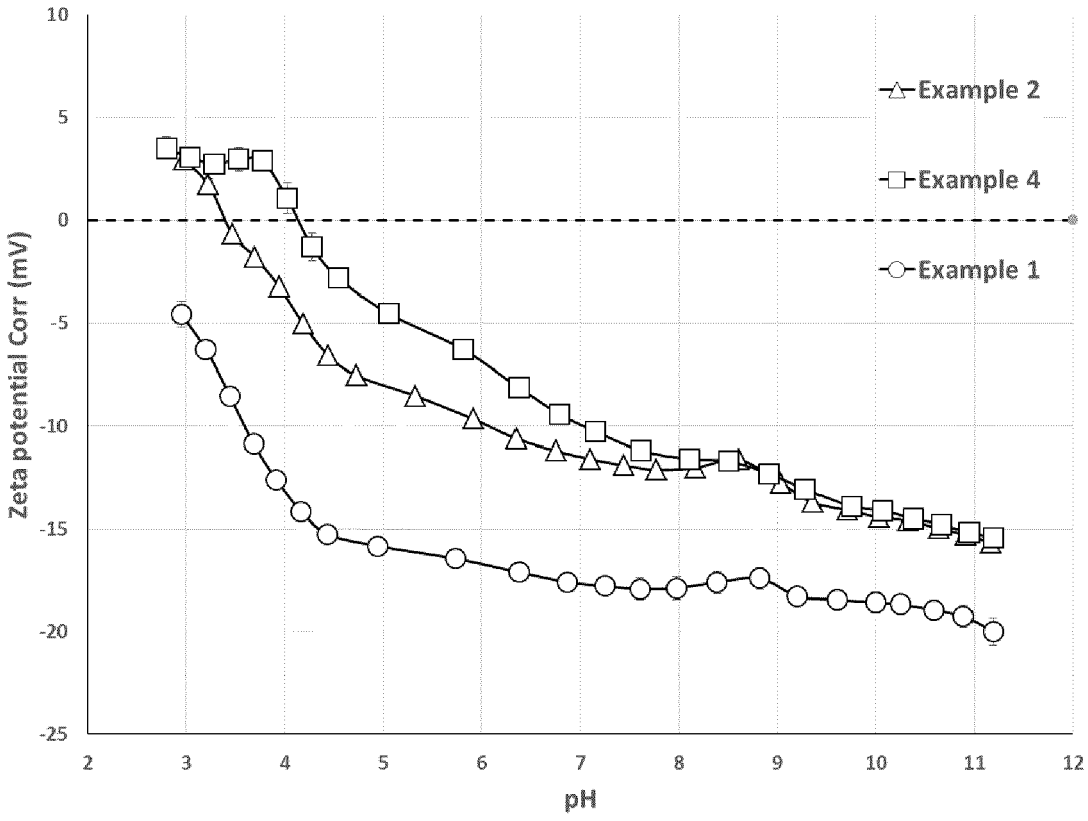
(71) Applicant: **LENZING AKTIENGESELLSCHAFT**
4860 Lenzing (AT)

(72) Inventors:
- **SUCHOMEL, Friedrich**
  4861 Schörfling (AT)
- **WESSELY, Peter**
  4840 Vöcklabruck (AT)
- **MOMMER, Claudia**
  4840 Vöcklabruck (AT)

(54) **SPUN-DYED FIBER AND METHOD FOR ITS MANUFACTURE**

(57) This invention relates to a spun-dyed man-made cellulosic fiber with incorporated color pigment wherein the fiber contains a polycationic compound on its outer surface. Furthermore a method for the manufacture of such a fiber is disclosed.

Fig. 2:



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Description

[0001] This invention relates to a spun-dyed man-made cellulosic fiber with incorporated color pigment which contains a polycationic compound on its outer surface. Furthermore a method for the manufacture of such a fiber is disclosed.

Prior Art

[0002] Spin-dyeing of fibers by incorporating the color pigments into the spinning dope before forming the fibers is in general a well-known and favourable dyeing method because of its better ecology. However often bleeding of the pigment occur during downstream processing of such fibers. Such bleeding is hardly accepted by the downstream processors, in particular in case of dark color pigments, for example black pigments like carbon black or blue pigments like oxidized indigo.

[0003] In the prior art there are several publications dealing with the fixation of dyestuffs on cellulosic fibers, mostly on cotton fibers. Poly(diallyldimethylammonium chloride) ("PolyDADMAC") dye-fixative (see e.g. Yu Y. and Zhang Y., Review of Study on Resin Dye-Fixatives on Cotton Fabrics, Modern Applied Science, Vol. 3, No. 10 (October 2009)) and quaternary ammonium salts (see e.g. Sharif et al. Role of quaternary ammonium salts, Color. Technol., 123 (2007), p. 8-17) are described as possible dye-fixative agents. However cotton obviously is not a spun-dyed fiber because cotton is not made by a solution spinning process.

[0004] WO 2004/081279 A1 discloses a method for dyeing cellulosic fibers, wherein a polycationic compound is incorporated into the cellulosic fibers during their manufacture. The cationic cellulose fibers thus obtained show improved affinity for direct dyestuffs, acid dyestuffs and reactive dyestuffs. The fibers according to this invention are not spun-dyed fibers and the applied dyestuffs are not pigments. EP 0683251 A1 discloses numerous polycationic compounds suitable for the process according to WO 2004/081279 A1. However, according to the experience, such polycationic compounds can decrease the spinnability of the spinning solution significantly, in particular in the viscose process. In particular long-chain polycationic compounds induce too early coagulation of the cellulose. Polycationic compounds with short chain length on the one hand have insufficient pigment fixation effect, on the other hand they are washed out in the spin bath and pollute the spin bath cycles.

[0005] WO 2014/118804A1 discloses black colored man-made cellulosic fibers and a black colorant formulation for preparing the same in a viscose process. According to this document a formulation containing among others a black color pigment, i.e. carbon black, as well as a surface active agent, an anti-coagulating agent and a steric stabilizer is mixed into a viscose dope. The surface active agent as well as the anti-coagulating agent should be anionic substances. While WO 2014/118804A1 is silent regarding the specific spinning process, it can be assumed that the viscose dope is extruded and further spun according to a regular viscose process. The black colored fibers were then washed for in total 15 minutes at the remarkably high washing bath temperature of 90°C with water, subsequently sulphuric acid and finally sodium hydroxide solutions. It must be assumed that during these washing steps all surplus black pigments are washed out of the fibers. But due to the harsh conditions, long processing times and the large quantities of washing lyes with black pigments such a process is neither economically nor ecologically feasible. However, in a usual commercially feasible fiber plant the washing steps cannot be washed for more than about 1 to 4 minutes in total.

Problem

[0006] In view of this prior art the problem to be solved consisted in providing spun-dyed cellulosic fibers without or with at least drastically reduced bleeding as well as a process for manufacturing such fibers without long processing times and without producing large quantities of used washing lyes containing black pigments.

Description

[0007] It is an object of the present invention to provide a spun-dyed man-made cellulosic fiber with incorporated color pigment, which contains a polycationic compound on its outer surface. Typically the fiber according to the invention shows a zeta potential of zero or positive at a pH of 3.0 or lower. All presently known spun-dyed cellulosic man-made fibers have a negative zeta potential. The incorporated color pigment in particular is a negatively charged color pigment, e.g. carbon black, but among others also indigo in the oxidized form would be suitable. Preferably the color pigment is carbon black.

[0008] The fiber according to the invention has a positive zeta potential in an acidic environment and at any pH value the zeta potential is significantly more positive (or less negative) than that of the untreated fiber without polycations. By the zeta potential the presence of the polycations can be detected over the whole pH range. The zeta potential of a fiber treated according to the invention may be at least 1mV more positive than that of the same fiber, i.e. containing the same incorporated pigment, but without the treatment of the invention, at the same pH value. Typically it may be about

3mV more positive over the whole pH range from pH 3 to pH 11.

[0009] In a preferred embodiment the polycationic compound is one out of the group containing polymeric quaternary ammonium compounds, in particular poly(diallyldimethylammonium chloride), cationically modified starch and polyethylenimines. In general for the purpose of the invention a high electrical charge density is beneficial because it allows obtaining the intended effect with low quantity of the polycationic compound. Polyvinylpyrollidon is a polycation as well, but shows significantly less performance in the present invention. Polyamines first have to be treated with an acid, e.g. acetic acid, before they can be applied to the fibers, which is a practical disadvantage. Poly(diallyldimethylammonium chloride) is a harmless compound which is e.g. used in cosmetics.

[0010] Preferably the fiber contains between 0,50 and 0,02 %(w/w), preferably between 0,2 and 0,04%(w/w), of the polycationic compound, in relation to the bone dry weight of the fiber. Preferably the fiber shows a bleeding number of between 4.0 and 5.0 according to the bleeding test.

[0011] In a particularly preferred embodiment of the present invention the fiber is a xanthate fiber. A xanthate fiber in the context of this invention is a cellulosic fiber which was manufactured by extrusion of a spinning solution containing a dissolved cellulosic compound into a spin bath, wherein the cellulosic compound is cellulose xanthate and wherein the cellulose xanthate is regenerated into cellulose while passing the spin bath. The most common xanthate fibers are called "Viscose" resp. "Modal" according to BISFA (International Bureau for the Standardization of Man-Made Fibres): "Terminology of man-made fibres", 2009 Edition (hereinafter the "BISFA terminology").

[0012] Viscose fiber is produced by extruding a solution of a cellulose derivative through very small spinneret holes and then coagulating by changing the pH and by converting the derivative back to cellulose.

[0013] Cellulose as wood pulp is usually used as the starting material although other sources of cellulose such as bamboo and cotton linters are also used. The wood pulp is steeped in sodium hydroxide and then reacted with carbon disulphide to convert it to cellulose xanthate. The xanthate is dissolved in a sodium hydroxide solution to yield a viscous, golden colored liquid which is commonly called viscose. The viscose is de-aerated and filtered. It is then extruded through precious metal spinnerets into a spinbath - a so-called wet spinning technology - consisting of sulphuric acid, sodium sulphate and zinc sulphate. The acid reacts with the sodium hydroxide in the viscose to cause coagulation of the cellulose xanthate. The acid also reacts with the cellulose xanthate converting it back to cellulose. While the newly formed fibre is still in a plastic state it is stretched to increase the orientation of the cellulose molecules with the axis of the fibre and encourage crystallization. The fibre may then be cut into lengths to form staple fibre or it may be kept as continuous filament or tow depending on the design of the spinning machine and the product required. In the remainder of the process the fibre is washed to remove non-cellulose products of the reaction such as sodium sulphate and hydrogen sulphide, finished with a spin finish and anti-stat to aid downstream processing and dried. Modern viscose plants are designed to recover as much of the by-products of the process as possible. This is essential to avoid environmental pollution and to ensure the safety of the workforce and surrounding community. Better recovery and recycling of by-products can also give a positive economic benefit.

[0014] Modal fibre is a high wet modulus fibre produced using a modified version of the viscose process. An additive is mixed with the spinning solution which slows down the regeneration of the cellulose during spinning. Together with modified spinbath and viscose composition, the additive allows the fibre to be stretched to a much greater extent than normal viscose. This gives a fibre with a higher orientation which is stronger than viscose and has a modulus closer to that of cotton. Modal fibre is often used in blend with cotton to give softer fabrics than would be made with cotton alone. It is used widely in knitted fabrics for lingerie and ladies apparel.

[0015] Lyocell is produced by a solvent spinning process. The solvent is a mixture of an amine oxide, in particular N-methylmorpholine-N-oxide ("NMMO") which is non-toxic, in water. A slurry of cellulose in a mixture of amine oxide and water is prepared. Water is removed from the slurry by evaporation and as the water content decreases, the cellulose dissolves in the amine oxide producing a solution which is a viscous liquid above 80°C. The solution is extruded through spinneret holes via an air gap into an aqueous coagulation bath - a so-called dry-jet wet spinning technology. The solvent is diluted by the water and the cellulose coagulates to form a fibre. In the remainder of the process, the fibre is washed to remove any amine oxide solvent, cut into staple fibre, finished with a lubricant and an antistatic agent and then dried. In another version of the process, the tow of newly formed fibre is cut into staple fibre of the required length and then washed on a moving wash bed. The washed fibre is dried in a flatbed dryer. In another version of the process, lyocell is produced as a continuous filament yarn by winding a bundle of filaments onto a package for subsequent use. In yet another version of the process, lyocell is produced directly as a nonwoven fleece by using a solution-blowing extrusion spinneret and subsequent coagulation, washing and winding. Such a process is disclosed among others in EP 1093536 B1. The amine oxide solvent used in the lyocell process is recycled in a closed loop in the factory. Recovery rates of greater than 99.5% are achieved. Recycling of the solvent means that the effect of the process on the environment is very low. It is also essential for the economics of the process.

[0016] In a preferred embodiment of the present invention the fiber is a Modal fiber (according to the BISFA terminology). In another preferred embodiment of the present invention the fiber is a Lyocell fiber (according to the BISFA terminology).

[0017] A fiber according to the invention which is dispersed in water may not show neutral behavior but may influence

the pH value of the water. This effect can be measured easily and is called the "fiber pH". The skilled in the art may consider this among others in further fiber processing within the textile chain. In a preferred embodiment the fiber pH of the fiber according to the invention is higher than 6.1. It may be preferably lower than 8,5 and in particular may be between 6.1 and 7.3.

[0018] Another aspect of the present invention is a method for the manufacture of a spun-dyed man-made cellulosic fiber with incorporated color pigment with the following steps:

a. Preparation of a spinning solution containing cellulose and at least one color pigment,
b. Extrusion of the spinning solution into a coagulation bath,
c. Coagulation of the cellulose and thereby forming of the fiber tow; usually there is a certain tension to apply a drawing force to the freshly formed fibers in the tow,
d. Optionally washing the fiber tow,
e. Cutting the fiber tow into staple fibers and forming a fiber fleece
f. Optionally washing the fiber fleece (according to well-known methods)
g. Impregnation of the fiber fleece with a treatment liquid, washing, pressing,
h. Application of a spin finish to the fibers, pressing,
i. Drying,

wherein in the treatment bath of step g. the fiber fleece is treated with a solution of a polycationic compound. A side effect is that only about half of the spin finish concentration in the spin finish bath is needed compared to the finishing of same fibers without PDADMAC treatment. In existing fiber plants the invention may be implemented at the bleaching stage of a conventional aftertreatment unit, because spun-dyed fibers, in particular for textile applications, require no bleaching.

[0019] The zeta potential is measured at pH=3; all presently known spun-dyed cellulosic man-made fibers have a negative zeta potential at pH=3.

[0020] The incorporated color pigment in particular is a negatively charged color pigment, e.g. carbon black, but among others also indigo in the oxidized form would be suitable. Preferably the color pigment is carbon black.

[0021] In a preferred embodiment of the present invention the polycationic compound is one out of the group containing polymeric quaternary ammonium compounds, in particular poly(diallyldimethylammonium chloride), cationically modified starch and polyethylenimines. Most preferably the polycationic compound is poly(diallyldimethylammonium chloride) ("PolyDADMAC").

[0022] In a preferred embodiment of the present invention the fibers between step c. and step g. always contain at least 50%(w/w), preferably at least 60%(w/w) water in relation to the cellulose content. Mostly they contain significantly more water, due to the nature of the process steps. For example after coagulation the fibers are highly swollen and may contain more than 200%(w/w) water in relation to the cellulose content. Even after washing and before drying the fibers contain more than 100%(w/w) water in relation to the cellulose content.

[0023] In a particularly preferred embodiment of the present invention the cellulose-containing spinning solution is a solution of the xanthate type - i.e. either according to the viscose process or according to the modal process, as described above - and step b. is performed according to a wet spinning technology and wherein the fiber tow is guided through a second drawing zone between step c. and step d..

[0024] In another particularly preferred embodiment of the present invention the cellulose-containing spinning solution is a solution of the lyocell type and step b. is performed according to a dry-jet wet spinning technology.

[0025] In a preferred embodiment of the inventive method step g. is characterized by the following parameters:

a. The polycation concentration in the treatment bath is between 0,1 and 10,0 g/l, preferably between 0,5 and 2,0 g/l, most preferably between 0,6 and 1,5 g/l,
b. A treatment time in the treatment bath of between 10 and 120 seconds, preferably between 45 and 135 seconds

[0026] Some commercial viscose fiber plants have aftertreatment units which allow a treatment time of about 60 seconds.

[0027] The polycation concentration required in the treatment bath depends on the content of the color pigment in the fibers, which itself depends on the fiber titer. In general thinner fibers, i.e. fibers with a lower fiber titer, need a higher pigment concentration than thicker fibers due to various optical effects depending on the fiber diameter and fiber surface. For example if a 1,5dtex modal fiber has a carbon black content of 4,3%(w/w), then a 1,0dtex modal fiber needs a content of 4,9%(w/w) of the same carbon black pigment in order to achieve the same black appearance in the end products (yarns, fabrics, garments). A thicker fiber, e.g. 1,7dtex viscose, will only require 3,8%(w/w) of the same carbon black pigment. Accordingly to obtain a bleeding number of 5,0, said 1,5dtex modal fiber had to be treated with a PolyDADMAC concentration of 0,75g/l in the treatment bath, while said 1,0dtex modal fiber required 0,85g/l and said 1,7dtex viscose

fiber required 0,5g/l, only.

[0028] Step g. may be characterized by a ratio of fiber mass to treatment liquid of between 1:0,1 and 1:5, preferably between 1:0,5 and 1:4, more preferably between 1:0,8 and 1:3.

[0029] In the method according to the invention PolyDADMAC with a molecular weight of more than 25.000 Dalton may be used. Preferably the molecular weight may be lower than 1.000.000 Dalton, preferably between 50.000 and 1.000.000 Dalton; if the molecular weight is higher, then the viscosity of the treatment liquid becomes too high and cannot be used effectively according to the invention. A molecular weight of 100.000 Dalton gives no significant viscosity increase; 400.000 Dalton still give no problems in terms of increased viscosity.

[0030] 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

Bleeding test method:

[0031] First the fiber samples are loosened by hand to obtain good accessibility for the liquid. 200ml of demineralized water are poured into a Labomat beaker of a Mathis laboratory dyeing device and are heated up to 85°C as fast as possible. 5g of the loosened fiber sample is put into the beaker and the whole beaker content is heated up to 98°C as fast as possible, kept at this temperature for 5 minutes and subsequently cooled down to 70°C as fast as possible. Then the water is poured into a 100ml glass bottle (colorless glass) until the bottle is completely filled. The bottle is allowed to cool down to room temperature. The color of the water is then compared to a grey scale according to (ISO 105-A03: 1993; augmented scale including four half-steps and, thus, 9 steps). The value obtained according to this ISO standard will be between 1 and 5 and, for the purposes of this invention, is called "bleeding number". A bleeding number of 5 means that there is no bleeding at all.

Zeta potential measurement method:

[0032] The measurements were performed with an Electrokinetic Analyzer (EKA) device supplied by company Anton Paar/Austria. A 5 l volume of streaming solution is prepared, containing 1 mM each of KCl and KOH. The fiber sample (0.5 g) is pre-wetted by immersion in 50 ml of the solution, which is then discarded.

[0033] 3.5 l of the streaming solution is used to rinse the Electrokinetic Analyzer (EKA) device, and then discarded. 500 ml of the streaming solution is used for the zeta potential measurements. The measuring cell of the Electrokinetic Analyzer (EKA) device is cylindrical with an inner diameter of 2 cm. The pre-wet fiber sample is placed in the approximate middle of the cell, and is book-ended on both sides by Ag/AgCl electrodes. The electrodes have perforations that allow the flow of streaming solution through the fiber sample. The fiber sample has to be tightly packed to ensure that there is no significant movement of the fibers with the flow of the streaming solution. The packing density can be controlled by the distance between the two electrodes, which in these measurements was between 0.5-0.6 cm. Thus the packing density was between 0.27-0.32 g/cm3 in these measurements. It is ensured there is no air trapped in the fiber sample by circulating the streaming solution through the fiber sample, and the measurement is started with the onboard software of the Electrokinetic Analyzer (EKA) device. The measurements were performed as the streaming solution pH was altered from the initial value of pH 11 to pH 3 in pH0.25 unit steps by the addition of 0.1 M HCl. This is performed with an autotitrator under software control (available among others from company Anton Paar/Austria. At the end of measurements, the streaming solution is replaced with a solution of 0.1 M KCl, and the solution is flushed through the system with repeated rinses. The cell resistance and solution conductivity values are then measured for the estimation of fiber plug dimensions to calculate the ZP corrected for surface conductance (= "Zeta potential Corr").

Nitrogen content:

[0034] The nitrogen content of the fibers was measured with a LECO FP 328 nitrogen analyzer (supplier: LECO Corporation/Saint Joseph, U.S.A.) according to the Dumas method. For this analysis the fibers were used in a conditioned state, conditioned until equilibrium is reached in a standard atmosphere at 20°C and 65% relative air humidity. The nitrogen content is given in relation to the weight of the fibers in conditioned state.

Examples 1 - 7:

[0035] Fibers of a linear density of 1,5dtex were manufactured according to a modal process as described in AT 287905 B, with a carbon black content of 4,3%(w/w). After coagulation the fiber tow was drawn, washed with water, cutted to a staple length of 39mm and laid down on the sieve belt of a conventional aftertreatment line in order to form

a fiber fleece. The fiber fleece was washed again with water and subsequently impregnated in a separate stage of the aftertreatment line for a retention time of 60 seconds with a treatment liquid containing a PolyDADMAC, at a PolyDADMAC concentration in the treatment liquid according to Table 1. The PolyDADMAC was supplied by company SNF (specification: "<100.000 Dalton"). Subsequently the fiber fleece was washed, most of the liquid phase squeezed off and finished with a spin finish at 5 g/l spin finish in the bath liquid. Thereafter the fibers were evaluated by the bleeding test for bleeding. The results are given in Table 1; the colors of the washing waters from the bleeding test are shown in Fig. 1; the numbers are the numbers of the examples; "0" is pure water. Acceptable fibers must have a bleeding number of 4 or higher. The pH value of all fibers, measured according to the method described above, was always pH 6.4.

[0036] The Zeta potential of the fibers of Example 1 (comparative, no polycationic treatment) and Example 4 (according to the invention) was measured as described above, in dependence of the pH of the surrounding liquid. Results are shown in Figure 2. Obviously the fiber according to the invention has a positive zeta potential in an acidic environment and at any pH value the fiber surface is significantly more positive (or less negative) than the untreated fiber without polycations. By the zeta potential the presence of the polycations can be detected over the whole pH range.

[0037] Further the nitrogen content of the fibers significantly increased with increasing concentration of the PolyDADMAC in the treatment bath: Example 1 showed a nitrogen content of 0,015 % (w/w), Example 2 showed 0,018% (w/w) and Example 4 showed 0,022% (w/w).

Example 8 + 9

[0038] Fibers with 1,0dtex resp. 1,7dtex were manufactured according to the same method as in Example 1 (see Table 1). A 1,0dtex modal fiber needs a content of 4,9%(w/w) of the same carbon black pigment in order to achieve the same black appearance in the end products (yarns, fabrics, garments). A thicker fiber, e.g. 1,7dtex viscose will only require 3,8%(w/w) of the same carbon black. Polycation concentration in the treatment bath and fiber properties see Table 1.

Table 1:

Example	Fiber titer [dtex]	carbon black content [%(w/w)]	Polycation conc. [g/l]	Bleeding number
1	1,5	4,3	0	3-4
2	1,5	4,3	0,5	4-5
3	1,5	4,3	0,5	4-5
4	1,5	4,3	0,75	5
5	1,5	4,3	0,75	5
6	1,5	4,3	1,0	5
7	1,5	4,3	1,0	5
8	1,0	4,9	0,85	5
9	1,7	3,8	0,5	5

Claims

1. Spun-dyed man-made cellulosic fiber with incorporated color pigment, **characterized in that** it contains a polycationic compound on its outer surface.

2. Fiber according to claim 1, wherein the polycationic compound is one out of the group containing polymeric quarternary ammonium compounds, in particular poly(diallyldimethylammonium chloride), cationically modified starch and polyethylenimines.

3. Fiber according to claim 1, wherein the fiber contains between 0,50 and 0,02 %(w/w), preferably between 0,2 and 0,04%(w/w), of the polycationic compound, in relation to the bone dry weight of the fiber.

4. Fiber according to claim 1, wherein the fiber shows a bleeding number of between 4.0 and 5.0 according to the bleeding test.

5. Fiber according to claim 1, wherein the fiber is a xanthate fiber.

6. Fiber according to claim 5, wherein the fiber is a Modal fiber.

7. Fiber according to claim 1, wherein the fiber is a Lyocell fiber.

8. Fiber according to claim 1, wherein the color pigment is carbon black.

9. Method for the manufacture of a spun-dyed man-made cellulosic fiber with incorporated color pigment, with the following steps:

a. Preparation of a spinning solution containing cellulose and at least one color pigment-,
b. Extrusion of the spinning solution into a coagulation bath,
c. Coagulation of the cellulose and thereby forming of the fiber tow,
d. Optionally washing the fiber tow,
e. Cutting the fiber tow into staple fibers and forming a fiber fleece
f. Optionally washing the fiber fleece,
g. Impregnation of the fiber fleece with a treatment liquid, washing, pressing,
h. Application of a spin finish to the fibers, pressing,
i. Drying,

characterized in that in the treatment bath of step g. the fiber fleece is treated with a solution of a polycationic compound.

10. Method according to claim 9, wherein the polycationic compound is one out of the group containing polymeric quaternary ammonium compounds, in particular poly(diallyldimethylammonium chloride), cationically modified starch and polyethylenimines.

11. Method according to claim 9, wherein the polycationic compound is poly(diallyldimethylammonium chloride) ("Poly-DADMAC").

12. Method according to claim 9, wherein the color pigment is carbon black.

13. Method according to claim 9, wherein the fibers between step c. and step g. always contain at least 50%(w/w), preferably at least 60%(w/w) water in relation to the cellulose content.

14. Method according to claim 9, wherein the cellulose-containing spinning solution is a solution of the xanthate type and step b. is performed according to a wet spinning technology and wherein the fiber tow is guided through a second drawing zone between step c. and step d..

15. Method according to claim 9, wherein the cellulose-containing spinning solution is a solution of the lyocell type and step b. is performed according to a dry-jet wet spinning technology.

16. Method according to claim 9, wherein step g. is **characterized by** the following parameters:

a. The polycation concentration in the treatment bath is between 0,1 and 10,0 g/l, preferably between 0,5 and 2,0 g/l, most preferably between 0,6 and 1,5 g/l,
b. A treatment time in the treatment bath of between 10 and 120 seconds, preferably between 45 and 135 seconds.

17. Method according to claim 9, wherein step g. is **characterized by** a ratio of fiber mass to treatment liquid between 1:0,1 and 1:5, preferably between 1:0,5 and 1:4, more preferably between 1:0,8 and 1:3

18. Method according to claim 9, wherein PolyDADMAC with a molecular weight of more than 25.000 Dalton is used.

Fig. 1:

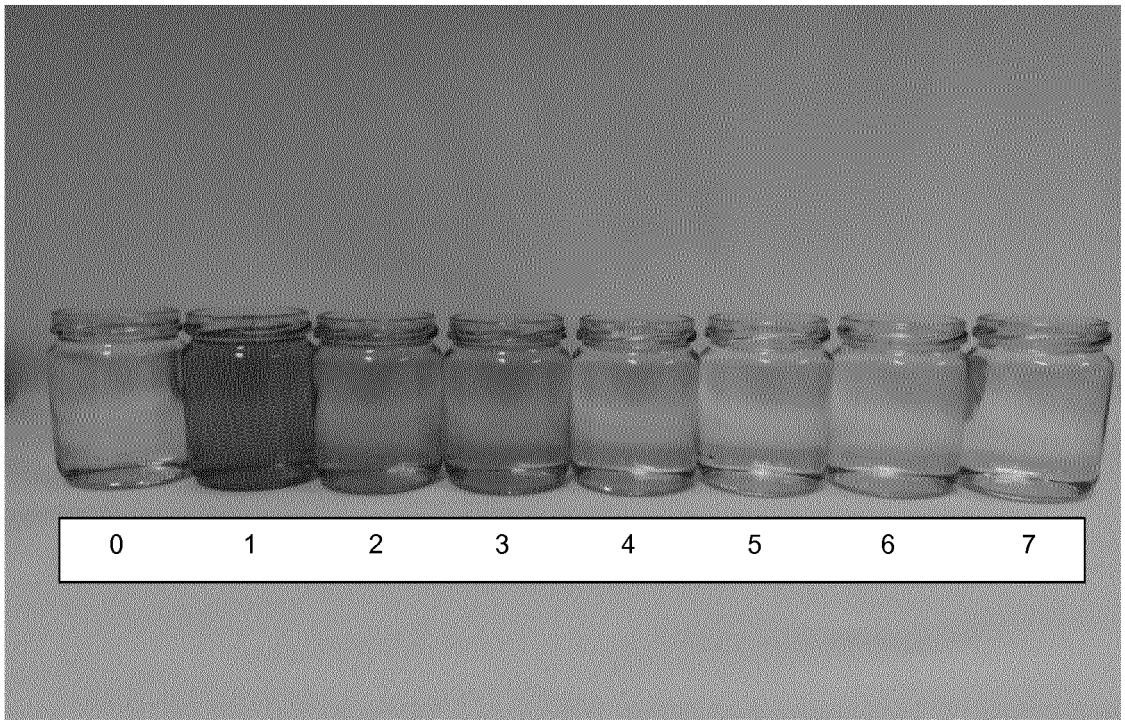
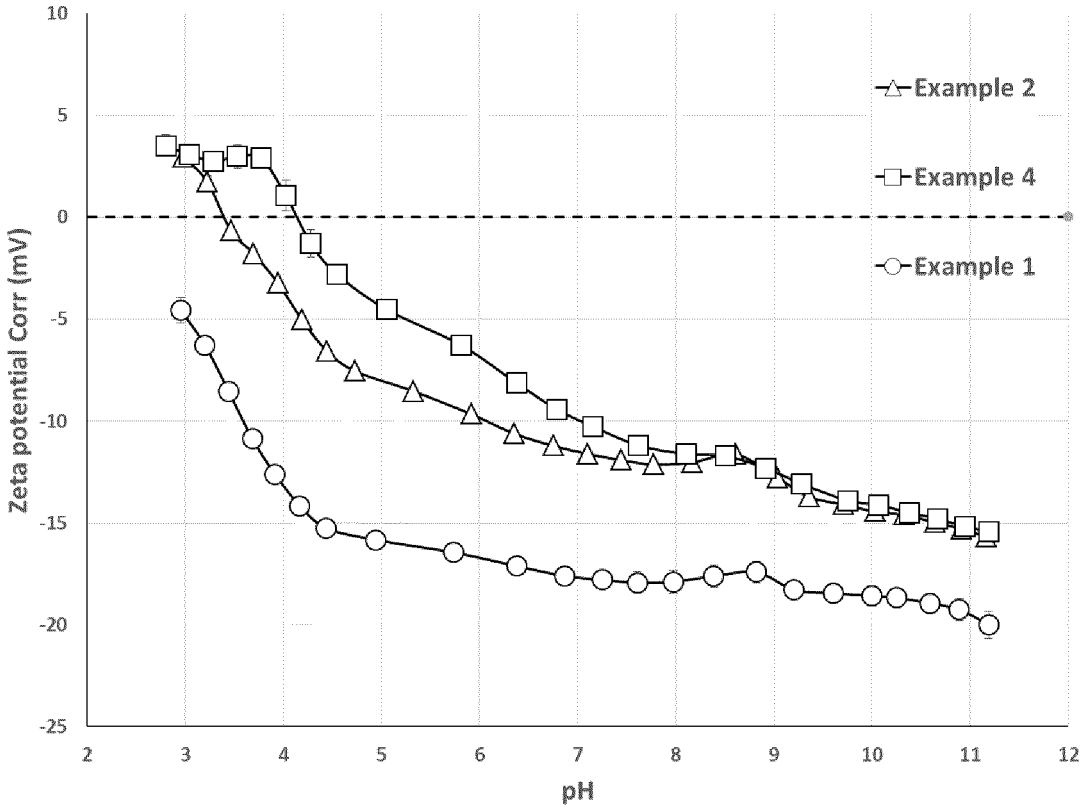

0
1
2
3
4
5
6
7

Fig. 2:


Example 2
Example 4
Example 1
Zeta potential Corr (mV)
pH
10
5
0
-5
-10
-15
-20
-25
2
3
4
5
6
7
8
9
10
11
12

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 19 02 0073

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	GB 885 462 A (COURTAULDS LTD) 28 December 1961 (1961-12-28)	1-8	INV. D06M15/11 D06M15/356 D06M15/61 D01F1/04 D01F2/00 D01F2/14
A	* page 1, line 47 - page 2, line 3 * * examples *	9-18	
A	WO 2015/154110 A1 (CHEMIEFASER LENZING AG [AT]) 15 October 2015 (2015-10-15) * page 2, line 20 - line 27 * * page 5, line 23 - line 25 *	1-18	
A	US 2007/180627 A1 (BECKER CHRISTOPH [DE]) 9 August 2007 (2007-08-09) * paragraph [0002] - paragraph [0006] * * paragraph [0010] - paragraph [0013] * * examples *	1-18	
A	EP 2 977 507 A1 (MITSUBISHI RAYON CO [JP]) 27 January 2016 (2016-01-27) * paragraph [0003] - paragraph [0009] * * paragraph [0016] * * paragraph [0068] * * examples *	1-18	
A	JP S63 303108 A (NIPPON CATALYTIC CHEM IND) 9 December 1988 (1988-12-09) * abstract *	1-18	

TECHNICAL FIELDS SEARCHED (IPC)
D06M
D01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	17 July 2019	Fiocco, Marco

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 19 02 0073

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