Jan. 21, 1969 B. S. V. MAREK ET AL 3,423,284

MODIFICATION OF REGENERATED CELLULOSE FIBERS BY SUBJECTING THE FIBERS TO A SWELLING AGENT AND MECHANICAL MOVEMENT

Original Filed Dec. 7, 1965

Fig. 1.

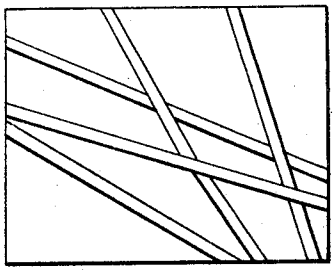


Fig. 2.

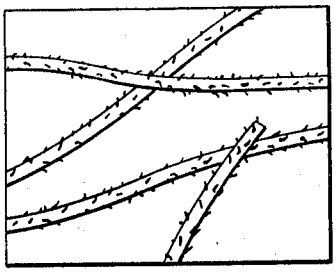


Fig. 3.

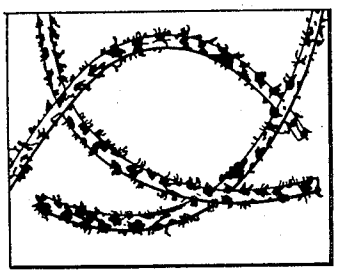
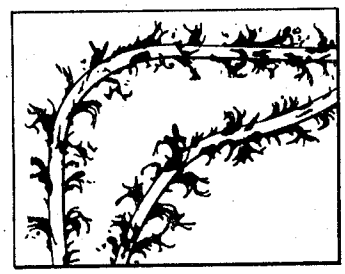


Fig. 4.



Bruno Stefan Vladimir Marek
Josef Gneisz
Inventors

By
Stevens, Davis, Miller & Mosher
Attorneys

United States Patent Office 3,423,284 Patented Jan. 21, 1969

3,423,284

MODIFICATION OF REGENERATED CELLULOSE FIBERS BY SUBJECTING THE FIBERS TO A SWELLING AGENT AND MECHANICAL MOVEMENT

Bruno S. V. Marek, Aarau, and Josef Gneisz, Rothenburg, Switzerland, assignors to Societe de la Viscose Suisse, Emmenbrucke, Switzerland, a Swiss corporation

Continuation of application Ser. No. 514,608, Dec. 7, 1965. This application June 28, 1966, Ser. No. 561,289
U.S. Cl. 162—157 9 Claims
Int. Cl. D21b 1/04; D21h 5/14

ABSTRACT OF THE DISCLOSURE

The process of the production of regenerated cellulose fibers with fine, hook-like filaments extending from the main fiber stem, which have a degree of polymerization of not less than 86 percent of that of the fibers from which they are made comprising subjecting a suspension of regenerated cellulose fibers in a liquid medium containing a swelling agent, such as an aqueous acid or an aqueous base. The suspension contains 3–13 percent by weight of fibers. The suspension is subjected to vigorous mechanical movement until fine hook-like filaments extend from the main fiber stem, following which the fibers are removed and washed.

This application is a continuation of United States patent application Ser. No. 514,608 filed Dec. 7, 1965, now abandoned, which was a division of application Ser. No. 210,176, filed July 16, 1962, now abandoned.

This invention relates to new forms of man-made fibres, to methods of their production, and to shaped structures made from such fibres.

The most important qualities of the new fibres are their felting and interlocking capacities which make them useful for many purposes, e.g. as a filling material and for the manufacture of felts. Their main application, however, is based on their ability to form coherent, self-supporting waterleaves which can be used for making sheet-like structures according to the methods of paper manufacture.

Numerous efforts have been made to transform man-made fibres into structures which, similar to fibrillated natural cellulose fibres, possess in the wet state sufficient coherence to enable them to be processed on conventional paper-making machines. However, unlike natural cellulose fibres, man-made fibres prepared according to ordinary production methods are usually not fibrillated when beaten in water, but only disintegrated into small chips. Fibrillation has been achieved with wet-spun polyacrylonitrile fibres and specially prepared viscose fibres; ordinary viscose fibres, however, reacted only after a preliminary treatment which resulted in a considerable degradation of the fibres. Polyamides and polyesters have only been fibrillated in the form of films or foils.

It is an object of the present invention to provide a method of treating ordinary man-made fibres of any titre and form produced by conventional spinning methods so as to produce novel fibrous structures having physical properties similar to those of fibrillated, natural cellulose fibres. It is a further object of the invention to provide such a method which is simple and easy to perform and scarcely damages the fibres.

According to the present invention there is provided a process for the production of man-made fibres with fine, hook-like filaments extending from the main fibre stem, which can be beaten and have a considerably higher water holding capacity than have the fibres from which they are made, which are capable of felting and interlocking with each other and with other fibres and which are capable of forming coherent, self-supporting waterleaves suitable for processing on paper machines, which comprises subjecting man-made fibres in the form of a suspension in a liquid medium to a vigorous mechanical movement in the presence of a swelling agent, the suspension containing 3 to 13% by weight of the fibres.

Fibres treated by the aforesaid process obtain their interlocking capacity by a peculiar change of the fibre surface. The surface of the fibre which is originally unbroken becomes densely and substantially uniformly covered with fine, and mostly curved, filaments extending from the main fibre stem in all directions like little hooks. The hooks have cylindrical, conical, or ribbon-like forms and are often curled and split-up. Their usual length is from one half to twice the diameter of the fibre. The fibre form is illustrated diagrammatically in the accompanying drawings, in which FIG. 1 depicts an untreated fibre and FIGURES 2, 3 and 4 show the hooked fibres in successive stages of development.

These "hooked fibres" possess a number of interesting qualities which are the result of their peculiar surface structure. As compared with untreated fibres they have a considerably higher water-holding capacity as expressed by their increased swelling factor determined by the centrifuging method. They further exhibit very good felting and interlocking properties and have also the new and surprising ability that, in contrast to untreated man-made fibres, they can be successful beaten in a Hollander beater or refiner. If required, the formation of hooked fibre structure can, by such a beating, be considerably intensified, and fibres with excellent capacity for mechanical entanglement are obtained.

The treatment by which hooked fibres are prepared does not seriously affect the quality of the original fibres. The fibres are not cut by the treatment, and no fibre fragments are obtained. The degree of polymerisation of the hooked fibres is only slightly different from that of the initial untreated fibres, and this is in marked contrast to other swelling methods which produce a considerable degradation of the fibre.

Both unbeaten and beaten hooked fibres can be used for all purposes, where fibres with interlocking capacities are required, e.g. as a filling material and for the manufacture of felts. But, above all, both fibre types are, similar to fibrillated natural cellulose fibres, capable of forming coherent, self-supporting waterleave which can be easily removed from a wire screen and further processed on conventional paper machines.

The present invention has proved especially successful in the treatment of fibres made from regenerated cellulose, cellulose esters, polyamides, polyesters, polyacrylonitriles including copolymers or graft copolymers of these substances. Fibres of any titre and form can be used, e.g. ordinary monofilaments or hollow or ribbon-like structures. Ordinarily, fibres of 1 to 10 mm. length are used, but with suitable apparatus fibres of greater length may be processed.

For every kind of fibre there exist one or more swelling agents which give best results, and, in many cases, aqueous acids and alkalies have proved to be very effective. Thus, for example, regenerated cellulose fibres react well on treatment with 13% hydrochloric acid or 4% sodium hydroxide solution. Cellulose triacetate fibres may be treated with 60% acetic acid, polyhexamethylene adipamide fibres either with 13% hydrochloric acid or with a mixture of 68% formic acid, 12% anhydrous sodium sulphate, and 20% water, and polycaprolactam fibres with a mixture of 2% hydrochloric acid, 40% acetic acid, and 58% water. For polyethylene terephthalate fibres a mixture of 23% phenol and 77% monochlorobenzene is suitable, while polyacrylonitrile fibres

may be treated with a mixture of 40% benzyl alcohol and 60% propylene carbonate. It is pointed out that these are only examples and that a great many organic and inorganic substances can be used as swelling agents for the fibres mentioned.

The vigorous movement of the fibres in the swelling agent can be produced by any suitable device, e.g. by an ordinary stirrer or high-speed mixer, by an electromagnetic vibrator, or by an ultrasonic apparatus, and can, on a technical scale, also be carried out in a continuous manner. Usually, the swelling agents are employed at temperatures between 20 and 30° C., but regenerated cellulose fibres already react well at 5–10° C. In cases where the mixing generates too much heat, outside cooling is applied, but for some fibres higher temperatures are preferred, as, for example, for polyacrylonitrile fibres which are treated with benzyl alcohol and propylene carbonate at 70–80° C.

As noted above, the fibre content of the suspension is not less than 3%. It is possible to work at lower fibre contents, but this does not produce such quick and good results. The upper limit of the fibre content of the suspension depends on the kind of apparatus used and on the length and titre of the fibres; usually it may be up to 13%.

The duration of the treatment depends on the nature of the fibre, on the swelling agent, and, above all, on the kind of apparatus used. With ordinary stirrers agitation for 30 to 100 minutes is usually necessary, but with strong mixers or ultrasonic devices only 5 to 15 minutes' treatment is usually sufficient to produce strongly developed hooked structures. In a continuously working process, the duration of treatment is, of course, considerably reduced. After being washed to remove the swelling agent and the possible addition of wetting or lubricating agents, the hooked fibres are ready for use. If required, they may be taken up in a neutral, faintly acid, or faintly alkaline aqueous suspension, beaten for 1 to 2 hours in a hollander or refiner and finally washed with water.

The drying and redispersion of the hooked fibres depends on their length and on the strength and character of the hooked structures. Hooked fibres up to a length of 2 mm., treated with a wetting agent and dried at 64° C. so that they contain only 1 to 3% moisture, can easily be redispersed in water. Hooked fibrous of greater length, however, are, when dried, already so strongly felted and entangled with each other that the fibre balls formed cannot be dispersed even on prolonged stirring.

For the production of sheet-like structures according to the methods of paper manufacture, the hooked fibres can be used in unbeaten or beaten condition. Any sizing material may be added, and the aqueous fibre suspensions are collected in the usual way on a wire screen. The wet waterleaves are then, with or without the addition of binders, pressed at various high temperatures, and the ultimate bonding of the fibre webs is effected by any binders present or by fusion of added thermoplastic fibres and/or thermoplastic hooked fibres. The shaped structures thus obtained possess good mechanical strength in the dry and wet state; their additional qualities depend on the nature of the fires used.

As all hooked fibres produced according to the present invention possess the felting and interlocking properties mentioned above, unbeaten and beaten hooked fibres of different origin can, of course, be mixed in any proportion. It is also possible to mix hooked fibres with untreated man-made fibres and with natural cellulose fibres. By varying proportions between all these kinds of fibres, sheet-like structures of widely different properties can be obtained, which have, as desired, a more textile or more paperlike character.

A change of surface structure similar to that of the hooked fibres of this invention has been reported of a special viscose rayon fibre made by the American Viscose Corporation (Man-made Textile Encyclopedia, New York, 1959, p. 500). An aqueous suspension of this fibre was beaten during three hours, the fibre content being not higher than 1½%, as it was found that, otherwise, the fibres were considerably damaged. According to British patent specification No. 687,041 the special fibre is produced by preparing a cellulose xanthate fibre which is stretched and then transformed into a regenerated cellulose fibre of low elongation. The specification states that "ordinary regenerated cellulose or viscose rayon fibre does not fibrillate when subjected to beating in an ordinary paper beater." In contrast, the present invention, using a swelling agent, permits fibre concentrations between 3 and 13%, requires for the treatment only 10 minutes when using a high-speed mixer or, at the most, 60 minutes when working with an ordinary stirrer, and is, above all, applicable to ordinary regenerated cellulose fibres of any elongation.

French patent specification No. 1,245,863 describes treatment of viscose fibres by hydrolysis with hot dilute acids, until the degree of polymerisation of the fibres is reduced by 20 to 75%. Hydrolysis is carried out without mechanical movement of the fibres and at temperatures between 50 and 120° C. When subsequently beaten in water at a fibre concentration of 1½%, the fibres show fibrillation. The specification states that, if hydrolysis is not sufficient to obtain the prescribed reduction of the degree of polymerisation, the fibres will not fibrillate. In contrast, the present invention, using simultaneous swelling and mechanical treatments, higher fibre concentrations, and lower temperatures, gives rise to hooked fibres showing a reduction in their degree of polymerisation of only 8 to 14%, when using dilute acids, and a mere 2% when using dilute alkalies as swelling agent. Accordingly, damage to the fibres is minimised or eliminated.

According to French patent specification No. 1,268,034, fibres made from mixtures of polyacrylonitrile copolymers with cellulose esters are beaten in the form of aqueous suspensions with a fibre content of 0.75% and yield fibres of a porous, sponge-like structure, quite different from the hooked fibres of the present invention. United States Patent No. 2,810,646 describes fibrillation of wet-spun polyacrylonitrile fibres by beating aqueous suspensions having a fibre content of 1%. By this process flattened filaments showing considerable splitting and striation are obtained. In contrast, the hooked fibres prepared according to the present invention which retain their form and do not show such deformations are obtained by working with a swelling agent and at much higher fibre concentrations.

It should also be mentioned that the great number of swelling treatments of fibres described in the literature have only produced crimping, shrinking and degradation effects, and have not produced fibre forms similar to the hooked fibres prepared according to the present invention. Polymer structures other than fibres have also been subjected to such swelling treatments. Thus, for example, British patent specification No. 810,001 proposes the production of spinnable fibres by mechanical friction or distortion or by supersonic vibration of swollen films or foils. However, in British patent specification No. 865,707, the same patentee notes that thick foils are damaged by these processes and that working with thin films is very slow and impractical.

In French patent specifications Nos. 1,214,126 and 1,246,379 fibrillated structures are produced by flash-spinning a polymer solution heated under pressure above its boiling point, or by heating either a suspension made by interfacial polymerisation or a dispersion prepared by mixing a polymer solution with a non-solvent. These methods do not use normally spun fibres, and the "structures plexifilamenteuses" and "fibrides" obtained are quite different in character from the hooked fibres made according to the present invention.

The following examples will serve to illustrate the invention. In these examples the swelling factor of the fibres is determined as an expression of their water-holding

capacity, the following method being adopted: The fibres are treated with an excess of water, centrifuged with 1,000 g. (gravity acceleration), weighed, dried and weighed again. Their swelling factor (f) is then:

$$f \text{ (in percent)} = \frac{\text{Wet weight} = \text{Dry weight}}{\text{Dry weight}} .100$$

EXAMPLE I

4 g. viscose fibres of 2 mm. length having a titre of 1.5 denier and an elongation of 16% are suspended in 96 g. of 13% hydrochloric acid and vigorously stirred during 60 minutes at a temperature of 10° C. by means of an anchor-type stirrer at about 2,000 r.p.m. The resulting fibres are washed with water and show under a microscope well developed hooked structures. When using, in place of a stirrer, a high-speed "Turmix" mixer of about 12,000 r.p.m. made by Turmix A.G., Kussnacht, Zurich, Switzerland, or an "Ultra-Turrax" ultrasonic apparatus made by Janke & Kunkel K.G., Staufen i.Br., Germany, and holding the temperature, by cooling, at 25° C., the same degree of hooked structures is already formed after only 10 minutes.

The hooked viscose fibres have a swelling factor of 126% as compared with 88% for the untreated fibres and a degree of polymerisation (Cuen) of 202 as compared with 235 for the untreated fibres, i.e., a DP-decrease of 14%.

EXAMPLE II

4 g. polynosic fibres (Silk and Rayon, 33 (1959) 1084) of 4 mm. length having a titre of 0.4 denier and an elongation of 8% are suspended in 96 g. of 13% hydrochloric acid and vigorously stirred during 45 minutes at a temperature of 10° C. by means of an anchor-type stirrer at about 2,000 r.p.m. The hooked fibres obtained are washed with water and show strongly developed hooked structures. They have a swelling factor of 238% as compared with 60% for the untreated fibres, and a degree of polymerisation of 381 as compared with 415 for the untreated fibres, i.e., a DP-decrease of 8%.

EXAMPLE III

510 g. viscose fibres of 2 mm. length and a titre of 1.5 denier having an elongation of 16% are suspended in 9,000 g. of a 4% aqueous sodium hydroxide solution and treated during 50 minutes with a "Polytron" ultrasonic apparatus made by Mobil Aarau AG., Aarau, Switzerland, holding the temperature of the suspension by cooling between 25 and 30° C. The fibres obtained are washed with water and show under a microscope well developed hooked structures. They have a swelling factor of 119% as compared with 88% for the untreated fibres and a degree of polymerisation of 252 as compared with 257 for the untreated fibres, i.e., a DP-decrease of 2%. From the aqueous suspension of the hooked viscose fibres leaves are formed on a small paper machine and dried. They have a pleasant soft hand and a dry breaking length of 610 m. When impregnated with a polyacrylic resin emulsion and dried, the leaves have a dry breaking length of 952 m., a wet strength equal to 40% of their dry strength, and an edge tearing resistance (Finch) of more than 2,800 grams (referring to leaves of 100 g./m.^{2}).

EXAMPLE IV

545 g. polynosic fibres (Silk and Rayon, 33 (1959), 1084) of 2 mm. length and a titre of 1.5 denier having an elongation of 9% are suspended in 6,500 g. of a 4% aqueous sodium hydroxide solution and vigorously stirred during 60 minutes at a temperature of 22–24° C. by means of an anchor-type stirrer at about 2,000 r.p.m. The fibres obtained are washed with water and show under a microscope strongly developed hooked structures. They have a swelling factor of 104% as compared with 59% for the untreated fibres. From an aqueous suspension of the hooked Polynosic fibres leaves are formed on a small paper machine which have a dry breaking length of 507 m. and, when impregnated with a polyacrylic resin emulsion and dried, have a dry breaking length of 1,046 m., a wet strength equal to 31% of their dry strength, and an edge tearing resistance (Finch) of more than 3,400 g. (referring to leaves of 100 g./m.^{2}).

Another portion of the hooked polynosic fibres is suspended in faintly alkaline water of pH=9.5, and the suspension beaten during 60 minutes in a Hollander beater. From the beaten fibres, which show considerably intensified hooked structures, leaves are formed on a small paper machine which have a dry breaking length of 893 m. When the leaves are impregnated with a polyacrylic resin emulsion and dried, their dry breaking length is 1,505 m., their wet strength equal to 43% of their dry strength, and their edge tearing resistance (Finch) more than 4,200 g. (referring to leaves of 100 g./m.^{2}).

EXAMPLE V

14 g. cellulose triacetate fibres of 2 mm. length and a titre of 3 denier are suspended in 186 g. of 60% acetic acid and vigorously stirred during 40 minutes at a temperature of 20° C. by means of an anchor-type stirrer at about 2,000 r.p.m. The hooked fibres obtained are washed with water and show distinct hooked structures. They have a swelling factor of 52% as compared with 19% for the untreated fibres, and contain 61.4% acetic acid as compared with 61.9% for the untreated fibres, i.e., practically the same.

EXAMPLE VI

15 g. polyhexamethylene adipamide fibres of 1.5 mm. length and a titre of 2 denier are suspended in 285 g. of 13% hydrochloric acid and vigorously stirred during 15 minutes in a "Turmix" mixer at about 12,000 r.p.m. The suspension is cooled during the treatment and the temperature kept at about 25° C. The hooked fibres obtained are washed with water and show strongly developed hooked structures. They have a swelling factor of 85% as compared with 17% for the untreated fibres.

EXAMPLE VII

16 g. polyhexamethylene adipamide fibres of 1 mm. length and a titre of 2 denier are suspended in 384 g. of 13% hydrochloric acid and treated during 5 minutes with an "Ultra-Turrax" ultrasonic apparatus. The suspension is cooled during the treatment and the temperature kept at about 25° C. The hooked fibres obtained are washed with water and show strongly developed hooked structures. They have a swelling factor of 45% as compared with 17% for the untreated fibres.

EXAMPLE VIII

15 g. polyhexamethylene adipamide fibres of 10 mm. length and a titre of 6 denier are suspended in 235 g. of 13% hydrochloric acid and treated during 100 minutes at a temperature of 20° C. with a dipping vibrator made by A.G. fur Chemie-Apparatebau, Zurich, Switzerland. The hooked fibres obtained are washed with water and show well-developed hooked structures. They have a swelling factor of 28% as compared with 15% for the untreated fibres.

EXAMPLE IX

100 g. polyhexamethylene adipamide fibres of 3 mm. length and a titre of 2 denier are suspended in 1,900 g. of a mixture containing 68% formic acid, 12% anhydrous sodium sulphate, and 20% water and vigorously stirred during 45 minutes at a temperature of 20° C. by means of an anchor-type stirrer at about 4,000 r.p.m. The hooked fibres obtained are washed with water and show well developed hooked structures. They have a swelling factor of 86% as compared with 15% for untreated fibres. Subsequently, in the form of a faintly acid aqueous suspension of pH=3, they are beaten during 100 minutes in a Hollander beater and then washed with water. The formation of hooked structures is thus considerably intensified. From

the aqueous suspension of a mixture containing equal parts of unbeaten and beaten polyhexamethylene adipamide hooked fibres, leaves are prepared on a small paper machine. The leaves are treated with a binder and heat-pressed for 10 seconds at a temperature of 120° C. The products have a wet strength of 36% of the dry strength and an Elmendorf tear strength of 234 g. (referring to leaves of 100 g./m.^{2}). The leaves are very porous and flexible and have a pleasant and soft hand.

EXAMPLE X

160 g. polyhexamethylene adipamide fibres of 1 mm. length and a titre of 2 denier are suspended in 1,840 g. of 13% hydrochloric acid and vigorously stirred during 30 minutes at a temperature of 20° C. by means of an anchor-type stirrer at about 4,000 r.p.m. The hooked fibres obtained are washed with water and show well developed hooked structures. A faintly alkaline aqueous suspension of the fibres at pH=9 is beaten during 100 minutes in a Hollander beater and then washed with water. Two mixtures are prepared, one containing 40% of unbeaten (1) and the other one 40% of beaten polyhexamethylene adipamide hooked fibres (2) and each of them containing 35% of untreated polyhexamethylene adipamide fibres and 25% of fibres of a copolymer made from 40% hexamethylene diamine adipate and 60% caprolactam. From the aqueous suspension of each of these two mixtures leaves are prepared on a small paper machine and either dried only (*a*) or dried and pressed during 10 seconds at 150° C. (*b*). Therefore, four different types of leaves are obtained.

1 (*a*) Leaves containing unbeaten hooked fibres, dried only.
1 (*b*) Leaves containing unbeaten hooked fibres, dried and heat-pressed.
2 (*a*) Leaves containing beaten hooked fibres, dried only.
2 (*b*) Leaves containing beaten hooked fibres, dried and heat-pressed.

All the leaves can be easily removed from the wire screen. Their mechanical strength is already good when dried only, but their tensile strength (calculated as breaking length) is considerably improved by heat-pressing. In the following table the figures for Elmendorf tear and burst strength refer to leaves of a weight of 100 g./m.^{2}:

Type of leaf	Breaking length (m.)	Elmendorf tear (g.)	Burst strength (kg./cm.^{2})
1 (a)	2,334	323	4.52
1 (b)	3,420	274	5.43
2 (a)	2,302	349	5.10
2 (b)	4,030	259	4.75

The leaves are very porous and flexible, possess a soft and pleasant hand, and have remarkable wrinkle-recovery properties.

EXAMPLE XI

6 g. polyhexamethylene adipamide fibres of 1.5 mm. length and a titre of 2 denier are suspended in 100 g. of 13% hydrochloric acid and vigorously stirred during 80 minutes at a temperature of 20° C. by means of an anchor-type stirrer at about 2,000 r.p.m. The hooked fibers obtained are washed with water and show well developed hooked structures. They are centrifuged during 10 minutes to remove the adhering water, treated with a 2% solution of an ethoxy polyamide wetting agent, and dried during 2 hours at a temperature of 64° C. When mixed with water and stirred for about one minute, the hooked fibres easily form again a finely divided fibre suspension. The same test with polyhexamethylene adipamide hooked fibres of 3 mm. length did not succeed; the fibres formed densely felted balls which could not be dispersed even on prolonged stirring.

EXAMPLE XII

5 g. polycaprolactam fibres of 4 mm. length and titre of 2.5 denier are suspended in 95 g. of a mixture containing 2% hydrochloric acid, 40% acetic acid and 58% water and vigorously stirred during 30 minutes at a temperature of 20° C. by means of an anchor-type stirrer at about 2,000 r.p.m. The hooked fibres obtained are washed with water and show well developed hooked structures. They have a swelling factor of 37% as compared with 13% for the untreated fibres. Subsequently a neutral aqueous suspension of the fibres is beaten during 1½ hours in a Hollander beater and then washed with water. The formation of hooked structures is thus considerably intensified.

From the aqueous suspension of a mixture containing 60% beaten polycaprolactum hooked fibres and 40% polynosic hooked fibres prepared according to Example II, leaves are formed on a small paper machine. The leaves are treated with a polyacrylic latex as binder and have a wet tensile strength of 55% of the dry tensile strength and a dry breaking length of 2,300 m.

EXAMPLE XIII

12 g. polyethylene terephthalate fibres of 2 mm. length and a titre of 1.5 denier are suspended in 88 g. of a mixture containing 23% phenol and 77% mono-chlorobenzene and vigorously stirred during 100 minutes at a temperature of 20° C. by means of an anchor-type stirrer at about 2,000 r.p.m. The hooked fibres obtained are washed with water and show well developed hooked structures. They have a swelling value of 21% as compared with 14% for the untreated fibres. From the aqueous suspension of a mixture containing equal parts of polyethylene terephthalate hooked fibres and beaten polyhexamethylene adipamide hooked fibres prepared according to Example IX, leaves are formed on a small paper machine which have a good wet and dry tensile strength and can be further processed. By contrast, leaves from untreated polyethylene terephthalate fibres and from untreated polyhexamethylene adipamide fibres could, in the wet state, be removed from the wire screen only with great difficulty and fell at once to pieces when dried.

EXAMPLE XIV

4 g. polyacrylonitrile fibres of 4 mm. length and a titre of 3 denier are suspended in 80 g. of a mixture containing 40% benzyl alcohol and 60% propylene carbonate and warmed to 75° C. The suspension is vigorously stirred at this temperature during 80 minutes by means of an anchor-type stirrer at about 2,000 r.p.m. The hooked fibres obtained are washed with 50% alcohol to remove the swelling agents and finally with water. They have well developed hooked structures and a swelling factor of 29% as compared with 14% for the untreated fibres. From the aqueous suspension of a mixture containing 40% polyacrylonitrile hooked fibres, 40% beaten polyhexamethylene adipamide hooked fibres prepared according to Example IX and 20% beaten sulphate cellulose, leaves are formed on a small paper machine. The leaves are treated with an emulisified thermoplastic polymer and have a bursting strength of 2.9 kg./cm.^{2} (referring to leaves of 100 g./m.^{2}).

We claim:

1. Process for the production of regenerated cellulose fibers with fine, hook-like filaments extending from the main fiber stem, which have a degree of polymerization of not less than 86% of that of the fibers from which they are made, which can be beaten and have a considerably higher water-holding capacity than have the fibers from which they are made, which are capable of felting and interlocking with each other and with other fibers and which are capable of forming coherent, self-supporting waterleaves suitable for processing on paper machines, which comprises subjecting a suspension of regenerated cellulose fibers in a liquid medium containing a swelling

agent selected from the class consisting of aqueous acids and aqueous bases, the suspension containing 3–13% by weight of the fibers, based on the total weight of the suspension, to a vigorous mechanical movement until fine hook-like filaments extending from the main fiber stem have formed on the said fibers, recovering the said fibers from the said medium, and washing the fibers to remove the swelling agent, said fibers having a reduction in their degree of polymerization of the order of 8 to 14% when the swelling agent is an aqueous acid, and of the order of 2% when the swelling agent is a dilute alkali.

2. Process according to claim 1 wherein the swelling agent is selected from the class consisting of aqueous mineral acids and aqueous alkali metal bases.

3. Process according to claim 1, wherein the swelling agent is aqueous hydrochloric acid.

4. Regenerated cellulose fibers produced by the process of claim 1.

5. Process for the production of regenerated cellulose fibers with fine, hook-like filaments extending from the main fiber stem, which have a degree of polymerization of not less than 86% of that of the fibers from which they are made, which can be beaten and have a considerably higher water-holding capacity than have the fibers from which they are made, which are capable of felting and interlocking with each other and with other fibers and which are capable of forming coherent, self-supporting waterleaves suitable for processing on paper machines,

which comprises subjecting a suspension of regenerated cellulose fibers in a liquid medium containing aqueous sodium hydroxide, the suspension containing 3–13% by weight of the fibers, based on the total weight of the suspension, to a vigorous mechanical movement until fine hook-like filaments extending from the main fiber stem have formed on the said fibers, recovering the said fibers from the said medium, and washing the fibers to remove the aqueous sodium hydroxide.

6. Process according to claim 5 wherein the suspension is subjected to a vigorous mechanical movement at a temperature of 5° to 30° C.

7. Process according to claim 5, wherein the regenerated cellulose is viscose.

8. Process according to claim 5 wherein the regenerated cellulose fibers are polynosic fibers.

9. Regenerated cellulose fibers produced by the process of claim 5.

References Cited

UNITED STATES PATENTS

3,052,593 9/1962 Battista ---------- 162—146

HOWARD R. CAINE, *Primary Examiner.*

U.S. Cl. X.R.

162—26, 146