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PROCESS FOR FIBRILLATING POLYAMIDE-CONTAINING  
FIBERS WITH AN ACID SWELLING AGENT  
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Fig. 1.

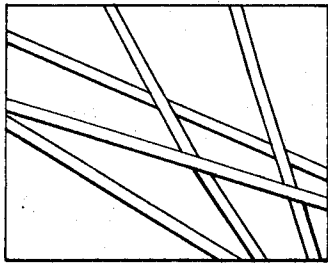


Fig. 2.

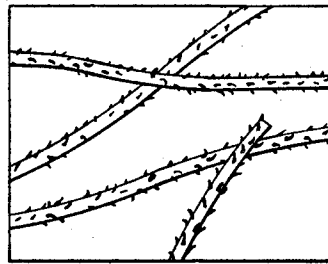


Fig. 3.

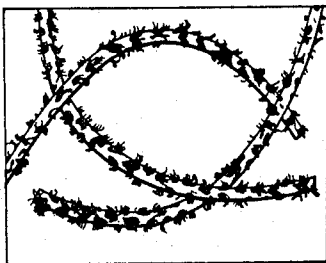


Fig. 4.



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**PROCESS FOR FIBRILLATING POLYAMIDE-CONTAINING FIBERS WITH AN ACID SWELLING AGENT**

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Continuation-in-part of application Ser. No. 547,111, Feb. 15, 1966, which is a continuation of application Ser. No. 210,176, July 16, 1962. This application May 23, 1967, Ser. No. 654,023  
8 Claims. (Cl. 162—157)

**ABSTRACT OF THE DISCLOSURE**

A process for fibrillating smooth-surface melt-spun monofilament polyamide-containing fibers which may be formed into felted material from self-supporting water-leaves, which comprises suspending up to 10 millimeter lengths of such fibers in an acid swelling agent, agitating the suspension so that the fibers form hook-like extensions, and dispersing the fibers in water and beating the dispersion. The fibers capable of felting and interlocking are also disclosed.

This application is a continuation-in-part of application Ser. No. 547,111 filed Feb. 15, 1966, which was a continuation of Ser. No. 210,176, filed July 16, 1962, both now abandoned.

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

The most important qualities of the new fibers or 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 water-leaves which can be used for making sheet-like structures according to the methods of paper manufacture.

Numerous efforts have been made to transform melt-spun man-made fibers into structures which, similar to fibrillated natural cellulose fibers, possess in the wet state sufficient coherence to enable them to be processed on conventional paper-making machines. However, unlike natural cellulose fibers, melt-spun man-made fibers 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 fibers and specially prepared viscose fibers; ordinary viscose fibers, however, reacted only after a preliminary treatment which resulted in a considerable degradation of the fibers. 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 melt-spun man-made fibers 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 fibers. It is a further object of the invention to provide such a method which is simple and easy to perform and scarcely damages the fibers.

According to the present invention, there is provided a process for the production of melt-spun man-made fibers having fine, hook-like filaments extending from the main fiber stem, 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

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which are capable of forming coherent, self-supporting water-leaves suitable for processing on paper machines. The process according to this invention comprises subjecting melt-spun man-made fibers in the form of a suspension of short lengths of such fibers 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 fibers.

Fibers treated by the aforesaid process obtain their interlocking capacity by a peculiar change of the fiber surface. The surface of the fiber which is originally unbroken becomes densely and substantially uniform covered with fine, and mostly curved, filaments extending from the main fiber stem in all directions like little hooks. The hook-like extensions 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 fiber. The fiber form is illustrated diagrammatically in the accompanying drawings, in which FIGURE 1 depicts an untreated fiber and FIGURES 2, 3 and 4 show the hooked fibers in successive stages of development.

These "hooked fibers" possess a number of interesting qualities which are the result of their peculiar surface structure. As compared with untreated fibers, 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 melt-spun man-made fibers, they can be successfully beaten in a Hollander beater or refiner. If required, the formation of hooked fiber structures can, by such a beating, be considerably intensified, and fibers with excellent capacity for mechanical entanglement are obtained.

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

Both unbeaten and beaten hooked fibers can be used for all purposes, where fibers with interlocking capacities are required, e.g., as a filling material and for the manufacture of felts. But, above all, both fiber types are, similar to fibrillated natural cellulose fibers, capable of forming coherent, self-supporting water-leaves 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 fibers made from melt-spun polyamides, and copolymers of polyamides. Fibers of any titre and form can be used, e.g., ordinary monofilaments or hollow or ribbon-like structures. Ordinarily, fibers of 1 to 10 mm. length are used, but with suitable apparatus fibers of greater length may be processed.

For every kind of fiber there exist one or more swelling agents which give best results, and, in many cases, aqueous acids have proved to be very effective. Thus, for example, polycaprolactam fibers can be treated with a swelling agent comprising a mixture of 2% hydrochloric acid, 40% acetic acid, and 58% water. It is pointed out that this is only exemplary and that a great many organic and inorganic substances can be used as swelling agents for melt-spun polyamide-containing fibers.

The vigorous movement of the fibers 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. In cases where the mixing generates too much heat, outside cooling can be applied to maintain a suitable temperature.

As noted above, the fiber content of the suspension is not less than 3%. It is possible to work at lower fiber contents, but this does not produce such quick and good results. The upper limit of the fiber 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 fiber, 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 fibers 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 fibers depends on their length and on the strength and character of the hooked structures. Hooked fibers 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 fibers of greater length, however, are, when dried, already so strongly felted and entangled with each other that the fiber 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 fibers can be used in unbeaten or beaten condition. Any sizing material may be added, and the aqueous fiber suspensions are collected in the usual way on a wire screen. The wet water-leaves are then, with or without the addition of binders, pressed at various high temperatures, and the ultimate bonding of the fiber webs is effected by any binders present or by fusion of added thermoplastic and/or thermoplastic hooked fibers. The shaped structures thus obtained possess good mechanical strength in the dry and wet state; their additional qualities depend on the nature of the fibers used.

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

According to French patent specification No. 1,268,034, fibers made from mixtures of polyacrylonitrile copolymers with cellulose esters are beaten in the form of aqueous suspensions with a fiber content of 0.75% and yield fibers of a porous, sponge-like structure, quite different from the hooked fibers of the present invention. United States Patent No. 2,810,646 describes fibrillation of wet-spun polyacrylonitrile fibers by beating aqueous suspensions having a fiber content of 1%. By this process flattened filaments showing considerable splitting and striation are obtained. In contrast, the hooked, melt-spun fibers prepared according to the present invention are obtained which retain their form and do not show such deformations or a substantial reduction in their degree of polymerization when worked with a swelling agent and at fiber concentrations of from about 3% to about 13% by weight.

It should also be mentioned that the great number of swelling treatments of fibers described in the literature have only produced crimping, shrinking and degradation effects, and have not produced fiber forms similar to the hooked fibers prepared according to the present invention. Polymer structures other than fibers have also been subjected to such swelling treatments. Thus, for example, British patent specification No. 810,001 proposes the production of spinnable fibers 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 polymerization or a dispersion prepared by mixing a polymer solution with a non-solvent. These methods do not use normally spun fibers, and the "structures plexifilamenteuses" and "fibrilles" obtained are quite different in character from the hooked fibers made according to the present invention.

The following examples will serve to illustrate the invention. In these examples, the swelling factor of the fibers is determined as an expression of their water-holding capacity, the following method being adopted: The fibers are treated with an excess of water, centrifuged with 1000 g. (gravity acceleration), weighed, dried and weighed again. Their swelling factor (*f*) is then:

$$f \text{ (in percent)} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \cdot 100$$

#### EXAMPLE I

15 g. polyhexamethylene adipamide fibers 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 fibers 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 fibers.

#### EXAMPLE II

16 g. polyhexamethylene adipamide fibers 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 fibers 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 fibers.

#### EXAMPLE III

15 g. polyhexamethylene adipamide fibers 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. für Chemie-Apparatebau, Zurich, Switzerland. The hooked fibers 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 fibers.

#### EXAMPLE IV

100 g. polyhexamethylene adipamide fibers of 3 mm. length and a titre of 2 denier are suspended in 1900 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 4000 r.p.m. The hooked fibers obtained are washed with water and show well-developed hooked structures. They have a swelling factor

of 86% as compared with 15% for untreated fibers. 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 fibers, 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.<sup>2</sup>). The leaves are very porous and flexible and have a pleasant and soft hand.

#### EXAMPLE V

160 g. polyhexamethylene adipamide fibers of 1 mm. length and a titre of 2 denier are suspended in 1840 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 4000 r.p.m. The hooked fibers obtained are washed with water and show well developed hooked structures. A faintly alkaline aqueous suspension of the fibers 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 fibers (2) and each of them containing 35% of untreated polyhexamethylene adipamide fibers and 25% of fibers of a copolymer made from 40% hexamethylene diamine adipate and 60% caprolactam. From the aqueous suspensions 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 fibers, dried only.

1(b)—Leaves containing unbeaten hooked fibers, dried and heat-pressed.

2(a)—Leaves containing beaten hooked fibers, dried only.

2(b)—Leaves containing beaten hooked fibers, 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.<sup>2</sup>:

| Type of leaf | Breaking length (m.) | Elmendorf tear (g.) | Burst strength (kg./cm. <sup>2</sup> ) |
|--------------|----------------------|---------------------|----------------------------------------|
| 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 VI

6 g. polyhexamethylene adipamide fibers 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 2000 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 fibers easily form again a finely divided fiber suspension. The same test with polyhexamethylene adipamide hooked fibers of 3 mm. length did not succeed; the fibers formed densely

felted balls which could not be dispersed even on prolonged stirring.

#### EXAMPLE VII

5 g. polycaprolactam fibers of 4 mm. length and a 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 2000 r.p.m. The hooked fibers 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 fibers. Subsequently a neutral aqueous suspension of the fibers 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 polycaprolactam hooked fibers and 40% polynosic hooked fibers prepared according to the procedure set forth in the next paragraph, 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 2300 m.

The procedure for preparing the polynosic hooked fibers referred to in the first sentence of the last paragraph is as follows: 4 g. polynosic fibers (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 fibers 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 fibers, and a degree of polymerization of 381 as compared with 415 for the untreated fibers, i.e., a DP-decrease of 8%.

It is claimed:

1. A process for fibrillating smooth-surface melt-spun monofilament polyamide-containing fibers comprising the steps of forming a suspension of smooth-surfaced melt-spun monofilament polyamide-containing fibers having a maximum length of about 10 millimeters; said suspension comprising from about 3% to about 13% by weight of said fibers, with the balance of said suspension consisting essentially of a liquid swelling agent selected from the class consisting of aqueous acids, mixtures of aqueous acids, and mixtures of an aqueous acid and an inorganic salt; agitating said suspension to form hook-like extensions from the smooth surface of said fibers, said extensions extending from the surface of said fibers a distance of about one-half to twice the diameter of said fibers; separating the treated fibers from the swelling agent; re-dispersing said separated fibers in water; and beating the resultant fiber-in-water dispersion to intensify the formation of said hook-like extensions.

2. A process for preparing a felted material, in the form of paper and the like, from self-supporting water-leaves, comprising forming a felted material from self-supporting water-leaves of the fibers produced by the process of claim 1.

3. Process according to claim 1 wherein the fibers are polyhexamethylene adipamide fibers and the swelling agent is aqueous hydrochloric acid.

4. Process according to claim 1 wherein the fibers are polyhexamethylene adipamide fibers and the swelling agent is a mixture of aqueous formic acid and sodium sulfate.

5. Process according to claim 1 wherein the fibers are polycaprolactam fibers and the swelling agent is a mixture of aqueous hydrochloric acid and aqueous acetic acid.

6. Process according to claim 1 wherein the fiber suspension is comprised of loose unwoven and unknitted fibers and which is agitated at a temperature in the range from about 20° C. to about 30° C. for between 5 and 100 minutes.

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- 7. Fibers formed by the process of claim 1.
- 8. Felted material formed by the process of claim 2.

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