Dec. 27, 1949 J. W. HALL ET AL 2,492,425

SPINNING ARTIFICIAL FILAMENTS

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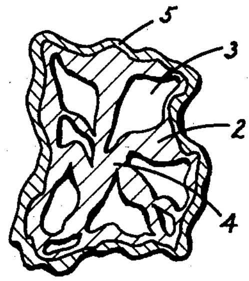

Fig. 1

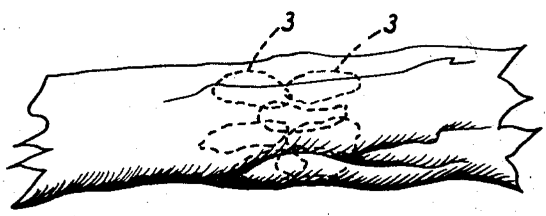

Fig. 2

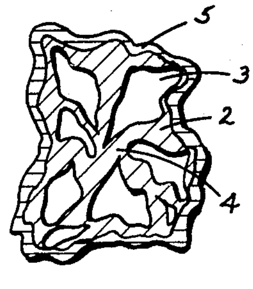

Fig. 3

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SPINNING ARTIFICIAL FILAMENTS

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6 Claims. (Cl. 18—54)

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This invention relates to novel hollow filaments of regenerated cellulose, products formed therefrom, and to processes for producing the same.

It has been proposed, heretofore, to produce hollow filaments by methods involving the emulsification of air in viscose prior to extrusion thereof, or the incorporation in the viscose of substances, commonly alkali carbonates, capable of reacting with acid to develop a gas, and extrusion of the mixture into an acid spinning bath.

All of the hollow regenerated cellulose filaments of the prior art, however produced, have had a common characteristic in that they have been tubular in cross-section, comprising either a hollow continuous canal, or a plurality of individual voids or lumens each taking up the entire cross-section area of the filament and spaced end to end along the length of the filament by transverse partitions. The hollow filaments of the prior art have numerous disadvantages. Most importantly, such filaments have extremely low tensile strength and extensibility, and, further, readily undergo considerable permanent collapse during manufacture, such as when they are passed over guides, about the godets, and under their own pressure as they are being collected on bobbins or in spinning buckets. Even after drying, should there be any appreciable residual inflation in the filaments having the tubular voids or lumens, additional permanent deflation occurs whenever articles formed therefrom such as cushions, mattresses, wearing apparel, etc., are subjected to compression, with a noticeable loss of buoyancy and increase in weight of the articles.

In our pending application Serial No. 557,004, filed October 3, 1944, now Patent Number 2,476,293 we have disclosed new hollow filaments of regenerated cellulose which, in cross-section, have a unique structure by virtue of which they are sharply distinguishable from hollow filaments of the prior art. Such filaments are illustrated in the accompanying drawing in which,

Figure 1 is a cross-sectional view of the filaments of our invention;

Figure 2 is a view taken along the length of the new filaments, and

Figure 3 is a cross-sectional view of the dyed filaments, the skin only being dyed.

Referring to Figure 1, it will be seen that our new filaments have in cross-section, a cellular type structure, the cross-section area being occupied by a plurality of partitions **2** which separate and define a plurality of voids or lumens **3**. The partitions **2** radiate irregularly from a point or points **4** within the filament, and lay more or less at random, and may have a regular or irregular contour, and the voids or lumens, which may vary in size from extremely small to much larger voids, are of varying shape, some being more elongated than others, for example, as determined by the contours of the dividing partitions. The voids **3** overlap one another and lie irregularly spaced along the fiber axis as shown in Figure 2. The separating partitions **2** present, as viewed in Figure 1, an essentially web-like configuration. All of the partitions radiate from a point within the filament but not necessarily all from the same point and the partitions may have a more or less complex shape constituted by a branched structure, one or more partitions branching off from one or more others which radiate from a common point, as shown in Figure 1.

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The new filaments having the cellular type structure may be obtained by extruding viscose containing a gas-developing substance, as for instance an alkali carbonate, such as sodium carbonate, into a high tenacity spinning bath which may contain a large proportion, not less than about 5%, of an inorganic salt of a polyvalent metal, which salt is soluble in concentrations of at least 5% in 6 to 15% sulfuric acid solutions. The salts which are useful for our purposes are inorganic acid salts of metals selected from the group consisting of zinc, iron, magnesium, chromium, cadmium, manganese, nickel and aluminum, as for instance, the sulfates of those metals. The salts mentioned in addition to zinc salts may be present in the spinning bath as substitutes for zinc sulfate, or they may be used in combination therewith. For example, spinning baths containing about 1% of zinc sulfate and about 5% of ferrous sulfate are very satisfactory for our purposes.

The spinning bath contains from 11.3 to 12.5% sulfuric acid; from 5 to 6% of the inorganic salt of a polyvalent metal; and from 21 to 25% sodium sulfate.

Generally, the viscose should analyze from about 1.9 to about 2.5% total sulfur, from about 6 to 9% sodium hydroxide (based on percent weight in viscose), from about 6 to 9% by weight cellulose, and should contain a large proportion of the gas-developing substance such as sodium carbonate, that is, from about 5 to 35% (based on the cellulose present). The viscose preferably should have a common salt (NaCl) point of from 5 to 6. The viscose may contain special modifying agents in addition to the sodium carbonate or other gas-developing substance, such as dyes, pigments, delustrants, etc., or any mixture of such materials.

The spinning bath should have a temperature between 40 to 60° C. The immersion depends, to some extent, upon the denier of the filaments, longer immersion periods being productive of better results in the case of filaments of larger total denier and denier per filament.

If desired, the filaments may be given a stretch up to about 40 to 50% of their length, by passing them between godets or rollers operating at different speeds, or by means of any other equivalent stretching procedure, and preferably the filaments are stretched soon after leaving the coagulating medium. When necessary, the stretching may be facilitated by passing the filaments through a plasticizing bath, such as hot water, hot acids, and the like.

Generally, the various factors involved in producing the fibers are correlated as indicated, and the various ingredients of the viscose and the spinning bath are used in proportions within the ranges stated, but when the sodium carbonate is present in the viscose in the higher amounts, the sulfuric acid, metal sulfate, and sodium sulfate contents of the spinning bath are not quite as critical as when the smaller quantities of sodium carbonate are employed.

For illustrative purposes, the following specific examples are given.

Example I

A viscose aged to a common salt point of 5.5 and having 8.4% by weight sodium hydroxide, 7.3% cellulose, 2.3% total sulfur and to which is added 25% by weight of sodium carbonate (based on cellulose) is extruded through a spinneret to produce a 120-filament thread having a total denier of 300, into a spinning bath maintained at 50° C. and containing 12.3% sulfuric acid, 22% sodium sulfate and 5.3% ferrous sulfate.

The immersion is 24''. After leaving the bath the filaments are passed over two godets in succession having a differential in speed which effects a 40% stretch of the filaments. Filaments which along their entire length show, in cross-section a cellular type structure are obtained.

Example II

A viscose aged to a sodium chloride salt point of 5.3, and having 8.1% by weight sodium hydroxide, 7.4% by weight cellulose, 2.3% by weight total sulfur and to which is added 20% of sodium carbonate (based on cellulose present) is extruded through a spinneret to produce a 200-filament thread having a total denier of 300, into a spinning bath maintained at about 45° C., and containing 12% sulfuric acid; 22.5% sodium sulfate, and 5.3% magnesium sulfate. The immersion is 14 inches. The filaments are stretched 40% between godets. Filaments which along 95% of the fiber axis show, in cross-section, a cellular type structure, are obtained.

Example III

A viscose aged to a sodium chloride salt point of 5, and having 9% by weight sodium hydroxide, 7.6% by weight cellulose, 2.3% by weight total sulfur and containing 25% of sodium carbonate (based on the cellulose) is extruded through a spinneret to produce a 490-filament thread of 1200 total denier, into a spinning bath maintained at 50° C., and containing 11.4% sulfuric acid, 23% sodium sulfate, and 0.85% zinc sulfate and 5% ferrous sulfate. The immersion is 14''. The filaments are stretched 40% between godets. Filaments are obtained which, along 95% of their length show, in cross-section, a cellular-type structure.

Example IV

A viscose aged to a sodium chloride salt point of 5.5, and having 8.5% by weight sodium hydroxide, 7.2% cellulose, 2.3% total sulfur and containing 25% sodium carbonate (based on the cellulose present) is extruded through a spinneret to produce a 24-filament structure of 300 total denier, into a spinning bath containing 12% sulfuric acid, 22.5% sodium sulfate, and 6% manganous sulfate. The immersion is 64''. The filaments leaving the bath are given a stretch of 40%. The filaments thus obtained show, in cross-section, at all points along the filament length, a cellular type structure.

Example V

A viscose aged to a common salt point of 5.5 and having 8.4% by weight sodium hydroxide, 7.3% cellulose, 2.3% total sulfur and to which is added 25% by weight of sodium carbonate (based on cellulose) is extruded through a spinneret to produce a 120-filament thread having a total denier of 300, into a spinning bath maintained at 50° C. and containing 12.3% sulfuric acid, 22% sodium sulfate and 5.3% zinc sulfate.

The immersion is 24''. After leaving the bath the filaments are passed over two godets in succession having a differential in speed which effected a 40% stretch of the filaments. Filaments which along their entire length show, in cross-section, a cellular type structure are obtained.

Example VI

A viscose aged to a sodium chloride salt point of 5.3, and having 8.1% by weight sodium hydroxide, 7.4% by weight cellulose, 2.3% by weight total sulfur and to which is added 20% of sodium carbonate (based on cellulose present) is extruded through a spinneret to produce a 200 filament thread having a total denier of 300, into a spinning bath maintained at about 45° C., and containing 12% sulfuric acid; 22.5% sodium sulfate, and 5.3% zinc sulfate. The immersion is 14 inches. The filaments are stretched 40% between godets. Filaments which along 95% of the fiber axis show, in cross-section, a cellular type structure are obtained.

Example VII

A viscose aged to a sodium chloride salt point of 5, and having 9% by weight sodium hydroxide, 7.6% by weight cellulose, 2.3% by weight total sulfur and to which has been added 25% of sodium carbonate (based on the cellulose) is extruded through a spinneret to produce a 490-filament thread of 1200 total denier, into a spinning bath maintained at 50° C., and containing 11.4% sulfuric acid, 23% sodium sulfate, and 5.5% zinc sulfate. The immersion is 14''. The filaments are stretched 40% between godets. Filaments are obtained which, along 95% of their length show, in cross-section, a cellular type structure.

Example VIII

A viscose aged to a sodium chloride salt point 5.5, and having 8.5% by weight sodium hydroxide, 7.2% cellulose, 2.3% total sulfur and to which has been added 25% sodium carbonate (based on the cellulose present) is extruded through a spinneret to produce a 24 filament structure of 300 total denier, into a spinning bath containing 12% sulfuric acid, 22.5% sodium sulfate, and 6%

zinc sulfate. The immersion is 64''. The filaments leaving the bath are given a stretch of 40%. The filaments thus obtained show, in cross-section, at all points along the filament length, a cellular type structure.

The filaments obtained as described have dry tensile strengths of approximately 2 or more grams per denier, and wet extensibilities of about 30%.

The individual filaments produced in accordance with this invention have in cross-section a cellular type structure at points along at least a substantial portion of the filament length which comprises a plurality of voids or gas pockets which are separated by partitions forming an internal support for the filaments.

The hollow continuous filaments of cellular cross-section initially obtained may be cut to staple length. For example, the filament bundles proceeding from several spinnerets over stretching godets may be combined into tows of 1200 up to 400,000 or so denier. The tows while still wet are cut to staple fibers, which are allowed to fall into a liquid bath which may serve merely to effect opening of the fiber clumps, or may also serve the purpose of an additional liquid treatment, such as washing or desulfurizing. The opened staple fibers are wet-treated, and finely dried in any appropriate manner.

Under the conditions of this invention, a skin of substantial thickness is set up on the filaments, as shown at 5 (Figures 1 and 3). The skin may be differentially dyed by the following procedure: A microtome section of one or more of the filaments mounted in a wax block is taken and mounted on a slide with Meyer's albumin fixative. After de-waxing in xylene, the section is placed in successive baths of 60% and 30% alcohol for a few moments each, and it is then stained in 2% aqueous solution of Victoria Blue BS conc. (General Dyestuffs Corp.) for 1 to 2 hours. At this point, the entire section is blue. By rinsing the section first in distilled waer and then in one or more baths composed of 10% water and 90% dioxane for a period varying from 5 to 30 minutes, the dye is entirely removed from the core, leaving it restricted to the skin areas. A cross-section of a filament in accordance with the invention and having the skin area only dyed is shown in Figure 3.

The thick skin, which is continuous and unbroken, completely surrounds each filament, aids in protecting the voids against collapse under compressional force and is, in turn, supported by the web-like cellular internal structure. The rigidity of the filaments is such that while they are flexible enough to enable their being easily manipulated and adaptable to various textile working processes, they do not tend to collapse even under the influence of very high compressional forces. Under such conditions, the filaments "give" but do not permanently collapse and upon removal of the compressing forces the inflated condition is immediately recovered. The filaments are characterized by a tensile strength which is unprecedentedly high for hollow filaments. The tensile strength is, generally, of the order of the tensile strength of standard viscose fibers and sharply distinguishes the new filaments over hollow filaments of the prior art.

The filaments or fibers have a delustered appearance, give full, deep dyeings in dull shades, and are characterized by a soft hand and feel, excellent water retentivity, light weight, and enhanced covering power. Those filaments that are made without much stretching are generally substantially cylindrical or long and oval in cross-section, depending upon the type of spinneret utilized, while those which have been given a greater amount of stretching exhibit numeraus points of necking down along their length, and due to this irregularity of configuration possessed by some of the filaments they exhibit fulling and felting properties resembling natural wool.

The new hollow fibers, either as continuous filaments or as staple fibers may be used in the production of textile yarns and knitted or woven fabrics which are especially useful in the manufacture of wearing apparel or bed clothing where lightness in weight, buoyancy, and protection from cold or heat are important factors. Carded mats of the material may be used as fillers for the production of comforts, wearing apparel, cushions, life preservers, vibration damping, sound insulating or generally as a heat insulating material for filling spaces between the walls of buildings or other structures to be insulated, such as ice boxes, cold rooms, ships, railway cars, automobiles, airplanes, and the like, and for any of these uses, where desired or necessary, the mats may be provided with a waterproof wrapping or the filaments may be impregnated with a resin, such as phenol-aldehyde and phenol-ketone resins, for example, phenol-formaldehyde resins, phenol-diphenylol propane-formaldehyde or ketone resins, phenol-furfural resins, aromatic sulfonamide-aldehyde resins, benzophenone aldehyde resins, and the polymerized vinyl resins.

The filaments either per se or in the form of a yarn-like bundle, or in the form of a mat, carded or otherwise, may be crimped by effecting shrinkage, which increases the bulk of the products. Further the filaments may be rendered potentially self-crimpable by stretching them while in a plasticized condition, removing the plasticizer while the stretched condition is maintained, fabricating the stretched filaments or fibers and permitting the development of crimp therein in situ in the fabricated structure by activating the filaments, as during a fulling or felting operation, and permitting the crimped filaments or fibers to dry while relaxed.

Since many variations and modifications may be made in practicing the present invention, it is to be understood that we are not to be limited except by the spirit and scope of the appended claims.

This application is a continuation-in-part of our pending application Serial No. 557,004, filed October 3, 1944, now Patent Number 2,476,293.

We claim:

1. A process for producing an inflated regenerated cellulose fiber showing in cross-section along at least a substantial portion of its length a web-like network constituted by a plurality of distinct radiating partitions which provide internal support for the peripheral wall of the fiber and separate and define a plurality of distinct individual voids between an internal point and said peripheral wall, which comprises extruding viscose having a common salt point of from 5 to 6 and containing from 1.9 to 2.5% by weight total sulfur, from 6 to 9% sodium hydroxide, from 6 to 9% cellulose, and from 5 to 35% added sodium carbonate based on the cellulose, into a spinning bath consisting of an aqueous solution of from 11.3 to 12.5% sulfuric acid, from 21 to 25% sodium sulfate, and at least 5% but not more than 6% of a

substance selected from the group consisting of zinc sulfate, iron sulfate, magnesium sulfate, chromium sulfate, cadmium sulfate, manganese sulfate, nickel sulfate, aluminum sulfate, and mixtures of such sulfates, at a temperature of from 40° to 60° C., withdrawing the fibers from the bath, and subjecting the fibers to a stretch of about 40% to 50%.

2. A process for producing inflated filaments of regenerated cellulose having a skin of substantial thickness surrounding a solid portion which occupies only a part of the filament cross-section and extends longitudinally of the filament, the solid portion being joined to the inner surface of the thick skin by partitions lying between the solid portion and the skin and defining an irregular cellular structure, which comprises extruding viscose having a common salt point of from 5 to 6, and containing from 1.9 to 2.5% by weight total sulfur, from 6 to 9% sodium hydroxide, from 6 to 9% cellulose, and from 5 to 35% added sodium carbonate based on the cellulose, into an aqueous acid spinning bath consisting of from 11.3 to 12.5% sulfuric acid, from 21 to 25% sodium sulfate, and 5% to 6% of zinc sulfate, withdrawing the fibers from the bath, and subjecting the fibers to a stretch of 40%.

3. Process for producing inflated filaments of regenerated cellulose having a skin of substantial thickness surrounding a solid portion which occupies only a part of the filament cross-section and extends longitudinally of the filament, the solid portion being joined to the inner surface of the thick skin by partitions lying between the solid portion and the skin and defining an irregular cellular structure, which comprises extruding viscose having a common salt point of from 5 to 6, and containing from 1.9 to 2.5% by weight total sulfur, from 6 to 9% sodium hydroxide, from 6 to 9% cellulose, and from 5 to 35% added sodium carbonate based on the cellulose, into an aqueous acid spinning bath consisting of from 11.3 to 12.5% sulfuric acid, from 21 to 25% sodium sulfate, and 5% to 6% of ferrous sulfate, withdrawing the fibers from the bath, and subjecting the fibers to a stretch of 40%.

4. Process for producing inflated filaments of regenerated cellulose having a skin of substantial thickness surrounding a solid portion which occupies only a part of the filament cross-section and extends longitudinally of the filament, the solid portion being joined to the inner surface of the thick skin by partitions lying between the solid portion and the skin and defining an irregular cellular structure, which comprises extruding viscose having a common salt point of from 5 to 6, and containing from 1.9 to 2.5% by weight total sulfur, from 6 to 9% sodium hydroxide, from 6 to 9% cellulose, and from 5 to 35% added sodium carbonate based on the cellulose, into an aqueous acid spinning bath consisting of 11.3 to 12.5% sulfuric acid, from 21 to 25% sodium sulfate, and 5% to 6% magnesium sulfate, withdrawing the fibers from the bath, and subjecting the fibers to a stretch of 40%.

5. Process for producing inflated filaments of regenerated cellulose having a skin of substantial thickness surrounding a solid portion which occupies only a part of the filament cross-section and extends longitudinally of the filament, the solid portion being joined to the inner surface of the thick skin by partitions lying between the solid portion and the skin and defining an irregular cellular structure, which comprises extruding viscose having a common salt point of 5.5, and containing 2.3% total sulfur, 8.4% sodium hydroxide, 7.3% cellulose, and 25% added sodium carbonate, based on cellulose, into an aqueous acid spinning bath consisting of 12.3% sulfuric acid, 22% sodium sulfate and 5.3% zinc sulfate, withdrawing the filaments from the bath and subjecting the filaments to a stretch of 40%.

6. Process for producing inflated filaments of regenerated cellulose having a skin of substantial thickness surrounding a solid portion which occupies only a part of the filament cross-section and extends longitudinally of the filament, the solid portion being joined to the inner surface of the thick skin by partitions lying between the solid portion and the skin and defining an irregular cellular structure, which comprises extruding viscose having a common salt point of 5.3 and containing 2.3% total sulfur, 8.1% sodium hydroxide, 7.4% cellulose, and 20% added sodium carbonate based on cellulose, into an aqueous acid spinning bath consisting of 12% sulfuric acid, 22.5% sodium sulfate and 5.3% zinc sulfate, withdrawing the filaments from the bath, and subjecting the filaments to a stretch of 40%.

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