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METHOD OF FORMING REGENERATED CELLULOSE FIBERS

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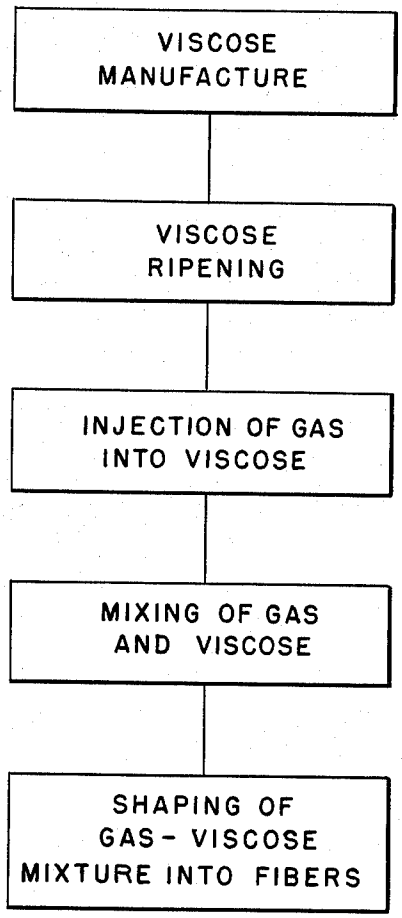

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METHOD OF FORMING REGENERATED CELLULOSE FIBERS

Joseph H. Anderer, Charlotte, N.C., Anthony P. Da Vinci, Chester, Pa., and Thomas F. McHugh, Leominster, Mass., assignors, by mesne assignments, to FMC Corporation, San Jose, Calif., a corporation of Delaware

Original application Mar. 25, 1960, Ser. No. 17,712, now Patent No. 3,156,605, dated Nov. 10, 1964. Divided and this application Aug. 28, 1962, Ser. No. 219,990

4 Claims. (Cl. 264—50)

This is a division of application Serial No. 17,712, filed March 25, 1960, now United States Patent 3,156,605.

This invention relates to a method of making a new form of regenerated cellulose filament and fiber.

In the manufacture of regenerated cellulose fibers and filaments, a cellulosic solution is extruded through orifices of a desired size and the cellulose subsequently regenerated from the shaped product. The spinning solution may be a viscose solution, a cuprammonium solution, or a cellulose ester solution and the like. The specific processing of the extruded liquid will, of course, be determined by the specific spinning liquid. Although filaments and fibers may be formed from spinning liquids consisting of solutions of cellulose nitrate and the like and by appropriate hydrolysis converted to regenerated cellulose, the most common method involves the regeneration of the cellulose from viscose. Accordingly, the invention will be described as applied to the viscose process but it is to be understood that these other methods may also be employed.

For most purposes, regenerated cellulose fibers and filaments are prepared by extruding viscose through orifices of a predetermined size into an aqueous acid bath wherein the extruded solution is coagulated and the cellulose regenerated from the plastic stream. The wet gel filaments are then subjected to a series of after-treatments wherein they are washed with water to remove acids and salts, treated with solutions to remove sulfides, are bleached, washed and finally dried. These after-treatments may be applied to the running tow or strand of filaments as in the continuous process or the filaments after leaving the spinning bath may be collected and the after-treatments applied after the cake has been removed from the spinning pot.

Various methods have been employed to form hollow or tubular filaments or regenerated cellulose for textile purposes. These filaments have an increased bulk factor, have a delustered appearance and present a full deep-dyed effect, particularly in dull shades. These filaments are further characterized by a soft hand and feel and are exceedingly supple and pliant. This type of product has been formed principally for what is commonly termed "novelty yarns." These tubular or hollow filaments may, in fact, be tubular or hollow and, in such filaments, the voids or gas pockets may be spaced longitudinally of the filament or they may be relatively short longitudinally of the filament and spaced both longitudinally and transversely to form a cellular type of structure. In the former structure, the particular method of handling the newly formed filaments may also result in the collapse of the hollow or tubular structure or the filaments may be subjected to suitable treatment to remove the gas from the pocket and form a filament with collapsed walls and or irregular configuration.

Fabrics formed from these types of filaments as by weaving have a very soft feel and are exceedingly supple and pliant. One of the disadvantages of rayon textile materials, such as woven piece goods formed from the hollow or tubular filaments of the prior art is their water-spotting characteristic.

It has now been discovered that hollow or tubular filaments of regenerated cellulose wherein the average wall thickness does not exceed about three microns and the width or breadth of the fiber is at least ten times the thickness of the wall, possess entirely different characteristics and properties from solid and prior "hollow" filaments.

The accompanying drawing illustrates the sequence of steps of the method of the present invention.

In forming the fibers in accordance with the present invention, any viscose such as normally employed in industry is satisfactory for the present purposes. Viscose generally contains from about 4% to 10% cellulose, about 4% to 10% sodium hydroxide and about 25% to 60% carbon disulfide based upon the weight of the cellulose. The viscose is prepared and ripened in accordance with usual commercial practice before spinning. The coagulating and regenerating bath and the after-treatments commonly employed may be also used in the present method. The coagulating and regenerating baths generally contain from about 15% to 25% sodium sulfate, from about 1% to 15% zinc sulfate and from about 6% to 12% sulfuric acid. In order to improve physical characteristics, such as tensile strength or tenacity and elongation or extensibility, the filaments after leaving the coagulating and regenerating bath are passed through a hot water bath which may contain a small amount of acid and while passing through the bath they are stretched from about 10% to about 85%. The hot water bath may, for example, contain 2% or 3% sulfuric acid and is generally maintained at a temperature between about 80° C. and about 95° C. Depending upon the intended use, the filaments may be cut to desired fiber lengths.

The fibers may be prepared from a cellulosic spinning solution such as viscose containing air, nitrogen or other gas in a range of approximately one cubic centimeter of gas to from about 0.1 gram to 5 grams of cellulose in the spinning solution or viscose. Where the ratio of gas to the weight of the cellulose is in the upper portion of the range, the fibers exhibit numerous ruptures along the side of the wall and the frequency of these open or broken side walls increases as the ratio between the volume of gas to the weight of the cellulose increases. In order to obtain a thorough and uniform distribution of small gas bubbles throughout the viscose, it is desirable that a surface-active agent be incorporated in the viscose. A wide variety of surface-active agents are satisfactory and the following are merely representative of these agents: sodium oleate, sodium lauryl sulfate, Turkey red oil, secondary amide derivatives of higher fatty acids, for example, the products known commercially as Detergent 1000 and Detergent 1011 as marketed by E. F. Drew and Company, Inc. and the like. These surface-active agents may be present in the viscose in amounts of from about 0.1% to about 5% based on the weight of the cellulose. In order to form a relatively stable dispersion of the gas bubbles and to uniformly distribute the bubbles in the viscose, the gas is preferably introduced by injection and the surface-active agent may be conveniently

injected simultaneously. The material is agitated vigorously in a closed mixing device or chamber, such as that shown in United States Patent 2,039,708. From this mixing device or blending device, the viscose may be passed through a second mixing device of the same type with the exception that no gas and surface-active agent need be introduced. From the second mixing device, the viscose is conducted directly to an extrusion device or spinneret.

In distributing the gas in the viscose, a vigorous blending or mixing is required to break the gas into small bubbles and disperse the small bubbles uniformly throughout the viscose. The bubbles should remain in a dispersed condition, that is, the dispersion should be relatively stable without a coalescene of the bubbles and consequent deaeration for a sufficient period so as to permit the gas-viscose mixture to be conducted to the spinneret orifices. In general, viscose is spun or extruded through the minute orifices of a spinneret at a guage pressure of about fifty to sixty pounds per square inch behind the orifices. We have found that at atmospheric pressures, the bubble size should not exceed roughly one-half the diameter of the orifices through which the viscose is to be extruded. Under the spinning pressure, the bubble size should not exceed about one-third the diameter of the orifice. For example, in spinning a 1.5 denier filament, the orifice size is 63.5 microns. At atmospheric pressure, the average bubble size of the gas should not exceed about thirty microns and under spinning pressure bubbles of this size will not exceed about twenty microns.

During the spinning operation, some escape of the gas from the freshly coagulated filaments is usually noticeable adjacent the spinneret particularly in the spinning of the smaller size filaments such as 1 denier and 1.5 denier filaments. In these small sized filaments, rupture of a portion of the side wall is common. The larger the size filament, the lower the number of noticeable ruptures. With an increase in the ratio of gas to cellulose, the number of ruptures also increases.

Considering a filament of a 1.5 denier size, the normal type filament such as used in the textile industry has a cross-sectional diameter of about thirteen microns whereas the thin-walled filament of this invention will have a wall thickness of between one and two microns and an average maximum transverse dimension of between about fifty microns and about eighty microns.

One of the remarkable characteristics of the filaments and fibers formed in accordance with the present invention is their ability to bond to themselves when wet with water or other liquid and subsequently dried. An explanation for this unique property is that the thin walls of the filaments and fibers are so compliant as to readily yield to strong attractive forces which result as the water is removed therefrom and thus establish strong hydrogen bonds between adjacent filaments and fibers as they become dry. In this respect, the wall thickness of the filaments and fibers here described is critical since no apparent bonding exists when the wall thickness exceeds about three microns.

As heretofore mentioned, the desired and dominant characteristic of the prior art hollow or inflated filaments was a soft hand and feel. The principal purpose was to provide a bulk yarn, that is, a yarn having a greater volume per unit of weight than conventional filaments and fibers. The fibers or filaments were very pliant and supple and were characterized by a soft hand and feel. The filaments and fibers formed in accordance with the present invention are clearly differentiated in that after spinning and the usual processing and drying, the hydrogen bonding forces unite the filaments and fibers at their points of contact so as to provide a bundle which is relatively stiff and rigid. In view of the very thin and compliant wall of the filaments and fibers formed in accordance with the present invention, substantial surface contact exist between adjacent fibers to thus enhance the

effect of the hydrogen bonding forces. For example, a 120 filament thread having a total denier of about 300 as produced in accordance with United States Patent 2,476,293 is very soft, pliant and flexible. A 120 filament thread having a total denier of 300 as produced in accordance with the method described above wherein the average maximum wall thickness of the filaments does not exceed about three microns is stiff and rigid being more comparable to a fine wire than to a bundle of regenerated cellulose filaments.

Another characteristic of the filaments and fibers of the present invention is their low strength in both the wet and dry state. For example, 1.5 denier to 2.0 denier thin-walled filaments and fibers have a wet strength of between 0.5 gram and 1.2 grams per denier and an extensibility of between 15% and about 35%. The tensile strength of the filaments which are dried and then conditioned by maintaining them in an atmosphere having a temperature of about 70° F. and a relative humidity of 58% for a period of about twelve hours lies between about 1.0 gram and about 1.5 grams per denier. Another characteristic of the fiber is its exceedingly high water-retention. The water-retention is, in general, of the order of two to four times that of corresponding conventional solid type fibers.

An entirely unique characteristic of the fabric form of the thin-walled filaments and fibers is the total absence of water-spotting which is characteristic of fabrics formed of prior art hollow or inflated regenerated cellulose fibers and filaments.

The production of the thin-walled regenerated cellulose fibers of this invention may be illustrated by the following example:

Viscose was prepared containing 5% cellulose, 6% caustic soda and 39% carbon disulfide based upon the weight of the cellulose. A greening agent consisting of a reaction product of ethylene diamine and fifty moles of ethylene oxide per mole of ethylene diamine was added to the viscose in an amount of about 3% based on the weight of the cellulose. The viscose was allowed to age to a sodium chloride salt test of 12. The viscose was then pumped into a closed mixing device such as shown in United States Patent 2,039,708. At the entrance to the mixing chamber, nitrogen was introduced at a guage pressure of fifty pounds per square inch. Sodium lauryl sulfate was pumped into the viscose in the mixing chamber to provide approximately 1% sodium lauryl sulfate based upon the weight of the cellulose in the viscose. In order to insure a complete distribution of the gas bubbles of the required size throughout the viscose, the viscose was then passed through a second closed mixing device of the same type. From this mixing device, the viscose was pumped to a spinneret. Various gas to cellulose ratios were employed for different samples as set forth in the table which follows. The spinneret was such as to produce a tow of 5000 filaments having a total denier of 7500 or roughly 1.5 denier per filament at a spinning speed of fifty meters per minute. The coagulating and regenerating bath contained 9.2% sulfuric acid, 8% zinc sulfate and 18% sodium sulfate and was maintained at a temperature of about 60° C. From the spinning bath, the tow passed through a water bath maintained at a temperature of about 90° C. containing 2.5% sulfuric acid. While in this bath, the filaments were stretched different amounts as set forth in the table which follows. In order to furnish a comparison, one sample was also prepared wherein no gas was injected into the viscose. The filaments were collected, washed, bleached and dried.

It will also be noted from the data in the following table that the water-retention which is expressed in terms of the weight of water which is absorbed by the fibers when wet with water and centrifuged to remove excess and surface-held water is of the order of at least about double that of the usual solid type regenerated cellulose fibers. Water-retentions as high as 300% have been attained in fibers of this type.

Sample	Gas (cc.) to cellulose (gms.) ratio	Stretch percent	Tenacity (gms./denier)		Extensibility Percent		Water retention percent
			Wet	Dry	Wet	Dry	
A	No gas	95	1.99	2.50	34.1	25.5	64
B	1:5	85	1.06	1.12	27.4	14.0	115
C	1:5	65	1.22	1.30	28.2	15.1	118
D	1:5	30	0.70	1.08	28.9	21.0	140
E	1:1	62	0.51	0.94	14.5	8.6	162
F	1:1	30	0.34	0.96	18.4	15.4	191
G	2:3	69	0.56	1.36	18.0	14.4	150

Although the total drying time for the fibers of this invention is about the same as that for conventional fibers, the fibers of this invention retain greater proportions of water over certain periods. For example, in the case of a sample of conventional fibers having a water-retention of 83%, the fibers contained 18% after two days in air at 75° C. and having a relative humidity of 58%. At the end of four days, the fibers were "conditioned;" that is, they contained about 10% moisture. Fibers of the present invention had a water-retention of 215% to 235%. At the end of two days at 75° C. and a relative humidity of 58%, the samples contained 85% to 115% moisture. At the end of four days, the fibers were "conditioned." Under damp or moist conditions, the fibers of this invention absorb greater proportions of moisture and will retain greater proportions for a longer period of time than conventional fibers.

The characteristics of the filaments and fibers produced in accordance with the present invention render the same suitable for a variety of uses which cannot be fulfilled by conventional solid filaments or fibers or inflated filaments or fibers formed by the known methods. In textile operations, the bonding forces are preferably masked by conventional yarn finishes to permit proper processing of the filaments and fibers into yarns and threads and weaving into textile fabrics. Once the desired fabric is obtained, the yarn finish is removed, as for example by scouring, to thus activate the hydrogen bonding forces.

Fabrics formed of the filaments and fibers of the present invention are relatively stiff and possess a crisp linen-like hand. These characteristics are, to a great degree, attributed to the strong cohesive forces acting between the adjacent filament and fibers, but are augmented by the unique configuration of the filaments and fibers themselves. Thus, at the collapsed areas of the filaments and fibers a relatively broad or flat structure is presented which enables them to entwine adjacent filaments and fibers, in addition to providing increased surface areas on which the hydrogen bonding forces may act.

The combined effects of the strong bonding forces and the entwinement of the filaments and fibers serve to restrict movement of the yarns and threads of a finished woven fabric and thus render the same highly satisfactory for use as filters in high velocity gas streams, as for example in air conditioning and heating systems.

More important, the stabilized character imparted to the woven fabric by these combined effects enables the finished farbic to be readily cut and folded with conventional apparatus into gauze or bandages which possess neither the limp nor slick properties associated with similar products formed of conventional rayon. Aside from the high liquid absorption and retention of the filaments and fibers, on wetting out and redrying the bond established between the crossing yarns of threads has been found to be of such magnitude that the force required to dislocate the yarns is about seven times that required in a comparable cotton construction. This bonding effect thus assures that the gauze or bandage will retain its desired shape and minimizes any tendency for the fabric edges to unravel, without interfering with its intended function or use. While such loose woven fabric normally presents a rather crisp or cotton-like hand, variations in the smoothness, flexibility and softness can be achieved by controlling the temperature and pressure or tension applied to filaments and fibers during drying.

The extremely high water absorption and retention characteristics also render the fibers particularly suited for certain surgical and medical uses such as absorbent fibrous products which, for example, may be formed as by a carding operation. The higher water absorption characteristic is also of distinct benefit in liquid filtration applications where, when the fibrous body or filter element is wet with water, the fibers swell appreciably to form a very firm filter body. Alternatively, the absorbent or filter body may be formed by dispersing fibers of uniform or of different lengths in a gas stream and depositing the fibers in a random arrangement and to a desired thickness on a foraminous collecting surface.

Another advantage of the fibers of the present invention is their ability to be blended with natural or synthetic fibers for producing radically new fabrics; that is, fabrics having characteristics which could not be achieved by other fibers or blends of fibers. In blends with natural, cellulosic, acrylic, and polyester fibers, the low wet modulus of the fibers here described contribute to wet wrinkle shedding with resulting improvement in wash and wear characteristics when fabrics are drip-dried. While similar results are generally achieved with fabrics formed of rayon blended with synthetic or cotton fibers, these known fabrics lack the desired "life-like" or crisp hand which is imparted by the fibers of the present invention. This crisp hand, as heretofore described, results from the hydrogen bonding forces acting between the fibers of the present invention as well as the ability of these broad or ribbon-like fibers to entwine about and restrict the movement of adjacent fibers. As the hydrogen bonds are broken during laundering operations, the resulting fabric exhibits superior wet wrinkle resistance, yet provides a crisp hand as the hydrogen bonds are restored upon drying. One of the remarkable aspects of such fiber blend is the bonding propensity of the fibers does not deteriorate upon repeated laundering so that the fabric possesses a permanent firmness without the use of any stiffening or bonding additives.

The amount of fibers of the present invention blended with other cellulosic or synthetic fibers is desirably within the range of from about 10% to about 40%, and preferably within the range of from about 25% to about 30%. When employing less than about 10% of the fiber here described, little opportunity exists for hydrogen bonding forces to fuse the fibers and thus no apparent crispness is imparted to the finished fabric. On the other hand, exceeding the maximum range of about 40% so greatly accentuates the bonding and entwining characteristics of the fibers of the present invention as to mask the desirable qualities of cellulosic or synthetic fiber which are blended therewith.

The following data is set forth as being illustrative of the improved properties which are achieved in blending the fibers of the present invention with other fibers. For the sake of clarity, the fiber of the present invention is designated as Fiber X in the following tables:

Yarn properties

	Nominal Yarn No.	Tenacity × Yarn Count	Oz. to break	Percent elongation
65% Dacron [1] (1.5 den.) and 35% Fiber X (1.0 den.)	40/1 cc.	328	8.19	20.7
	60/1 cc.	301	4.19	18.6
65% Dacron [1] (1.5 den.) and 35% Rayon (1.5 den.)	50/1 cc.	230	4.63	12.9
70% Acrilan [2] (2.0 den.) and 30% Fiber X (1.5 den.)	30/1 cc.	239	8.4	19.5
	35/1 cc.	225	6.3	17.5
	40/1 cc.	228	5.8	16.9
	45/1 cc.	219	4.8	14.3
	50/1 cc.	207	4.0	13.7
70% Acrilan [2] (2.0 den.) and 30% Pima Cotton.	30/1 cc.	218	7.3	7.5
	35/1 cc.	210	5.8	7.3
	40/1 cc.	207	5.0	6.7
	45/1 cc.	206	4.5	6.1
	50/1 cc.	200	3.8	5.9
70% Acrilan [2] (2.0 den.) and 30% Rayon (1.5 den.).	30/1 cc.	206	6.7	11.8
	35/1 cc.	198	5.8	10.9
	40/1 cc.	196	4.8	9.9
	45/1 cc.	198	4.4	10.1
	50/1 cc.	183	3.7	8.1

[1] Dacron—Registered trademark. A fiber composed of a polyester condensation polymer.
[2] Acrilan—Registered trademark. A fiber prepared from acrylonitrile and vinyl derivatives.

Fabric stiffness (as determined by Cantilever Method, ASTM D1388–55T)

	Milligram centimeters
100% Fiber X	410.35
100% Rayon	47.79
67% Polyester, 33% Rayon	58.35
67% Polyester, 33% Fiber X	105.76

It is obvious that the properties and characteristics of filaments and fibers prepared as described herein may be altered by the application of various finish compositions such as those commonly employed in the manufacture of the conventional regenerated cellulose fibers and filaments. The finish material may be such as to merely render the fibers and filaments amenable to textile operations such as carding, knitting, weaving and the like. The finish may be subsequently removed as described above, or the finish may be such that it will be retained in the completed fibrous product to alter the characteristics of the products formed from the fibers and filaments.

Other modifications may also be made to alter the characteristics of the fibers as is well known in the art. For example, various dyes and pigments may be incorporated in the viscose to provide fibers of desired color and shape. Resins may be incorporated in the viscose to provide desired properties. These modifications are to be considered within the scope of the invention.

We claim:

1. The method of forming thin-walled regenerated cellulose fibers having an average wall thickness not exceeding about three microns which comprises adding to and incorporating in viscose a small amount of a surface-active agent, mixing a gas into the viscose, vigorously agitating the mixture to disperse the gas in the viscose and form a uniform, stable dispersion of the gas in the form of small bubbles and extruding the viscose into an acid bath through an orifice having a diameter of about twice the average diameter of the bubbles at atmospheric pressure.

2. The method as defined in claim **1** wherein the amount of gas mixed into the viscose is in a ratio of one cubic centimeter of gas to form 0.1 gram to 5 grams of cellulose in the viscose.

3. The method of forming thin-walled regenerated cellulose fibers having an average wall thickness not exceeding about three microns which comprises adding to viscose small amount of a surface-active agent, mixing a gas into the viscose in a ratio of one cubic centimeter of gas to from about 0.1 gram to 5 grams of cellulose in the viscose, vigorously agitating the mixture to disperse the gas in the viscose and form a uniform, stable dispersion of the gas in the form of small bubbles, extruding the viscose into an acid bath through an orifice having a diameter of about twice the average diameter of the gas bubbles at atmospheric pressure and stretching the freshly formed fibers from 10% to 85%.

4. The method of forming thin-walled regenerated cellulose fibers having an average wall thickness not exceeding about three microns which comprises adding to and incorporating in viscose a small amount of sodium lauryl sulfate, mixing an inert gas into the viscose in a ratio of one cubic centimeter of gas to from 0.1 gram to 5 grams of cellulose in the viscose, vigorously agitating the mixture to disperse the gas in the viscose and form a uniform, stable dispersion of the gas in the form of bubbles having an average diameter not exceeding about thirty microns, extruding the viscose through an orifice having a diameter of about twice the average diameter of the gas bubbles into an acid spinning bath to provide filaments and stretching the freshly formed filaments 10% to about 85%.

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ALEXANDER H. BRODMERKEL, *Primary Examiner.*
WILLIAM J. STEPHENSON, *Examiner.*