

June 19, 1962

A. J. MEHLER, JR., ETAL

3,039,173

CRIMPED TEXTILE PRODUCTS

Filed Feb. 12, 1958

2 Sheets-Sheet 1

Fig. 1

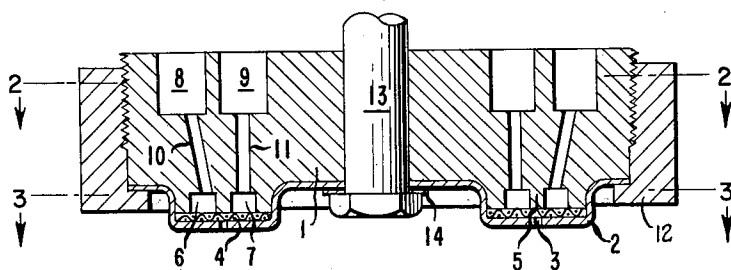


Fig. 1a

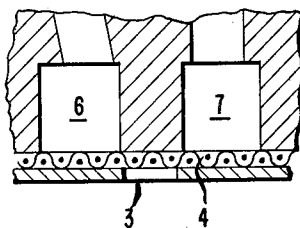
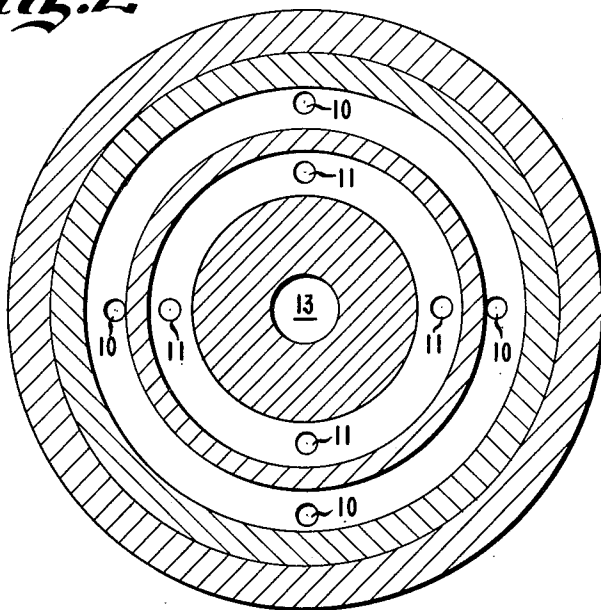


Fig. 2



INVENTORS
ALBERT JOSEPH MEHLER, JR.
JOHN ROSCOE PROFFITT, JR.
ROBERT BURNS TAYLOR, JR.

BY *Raymond J. Blumfeld*

ATTORNEY

June 19, 1962

A. J. MEHLER, JR., ETAL

3,039,173

CRIMPED TEXTILE PRODUCTS

Filed Feb. 12, 1958

2 Sheets-Sheet 2

Fig. 3

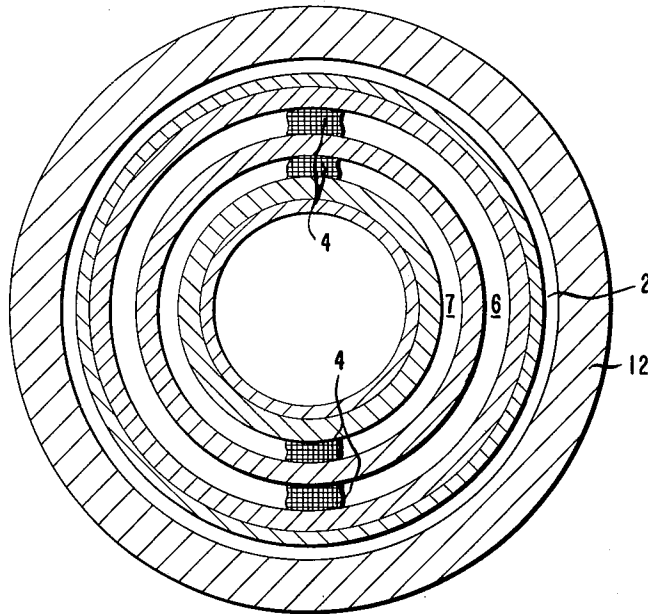
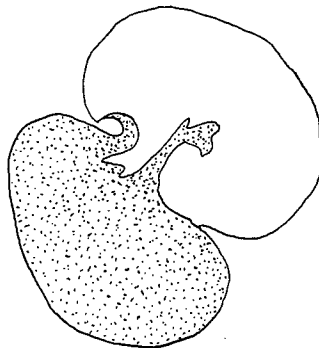


Fig. 4



INVENTORS
ALBERT JOSEPH MEHLER, JR.
JOHN ROSCOE PROFFITT, JR.
ROBERT BURNS TAYLOR, JR.

BY *Raymond E. Blount*

ATTORNEY

1

3,039,173

CRIMPED TEXTILE PRODUCTS

Albert Joseph Mehler, Jr., New Hope, and John Roscoe Proffitt, Jr., Waynesboro, Va., and Robert Burns Taylor, Jr., Wilmington, Del., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Filed Feb. 12, 1958, Ser. No. 714,772
11 Claims. (Cl. 28—82)

This invention relates to textile fibers of cellulose derivatives and particularly improved, crimped composite filaments. In the course of the development of the synthetic textile industry, much effort has been expended toward the production of wool-like fabrics. Unlike wool, most of the synthetic textile fibers are relatively straight with a smooth slick surface and are not adapted to being spun into a yarn on either the cotton or woolen systems. To facilitate the carding and/or combing drafting operations to which the man-made staple fibers are subjected before spinning them into yarn, it is essential to crimp them so they will exhibit sufficient coherence, at least during the early stages of the yarn spinning operations, so that the yarns can be processed on conventional textile processing equipment.

Various methods have been proposed to crimp synthetic filaments. These methods comprise mechanical treatment of the filaments spun in normal fashion as well as the use of special spinning conditions or after-treating which bring about differential physical properties over the cross section of the single filaments that will thereby cause a crimp. It has also been proposed to extrude two or more different materials together to form a composite filament which contains the components in an eccentric relation over the cross section of the filaments. When the two components possess substantially different shrinkage, a crimp is caused by the differential shrinkage of the spun and drawn components.

When such methods of crimping filaments are used and the filaments cut into staple and yarn spun therefrom, the resulting fabrics are not completely satisfactory. Although such fabrics have a different hand from a woven fabric of continuous filaments, they are usually deficient in bulk and cover due to the fact that the crimped filaments in the yarn tend to stay as they are and cannot be worked out or full by finishing operations to obtain a pleasing handle and good cover. In addition, the fabrics are deficient with regard to recovery from deformation, such as crushing or glazing. The fabrics are usually deficient also in elastic properties, such as stretchability, compressional resilience and liveliness and usually have the harsh, slick handle of a typical synthetic filament.

In addition to modifying synthetic filaments in order to make spun yarns from them, much effort has been expended on the production of continuous filaments such that fabrics made therefrom will resemble fabrics woven from spun yarn rather than from continuous-filament yarn. Various means of doing this have been proposed including the aforementioned self-crimping filaments, but again the products have more nearly resembled those fabrics made of continuous filaments in that the yarns were not responsive to a finishing and fulling operation and did not display a renewable surface.

It is, therefore, an object of the present invention to provide crimped multicomponent composite filaments of cellulose derivatives having improved crimp characteristics and imparting improved properties to textile fabrics containing synthetic yarns. It is a further object of the invention to provide filaments and yarns composed of such filaments which exhibit improved covering power when embodied into fabrics. A further object of the invention is to provide yarns which when embodied in a fabric dis-

2

play a renewable surface. Further objects will appear hereinafter.

The objects of this invention have been attained by producing a crimpable composite filament comprising at least two cellulosic components having substantially different shrinkages when treated with a swelling agent. Also, the composite filament has the capacity for spontaneously changing its extent of crimp (the number of crimps per inch) upon being exposed to the effect of a swelling agent and substantially reverting to the original state of crimp upon removal of the swelling agent. This latter characteristic, which, for convenience, is referred to as "crimp reversibility," is characteristic of the filaments of this invention and is manifested by the "squirming" of the filaments upon both application and removal of the swelling agent. The composite filaments of this invention have a crimp reversibility of at least 5 crimps per inch.

According to one embodiment of this invention, the new filaments of this invention are prepared by spinning together two or more cellulosic derivatives, at least one of which is fiber-forming, in such a way that the derivatives are not appreciably blended together but form over the cross section of the single composite filament two or more distinct zones which extend through the entire length of the filament in eccentric fashion, whereby only one or, alternatively, part of or all the components form the surface of the single composite filament. The extrusion can be such that the components are localized and held together in a "side-by-side" arrangement in which both components form part of the surface of the composite, or the extrusion may be such that one component forms a core and the other a sheath to form a composite referred to hereinafter as a "sheath-core" structure. In this latter structure only the sheath contributes to the surface of the composite. After further treating the composite filament as desired (as by drawing), the treated composite filament is shrunk by being subjected, while in a substantially tensionless state, to a shrinking treatment. (For convenience, the following discussion will refer to two-component filaments, although the filaments may, if desired, have more than two components.)

In accordance with the present invention, one component of the composite filaments has a substantially greater initial shrinkability than the other component, and one component of the crimped filaments of the present invention undergoes a reversible length change (after an initial shrinkage) to a substantially greater degree than the other component. By virtue of the above-described characteristics, composite filaments of this invention under the influence of a shrinking agent develop a crimp which upon subsequent exposure of the filament to a swelling agent is, at least in part, altered but is regained upon removal of the swelling agent. The value of this crimp reversibility is evidenced by the ability of the filaments in yarns of this invention when embodied in a fabric to squirm about in the fabric under the influence of a swelling agent such as water, but, nevertheless, to regain the original crimp in the fabric with removal of the swelling agent, as by drying. Fabrics containing these novel filaments acquire a high degree of fullness or covering power after the swelling treatment and retain this fullness even after being subjected to such treatment repeatedly. It will be understood that fabrics composed of the novel filaments can also be subjected to a physical working of the fabric to develop fullness and covering power to the greatest degree. This invention offers a new degree of freedom to the fabric finisher by allowing him to work a fabric into the desired hand.

To develop adequate crimp in a composite filament, the shrinkability of one component should be at least 3% and preferably 8% greater than the shrinkability of the other component, that is, said component has at least

3% greater loss of original length upon shrinking than the other component. The shrinkability of a component is determined by measuring the shrinkage, upon treating with a shrinking agent under no tension, of a mono-component filament made from the component polymer (spun and treated under substantially the same conditions as the composite filament to be prepared therefrom). The shrinking agent may be boiling water, or saponifying alkaline solution, or the like.

In order to develop the crimp reversibility characteristic of filaments of this invention, one component of the composite filament preferably has a reversible length change after shrinkage of at least 4.0% and desirably at least 6.0% more than that of the other component. The reversible length change of a component is determined by measuring the increase in length of a monocomponent filament of the component polymer (spun, treated, and shrunk under the same conditions as the composite filament) upon being immersed in an aqueous medium used for testing the reversible length change of both components.

Crimp intensity in the dry and wet states expressed in crimps per inch of crimped length is determined by the following procedure: seven filaments are selected from a yarn bundle and mounted on a metal frame with 10 cm. between the ends. The length of fiber is adjusted to 12 cm., approximately after a 10-minute slack boil-off. This gives 20% slack in a fiber after boil-off. If either of the two components has less than 5% shrinkage, no adjustment is made, i.e., 12 cm. of the original fiber is used. The fibers on the frame are then crimped by immersing in boiling water for 10 minutes, removed, dried, and then photographed. Saponification may be substituted for the boil-off if this is the crimp-activating step.

The same (crimped) fibers are then immersed in water at 25° C. and photographed under water. After drying, the fibers are again photographed. By carefully studying the photographs, the total crimps are counted for each fiber, then averaged for each condition, and calculated as crimps per inch. Crimp reversibility is the difference in the number of crimps per inch between a dry and wet state.

Referring to the drawings:

FIGURE 1 is an axial longitudinal section of a spinneret assembly which can be used to make the composite filaments of this invention.

FIGURE 2 is a transverse cross section of the apparatus of FIGURE 1 taken at 2—2 thereof and showing a plan of the top of the spinneret plate.

FIGURE 3 is a transverse cross section taken at 3—3 of FIGURE 1 to show the plan of the bottom section of the plate thereof.

FIGURE 1A is an enlarged portion taken from FIGURE 1 to show details of the spinneret at the orifice.

FIGURE 4 shows a typical cross section of filaments of this invention produced by dry spinning. In these drawings one component is shaded to show the separation between components.

With reference to FIGURE 1, the bottom spinneret proper 2 which contains a circle of orifices 3 is held in place against back plate 1 by retaining rings 12, 14 and bolt 13. Orifices 3 are uniformly spaced around the spinneret plate 2 with each orifice being positioned to receive spinning solutions which are fed from annular grooves 8 and 9 through holes 10 and 11 to annular spaces 6 and 7. A fine mesh screen 4 (325 mesh) is located between the spinneret plate 2 and the back plate 1. The back plate 1 contains two annular grooves 8, 9 which are connected to suitable piping and filtration apparatus to receive different spinning solutions. Holes 11 go from annular groove 9 to annular space 7. Holes 10 lead from annular groove 8 to annular space 6. As illustrated in FIG. 1, annular spaces 6 and 7 are separated by wall 5 which is positioned above orifice 3 and spaced from spinneret plate 2 by screen 4 to permit the passage of

the spinning solutions from the annular spaces 6 and 7 through orifice 3.

FIGURE 2 shows a plan of the back plate. Appearing in this view are eight lead holes 10 and 11 equally spaced within the concentric grooves 8 and 9, respectively.

FIGURE 3 shows the appearance of the back plate 1 sectioned as indicated on FIGURE 1. Visible are the concentric inner and outer annular spaces 6 and 7 and the fine mesh screen 4.

Operation of the described apparatus in the practice of this invention is readily understood. Separate spinning material is supplied to the inner annular groove 9 and outer annular groove 8, respectively, of the back plate; the former flows from groove 9 through the openings 11 into the inner annular space 7 and thence through orifice 3 to form a part of a composite filament, while the latter passes through the lead hole 10 to the outer annular space 6 and thence through the outer side of the orifice 3 to form the other part of a composite filament of the type illustrated in FIG. 4. Referring to FIG. 4, as the separate spinning materials are extruded from orifice 3, a composite filament is formed with the components eccentrically disposed towards each other in distinct zones. The adjoining surfaces of the components are in intimate, adhering contact with each other.

The expression "intrinsic viscosity" with the symbol (η) as used herein signifies the value of $\ln \eta_r$ at the ordinate axis intercept (i.e., when c equals 0) in a graph of

$$\frac{\ln \eta_r}{c}$$

as ordinate with c (grams of polymer per 100 ml. of solution) values as abscissas. η_r is a symbol for relative viscosity, which is the ratio of the flow times in a viscosimeter of a polymer solution and the solvent. $\ln$ is the logarithm to the base e .

WS viscosity is used as a measure of molecular weight or degree of polymerization of cellulose esters and ethers. This is calculated from measurements on a 0.0913% solution of polymer in 92% acetic acid at 25° C. in a modified Ostwald viscometer as follows:

WS viscosity = $(\eta_r - 1) (1000) = 1000 \eta_{sp}$ where the relative viscosity (η_r) is the ratio between the flow times of the solution and solvent in the viscometer.

In the following examples specific products of this invention are compared with prior known products. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Cellulose triacetate containing 2.9 acetyl groups per glucose unit (equivalent to 61.3% combined acetic acid) with a WS viscosity of 240 is dissolved in a 90/10 mixture of methylene chloride/methanol, to make a 21% solids spinning solution for one component (B) of a composite fiber.

Cellulose acetate containing 2.4 acetyl groups/glucose unit (equivalent to 55% combined acetic acid) with a WS viscosity of 185 is dissolved in acetone to make a 25% solids spinning solution for another component (A) of a composite fiber.

The two solutions are extruded at 60° C. through a spinneret similar to that shown in FIGURES 1 to 3 with 18 holes of 0.06 mm. in diameter into air at 100° C. and the two-component 18-filament yarn wound up at 200 yards per minute (y.p.m.).

The two solutions are also separately spun in a similar manner to make monocomponent filaments. All filaments are boiled in water for 1 minute, which causes the composite filaments to crimp. The monocomponent filaments remain uncrimped.

EXAMPLE II

The solution of cellulose triacetate in Example I is simultaneously extruded as component B with an 18.5%

5

solution of cellulose acetate (2.01 acetyl groups/glucose unit (49% combined acetic acid) and a WS viscosity of 175) in an 85/15 mixture of methylene chloride/methanol as component A. The resulting two-component 18-filament yarn is prepared as in A. Monocomponent filaments are prepared separately from each of the two solutions. A portion of each of the samples is boiled in water which crimps the composite (two-component) filaments, but leaves the monocomponent filaments uncrimped.

EXAMPLE III

Portions of the as-spun composite and monocomponent filaments of Example II are saponified in an aqueous solution containing 1% sodium acetate and 0.3% NaOH at 60° C. for 40 minutes in a slack (tensionless) condition. This treatment causes the composite filaments to crimp, but fails to crimp the monocomponent filaments. All samples are subjected to steam (while in a slack condition) at 25 p.s.i. for 30 minutes, which intensifies the crimp of the composite fibers. Analysis of the yarn shows that the cellulose triacetate is chemically unchanged by the saponification conditions, while the acetic acid content of the second component is reduced from 49 to 0%. Staple cut from the crimped product has the soft bulky luxurious handle associated with cashmere wool. Crimped fibers of this example have a tenacity of 1.0 gram per denier, an elongation at the break of 25%, and initial modulus of 35 grams per denier.

Similar results are obtained when as-spun composite fibers are saponified in a taut condition, but the level of crimp is decreased.

Data on the composite filaments and the corresponding monocomponent filaments are given in Table I, where it can be seen that as the difference in shrinkability between the two components increases (at a given denier), the intensity of the crimp increases under like conditions.

Data obtained from the readily spun items (Examples I and II) would not lead one to anticipate that the observed shrinkage trend would reverse itself at lower levels of acetic acid content or, alternatively, at higher content of hydroxyl groups. Thus, the results with the filaments of Example III are quite surprising.

6

2-inch lengths, hand-carded and made into pellets weighing 0.30 gram. These pellets are placed in a cylinder (0.5 inch diameter hole) under a freely sliding piston that exerts 5000 p.s.i. for two minutes. The height of the pellet is measured while under compression and also immediately after the pellet is removed. The pellet then is placed in 25° C. water and its height measured. The pellet is then removed from the water, air dried and its height again measured. The ratio of the immediate, wet and dried heights to the compressed height are expressed below, as "recovery."

Item	RECOVERIES		
	Immediate Compressed	Wet Compressed	Dried Compressed
I.....	1.5	6.5	8.3
II.....	1.4	4.2	4.8
III.....	1.3	12.1	13.1
Control.....	1.4	6.5	5.8

The Control, a self-crimped cellulose acetate filament, made according to U.S. Patent 2,431,435 issued to W. Taylor, is included for comparative purposes.

The data indicate the unusual recovery properties of filaments having the crimp reversibility (as shown by Item III) of this invention. The pellet behavior is directly analogous to the behavior of a fiber in a pile fabric and demonstrates the superior recovery from compaction of the filaments having crimp reversibility.

A soft, twill-woven fabric of the Surah type is woven from as-spun (uncrimped) yarn similar to that of Example II, and another fabric is woven from 80 and 150 denier yarns of single component filaments of cellulose acetate (54.9% combined acetic acid) having deniers per filament (d.p.f.) of 2.2 and 2.8. The fabrics are designated (a) and (b), respectively. Portions of each of the two fabrics are saponified in a slack condition according to conditions of Example III. Both saponified and unsaponified fabrics are then rinsed, scoured at the boil and dried.

Fabric (b) (unsaponified) has the appearance and

Table I

Example	Polymer Components				Monocomponent Filament Data						Composite Filament Data		
	A		B		Reversible Length Change, Percent			Shrinkability, Percent			Crimps/Inch		denier/ fila- ment
	OH glucose	Combined Acetic Acid, Percent	OH glucose	A	B	A—B	A	B	A—B	Dry	Wet		
I.....	0.59	55	61.3	0.10	2.0	0.80	1.2	1.5	0.8	0.7	2.0	0.0	10
II.....	0.99	49	61.3	0.10	3.3	0.80	2.5	0.0	0.8	-0.8	5.0	1.0	10
III.....	3.00	0.0	61.3	0.10	13.4	0.80	12.6	36.1	0.8	35.3	9.0	1.0	10
IV.....	0.17 sulfoethyl/ glucose, 2.41 acetyl/ glucose.		61.3	0.10	56.0	0.80	56.0	52.5	0.8	51.7	9.0	2.0	10
V.....	0.62 succinyl/ glucose, 1.86 acetyl/ glucose.		61.3	0.10	3.4	0.80	2.6	14.1	0.8	3.3	14.0	3.0	10

¹ Estimated from crimp dimensions.

In addition to possessing a differential shrinkability high enough to give a useful crimp level, the components of a composite filament should have a differential reversible length change of at least 4.0% and preferably 6.0% in order to provide filaments with a useful extent of reversible crimp. It has been found that a fiber should have a crimp reversibility of at least 5 and preferably 7 crimps per inch in order to exhibit in a fabric the beneficial results of this invention.

The crimped fibers of the above examples are cut into

handle of a typical known fabric of cellulose acetate continuous filaments.

Fabric (b) (saponified) has the appearance and very slick handle typical of continuous filament rayon fabrics

Saponification of fabric (a) converts the fibers therein to those of Example III. The saponification step causes the composite filaments present in fabric (a) to crimp, so that the finished fabric has a resilient, spun-yarn-like handle and an appearance similar to that of fine cotton.

The composite filaments in unsaponified fabric (a) crimped during the scouring and the finished fabric has a handle and appearance intermediate between fabric (a) saponified and fabric (b).

Samples of fabrics (a) saponified and (b) unsaponified of a size $\frac{1}{2}$ " by 1" are inserted in a holder, folded double and creased dry for 5 minutes under a 1 kilogram weight. Recovery of the creased member is then measured at the end of 300 seconds. Both fabrics show about 56% recovery. (Monsanto Wrinkle Recovery method—Monsanto Chemical Co., Textile Chemicals Dept., Boston, Mass.) The samples in their holder are then carefully immersed in 25° C. water, removed and dried in a gentle stream of 25° C. air. At the end of 30 minutes, the fabrics are dry and the control fabric ((b) unsaponified) shows 60% recovery, whereas the fabric made up of the fibers of this invention ((a) saponified) has straightened out almost completely so that it shows a recovery of 90%.

In a second series of evaluations, 2-inch squares of fabrics are wadded into a ball and pressed into a 20 mm. diameter test tube for 5 minutes. All samples upon standing in air for 5 minutes are quite wrinkled and show many sharp creases. The samples are then immersed in water and allowed to dry in a tensionless state. When dry, the fabric containing the filaments of this invention ((a) saponified) shows very diffuse creases which are much less noticeable than the very sharp and distinct creases found in the samples of control fabric (b) unsaponified. The fabric (a) unsaponified shows even poorer recovery from crease recovery than does the control fabric. The advantages of the higher level of crimp and crimp recovery in the filaments of this invention are quite obvious.

EXAMPLE IV

A sulfoethyl cellulose containing 0.17 sulfoethyl and 2.54 acetyl groups per glucose unit (total degree of substitution 2.71 per glucose unit) with a WS viscosity of 138 is prepared by acetylation and subsequent hydrolysis of sulfoethyl cellulose. An 18% solution of this product in a 90/10 mixture of methylene chloride/methanol is co-spun as component A with the solution of cellulose triacetate of Example I as component B under the conditions of that example. Sufficient shrinkage occurs on wetting and drying the as-spun yarn at room temperature, to crimp the composite filaments. Data on the homocomponent filaments and composite filaments are presented as item IV in Table I.

The advantages of using ionizable groups, such as sulfonic acid on a cellulose chain to promote crimp and crimp reversibility are evident upon comparison of component A of item IV with component A of item I in Table I. Both polymers have essentially the same degree of substitution of the cellulose chain (about 2.41).

EXAMPLE V

A cellulose acetate-hydrogen succinate containing 0.62 hydrogen succinyl and 1.86 acetyl groups per glucose unit with a WS viscosity of 216 is prepared by reaction of succinic anhydride with cellulose acetate of 1.86 acetyl groups per glucose unit using acetic acid as a solvent and sodium acetate as a catalyst. An 18% solution of this polymer in the solvent of Example IV is spun as component A using the cellulose triacetate solution of Example I as component B under the conditions of Example I. The as-spun composite filament develops a helical crimp upon boiling in water. Data on the crimped composite filaments and corresponding homocomponent filaments from components A and B are given in Table I as item V.

The above filament can be directly compared with item I in Table I, since component A of item V has a total degree of substitution of 2.48 acetyl groups per glucose unit (equivalent to 56% combined acetic acid)

and a similar WS viscosity. The advantage of using even as weak an ionizable group as hydrogen succinate over a filament containing no ionizable groups is readily seen.

EXAMPLE VI

This example illustrates the effect of adding certain modifiers to one of two otherwise equivalent cellulose ester components in a composite fiber so that the rate of saponification of one of the cellulose esters is altered and composite fibers of this invention are produced.

Spinning solutions are prepared from a cellulose acetate with 2.4 acetyl groups/glucose unit (i.e., 0.6 hydroxyl groups/glucose unit and containing 54.9% of combined acetic acid) with a WS viscosity of 185. A 25% solution in acetone is spun as one component of filaments B to J in Table II. Various modifiers are added to portions of one cellulose acetate, and acetone solutions of each portion, containing 25% of total solids, are co-spun as in Example I with component of items B to J. For comparison, item A in Table II is co-spun as in Example I from 21% and 25% solutions in 90/10 methylene chloride/methanol and acetone of two cellulose acetates containing 60.0 and 54.9% combined acetic acid (0.21 and 0.60 hydroxyl/glucose), respectively. All items have a total denier of 75 for the 18-filament yarn.

The crimp of the fibers is measured after a boil-off and also after a 10, 20 or 40 minute saponification treatment in a tensionless condition in an aqueous bath containing 0.3% sodium hydroxide and 1% sodium acetate at 60° C. The results are given below in Table II.

Table II

Item	Additive in 1 Component	Composite Filaments, Crimps per Inch at 25° C.—Dry/Wet			
		After Boil-off	After Saponification for		
			10 min.	20 min.	40 min.
A-----	none-----	6.1/4.8	8.6/7.9	-----	25.4/10.7
B-----	20% polyvinyl acetate.	12.6/12.4	26/11	18/11	-----
C-----	5% polyvinyl acetate.	-----	10/1.7	9.6/4.1	-----
D-----	5% Sorbitan monostearate.	6.3/5.5	9.6/3.8	11/3.4	-----
E-----	5% stearic acid-----	6.3/4.3	8.3/1.7	6.3/3.6	-----
F-----	5% calcium stearate.	-----	9.4/9.1	10/3.9	14/7.2
G-----	5% sucrose octaacetate.	9.1/9.1	8.1/3.5	12/1	14/4.9
H-----	5% carbowax 4000.	8.1/7.3	12/3.9	9.6/0	-----

In order to determine the effect of the modifier on the saponification of the fiber, single component filaments are also spun of the solutions containing the modifiers, and as-spun fibers submitted to a similar saponification treatment. These results show that polyvinyl acetate and sorbitan monostearate accelerate the saponification of the cellulose ester in which it is located. These results also indicate that the modifiers added in items E to H, respectively, retard the saponification of the cellulose ester in that component. It is obvious that such modifiers can be used to attain the required differential hydroxyl/glucose content of the two components in the composite fibers to obtain the fibers of this invention having crimp reversibility.

In addition to being able to control the extent of saponification by the presence of modifiers, it will be obvious to those skilled in the art that the saponification step can be altered within wide ranges by changing the time, temperature, kind and/or concentration of reagents used.

In accordance with one embodiment of this invention, cellulose derivatives which exhibit different rates of saponification are co-spun into a composite filament. For example, cellulose triacetate, which is essentially unaffected by some saponification procedures, is co-spun with

another cellulose ester that has at most a 2.6 and preferably 2.0 degrees of substitution per glucose unit. Alternatively, two cellulose derivatives, which are saponified at appreciably different rates, are co-spun as, for example, two cellulose esters containing 57.5 and 49%, respectively, combined acetic acid. The two components should differ in their degree of substitution by at least 0.4 and preferably 0.6 unit per glucose, although one skilled in the art will realize that the differential saponification rate will vary as the absolute level of substitution.

According to another embodiment there is added to one of the cellulose derivative components a modifying agent which either retards or accelerates the normal saponification rate. Proper selection of the second component with respect to saponification rate will then result in the required differential hydroxyl content between the components after saponification.

According to still another embodiment, cellulose derivatives which differ in ionizable group content by at least about 0.01 group per glucose unit may be utilized to provide the novel composite filaments of this invention. The best products containing a cellulose derivative with attached ionizable groups are those in which the cellulose derivatives differ by at least 0.05 ionizable groups. Ionizable groups in cellulose derivatives as a means of causing a differential reversible length change can be selected from acidic or basic groups. The invention has been illustrated by a sulfonic acid group connected to cellulose by an ether linkage (cellulose acetate-sulfo-ethyl cellulose) and by a carboxylic acid connected to the cellulose through an ester linkage (cellulose acetate-hydrogen succinate). Sulfonic acid derivatives are preferred to carboxylic acids due to their greater effectiveness. Suitable cellulose derivatives containing sulfonic acid by means of an ester linkage include: the sulfoacetate, sulfopropionate, sulfobutyrate, sulfoisobutyrate, sulfoisovalerate, sulfohexahydrobenzoate, sulfolaurate, sulfobenzoate, and sulfophthalate of cellulose.

Although this invention has been illustrated with cellulose acetates, suitable components may be found among all classes of fiber-forming cellulose derivatives, such as cellulose esters of single and mixed organic and inorganic acids, simple and mixed cellulose ethers and mixed cellulose ethers-esters. The term "cellulose derivative" refers to cellulosic compounds in which one or more hydroxyl groups has been replaced by another substituent group. Viscose rayon is not a "cellulose derivative."

Filaments of this invention may be drawn or not prior to crimping. If one of the cellulosic compounds does not contain more than 0.01 ionizable groups per glucose unit than another cellulose component in the composite filament, the shrinkability of one cellulosic component must be at least 3% and preferably 8% greater than the shrinkability of another component (as measured on homopolymer filaments) and one component of the crimped filament must have a reversible length change after the shrinkage of at least 4.0% and preferably at least 6% more than that of another component. The cellulosic components can be selected such that there will be a difference in hydroxyl content between two of the components of at least 1.1 and preferably 2.8 hydroxyls per glucose unit. This difference may be created by preferential saponification of one of the cellulosic components in the composite fiber. As illustrated in the examples, suitable modifiers may be added to one of the components prior to spinning so that the required differential shrinkage and reversible crimp is present in the composite fiber. In the case of cellulose derivative components containing ionic groups (i.e., sulfoethyl cellulose), the above criteria as to reversible length change need not obtain because such components may possess lower reversible length change values and still produce the composite filaments of this invention.

The amount of modifier to use will depend upon the

actual level of crimp and crimp reversibility desired in the crimped fiber and can be readily evaluated in single component filaments. There may also be added a modifier which becomes water sensitizing upon a brief saponification step which is insufficient to bring about the required differential properties between the two cellulose derivative components in the absence of the modifier.

Suitable cellulose ethers for use in this invention are sulfopropyl-, sulfobutyl-, sulfoisobutyl-, sulfobenzyl-, and sulfoethoxyethyl-cellulose, and similar carboxyl alkyl ethers of cellulose as, for example, carboxymethyl cellulose.

Suitable cellulose esters include cellulose propionate, cellulose butyrate, etc., mixed cellulose esters such as cellulose acetate propionate, cellulose acetate butyrate, etc., as well as mixed ether-esters of cellulose.

All manner of dibasic acids as oxalic, adipic, sebacic, phthalic, etc., can be used to make cellulose derivatives having one available carboxylic group in the acid or salt form.

Sulfonated cellulose derivatives made by treating an unsaturated cellulose derivative (as cellulose crotonate) with a bisulfite as taught by Dreyfus in U.S. Patent 2,321,069 issued June 8, 1943, are also useful in this invention.

Quaternary ammonium groups prepared, for example, by the reaction of pyridine with cellulose acetate-chloroacetate are also suitable for use in this invention.

The level of ionic modification to be selected will depend upon the physical properties desired as solubility, initial modulus, dyeability, etc.

The shrinking of the composite filaments in order to effect crimping may be carried out by the use of any suitable known shrinking agent. Shrinking may be done simultaneously with an after-treatment, such as saponification. Shrinking will ordinarily be carried out by the use of hot aqueous media, such as hot or boiling water, steam, or hot highly humid atmosphere, or by the use of hot air or other hot gaseous or liquid media inert to the polymers of the composite filaments. The shrinking temperature is generally in the neighborhood of 100° C. but may be higher or lower, e.g., 50° C. up to about 150° C. or even up to a temperature not exceeding the melting point of the lowest melting polymeric component of the fiber.

Although this invention has been illustrated with dry spinning, it is, of course, applicable to filaments prepared by wet spinning, plasticized melt spinning, as described in U.S. Patent 2,706,674 issued to Rothrock on April 19, 1955, or melt spinning.

The filaments of the above examples and yarns produced therefrom possess in common with all the filaments of this invention the characteristic of crimp reversibility, that is, the ability to return to the original crimp state spontaneously after having been treated with a swelling agent and after removal of the swelling agent following such treatment. Thus, these yarns impart a renewable surface to fabrics prepared therefrom. One of the important novel features of this invention is that crimp may be imparted to a fabric filament without the stretching or drawing step of the prior art.

The preferred filaments of this invention are those which have been crimped by a suitable shrinking treatment and which upon being swollen lose a portion of the crimp. Such filaments may be woven or knitted, either in the potentially crimpable or in the crimped state, as continuous filaments or as staple fibers, and if woven in the uncrimped or potentially crimpable state, the crimp may be developed in the fabric by treatment with a suitable shrinking agent. The crimped filaments of the fabric will, upon treatment with a swelling agent, as by aqueous treatment in the washing, scouring, dyeing, and other treatments normally applied to fabrics, move around or squirm during such treatments with considerable freedom and upon removal of the swelling agent

regain the lost crimp with the imparting of a fullness and highly increased covering power to the fabric.

Not only is this "renewable" characteristic of advantage in the type of fabric used for clothing, but it is of great importance in pile fabrics such as those used in carpets and upholstery, where the compacting of the fibers under compression incident to use may be overcome by treatment with water or other swelling agent to cause the fibers to squirm or work out of the compressed state, but, upon drying, the fibers will again revert to their highly crimped and voluminous state prior to their having been compressed.

Although the invention has, in its preferred form, been applied to filaments which lose at least a part of their crimp upon the swelling treatment, it is within the scope of this invention to utilize a reversible crimp wherein the crimped filaments actually gain additional crimp upon treatment with a swelling agent; in this case, also, the filaments squirm and work around with respect to each other upon treatment with a swelling agent and also upon removal of the swelling agent as by drying, thereby, because of the freedom of movement of the filaments even with increased crimp, insuring the imparting of increased fullness, bulk and covering power to the fabric.

The claimed invention:

1. A freshly formed essentially undrawn composite cellulosic filament crimpable from the straight state upon shrinking comprised of at least two cellulosic components having substantially different shrinkages, said components being eccentrically disposed towards each other in distinct zones with adjoining surfaces being in intimate adhering contact with each other, said filament having a crimp reversibility after shrinkage of at least five crimps per inch characterized by squirming of said filament upon treatment in a relaxed condition with a swelling agent and upon subsequent removal of a swelling agent, at least one of said components being a polymeric derivative of glucose units selected from the group consisting of cellulose ethers and esters and mixed cellulose ether-esters, one of said components having a reversible length change of at least 4% greater than any of said other components when treated with a swelling agent with said component substantially returning to its original length upon removal of said swelling agent.

2. The filament of claim 1 in which two of the components have a shrinkability difference of at least 3% and one component has a reversible length change after shrinkage at least 6% more than the other component.

3. The filament of claim 2 in the crimped state.

4. A fabric comprising filaments of claim 2.

5. The filament of claim 2 in which two of the cellulosic components have a shrinkability difference of at least 8% and one component has a reversible length change after shrinkage of at least 6% more than the other component.

6. The filament of claim 5 in which the cellulosic components are cellulose acetate.

7. A freshly formed essentially undrawn composite cellulosic filament crimpable from the straight state upon shrinkage comprising at least two cellulosic polymer com-

ponents having a difference in shrinkage of at least 3%, said components being eccentrically disposed towards each other in distinct zones with adjoining surfaces being in intimate adhering contact with each other, at least one of said components having ionizable groups selected from the group consisting of sulfonic and carboxylic acid derivatives attached to said polymer through linkages selected from the class consisting of ether and ester linkages, said two cellulosic components having a crimp reversibility after shrinkage of at least five crimps per inch characterized by squirming of said filament upon treatment in a relaxed condition with a swelling agent and upon subsequent removal of said swelling agent, said two cellulosic components having a difference in ionizable groups of at least 0.01 per glucose unit of said cellulosic polymer, one of said components having a reversible length change after shrinkage evidenced by an increase in length of at least 4% greater than any of said other components when treated with a swelling agent with said component substantially returning to its original length upon removal of said swelling agent.

8. The filament of claim 7 in the crimped state.

9. The filament of claim 7 in which one of the components contains at least 0.05 more ionizable groups per glucose unit than the other component.

10. A fabric comprising filaments of claim 1.

11. A freshly formed essentially undrawn composite cellulosic filament crimpable from the straight state upon shrinkage comprising at least two cellulosic polymer components having a difference in shrinkage of at least 3%, said components being eccentrically disposed towards each other in distinct zones with adjoining surfaces being in intimate adhering contact with each other, at least one of which is selected from the group consisting of cellulose ethers, cellulose esters, and mixed cellulose ether-esters having substantially different shrinkages, said filament having a crimp reversibility after shrinkage of at least five crimps per inch characterized by squirming of said filament upon treatment in a relaxed condition with a swelling agent and upon subsequent removal of said swelling agent, said two components having a difference in hydroxyl content of at least 1.1 hydroxyl groups per glucose unit of said cellulosic polymer, one of said components having a reversible length change after shrinkage evidenced by an increase in length of at least 4% greater than any of said other components when treated with a swelling agent with said component substantially returning to its original length upon removal of said swelling agent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,428,046	Sisson et al.	Sept. 30, 1947
2,439,813	Kulp et al.	Apr. 20, 1948
2,439,814	Sisson	Apr. 20, 1948
2,439,815	Sisson	Apr. 20, 1948
2,517,694	Merion et al.	Aug. 8, 1950
2,686,709	Woodell	Aug. 17, 1954
2,775,505	Pedlow	Dec. 25, 1956