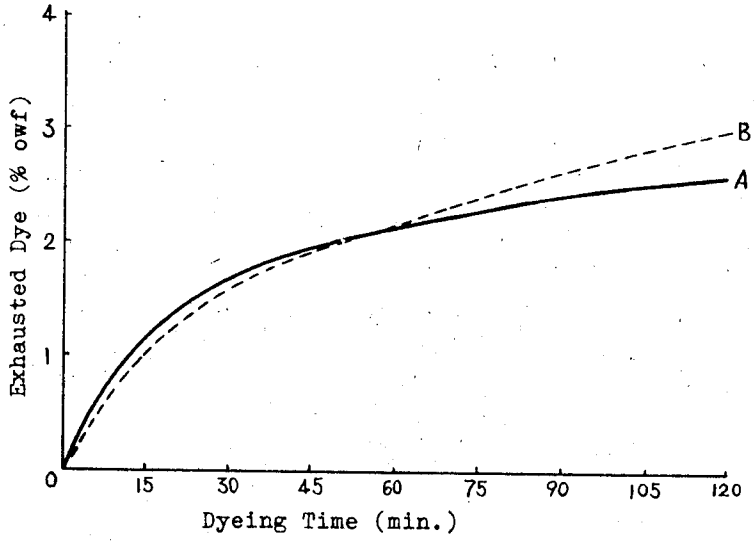
June 2, 1970 HIDETO SEKIGUCHI ET AL 3,515,627

ACRYLIC COMPOSITE FIBERS HAVING IRREVERSABLE THREE DIMENSIONAL COIL CRIMPS

Filed March 24, 1967



Hideto Sekiguchi, Keitaro Shimoda and Kenji Takeya, Inventors

By Wenderoth, Lind and Ponack, Attorneys

United States Patent Office 3,515,627 Patented June 2, 1970

3,515,627

ACRYLIC COMPOSITE FIBERS HAVING IRREVERSIBLE THREE-DIMENSIONAL COIL CRIMPS

Hideto Sekiguchi, Keitaro Shimoda, and Kenji Takeya, Saidaiji, Japan, assignors to Japan Exlan Company Limited, Osaka, Japan

Filed Mar. 24, 1967, Ser. No. 625,781
Claims priority, application Japan, Mar. 26, 1966, 41/18,866
Int. Cl. D01a 5/22; D02g 3/04
U.S. Cl. 161—173 6 Claims

ABSTRACT OF THE DISCLOSURE

An acrylic composite fiber comprising two different acrylic polymer components laminarly conjugated together along the length of the fiber, said components consisting predominantly of acrylonitrile but copolymerized with at least one hydrophobic non-crystalline high polymer-forming comonomer in different proportions so as to cause difference in thermal shrinkage between said components, the high shrinkage component containing a strong acidic group providing dyeing site for a cationic dye in an amount less than that in the other fiber component so that the initial dyeing rates of these two components are substantially equal and the fiber has three-dimensional coily crimps which are irreversible even when exposed to water or other swelling agent. Each component contains 5–15% by weight of the hydrophobic non-crystalline high polymer-forming comonomer, but there is a difference of 0.5–6% by weight in content of said comonomer between the two acrylic polymer components.

This invention relates to acrylic composite fibers which have improved crimp characteristics and can be well dyed with cationic dyes. More particularly the present invention relates to acrylic composite fibers having various characteristics wherein two types of acrylic polymer components are uniformly laminarly arranged along the entire lengths of the fibers, three-dimensional coily crimps being formed due to the difference in thermal shrinkage between the two components. Once developed these coily crimps have no water-reversibility, and therefore defects such as are often observed in conventional acrylic composite fibers, e.g. a part of the crimps vanishing when the fibers are washed, causing elongation and therefore a decrease in the dimensional stability, are eliminated. In the present invention, dimensions are stable even if the fibers are washed, and the two acrylic polymer components of different shrinkage characteristics in the same single fiber are not delaminated or separated from each other, nor is thread splitting caused. Further, the initial rates of dyeing of both components forming the acrylic composite fibers of the present invention, with a cationic dye, are substantially equal, and both components have an even or level dyeability. The fibers of this invention have an excellent woolly elasticity and hand.

Many efforts have been made to impart excellent woolly elasticity and hand to synthetic fibers. This has been attained to a considerable degree in certain acrylic composite fibers. However, the conventional acrylic composite fibers exhibit only an imitation of a part of the properties of wool and are neither woolly in their entirety nor have characteristics superior to the properties of wool. As regards the dimensional stability, for example, in washing, woolen products have a defect in that, as washing is repeated, due to the peculiar shrinkability in addition to the water-reversibility of the crimps, they will shrink remarkably. Further, the invention of Breen disclosed in U.S. Pats. Nos. 3,038,236, 3,038,237 and 3,039,524, which is considered to be one providing typical conventional acrylic composite fibers, gives a product having water-reversible crimps by conjugating two components having a difference in the ionizing radical contents. In addition the principle of Sisson, noted in U.S. Pat. No. 2,439,815, gives an excellent elasticity and hand. However, acrylic composite fibers based on this principle have great disadvantages. The dimensional instability in washing is one of such defects. That is to say, there is a defect in that, since a part of crimps will vanish and decrease when wet, the fibers will elongate when the fibers are washed. Thus, while wool has a defect in that it will shrink remarkably, the acrylic composite fibers by the invention of Breen have a defect in that they will elongate.

According to Breen, the water-reversible crimps are of such property that, with the action of water or other swelling agent, the amount of crimps will vary and, when the swelling agent is removed, the original crimped state will be restored. In the testing method shown in the example of Breen's U.S. patents, this is called an equilibrium crimp reversibility, which is a value obtained after the fibers are left in a wet state at 70° C. for 6 hours and are then dried at 70° C. for 16 to 24 hours and this treatment is repeated until the dry-wet crimp difference becomes constant. However, in the step of processing fiber products or in the process of wearing them as clothes or repeating the washing and drying of them, the conditions of such high temperature and long time as 70° C. in a wet state for 6 hours and 70° C. in a drying process for 16 hours cannot feasibly be adopted. In case the crimps vary in the dry and wet states, such deformations as extension, shrinkage, bend and twist will occur in every part of the fibers. However deformations of the fibers will be subject to a decisive velocity influence from the temperature, medium and time in the environment. For example, even if fibers have fixed crimps in equilibrium at a fixed temperature in a fixed medium, the equilibrium value will be obtained only when the fibers are placed in the particular environment for a sufficient length of time. Even if the equilibrium value is obtained under such testing conditions as are defined by Breen, in practical use there will be obtained only a value in the course of variation proceeding to the equilibrium value. That is to say, formation of the crimps will be determined by the velocity of the variation to the equilibrium value and the crimps will be obtained only when sufficient time has lapsed to achieve the equilibrium value. More particularly, if the wetting and drying temperature and time conditions are respectively different, the water-reversible crimps will be of degrees which differ accordingly. For example, in summer and winter, the washing and drying temperatures are different. Further, in domestic washing and commercial washing, the respective temperature and time conditions are different. Even in the dyeing process, the same thing is presumed. Even if any one of these different conditions is present, no sufficient equilibrium crimp value will be obtained. In all cases, only crimps of respectively different degrees will be obtained. products having many crimps shrink well and are high in the elasticity. On the other hand, products having few crimps tend to extend, are low in the elasticity, are therefore low in the dimensional stability and fluctuate remarkably in elasticity and hand. What is more important is that generally, in the process of working or practicing clothing products, under wet conditions the deformations of the fibers are more in a process of a higher variation velocity. It has been discovered that synthetic fibers containing a large amount of an ionizing radical in the invention of Breen, which is deemed specifically as a typical ex-

ample of acrylic composite fibers, tend strongly to become deformed by water so that the variation velocity of crimps is higher in the wet state even under the same temperature and time conditions. Therefore, generally, in the water-reversible crimps, the rate at which the crimps vanish and the dimensions elongate due to water is higher than the rate at which the crimps return and shrink due to drying. That is to say, in the known process, as the wetting and drying are repeated, the crimps will tend to decrease and the dimensions will tend to extend.

It has been discovered that, due to coily crimps of composite fibers, the elastic recovering property will rise and therefore an excellent woolly elasticity and hand will result, but in fibers having water-reversible crimps, the crimp retention and dimensional stability are so low that coily crimps cannot be a feasible means of overcoming the defects of the deterioration of the elasticity and hand, due to washing and the dimensions being likely to extend.

Therefore, an object of the present invention is to provide an acrylic composite fiber product which has the same elasticity as wool, due to irreversible coily crimps of acrylic composite fibers, does not so remarkably shrink as wool as regards the stability of the dimension and form, does not have the defect that, in the repetition of wetting and drying, the crimps vanish and the fibers extend as in conventional water-reversible acrylic composite fiber products, and has a permanently stable crimpability.

Another object of the present invention is to make the initial rates of dyeing of both components (referred to as A and B) of acrylic composite fibers, with a cationic dye, equal to each other. This is very important in the dyeing process.

In Breen's U.S. patents considered to be a typical example of conventional acrylic composite fibers, the difference in the content of an ionizing radical which is a dyeing site of acrylic fibers in both components is utilized as a means of giving water-reversible crimps. This results in some difficulties, as the ionizing radical is used for both the dyeing site and the means of obtaining water-reversible crimps. Specifically, from the viewpoint of dyeing, the difference in the content of the ionizing radical between the two components of composite fibers is unduly large so that the dyeability will become different between the two components and therefore the uniform property of dyeing will deteriorate. After dyeing, the degree of dissociation of the ionizing radical will diminish and hence the hydrophilicity will decrease, resulting in a remarkable decrease of crimps. Further, the difference in the properties of both components of the composite fibers will be so remarkably large that the yarn will be likely to delaminate or split into the two components.

It has been discovered that the above drawbacks are overcome and the objects of the invention are accomplished by providing acrylic composite fibers which have been wet-spun and in which two or more types of acrylic polymer components, different in their thermal shrinkage, are uniformly laminarly arranged along the entire lengths of the fibers. Each component contains at least 5 to 15% by weight of a hydrophobic noncrystalline high polymer-forming comonomer in the form of a copolymer with acrylonitrile, there being a difference of less than 6% by weight in the content of said hydrophobic noncrystalline high polymer-forming comonomer between the acrylic polymer components. Further, the acrylic copolymer component which is higher in the content of the hydrophobic noncrystalline high polymer-forming comonomer (that is, the component exhibiting higher thermal shrinkage) is made to contain a strong acid radical, forming a dyeing site for a cationic dye bonded with the polymer, in an amount which is smaller by 4 to 30 milliequivalents per 10^3 grams of the polymer than the amount which is contained in the copolymer component which is lower in the content of the hydrophobic noncrystalline high polymer-forming comonomer (that is, the copolymer component exhibiting lower thermal shrinkage). In this way the initial dyeing rates of both components with the cationic dye will be substantialy equal to each other. The resulting heat treated fibers have three-dimensional coily crimps irreversible in water and other swelling agents.

According to the present invention, each component is copolymerized with at least 5% by weight and at most 15% by weight of a hydrophobic noncrystalline high polymer-forming comonomer, and there is a difference of less than 6% by weight of the hydrophobic noncrystalline high polymer-forming comonomer between the two components. The respective polymers are simultaneously and compositely spun, through a common orifice in an art-recognized manner. Thus a difference of more than 1% in the thermal shrinkage between the components during drawing and heat-treating the spun yarn is created due to the difference in content of the said comonomer. Further, the content of the strong acid radical in the high shrinkage component is from 4 to 30 milli-equivalents per 10^3 grams of the polymer less than the content in the low shrinkage component, thus cancelling the difference in the water-swellability (and hence water-reversibility of crimps) caused by the differences in the degree of orientation and the cohesive energy in the noncrystalline regions of both components. The coily crimps to be developed due to the differences in the degree of orientation and the cohesive energy in the noncrystalline region are indicated by the likelihood of the fibers being deformed in hot water at 90° C. or, for example, the reciprocal number of the modulus of elasticity in hot water at 90° C., that is, a compliance J_w^{90}. But the fiber components higher in the compliance J_w^{90} in hot water are much higher in their swellability in hot water that, even if the ionizing radicals of both components are made equal, the water-reversibility of the crimps will not be able to be removed. Each component is made to contain 5 to 15% by weight of the hydrophobic noncrystalline high polymer-forming comonomer. In case the content is less than 5% by weight, in the aqueous wet spinning, the fiber gel swelling degree after coagulation will be so high that the shrinkage in drying will be high, and therefore substantially no shrinking performance will be observed in the subsequent heat-treating operation, and the degree of the noncrystalline region production will be low. Further, a content of less than 5% of said comonomer will not be desirable from the viewpoint of dyeability. When the content is more than 15% by weight, the softening point will be lower, and the heat-resistance will be remarkably lower.

The difference in the hydrophobic noncrystalline high polymer-forming comonomer content between both components is kept 6% or less by weight. If there is a difference of 6% by weight at most, coily crimps necessary and sufficient to elevate the elasticity, as of knitted and woven products, will be obtained. If there is a difference larger than that, the degree of yarn delamination in the two components will be so high that acrylic composite fibers having permanent crimps will not be obtained. Further, if the difference in content of the non-crystalline high polymer-forming comonomer between both components is 0.5% by weight, the objects of the invention are attained.

The high thermal shrinkage component polymer is made to contain, as bonded with the polymer, the strong acid radical forming a dyeing site for a cationic dye in an amount smaller by 4 to 30 milli-equivalents per 10^3 grams of the polymer than in the other component (that is, the low thermal shrinkage component polymer). This is based on the fact that the water-reversibility of the crimps produced due to the difference in the content of the hydrophobic noncrystalline high polymer-forming comonomer between both components can be thereby

cancelled. Furthermore, only when the amount of strong acid radical, forming the dyeing site of the high shrinkage component polymer is made less than that of the low shrinkage component polymer by an amount of 4 to 30 milli-equivalents per 10^3 grams of the polymer, will the initial dyeing rates of the two components with a cationic dye become substantially equal to each other.

The respective components having equal initial rates of dyeing with a cationic dye will not only be able to be very uniformly dyed even if composite fibers having any component ratio or any distribution of component ratios are made, or even in the case of yarns spun as blended with yarns of an acrylic single component corresponding to one of the components, but also will have a tendency to exhibit similar hydrophilicity and other physical properties of fibers equal in dyeing rate. Therefore, it is very rare that the yarn will split into the two components. These facts are one of the most important features of the present invention.

In the high shrinkage component of the fiber of the present invention, the hydrophobic noncrystalline high polymer-forming comonomer is contained in an amount higher than in the low shrinkage component but the content of the strong acid radical which is a dyeing site for a cationic dye is less than that in the low shrinkage component. Therefore, such physical properties as the swellability with water of both components are substantially equal and the uniform dyeing effect of both components in the initial period of dyeing with the cationic dye is remarkably promoted. Therefore, the yarn split is less than in the conventional acrylic composite fibers. The difference in the thermal shrinkage between both components which can be utilized to obtain the practically necessary permanence of crimps and even dyeability, that is, the range of the copolymer composition can be adopted more widely than in conventional composite fibers.

In the present invention, the initial dyeing rates of both components of composite fibers with a cationic dye are made substantially equal. Uniform dyeing is important particularly in the case of light color dyeing. Its decisive influence is given by the initial dyeing rate at the beginning of dyeing. Therefore, the dyeing is begun generally at a low dyeing rate by a method of gradually elevating the dyeing bath temperature so that an even dyeing may be obtained.

Tentatively, the initial dyeing rate has been determined by the following manner. The filters are dyed at a dyeing bath temperature of 90° C. for 60 minutes with Sumiacryl Orange 3R (produced by Sumitomo Chemical Co., Ltd.) as a cationic dye, under the following dyeing bath conditions: a dye concentration of 7% of the weight of the fibers (abbreviated as % OWF hereinafter), 3% OWF acetic acid and a bath ratio of 1/100. The initial dyeing rate is represented by the exhausted amount of the dye on the fibers in percent OWF in this standard condition. We further obtained isothermal dyeing curves and investigated the initial dyeing performances. It has been recognized from the dyeing curves shown in the accompanying drawing that, as the number of dyeing sites of the high shrinkage component is made less than the number of dyeing sites of the low shrinkage component to make the initial dyeing rate of both components substantially equal, and as the equilibrium is approached due to dyeing for a long time, the dyed amount of the high shrinkage component will decrease. In order to make the dyeing rates of the high shrinkage component and low shrinkage component equal to each other and to eliminate the water-reversibility of the fibers, though the dyeing rate will differ depending on the difference in the compliance J_w^{90} between both components, the number of coily crimps, and the level of the total amount of the dyeing sites and also depending on whether the level of such total amount of the dyeing sites is to be equal to the number of woolly crimps as is required for thick color dyeing of acrylic fibers with a cationic dye, it will be necessary to make the content of the strongly acid radical in the high shrinkage component less than the content of the strongly acid radical in the low shrinkage component by at least 4 milli-equivalents per 10^3 grams of the polymer at the minimum. Further, as a result of investigations, it has been found that, when a difference of 30 milli-equivalents per 10^3 grams of the polymer is given as the maximum, the objects of the present invention will be attained. When a difference larger than 30 milli-equivalents per 10^3 grams of the polymer is given, the water-reversibility of the crimps will be in the negative direction, that is, the crimps will increase when wet but will decrease when dry and therefore it will not be desirable from the viewpoint of the stability of the crimps.

The hydrophobic high polymer-forming comonomers to be copolymerized with acrylonitrile in the present invention are those which are substantially insoluble in water, and do not readily form crystalline high polymers. Examples of such comonomers are acrylic esters such as methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, methoxyethyl acrylate, phenyl acrylate, cyclohexyl acrylate, dimethylaminoethyl acrylate; the corresponding methacrylic esters; vinyl chloride, vinylidene chloride, vinylidene cyanide, styrene, their alkyl substitutes; unsaturated ketones such as methyl vinyl ketone, phenyl vinyl ketone, isopropenyl methyl ketone; carboxylic acid vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl thiol acetate, vinyl benzoate; vinyl ethers and esters of ethylene α,β-carboxylic acids such as fumaric acid, citraconic acid, mesaconic acid, aconic acid, etc.

For introducing the strong acid radical into the copolymers forming the acrylic composite fibers in the present invention, there may be utilized a method wherein a sulfonic acid radical produced by the decomposition of a catalyst in the polymerizing reaction is introduced into the terminal radical of the polymer. However, the most general method is wherein sulfonic acid radicals are positively introduced into the copolymer. For example, a monomer which contains unsaturated sulfonic acid radical such as an alkenyl aromatic sulfonic acid, p-styrene sulfonic acid, vinyl sulfonic acid, allyl sulfonic acid or methallyl sulfonic acid or their salts, and can be copolymerized with acrylonitrile, is copolymerized with acrylonitrile. Other unsaturated organic sulfonic acids such as o- and m-styrenesulfonic acid, allyloxyethylsulfonic acid, methallyloxyethylsulfonic acid, allyloxypropanolsulfonic acid, allylthioethylsulfonic acid, allylthiopropanolsulfonic acid, isopropenylbenzenesulfonic acid, vinylbromobenzenesulfonic acid, vinylfluorobenzenesulfonic acid, vinylmethylbenzenesulfonic acid, vinylethylbenzenesulfonic acid, isopropenylbenzenesulfonic acid, vinylhydroxybenzenesulfonic acid, vinyldichlorobenzenesulfonic acid, vinyltrihydroxybenzenesulfonic acid, vinylhydroxynaphthalenesulfonic acid, sulfodichlorovinylnaphthalenesulfonic acid, vinylhydroxyphenylmethanesulfonic acid, vinyltrihydroxyphenylethanesulfonic acid, 1-isopropylethylene-1-sulfonic acid, 1-acetylethylene-1-sulfonic acid, naphthylethylenesulfonic acid, propenesulfonic acid, butenesulfonic acid, hexenesulfonic acid and their salts may also be used.

It is not desirable that the content of the strong acid radical in the polymer forming the acrylic composite fibers in the present invention exceed 100 milli-equivalents per 10^3 grams of the polymer. That is to say, in the acrylic composite fibers of a composition in which more than 5% by weight of a hydrophobic noncrystalline high polymer-forming comonomer is copolymerized, as the content of the strong acid radical exceeds 80 milli-equivalents per 10^3 grams of the polymer, defects result, such that the water absorption even at the normal temperature will increase, Young's modulus will be likely to diminish due to the action of water or other swelling agents, the reversibility of the crimps will be likely to develop, the dyeing rate will become unduly high, and spots or uneven dye-

ing will occur in dyeing, or specifically light color dyeing.

It is preferable that each of the composite fiber components comprises at least 85% by weight of acrylonitrile.

The composite fibers of this invention may be spun in any proper device known in the art of the production of composite fibers. For example, a spinning apparatus of the type shown and described in U.S. Pat. No. 3,182,106 may conveniently be used.

The invention will be described in more detail by referring to the following examples wherein all percentages are by weight unless otherwise specified and wherein various values have been determined in the following manners:

The content of the strong acid radical in the acrylic polymer was measured by passing a dimethyl formamide solution of the copolymer through an ion exchange resin to convert the strong acid radical into the form of a free acid and then conductometric titration with a caustic soda solution was employed. The results of the analysis are represented in milli-equivalents of the acid radical per 10^3 grams of the copolymer. The molecular weight of the polymer was calculated by converting the measured value of the viscosity of the dimethyl formamide solution at 30° C. by using Standinger's formula.

The fundamental crimp frequency (C_f) was measured by the formula:

$$C_f = \text{number of crimps} \left(1 - \frac{\text{crimp index}}{100}\right) \quad (1)$$

by determining the number of crimps and crimp index in respect to crimped fibers which have been relaxed in boiling water. The crimp frequency (number of crimps) was determined by counting the crimp number per 25 mm. of the fiber under an initial load of 2 mg./denier. The test was repeated 20 times and the average value was taken.

The crimp index was measured by the formula:

$$\text{Crimp index} = \frac{b-a}{b} \times 100 \quad (2)$$

wherein a is the length of the sample fiber under the initial load of 2 mg./denier and b is the length at 30 seconds later after an additional load of 50 mg./denier has been placed on the fiber.

The value of the water-reversibility of the crimps, as represented by ΔC_f in Formula 3, is determined by the difference between the value C_f (wet at 70° C.) obtained by measuring C_f defined as mentioned above after the crimps were relaxed in water at 70° C. for 6 hours, and the value C_f (dry at 20° C.) obtained by measuring C_f after the crimps were dried at 70° C. for 16 hours and were cooled to room temperature:

$$\Delta C_f = C_f \text{ (dry at 20° C.)} - C_f \text{ (wet at 70° C.)} \quad (3)$$

As C_f and ΔC_f are inversely proportional to the diameter of the fiber under a fixed shrinkage difference and a fixed environment, it is necessary to represent fibers of different diameters as converted to a fixed standard. A fiber of 3 deniers was used as a standard. It is necessary that the water-reversibility ΔC_f should be less than 0.85 at 3 deniers in order that the crimps may be substantially irreversible. The thread split of acrylic composite fibers was represented by the percentage (%) of the fiber which peeled into two components when the fiber suspended under a load of 0.4 g./d. was rubbed with the side of a hard chrome-plated stainless steel bar of an octagonal cross-section rotated at 3500 r.p.m. for 10 minutes, and the cross-section of the fiber was subsequently observed with a microscope.

EXAMPLE 1

For the component A of acrylic composite fibers, in obtaining a copolymer of 89.0% acrylonitrile, 11.0% methyl acrylate and a molecular weight of 74,000, a chloric acid-sulfurous acid catalyst system was used. A slight amount of sodium methallylsulfonate was also copolymerized with the acrylonitrile, and the content of the sulfonic acid radical introduced at the terminal of the polymer both by means of the decomposition of the catalyst and positive introduction, was adjusted to 38 milli-equivalents per 10^3 grams of the polymer. For the component B, in obtaining a copolymer of 91% acrylonitrile, 9% methyl acrylate and a molecular weight of 74,000, the amount of sodium methallylsulfonate copolymerized with acrylonitrile, was adjusted in the same manner as in the copolymer of the component A so that the total sulfonic acid radical content was 50 milli-equivalents per 10^3 grams of the polymer. Each of both copolymers A and B was dissolved in an aqueous solution of 48% sodium thiocyanate to prepare a spinning solution so that the copolymer concentration was 9%. Filaments wet-spun into an aqueous solution of 10% sodium thiocyanate at 0° C. with a composite fiber spinning apparatus shown in U.S. Pat. No. 3,182,106, in a manner such that the amounts of both components A and B were equal to each other, were drawn to 10 times their length in boiling water and were dried in hot air at 115° C. When the obtained acrylic composite fibers were heated in pressure steam at 123° C. for 10 minutes, due to the difference in the thermoshrinkage between both components, coily three-dimensional crimps of fundamental crimp frequency C_f of 22 developed in the fibers of 3 deniers. These crimps showed a water-reversibility value ΔC_f of 0. When each of both components A and B was singly spun, drawn and heated under the same conditions as above, the amount of dye exhaustion on the single component fibers was shown to be 2.12% OWF in the component A and 2.16% OWF in the component B, thus indicating substantially equal values. The isothermal dyeing curves of the respective components A and B at 90° C. coincided with each other very well at the initial dyeing rate as shown in the drawing. Therefore, when the composite fibers were dyed under the same conditions to prepare samples of fiber cross-sections and the dye concentrations in both components were compared with each other under a microscope, it was quite impossible to distinguish the two components from each other. The yarns spun of these composite fibers and the products knitted or woven from the yarns were very high in uniformity of dyeing, specifically in light color dyeing, and showed a very fine finish. Further, no thread splitting into the two components was observed.

EXAMPLE 2

The adjustment of the content of a strong acid radical for making the dyeing rate uniform, and obtaining acrylic composite fibers having no water-reversibility of crimps, can also be achieved by employing a difference between the molecular weights of the polymers. The component A was obtained by aqueous suspension polymerization of a copolymer of 90% acrylonitrile, 10% methyl acrylate and had a molecular weight of 75,000. This copolymer contained 20 milli-equivalents of a sulfonic acid radical per 10^3 grams of the polymer, introduced by the decomposition of the catalyst system of Example 1. The component B was obtained by aqueous suspension polymerization of a copolymer of 92% acrylonitrile, 8% methyl acrylate and had a molecular weight of 53,000. This copolymer contained 44 milli-equivalents of a sulfonic acid radical per 10^3 grams of the polymer, by the same mechnism as in component A.

The component A copolymer was dissolved in an aqueous solution of 47% sodium thiocyanate, the copolymer concentration being 9%, to prepare a spinning solution. The component B copolymer was dissolved in an aqueous solution of 47% sodium thiocyanate, the copolymer concentration being 12%, to prepare a spin-

ning solution. The respective solutions of the components A and B were spun into an aqueous solution of 5% sodium thiocyanate at 0° C. with the same composite fiber spinning apparatus as in Example 1, so that the net weights of the respective copolymers were equally delivered. The thus obtained filaments were drawn to 10 times their length in boiling water, were then dried in hot air at 115° C. and were heated with pressure steam at 125° C. for 10 minutes, resulting in coily three-dimensional crimps being developed by means of the difference in the thermoshrinkage between both components. These acrylic composite fibers were fibers of 3 deniers. Their fundamental crimp frequency C_f was 20. Their water-reversibility value ΔC_f was −0.4. This water-reversibility value was negligible. Thus, products very high in dimensional stability were obtained. These composite fibers were so high in the molecular weight of the high shrinkage component and in the elatsicity and strength of the load supporting component in stretching the crimps that the permanence of the crimps was very high. The amount of dye exhaustion on single component fibers of 3 deniers obtained by singly spinning, drawing and heating each of the components A and B under the same conditions as are mentioned in Example 1, was shown to be 1.08% OWF in the component A and 1.16% OWF in the component B. Thus they had substantially equal dyeing rates.

EXAMPLE 3

The adjustment of the strong acid radical can be achieved by a method which combines the adjustment of the molecular weight of only one fiber component, and the adjustment of the addition amount of a monomer, containing a strong acid radical, to be copolymerized with acrylonitrile in the polymer chain of the same fiber component. It is also possible to vary the kind of hydrophobic non-crystalline high polymer forming comonomer to obtain a difference in the non-crystalline structure. In this example, for the component A, in copolymerizing 89% acrylonitrile and 11% vinyl acetate, a copolymer resulted in which the content of a sulfonic acid radical was adjusted with the addition of nonaddition of sodium methallylsulfonate. The variation of the molecular weight was as shown in Table 1. For component B, in the copolymerization of 91% acrylonitrile and 9% methyl acrylate, a slight amount of sodium methallylsulfonate was copolymerized with the acrylonitrile, and, the content of a sulfonic acid radical was adjusted to 50 milli-equivalents per 10^3 grams of the polymer. The copolymer had a molecular weight of 58,000. Each of both component polymers was dissolved in an aqueous solution of 48% sodium thiocyanate, the copolymer concentration being 11%, to prepare a spinning solution. Composite fibers and single component fibers were spun under the same conditions as in Example 1, were drawn to 10 times their length, and were treated with pressure steam to obtain fibers of 3 deniers. The characteristics of the resultant fibers are shown in Table 1.

TABLE 1

	Experiment No.						
	I	II	III	IV	V	VI	VII
	Pressure steam treating temperature (° C.)						
	120	123	123	123	121	121	130
Component A copolymer composition:							
Molecular weight	58,000	58,000	62,000	66,000	67,100	73,900	84,500
Total sulfonic acid amount in milli-equivalents per 10^3 grams of the copolymer	46	43	41	39	36	32	27
Single component fibers:							
Amount of dye exhaustion:							
A (percent OWF)	2.30	2.28	2.24	2.08	2.00	1.92	2.28
B (percent OWF)	1.96	2.16	2.16	2.16	2.04	2.04	2.40
Composite fibers:							
C_f	16.9	24.0	26.6	20.0	21.6	21.0	16.4
ΔC_f	0.3	0.1	0.1	−0.1	−0.2	−0.6	−0.4
Thread split (percent)	0	0	0	0	0	0	0

These acrylic composite fibers showed very similar initial dyeing characteristics, their water-reversibility was so low as to be substantially negligible, and they showed a feature of irreversible crimps.

EXAMPLE 4

The component A was comprised of 91% acrylonitrile and 9% methyl acrylate, and had a molecular weight of 58,000. The content of a sulfonic acid radical at the terminal of the polymer, introduced by means of the decomposition of the catalyst system of Example 1, was 40 milli-equivalents per 10^3 grams of the polymer. For the component B, in the copolymerization of 95% acrylonitrile and, 5% methyl acrylate, resulting in a molecular weight of 58,000, the total sulfonic acid radical content, introduced by copolymerizing a slight amount of sodium methyallylsulfonate with the acrylonitrile, was 52 milli-equivalents per 10^3 grams of the polymer. Both components were spun, drawn and dried by the same process as in Example 3, were heated in pressure steam at 130° C. for 10 minutes. The fundamental crimp frequency C_f of the coily crimps of these acrylic composite fibers was 23 and their water-reversibility value ΔC_f was 0.1.

What we claim is:

1. A wet-spun acrylic composite fiber comprising,
   (a) two different acrylic polymer components laminarly conjugated together along the length of the fiber,
   (b) each of said components being a copolymer consisting predominantly of acrylonitrile which has been copolymerized with 5–15% by weight of at least one comonomer selected from hydrophobic non-crystalline high polymer-forming monomers,
   (c) said components having a difference of 0.5–6% by weight in the content of said comonomer between them,
   (d) said components respectively containing different amounts of strong acid groups of at most 100 milli-equivalents per 10^3 grams of the polymer,
   (e) the smaller amount of the said acid group being present in the higher shrinkage component which contains a larger amount of the hydrophobic non-crystalline high polymer-forming monomer,
   (f) the respective components having a difference of 4 to 30 milliequivalents per 10^3 grams of the polymer in the proportion of the strong acid groups which impart to each of the components an equal initial rate of dyeing,
   (g) and exhibiting irreversible three dimensional coil crimps even when the resulting fiber is exposed to water or other swelling agent.
2. An acrylic composite fiber as in claim 1 wherein

each component contains at least 85% by weight of acrylonitrile.

3. An acrylic composite fiber as in claim 1 wherein the hydrophobic non-crystalline high polymer-forming comonomer is methyl acrylate.

4. An acrylic composite fiber as in claim 1 wherein one component contains methyl acrylate and the other component contains vinyl acetate.

5. An acrylic composite fiber as in claim 1 wherein the strong acidic group is a sulfonic acid group.

6. An acrylic composite fiber as in claim 5 wherein the sulfonic acid group is introduced into the polymer by copolymerizing a compound selected from the group

consisting of methallyl sulfonic acid and salts thereof with the monomers for forming said polymer.

References Cited

UNITED STATES PATENTS

3,039,524 6/1962 Belck et al. ---------- 161—177

ROBERT F. BURNETT, Primary Examiner

R. O. LINKER, JR., Assistant Examiner

U.S. Cl. X.R.

161—177; 264—168, 171