

- [54] **METHOD OF PRODUCING ACRYLIC COMPOSITE FIBERS**
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| Oct. 7, 1966 | Japan..... | 41-68532 |
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[51] Int. Cl..... **D01d 5/22**
[58] Field of Search..... **264/168, 171, 182**
- [56] **References Cited**
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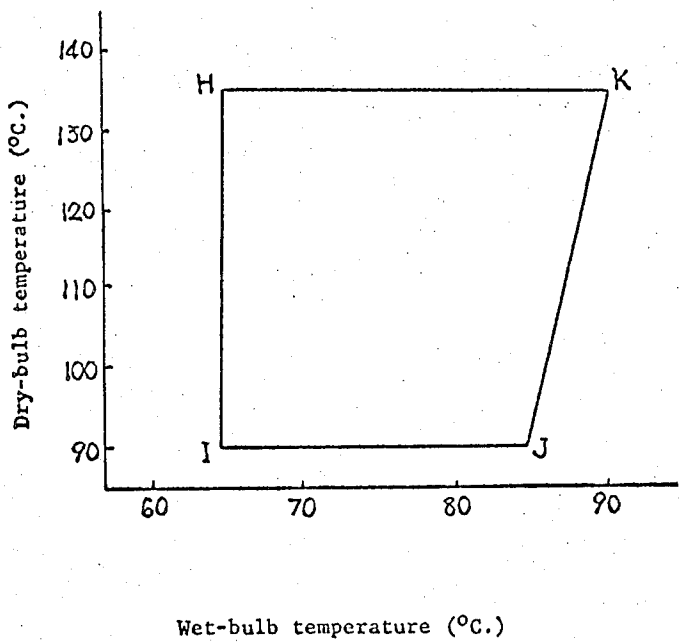
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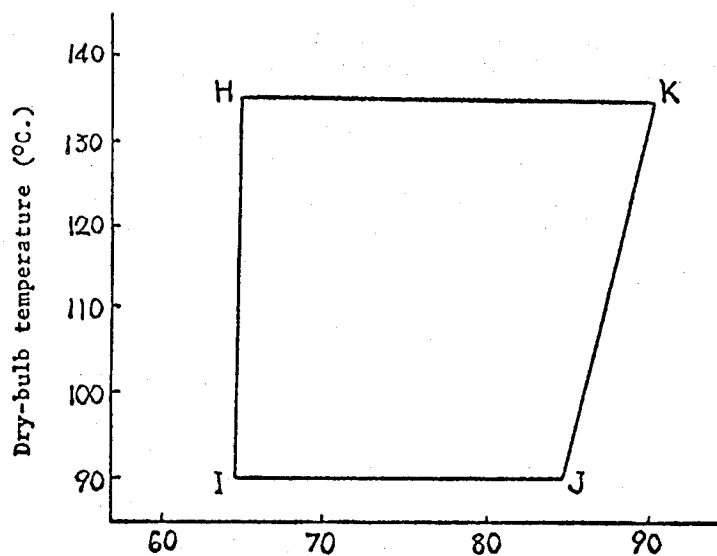
[57] **ABSTRACT**

Acrylic composite fiber having a three-dimensional spiral crimp is produced by the wet-spinning of acrylonitrile or substantially acrylonitrile polymer, using two polymeric components which exhibit dissimilar degrees of swelling in a gel state, arranged in side-by-side relation through the entire length of the fiber, washing the resulting swollen gel composite fiber with water, drawing the washed fiber, relaxing the swollen fiber—the water content of which relative to the dry weight of the fiber is 40% or higher under no tension in hot water or water vapor at 60° to 130°C, and finally drying the fiber, the three-dimensional spiral crimp being produced by the shrinkage differential due to difference in gel swelling of the two components.

11 Claims, 1 Drawing Figure



	Dry-bulb temperature (°C.)	Wet-bulb temperature (°C.)
H	135	65
I	90	65
J	90	85
K	135	90



	Dry-bulb temperature (°C.)	Wet-bulb temperature (°C.)
H	135	65
I	90	65
J	90	85
K	135	90

METHOD OF PRODUCING ACRYLIC COMPOSITE FIBERS

This is a continuation of application Ser. No. 672,634, filed Oct. 3, 1967, now abandoned.

This invention relates to a novel method of producing acrylic composite or conjugated fiber and, more particularly, to a novel method of producing an acrylic composite fiber having a three-dimensional spiral crimp through the wet-spinning of an acrylonitrile polymer or an acrylonitrile copolymer composed mainly of acrylonitrile, which comprises carrying out said spinning in such a manner that two polymeric components which exhibit dissimilar degrees of swelling in a gel state are arranged in layers in side-by-side relation through the entire length of the fiber, washing the resulting swollen gel composite fiber with water, drawing the said fiber, relaxing the swollen gel fiber whose water content relative to the dry weight of the fiber is 40% or higher (hereinafter referred to as moisture content) under no tension in hot water or water vapor at a temperature from 60°C. to 130°C., and finally drying the fiber, whereupon said three-dimensional spiral crimp is produced by the shrinkage differential derived from the difference in gel swelling between the two components.

A number of techniques have been proposed for the production of composite fibers possessing wool-like spiral crimps by imparting a superior wool-like elasticity and feeling to synthetic fiber, and the Sisson U.S. Pat. No. 2439815 was the first attempt.

Representative of such technique are those disclosed in U.S. Pat. Nos. 3038239, 3038236, 3038237 and 3039524. The composite fibers obtained by those techniques are invariably based on the principle disclosed in the Sisson U.S. Pat. No. 2439815 that the two acrylic polymer components of a composite fiber are different in thermal shrinkage (hereinafter referred to as Sisson type), or on the principle disclosed in the Breen U.S. Pat. Nos. 3038236, 3038237 and 3039524 that the crimp is rendered water-reversible by spinning conjugatedly two acrylic polymer components containing ionizable groups in dissimilar concentrations (hereinafter referred to as Breen type), or have both the characteristics of Sisson and Breen types.

Those acrylic composite fibers are more akin to wool in feeling than the conventional acrylic fiber of monocomponent type, but they have serious disadvantages.

Thus, the most salient disadvantage of practical significance is that the fibers are seriously lacking in dimensional stability under humid, hot conditions. Though changes in fiber length of the order of 2 and 3 percent are substantially negligible in the case of a fiber of the monocomponent type, a similar disparity of 2 to 3 percent in length between the two components of an acrylic composite fiber of the described type will result in a significant change in the amount of the spiral crimp, as will be readily presumed from the principles responsible for the formation of spiral crimps. Thus, such a change considerably affects the feeling and dimensional stability of the product made of these composite fibers.

In both acrylic composite fibers of the Sisson and Breen types, the acrylonitrile content of the high-shrinkable component, i.e. the inner element of the spiral crimp, is lower than that of the low-shrinkable component, i.e. the outer element of said crimp. With respect to the acrylic composite fiber of the Sisson type

which is based on the difference in thermal shrinkage, the glass transition point of the acrylic polymer constituting the inner element of the spiral crimp is lower than that of the acrylic polymer constituting the outer element of the spiral crimp and, accordingly, the thermal shrinkage of said inner element is higher than that of said outer element. This fact necessarily means that, at temperatures above the glass transition point, the inner element of the spiral crimp has a lower Young's modulus than the outer component of the same crimp, and if a tension force is applied to an acrylic composite fiber having such spiral crimps, a greater strain is naturally induced in the inner element of the crimp. Therefore, when an acrylic composite fiber of the Sisson type is dyed, washed, or otherwise treated under hot, humid conditions, the highest degree of care and skill is required, for subjecting the fiber to a slight tension could result in the decrimping and serious loss of the feeling and dimensional stability of the fiber or its product.

An acrylic composite fiber of the Breen type swells under hot, humid conditions, and due to the differential swelling of the two dissimilar components, its spiral crimp is partially stretched and lost. Upon drying the fiber, the spiral crimp is restored, but this restoration of crimp varies in degree according to the drying temperature and the tension to which the fiber is subjected, thus necessitating the exercise of special care and skill in the drying step. Moreover, the ionizable groups responsible for the development of the water-reversibility of the spiral crimp lose their dissociability because of their combination with cationic dyes, cationic retarders, or multivalent metal ions in the dyeing process or else, and, hence, the hydrophilic nature of the component polymer is lost. It entails a lowered water-reversibility of the spiral crimp so that the re-development of the spiral crimp upon drying is considerably affected.

Further, in the composite fibers of Sisson type as well as Breen type, the acrylic polymer composition is different between the two fiber components. Therefore, there is naturally a difference in the dyeing velocities between the two components. It has therefore been difficult to obtain acrylic composite fibers high in even dyeability. Further, in order to obtain these acrylic composite fibers by a wet-spinning process, it is usual to produce them by relaxing the fibers after carrying out composite spinning, water-washing, stretching and drying treatments. However, generally, in acrylic synthetic fibers, with the increase of the acrylonitrile content, the glass transition temperature will rise and therefore the heat movement of polymer molecules will be inhibited. As a result, in case the acrylonitrile content in the fibers is high, the spun, water-washed, stretched and then once dried fibers will reduce in the amount of shrinkage in the heat relaxing treatment and it will be difficult to obtain a sufficient relaxing effect. Thus, for example, the total of the shrinkages in the drying and relaxing thermal treatments or the so called in-process shrinkage will remarkably reduce. Therefore, the three-dimensional spiral crimps characterizing acrylic composite fibers will not develop satisfactorily and no satisfactory knot strength or knot elongation will be obtained. Further, if the temperature for the relaxation treatment is elevated to compensate these defects, the whiteness of the fibers will remarkably reduce, the dyeing velocity will remarkably increase and uneven dyeing will occur in the dyeing step.

U.S. Pat. No. 3,084,993 to Dawson refers to a method of making acrylic composite fibers from a single polymer. In said method, acrylic composite fibers having crimps are obtained by compositely wet-spinning two kinds of spinning solutions of different polymer concentrations of a single acrylic polymer, stretching the fibers and then drying them at a temperature below 100°C. in a shrinkable state (this will be referred to as Dawson type hereinafter.). However, the acrylic composite fibers of the Dawson type are not subjected at all to a relaxing treatment which is generally an important treatment for synthetic fibers, are therefore very brittle or remarkably low in knot strength and are so apt to fibrillate that they can be hardly used in practice as fibers for clothing. Further, when a relaxing treatment is applied by such known process as, for example, with hot water or steam to overcome the above mentioned defects of acrylic composite fibers of the Dawson type, the spiral crimps will substantially disappear and the important feature of the composite fibers will be lost. Therefore, the acrylic composite fibers of the Dawson type will lose the spiral crimps in the dyeing step or the like and therefore can be hardly used in practice.

A primary object of the present invention is to provide an improved acrylic composite fiber which has no such disadvantage as mentioned before in respect of conventional acrylic composite fiber.

Another object is to obtain fiber which not only has a satisfactory dimensional stability and three-dimensional spiral crimp, but also is excellent in physical properties, from polymers containing high percents of acrylonitrile.

Still another object of the invention is to obtain an acrylic composite fiber having a comparatively low rate of dye adsorption and, hence, superior even dyeability.

Other objects will become apparent from the following description which will be made partly by referring to the accompanying drawing which is a graph showing a temperature and humidity range within which the drying of the present acrylic composite fibers is preferably conducted.

As regards the thermal properties of an acrylic polymer, its apparent glass transition point is lowered as the amount of a swelling agent or plasticizer contained in the polymer is increased. In the wet-spinning of fiber, the fibrous polymer extruded into a coagulating bath will be obtained in the state of a gel fiber swollen with a coagulating agent, and when this gel fiber is stretched under hot, humid conditions, a swollen stretched gel fiber is obtained. Depending on its degree of irreversible swelling, the stretched gel fiber exhibits a varying thermal behavior. Thus, it has been found that when such a stretched swollen gel fiber is relax-treated under hot, humid conditions, the higher its degree of irreversible swelling, the more the fiber shrinks, assuming that the relax-treatment is carried out at a given temperature. The present invention is based on the above finding.

The present invention is based on the further finding that when a swollen gel fiber prepared by stretching a wet-spun acrylic composite fiber is not preliminarily dried but is directly relax-treated under hot, humid conditions and in the absence of tension, its shrinkage varies according to the swelling degree of the components constituting the composite fiber, and also that the decrease in volume of the fiber which is observed when

it is subsequently dried varies according to the swelling degree of the original gel fiber.

The swelling of such a swollen gel fiber is so irreversible that, once the fiber is dried, it will no longer return to the initial swollen state even if it is in a wet state, and we call this phenomenon "irreversible swelling". As a measure of said irreversible swelling, we employ the concept of irreversible swelling, which is expressed as follows.

$$\text{Irreversible swelling} = W_G/W_D$$

Wherein W_G is the weight of a swollen gel fiber which has been hot-stretched, and W_D represents the weight of the same gel fiber after drying.

An acrylic composite fiber of this invention consists of two acrylonitrile polymer components which differ from each other in irreversible swelling by 0.05 - 3%, the inner element of the crimp being the component possessing a high irreversible swelling, that is to say, the higher-shrinking component. If the difference in irreversible swelling between the two components constituting the acrylic composite fiber is less than 0.05, it will be found difficult to obtain a fully developed spiral crimp. On the other hand, if the difference in irreversible swelling between the two components becomes greater, the difference in shrinkage between two components will also be increased to the extent that the number of spiral crimps per unit fiber length will be large. However, if the difference in irreversible swelling between the two components exceeds 3, the number of spiral crimps will be excessively increased and the resulting fiber will be rather poor in spinning property and feeling.

According to the invention, various methods may be used in order to create at least 0.05% of difference in irreversible swelling between the two polymeric components or layers constituting the acrylic composite fiber. Thus, the following METHOD I, II and III may be employed.

METHOD I

The initial Young's modulus of an acrylic fiber at temperatures above the glass transition point increases as the acrylonitrile content of the polymer becomes higher. Therefore, if acrylic polymers containing different amounts of acrylonitrile are used as the two components of an acrylic composite fiber and the irreversible swelling of the higher-acrylonitrile component is made greater by least 0.05 than the irreversible swelling of the lower-acrylonitrile component, there is obtained an acrylic composite fiber consisting of a high-shrinkable component, i.e. the higher-acrylonitrile component, and a low-shrinkable component, i.e. the lower-acrylonitrile component, in which the initial Young's modulus of the high-shrinkable component constituting the inner element of the spiral crimp at temperatures above the glass transition point is higher than the comparable modulus of the outer element of the same crimp. In order to ensure that, at temperatures above the glass transition point, the Young's modulus of the high-shrinkable component constituting the inner element of the spiral crimp is higher than, or at least equal to, the initial Young's modulus of the low-shrinkable component constituting the outer element of said crimp, the acrylonitrile content of the polymer which is used as the high-shrinkable component should be higher by at least 0.5 percent than that of the polymer

to be used as the low-shrinkable component. While the initial Young's modulus of the inner component of the spiral crimp at temperatures above the glass transition point becomes high as the acrylonitrile content of the high-shrinkable component is increased relative to the acrylonitrile content of the low-shrinkable component, the difference in irreversible swelling between the two components becomes higher than 3 when the difference in acrylonitrile content between them exceeds 10 percent by weight, so that a considerably great number of extremely fine spiral crimps will be produced, with the result that the fiber has poor spinning property and feeling.

The irreversible swelling of an acrylic polymer containing 88 percent or more by weight of acrylonitrile increases as the acrylonitrile content of the polymer gains, but in order to ensure that the difference in irreversible swelling due exclusively to the difference in acrylonitrile content between the two components is 0.05 or more, it is necessary that the difference in acrylonitrile content between the two components is 2 percent or more by weight. As explained above, in order to satisfactorily develop a spiral crimp in the composite fiber, there must be an acrylonitrile content differential of 2 percent or more in order to give a difference of 0.05 or more in irreversible swelling between the two components. However, if it is impossible to attain a sufficient difference in irreversible swelling between the two components due exclusively to the acrylonitrile content differential, the difference may be made up if, as an auxiliary means, the concentration of strongly acidic groups in the higher-shrinkable component polymer is higher by 30 milli-equivalents or less per 10^3 grams of polymer than the concentration of strongly acidic groups in the low-shrinkable component polymer, or alternatively, if the concentration of hydrophilic groups in the high-shrinkable acrylic polymer is higher by 10 percent or less by weight than the concentration of such groups in the low-shrinkable acrylic polymer. However, if the difference in concentration of the strongly acidic groups or hydrophilic groups between the two components exceeds the above-mentioned range, the undesirable effects result that the difference in irreversible swelling between the two components is unduly great and also that the crimp is rendered water-reversible.

As an auxiliary means of more effectively making the irreversible swelling of the high-shrinkable component greater than the irreversible swelling of the low-shrinkable component, it is possible to prepare a spinning solution of the high-shrinkable component in a concentration 0.3 to 5 percent lower than the concentration of its counterpart solution of the low-shrinkable component. No beneficial effect is expected when the difference in concentration between the two spinning solutions is less than 0.3 percent, whereas a difference of more than 5 percent proves undesirable, for it gives rise to an unduly great difference in irreversible swelling.

It is also possible to increase the difference in irreversible swelling by arranging so that the molecular weight of the high-shrinking polymer is lower than that of the low-shrinking polymer.

Further it is possible to create the desired difference in the irreversible swelling degree between the polymeric components by differentiating the comonomer

(e.g. vinylidene chloride, vinylidene cyanide, etc.) content in these polymeric components.

Of course, any two or more of the above explained measures may be suitably combined in order to obtain the desired result.

It is also possible to make the content of strongly acidic groups in the low shrinking polymeric component (i.e. the polymer which would constitute the outer element of the crimp of the coily crimped acrylic composite fiber) higher than that in the other or high shrinking polymer. In this way, the dyeability of the outer element of the coil crimp is rendered higher than that of the inner element. However, in this case, there is a tendency toward decreasing the difference in shrinkage between the high and low shrinking components due to the strong acidic groups. In order to overcome this tendency, it is recommended to increase the difference in acrylonitrile content between the two component polymers or to lower the polymer concentration in the spinning solution of the high shrinking component to less than that in the spinning solution of the low shrinking component, depending upon the difference in the content of the strong acidic groups between the high and low shrinking components.

METHOD II

An acrylic composite fiber is made so as to consist of two acrylic polymer components which differ from each other by 0.5 percent or less in the acrylonitrile content and which differ from each other in irreversible swelling by at least 0.05, the inner element in the crimp of the resulting crimped fiber being the component possessing a high irreversible swelling degree, that is the high-shrinking component.

To ensure that, in a composite fiber made up of two components which differ in acrylonitrile content by 0.5 percent or less, the difference between said two components in irreversible swelling is at least 0.05 or greater, the following various means may be employed.

A. It is so arranged that the concentration of strongly acidic groups in an acrylic polymer which is to be used as the high-shrinking component is higher than the comparable concentration in another polymer which is to be used as the low-shrinking component by 10 to 30 milliequivalents per 10^3 grams of polymer. When the difference in the concentration of strongly acidic groups between the two components is less than 10 milliequivalents per 10^3 grams of polymer, the difference in irreversible swelling between said components cannot reach 0.05, with the result that no adequate development of the desired spiral crimp can be attained. On the other hand, when the difference in concentration of strong acid groups between the two components exceeds 30 milliequivalents per 10^3 grams of polymer, the difference in irreversible swelling will be unduly great, so that the crimp is rendered water-reversible.

B. It is so arranged that the content of neutral and weakly acidic hydrophilic groups in a polymer to be used as the high-shrinking component is higher by 3 to 10 percent by weight than that in another polymer to be used as the low-shrinking component. When the difference between the two components in the content of said hydrophilic groups is less than 3 percent by weight, the difference in irreversible swelling between the components does not reach 0.05, with the result that no adequate development of spiral crimps can be expected. If the difference in content of such hydrophilic groups

exceeds 10 percent by weight, not only an unusually large difference is created between the degrees of irreversible swelling between the two components, but the crimps are rendered water-reversible. Thus, undesirable results ensue.

C. It is so arranged that the concentration of acrylic polymer in the spinning solution to be used as the high-shrinking component is lower than that of the spinning solution to be used as the low-shrinking component by 0.3 to 5 percent by weight. Should the difference in polymer concentration between the two components be less than 0.3 %, there would not be obtained any appreciable effect, while if the difference exceeds 5 percent, the difference in irreversible swelling will become undesirably high.

D. In using acrylic polymers having similar compositions as the two components of the fiber, it is so arranged that the molecular weight of the polymer to be used as the high-shrinking component is lower in viscosity than that of the polymer to be used as the low-shrinking component by at least 0.1 in terms of intrinsic viscosity $[\eta]$ as measured in dimethylformamide at 30°C. There is observed no appreciable effect when the difference in intrinsic viscosity $[\eta]$ between the two components is less than 0.1, while an unusually high difference in $[\eta]$ between the components gives rise to an undesirably large difference in irreversible swelling and, at the same time, increases the difference in dyeing velocity to the extent that uneven dyeing results.

E. Among other methods, there is a method which provides a difference in content of comonomer (e.g. vinylidene chloride, vinylidene cyanide, etc.) between the two acrylic polymers which respectively constitute the fiber components.

It is also possible to employ the above enumerated measures in various combinations.

METHOD III

The same acrylonitrile polymer is employed but its concentration is differentiated between the two spinning solutions from which the respective components of the composite fiber are formed. In this case, the difference in polymer concentration is so selected that the difference in irreversible swelling between the two components or layers of the resulting composite fiber will be at least 0.05. The fiber component formed from the spinning solution low in the polymer content and high in the irreversible swelling will become a high shrinkable layer and will be a spiral crimped inner element or layer.

In order to make the difference in irreversible swelling between the two layers or components at least 0.05 by using the same acrylic polymer, the concentration of the acrylic polymer in the spinning solution to be used for the formation of the high-shrinkable layer should be lower by 0.3 to 5 % by weight than the concentration of the same acrylic polymer in the spinning solution for the formation of the lowshrinkable layer of the composite fiber.

In case the difference of the acrylic polymer concentration between the two kinds of spinning dopes is less than 0.3 % by weight, the difference in irreversible swelling between two layers will not reach 0.05 and the development of spiral crimps will be poor. In case it exceeds 5 %, the difference in irreversible swelling between two layers will become unduly large and the result will not be desirable.

For introducing strongly acidic groups into an acrylic polymer, the method consisting in allowing the sulfonic groups formed on decomposition of a catalyst during the polymerization reaction to find their way into the terminal groups of the polymer, or the method of introducing sulfonic groups positively into the copolymer may most ordinarily be employed. Thus, a monomer or monomers containing sulfonic groups, e.g. elkenyl aromatic sulfonic acids, para-styrene-sulfonic acid, vinyl sulfonic acid, allylsulfonic acid, or methallylsulfonic acid, as well as salts thereof, may be copolymerized with acrylonitrile. In order to introduce hydrophilic groups into an acrylic polymer, acrylonitrile may be copolymerized with alcohols, e.g. allyl alcohol, methallyl alcohol, etc., beta-hydroxyethyl acrylate, beta-hydroxypropylacrylate, acrylic acid, methacrylic acid, itaconic acid, maleic acid and other unsaturated carboxylic acids, the alkali or ammonium salts of such acids, acrylamide, methacrylamide and other monomers which contain hydrophilic groups and are copolymerizable with acrylonitrile.

Now, the method of manufacturing the acrylic composite fiber of the present invention will be described in detail.

The acrylonitrile polymers mentioned hereinbefore include both acrylonitrile homopolymers and copolymers, the latter being copolymers of at least 80 percent acrylonitrile with one or more monomeric compounds copolymerizable with acrylonitrile, irrespective of the manners in which such polymers and copolymers are produced. The "one or more monomeric compounds copolymerizable with acrylonitrile" mentioned above may be selected from the group consisting of, for example, the monomers specifically named hereinbefore as well as methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, methoxyethyl acrylate, phenyl acrylate, cyclohexyl acrylate and dimethylaminoethyl acrylate; the corresponding esters of methacrylate; the alkyl or nitrogen substituted products of acrylamide and of methacrylamide; unsaturated ketones such as methylvinyl ketone, phenylvinyl ketone, methylisopropenyl ketone, etc.; vinyl carboxylates such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, etc.; the esters of ethylene-alpha-beta-carboxylic acids such as fumaric acid, citraconic acid, methaconic acid, animaic acid, etc.; N-alkylmaleimide; N-vinylcarbasole; N-vinylsuccinimide; N-vinylphthalimide; vinyl ether; N-methylolacrylamide; vinyl pridines such as 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl 5-vinyl pyridine etc.; styrene and the alkylation products thereof; vinyl chloride, vinylidene chloride; vinylidene cyanide and the like.

The acrylic composite fiber of the present invention is obtained only by the so-called wet-spinning method, and the solvents which are used in the preparation of spinning solutions may be selected from the conventional wet-spinning solvents for acrylic polymers such as concentrated aqueous solutions composed predominantly of inorganic salts such as the thiocyanates of alkali metals, e.g. lithium thiocyanate, potassium thiocyanate, sodium thiocyanate, etc.; ammonium thiocyanate, zinc chloride, perchlorates, etc., concentrated aqueous solutions of inorganic acid such as sulfuric acid, nitric acid, etc., and various organic solvent such as dimethylformamide, dimethylacetamide, dimethylsulfoxide and the like.

In preparing spinning solutions, it is essential to select the acrylic polymers and/or the polymer concentrations in the spinning solutions in such a manner that the difference in irreversible swelling between the resulting two fiber components is 0.05 - 3. The concentration of the acrylic polymer in a spinning dope should vary depending on the particular solvent, but generally speaking, it is advisable to so select that the viscosity of the spinning solution at 30°C. lies somewhere between 5 and 50 poises. The spinning solution may be the one obtained directly from a solution polymerization process. In this instance, the same requirements as above also apply. The two different spinning solutions are respectively deaerated and filtered in the conventional manner before being fed to the composite fiber spinnerette.

The above-mentioned spinning solutions are extruded in a coagulating bath through a spinning device such as that disclosed in U.S. Pat. No. 3,182,106 or British Pat. No. 1,030,005, or any other equipments known for the spinning of composite fibers.

As said coagulating bath, water or a dilute aqueous solution of the same solvent as the one used in the preparation of said spinning dopes may be employed as well known in the art.

The swollen gel composite fiber emerging from the coagulating bath is washed with water, and then stretched 3 - 20 times the initial length, whereby the fiber assumes the practical degree of strength and elongation. The stretching may be carried out in one step, but by taking advantage of the cold-stretchability of the unstretched fiber, it is possible to stretch the fiber 1.1 - 4 times in the washing water bath at room temperature and, then, hot-stretch the same so that the total stretch ratio would be 3 - 20 times the initial length. It is also possible to carry out a hot-stretching of the fiber in several steps. The hot-stretching may also be carried out in steam at 100°- 140°C.

The swollen gel composite fiber stretched as above is relaxed by treating it under no tension with hot water or steam, whereby the fiber is homogenized and its knot strength and elongation improved. By the above treatment, part of the latent spiral crimp is developed, due to the shrinkage differential which is derived from the irreversible swelling differential mentioned before. The swollen gel composite fiber stretched and oriented, before being subjected to the subsequent hot, humid treatment, must have a moisture content (hereinafter referred to as % moisture content) of 40 percent or more relative to the dry weight of the fiber. If the % moisture content of the oriented swollen gel composite fiber is less than 40 percent, its plasticity due to water is reduced and, accordingly, its apparent glass transition temperature is increased. As a result, the effect of said hot, humid relaxing treatment cannot be attained to the desired extent. Moreover, the latent spiral crimp cannot be fully developed in the subsequent drying for collapsing or compacting. The swollen gel composite fiber of 40% or more moisture content as referred to in the present specification is a swollen gel composite fiber which has not yet been dried. The above-mentioned hot, humid relaxing treatment is carried out in hot water or water vapor. The treating temperature may range from 60°C. to 130°C. To obtain satisfactory effects from the hot, humid relax treatment, and an effective development of the spiral crimp, it is sufficient to carry out the relaxation treatment for 5 to 20 min-

utes. If the treating temperature is below 60°C., it is impossible to sufficiently relax the fiber, or allow the spiral crimp to develop sufficiently. As a result, it is impossible to obtain a fiber having satisfactory spiral crimp and excellent knot strength and elongation properties. On the other hand, if the temperature exceeds 130°C., there occurs coloration of the swollen gel composite fiber, whereby the final fiber assumes a yellow shade. The dye-absorbing velocity of the fiber depends upon the temperature at which the hot, humid treatment is conducted and, therefore, increasing the temperature of said hot, humid treatment excessively will result in a remarkable increase in dyeing velocity, which leads to uneven dyeing.

The swollen gel fiber which has been relaxed in hot, humid atmosphere to have its spiral crimp developed is then dried under no tension in the conventional manner, preferably within the controlled temperature-humidity range defined by H, I, J and K shown in the accompanying drawing wherein the points H, I, J and K are defined as follows:

	Dry bulb temperature (°C.)	Wet bulb temperature (°C.)
H	135	65
I	90	65
J	90	85
K	135	90

By the above drying, the fiber has its latent spiral crimp fully developed and, at the same time, is compacted owing to the shrinkage differential derived from the difference in irreversible swelling between the two components.

The acrylic composite fiber which has been compacted and the spiral crimp of which has been fully developed due to the shrinkage differential derived from said difference in irreversible swelling, when heat-treated a second time, is further structurally stabilized, whereby the initial Young's modulus at temperatures above the glass transition point is further increased. The second heat-treatment mentioned above may be carried out in the conventional manner, either under dry, hot or humid, hot conditions. For example, the above treatment may thus be effected in relaxed state by means of hot, humid media, such as hot water, steam, etc., hot liquids such as glycerin, hot air or radiation heat and the like, at 80°C. to 130°C. In this heat-treatment, the acrylic composite fiber of this invention does not substantially shrink and, therefore, the number of spiral crimps, as well as the degree of crimping, remains substantially unaffected.

The acrylic composite fiber of this invention, unlike the fiber manufactured through the application of the Sisson principle to acrylic composite fiber, has its spiral crimp developed by the difference in irreversible swelling between the two components constituting the composite fiber. Therefore, the number of crimps is not increased by dyeing at high temperature and, accordingly, the diameter of the spiral crimps is not reduced. Thus, the bulkiness and the concomitant wooly "feel" of the composite fiber is maintained.

In the conventional acrylic composite fiber, the component which is lower in acrylonitrile content and has a greater thermal shrinkage constitutes the inner element of the spiral crimp, with the result that when the fiber is heated, as in the case of dyeing at high tempera-

ture, the inner element of the spiral crimp undergoes a greater thermal shrinkage than the outer element of the crimp. This entails an increased number of crimps and a reduced diameter of each crimp. That is to say, the individual crimp becomes considerably small in size. The greatest factor responsible for the bulkiness of a textile product is the diameter of the spiral crimp. The diameter of the spiral crimp of wool is comparatively large, and it is mainly responsible for the characteristically kind feel of wool. Therefore, the conventional acrylic synthetic fiber in which a thermally high-shrinking polymer constitutes the inner element suffers a reduction in crimp diameter when it is subjected to dyeing or other high temperature treatment. The result is that the surface of the product has a harsh feel and, in some instances, assumes a "felt" -like hand. The acrylic composite fiber of this invention is completely free from such disadvantages.

The acrylic composite fiber of this invention obtained by differentiating the irreversible swelling between the two components according to the methods of this invention, especially Method I or Method III mentioned hereinbefore. Has dimensional stability because of its freedom from partial loss of the spiral crimp on dyeing or laundering as would be the case with conventional acrylic composite fibers, said freedom being derived from the fact that the initial Young's modulus of the higher-shrinkable component constituting the inner element of the spiral crimp at temperatures above the glass transition point is equal to, or higher than, the initial Young's modulus of the lower-shrinkable component constituting the outer element of said crimp at the same temperatures as above, with the result that the feeling or hand of the final product is substantially not affected by humid-heat treatments, in addition to the advantage that the dissimilar acrylic polymer components having dissimilar shrinking characteristics remain permanently inseparable, that is to say, there is no splitting of the fiber into the components.

Further, the acrylic self-crimped fibers according to the present invention have nothing of such defect caused by having such water-reversibility of spiral crimps as is seen in acrylic composite fibers of the Breen Type as is described above. Thus, the spiral crimp developed by virtue of the difference in irreversible swelling, once dried, cannot revert to its initial swollen state even if it is allowed to stand in a wet atmosphere, and since there is no substantial difference in content of ionizable or hydrophilic groups between the two components, when the METHOD I or METHOD II mentioned before is employed, its water-reversibility is extremely small. Further, according to the METHOD III, the content of ionizable groups and hydrophilic groups in the two components is equal so that no water reversibility of crimp is observed. Therefore, in any case, the spiral crimp remains extremely stable even in a wet state.

Furthermore, in accordance with the present invention, when the stretched swollen gel fiber is not dried but directly relaxed under hot, humid conditions and under no tension, a sufficient shrinking effect may be had even if the treating temperature is as low as about 60°C. This phenomenon is accounted for by the fact that as the swollen gel fiber is plasticized by a relatively large amount of a swelling agent, e.g. water, its apparent glass transition point is appreciably lowered. Therefore, even with acrylic polymers rich in acrylonitrile

and acrylonitrile homopolymers, which has heretofore been considered not adaptable for the conventional techniques, it is now made possible by the invention to produce acrylic composite fibers possessing excellent physical properties and superior spiral crimps. Furthermore, the dye-absorption velocity of acrylic synthetic fiber depends on the temperature at which a relaxing treatment is carried out. Therefore, since the relaxing treatment of this invention may be effected at a relatively low temperature, the dye-absorption velocity of fiber is lowered, with the result that acrylic composite fibers which is high in even dyeability may be produced by the method of this invention.

As regards the distribution of dye between the two components of an acrylic composite fiber, the inner element of the spiral crimp of the conventional Sisson or Breen type composite fiber has a greater affinity for dyes than that of the outer element of the crimp. In contrast thereto, the composite acrylic film of this invention prepared on the principle of the METHOD I, exhibits an opposite dyeing behavior. Thus, the polymeric component constituting the outer element of the spiral crimp is more receptive to dye than the polymeric component constituting the inner element of the crimp. When there are substantially equal numbers of "dyeable seats" in two substrates, the diffusion velocities of a dye depend on the physical compactness of the two substrates. Thus, the substrate containing a greater amount of acrylonitrile is higher in compactness than the substrate containing less acrylonitrile, and, therefore, is less receptive to dye than the latter. The dye-stuffs usable include cationic and dispersive dyes, as well as all other dyes that can be applied to acrylic synthetic fibers in general, and since the outer element of the spiral crimp of the fiber of this invention has a greater affinity to dyestuffs, it is possible to obtain a product of brilliant, deep shade by making use of this outer element as a dyeing-substrate component. On the other hand, the inner element of the spiral crimp which exhibits a higher Young's modulus in hot water acts as a load-bearing component which prevents elongation of the crimp by resisting the external force arising from the turbulent flow of the dyeing solution.

The composite acrylic fiber prepared by the METHOD III of this invention is uniform throughout the fiber in the kind of polymer employed and therefore can be dyed evenly like mono-component fiber.

The invention will be explained more concretely by means of the following Examples wherein all parts are by weight. The molecular weight of polymer was calculated by measuring the intrinsic viscosity $[\eta]$ of the polymer in dimethylformamide at 30°C. and was expressed in $[\eta]$.

The fundamental crimp frequency $[C_f]$ is a characteristic which is proportional to a difference in the lengths of the two components, and is a value calculated from the crimp index and crimp frequency by means of equation (1), and is the crimp number per 25 millimeters of the fiber as relaxed in boiling water.

$$[C_f] = \text{Crimp frequency} (1 - \text{Crimp index}/100) \quad 1.$$

Crimp frequency — The number of crimps per 25 mm. was counted for the sample under the initial load (2 mg. per denier). The test was repeated 20 times and average value was taken.

Crimp index — The length (a) of the sample under the initial load (2 mg. per denier), and the length (b) of the same sample at the time of lapse of 30 seconds after loaded with 50 mg. per denier were respectively measured. The crimp index was calculated by the following formula:

$$\text{Crimp index} = b - a/b \times 100$$

The diameter of crimp (C_d^{cat}) was calculated from the C_f and the crimp index by means of equation (2) showing geometry of an ideal spiral form.

$$C_d^{cat} = 25 \sqrt{C_i(2 - C_i)/2 C_f}$$

wherein

$$C_i = \text{Crimp index}/100$$

C_d^{cat} represents the width of spiral, and according to an actual measurement of the width of spiral crimps of the composite fibers by the present invention, every width shows the degree of 80 % of C_d^{cat} and this means an excellent correlation. That is to say, the diameter of spiral crimp actually measured (C_d^{obs}) has a relationship shown in equation (4), and as the value of C_d^{cat} becomes greater, the fiber provides a better bulkiness and more wool-like good hands.

$$C_d^{obs} = 0.8 C_d^{cat}$$

The elastic recovery of crimp was measured by the following standard method. However, since the fibrous products are so often attacked by loads under more hard conditions than that in the said measuring method, the sample was loaded with 300 mg. per 1 denier for elongation of crimp for 2 minutes, and thereafter, was left being loaded 2 mg. per 1 denier without taking off the whole load.

Elastic recovery of crimp: The length (a) of the sample under the initial load of 2 mg. per denier was measured, and then the length (b) of the same sample at the time of lapse of 30 seconds after being loaded with 50 mg. per denier was measured. Then the whole load was removed and after 2 minutes the initial load (2 mg. per denier) was again applied and the length (c) was measured. The elastic recovery of crimp was calculated by the following formula:

$$\text{Elastic recovery of crimp (\%)} = b - c/b - a \times 100$$

The Young's modulus E_r^{95} in hot water was measured as follows. Thus a constant-speed elongation tester (Toyo Sokki K.K., Tensilon III) was equipped with a 95°C. hot water thermostatic vessel, by means of which a 30 mm-long sample was stretched at a speed of 30 mm/min. or 100 % per minute, and the loads detected by a load cell of the resistance coil strain gauge type (Toyo Sokki Co., Ltd., TLU 0.03 kg.) were self-recorded. From the results, a load/elongation curve was drawn, and based on the initial gradient of the curve, the Young's modulus per denier of the sample was calculated.

Dyeing tests were carried out at high temperatures, i.e. 110°C. or 120°C. The cationic dye used was C.I. Basic Blue 47, while the disperse dyes were C.I. Disperse Blu 1 and C.I. No. 64500. The dyeing conditions: 100 parts water, 0.5 part dye, 5 parts fiber, 60 minutes. The dyed fiber was washed with water, dehydrated, and dried. Then, the sample fiber was observed under microscope to compare the difference in shade between the inner and outer components of the spiral crimp. The abbreviation C.I. means the Colour Index, Second Edition, 1956, and Supplement, 1963, issued by the Society of Dyers and Colourists, Bradford, England and the American Association of Textile Chemists and Colorists, Lowell, Mass., U.S.A.

2. 15 The splitting of the fiber into the two components was measured in such a manner that the sample was hung under a load of 0.4 g/denier and was rubbed with one end of an octagonal rod of stainless steel, hard-chrome-plated, which was revolving at 3500 r.p.m. The worm fiber was observed microscopically and the degree of splitting was expressed in percentage.

EXAMPLE 1

- 25 In the preparation of copolymers, which are to be used as the inner element of the spiral crimp (hereinafter referred to as component A), from acrylonitrile and methyl acrylate in the ratios by weight of 100/0, 97/3 and 95/5, $[\zeta] = 1.5$, small amounts of sodium methallylsulfonate were copolymerized with the above monomers, whereby the sulfonate groups content of the polymers is 50 milliequivalents per 10^3 grams of polymer. To prepare a copolymer, which is to be used as the (hereinafter referred to as component B) outer element of the spiral crimp, from acrylonitrile and methyl acrylate in the ratio by weight of 93/7, $[\zeta] = 1.5$, small amounts of sodium methallylsulfonate are added so that the sulfonate groups content of the copolymer is 50 milliequivalents per 10^3 grams of polymer. Both components, A and B, are respectively dissolved in 48 % aqueous solution of sodium thiocyanate, so that the resulting spinning dopes contain 11 % of the copolymers, respectively. Equal amounts of the dopes are wet-spun in a 10 % aqueous solution of sodium thiocyanate at 0°C. by means of a composite fiber spinnerette of the type disclosed in U.S. Pat. No. 3,182,106. The resulting filaments are guided through a washing bath, whereby they are thoroughly washed with water. The filaments are then stretched 10 times the original length in boiling water to obtain gel filaments with water contents of 130, 106 and 88 % respectively, followed by a 15 minutes' relaxing treatment in boiling water under no tension. Then, the filaments are compacted by drying them under no tension in a controlled atmosphere at a dry-bulb temperature of 110°C. and a wet-bulb temperature of 78°C., followed by a heat-treatment in boiling water for 15 minutes. The filaments are finally dried at about 100°C. The spiral crimps are mostly developed in the compacting drying step. The characteristics of the composite fibers, as well as the results obtained when these fibers are dyed with cationic dye at 120°C., are summarized in Table 1. On the other hand, components A and B are respectively spun into separate filaments under the same conditions as above, and the degrees of irreversible swelling, as well as the degrees of in-process shrinkage, of the two components are measured. The results are also given in Table 1.

Table 1

Polymer ingredients				
Acrylonitrile/methyl acrylate				
Component A	100/0	97/3	95/5	93/7
Component B	93/7	93/7	93/7	95/5
Mono-component filaments				
Irreversible swelling (Q)				
Component A	2.82	2.36	1.98	
Component B	1.77	1.77	1.77	
Difference in irreversible swelling	1.05	0.59	0.21	
In-process shrinkage				
Component A (%)	46.7	37.5	33.7	22.6
Component B (%)	31.1	31.1	31.1	20.4
Difference in shrinkage (%)	15.6	6.4	2.6	2.2
E_{cr}^{95}				
Component A (g/d)	1.56	1.40	1.38	0.98
Component B (g/d)	0.94	0.94	0.94	1.41
Composite fibers				
C_f	33.9	20.4	9.0	3.1
C_{f}^{rel}	0.19	0.30	0.46	0.70
Elastic recovery of crimp				
Splitting (%)	57.0	58.4	62.7	49.6
Dry strength (g.d)	0	0	0	0
Knot strength (g.d)	2.34	3.25	3.82	3.97
Dry elongation (%)	1.99	2.92	3.00	2.48
Knot elongation (%)	37.4	45.8	47.2	31.1
	24.5	35.2	37.4	15.3
Dyed fibers				
C_f	32.5	19.0	5.1	6.1
C_{f}^{rel}	0.19	0.31	0.66	0.39
Shade of dyed fibers				
Component A	pale	pale	medium	dark
Component B	dark	dark	dark	medium

It will be apparent from Table 1 that the initial Young's modulus of component A which is the inner element of the spiral crimp, is higher than that of B in hot water at 95°C. This is a characteristic of the present fiber, which is not seen in the conventional acrylic composite fibers. The results of high-temperature dyeing with cationic dye suggest that the outer element of the spiral crimp has a great dyeability than the inner element and, also, that even after such a C_d^{rel} values of the samples are now lowered, but are rather increased, and there is no loss of the bulkiness of the fibers.

The control given in Table 1 relates to the characteristics of the fiber prepared by applying the conventional compacting-drying and hot wet relaxing treatments after thermal stretching, and the results show that both the acrylonitrile content and initial Young's modulus in hot water at 95°C. of the control sample is greater for B and A; that is to say, the inner and outer elements of the spiral crimp are reversed. Since the component having a greater Young's modulus at 95°C. water constitutes the outer element of the crimp, the C_d^{rel} value of the fiber after dyeing is inferior and the elastic recovery of the crimp is also low.

EXAMPLE 2

In the preparation of component A copolymer of acrylonitrile and methyl acrylate in the ratios by weight of 100/0, 97/3 and 94/6, $[\zeta] = 1.5$, azobisisobutyronitrile is used as polymerization initiator so that no sulfonate groups are introduced into the terminal of the copolymer. Component B is also prepared from acrylonitrile and methyl acrylate in the ratio by weight of 93/7, $[\zeta] = 1.5$, in a similar manner so that no sulfonate groups are introduced into the terminal of the copolymer. Component A is dissolved in 48 % aqueous solu-

tion of sodium thiocyanate to prepare a spinning dope, the copolymer concentration of which is 1.1 %. Component B is also dissolved in 48 % aqueous solution of sodium thiocyanate to prepare another spinning dope, the copolymer concentration of which is 1.3 %. From the two dopes, an acrylic composite fiber is prepared in a manner similar to Example 1. The characteristics of the acrylic composite fiber, as well as the results obtained when the fiber is dyed with a disperse dye at 120°C., are summarized in Table 2.

Table 2

Polymer ingredients				
Acrylonitrile/methyl acrylate				
Component A	100/0	97/3	94/6	
Component B	93/7	93/7	93/7	
Mono-component filaments				
Irreversible swelling (Q)				
Component A	3.72	2.52	2.91	
Component B	1.86	1.88	1.86	
Difference in irreversible swelling	1.86	0.66	0.33	
In-process shrinkage (%)				
Component A	37.5	29.0	25.4	
Component B	21.6	21.6	21.6	
Difference in shrinkage	15.9	7.6	3.8	
D_{cr}^{95} (g/d)				
Component A	3.15	2.25	2.02	
Component B	1.54	1.54	1.54	
Composite fibers				
C_f	31.1	22.9	15.0	
C_{f}^{rel}	0.22	0.29	0.37	
Elastic recovery of crimp				
Splitting (%)	53.3	55.3	56.9	
	0	0	0	
Dyed fibers				
C_f	27.0	17.8	11.0	
C_{f}^{rel}	0.23	0.32	0.45	
Shade of dyed fibers				
Component A	especially dark	pale dark	medium dark	
Component B				

EXAMPLE 3

In the preparation of component A copolymer of acrylonitrile and methyl acrylate in the weight ratio of 99/1, $[\zeta] = 1.5$, a small amount of sodium methallylsulfonate is copolymerized with the above monomers, whereby the sulfonate groups content of the resulting copolymer is 50 milliequivalents per 10^3 grams of copolymer. As for component B, a small amount of sodium methallylsulfonate is copolymerized with acrylonitrile and methyl acrylate (97/3 by weight) to prepare a copolymer $[\zeta] = 1.7$, the sulfonate group content of which is 33 milliequivalents per 10^3 grams of copolymer. Both components A and B are respectively dissolved in 48 % aqueous solutions of sodium thiocyanate to prepare spinning dopes, the copolymer concentration of which is 10 %. The dopes are extruded into a composite fiber and the latter is washed and stretched, in a manner similar to Example 1 to obtain gel film of moisture content 210 %. The fiber is immediately treated in relaxed state in hot water at 98°C. for 15 minutes, at the end of which time the fiber is compacted by drying the same under no load tension in a controlled atmosphere at a dry-bulb temperature of 110°C. and a wet-bulb temperature of 77°C. Finally, the fiber is further heat-treated with pressurized water vapor at 110°C. for 15 minutes. The characteristics of the final composite fiber, as well as the results attained when the fiber is dyed with a cationic dye at 120°C., are summarized in Table 3. On the other hand, components A and B are independently spun and treated under the same conditions as above, and the degrees of irreversible swelling and in-process shrinkage of the two components are measured. The results are also given in Table 3.

Table 3

Copolymer ingredients	Component A	Component B	Composite fiber
Acrylonitrile/methyl acrylate	99/1	97/3	
Sulfonate group content (milliequivalent per 10^3 gram copolymer)	50	33	
Irreversible swelling (Q)	3.33	2.86	
Difference		0.47	
In-process shrinkage (%)	42.1	37.0	
Difference (%)		5.1	
E_w^{90} (g/d)	3.00	2.55	
C_f			18.2
$C_{f,rel}$			0.35
Elastic recovery of crimp			59.7
Splitting (%)			0
Dyed fiber			17.0
C_f			0.39
$C_{f,rel}$			
Shade of dyed fibers	pale	pale	

EXAMPLE 4

In the preparation of component A copolymer of acrylonitrile and methyl acrylate (99/1 by weight), a small amount of sodium methallylsulfonate is copolymerized with the above monomers to prepare a copoly-

mer, $[\zeta] = 1.4$, the sulfonate group content of which is 37 milliequivalents per 10^3 grams of copolymer. This copolymer is dissolved in 48 % aqueous solution of sodium thiocyanate to prepare a spinning dope the copolymer concentration of which is 10 percent. In the preparation of component B from acrylonitrile and methyl acrylate (93/7 by weight), a small amount of sodium methallylsulfonate is copolymerized with the above monomers to prepare a copolymer, $[\zeta] = 1.4$, the sulfonate groups concentration of which is 66 milliequivalents per 10^3 grams of copolymer. The resulting copolymer is dissolved in 48% aqueous solution of sodium thiocyanate to prepare a spinning dope, the copolymer concentration of which is 13 percent. Equal amounts (on a copolymer basis) of the above spinning dopes are wet-spun by means of a spinnerette of the type disclosed in U.S. Pat. No. 3,182,106, to which metering pumps are connected, into 10 % aqueous solution of sodium thiocyanate at 0°C. The resulting swollen gel composite fiber is passed through a washing water bath, whereby the fiber is thoroughly washed with water, while it is stretched 2.5 times its initial length. The fiber is further stretched 4 times its length in boiling water to obtain gel fiber of a moisture content of 230 %, followed by a 15-minute hot wet relaxing treatment under no tension in hot water at 90°C. The swollen gel fiber treated under hot wet conditions as above is then compacted by drying the same under no tension in an atmosphere at a dry-bulb temperature of 110°C. and a wet-bulb temperature of 75°C., further followed by a heat treatment in boiling water for 15 minutes. The characteristic of the resulting fiber, as well as of the fiber dyed with a cationic dye at a high temperature of 110°C., are summarized in Table 4.

On the other hand, components A and B are independently spun and treated under the same conditions as above, and the degrees of irreversible swelling and in-process shrinkage of the fiber are measured. The results are also given in Table 4.

Table 4

Copolymer ingredients	Component A	Component B	Composite fiber
Acrylonitrile/methyl acrylate	99/1	93/7	
Sulfonate group content (milliequivalents per 10^3 grams copolymer)	37	66	

Table 4—Continued

Copolymer ingredients	Component A	Component B	Composite fiber
Copolymer concentration of spinning dope (%)	10	13	
Irreversible swelling (Q)	3.86	2.81	
Difference	1.05		
In-process shrinkage (%)	33.4	27.4	
Difference	6.0		
E_{ir}^{95}	1.47	0.85	
C_{ir}^{ent}			19.5
Elastic recovery of crimp (%)			0.35
Splitting (%)			62.3
Dyed fiber			0
C_{ir}^{ent}			16.2
Shades of dyed fibers	pale	dark	0.38

EXAMPLE 5

In the preparation of component A copolymer of acrylonitrile and vinyl acetate (97/3 by weight) and having a viscosity $[\eta]$ of 1.4, a small amount of methallyl sulfonic acid is copolymerized with the above monomers, whereby the content of sulfonate groups in the resulting copolymer is 40 milliequivalents per 10^3 grams of copolymer. As for component B, a small amount of sodium methallyl sulfonate is copolymerized with acrylonitrile and vinyl acetate (91/9 by weight) to prepare a copolymer $[\eta] = 1.4$, the sulfonate group content being 40 milliequivalents per 10^3 grams of copolymer. These two copolymers A and B are separately

and B component polymers are separately dissolved in 45 % aqueous solutions of sodium thiocyanate to prepare different spinning solutions both 11 % in the polymer content. These spinning solutions are spun into composite fiber, which is washed with water and stretched in the same manner as in Example 1 to obtain swollen gel fiber of a moisture content of 150 %. Immediately thereafter, the gel fiber is relaxed for 15 minutes in hot water of 90°C. under non-tensioned state and then dried in a moisture-controlled atmosphere of a dry-bulb temperature of 110°C. and wet-bulb temperature of 77°C. in a non-tensioned state. The dried fiber is then heat-treated for 15 minutes in pressurized steam of 110°C. The results are shown in Table 6.

Table 5

Copolymer ingredients	Component A	Component B	Composite fiber
Acrylonitrile/vinyl acetate	97/3	91/9	
Sulfonate content (milliequivalents/ 10^3 copolymer)	40	40	
Irreversible swelling (Q)	3.33	2.03	
Difference	1.30		
In-process shrinkage (%)	39.9	29.2	
Difference (%)	10.7		
C_{ir}			21.2
Elastic recovery of crimp (%)			56.9

dissolved in 48 % aqueous solutions of sodium thiocyanate to prepare two spinning solutions both 12 % in polymer concentration, which are spun into composite fibers, which are washed with water; stretched in the same manner as in Example 1 to obtain swollen gel fiber of a moisture content of 170 %. The fiber is immediately relaxed for 15 minutes in hot water of 98°C. under non-tensioned state and then dried under non-tension in a moisture controlled atmosphere of 110°C. in dry-bulb temperature and 77°C. in wet-bulb temperature, and further heat-treated for 15 minutes in a pressurized steam of 110°C. The properties of the resulting fiber are shown in Table 5.

EXAMPLE 6

In the preparation of component A copolymers of acrylonitrile and acrylamide (91/9 and 94/6 by weight) and having a viscosity $[\eta]$ of 1.5, azobisisobutyronitrile is used as the polymerization initiator so that no sulfonate is contained in the polymer terminal. As for component B, a copolymer ($[\eta] = 1.5$) is prepared from acrylonitrile and methyl acrylate (91/9 by weight) with azobisisobutyronitrile as the initiator so that no sulfonate is introduced in the polymer terminal. These A

Table 6

Copolymer ingredients		
Component A (acrylonitrile/acrylamide)	91/9	94/6
Component B (acrylonitrile/methyl acrylate)	91/9	91/9
Mono-component fiber		
Irreversible swelling (Q)		
Component A	2.98	2.92
Component B	2.08	2.08
Difference	0.90	0.84
In-process shrinkage (%)		
Component A	35.3	34.7
Component B	28.0	28.0
Difference	7.0	6.7
E_{ir}^{95} (g/d)		
Component A	0.42	0.56
Component B	0.60	0.60
Composite fiber		
Fundamental crimp frequency (C_f)	24.2	18.1
Elastic recovery of crimp (%)	58.1	65.9
Denier (d)	3.04	2.35
Dry strength (g/d)	3.39	3.14
Knot strength (g/d)	2.88	3.07
Dry elongation (%)	47.7	42.0
Knot elongation (%)	41.3	37.6

EXAMPLE 7

In the preparation of component A copolymers of acrylonitrile and vinylidene chloride (91/9 and 93/7 by weight) and having a viscosity $[\eta]$ of 1.5, azobisisobutyronitrile is used as the polymerization initiator so that no sulfonate is introduced in the polymer terminal. As for component B, copolymers ($[\eta]=1.5$) are prepared from acrylonitrile and methyl acrylate (93/7 by weight) and also from acrylonitrile, methyl acrylate and vinylidene chloride (84/7/9) with azobisisobutyronitrile as the initiator so that no sulfonate is introduced in the polymer terminal. These components A and B polymers are separately dissolved in 52 % aqueous solutions of sodium thiocyanate to prepare different spinning solutions all 11 % in the polymer content. These spinning solutions are selected in such combinations as indicated in Table 7 and spun into composite fiber, which is then treated in the same manner as in Example 1. The results are shown in Table 7.

Table 7

Polymer ingredients	(acrylonitrile/methyl acrylate/vinylidene chloride)	91/0/9	93/0/7
Component A		91/0/9	93/0/7
Component B		84/7/9	93/7/0
Mono-component fiber			
Irreversible swelling (Q)			
Component A		2.88	2.88
Component B		1.81	2.24
Difference		1.07	0.64
In-process shrinkage (%)			
Component A		37.7	37.7
Component B		27.2	32.1
Difference		10.5	5.6
E_{α}^{95} (g/d)			
Component A		1.48	1.48
Component B		0.80	0.95
Composite fiber			
C_f		22.0	12.7
Elastic recovery of crimp (%)		66.2	63.7

EXAMPLE 8

In preparing three different copolymers from 91 % acrylonitrile and 9 % methyl acrylate, with viscosity of $[\eta]=1.0, 1.4$ and 1.7 , respectively, small amounts of sodium methacrylate are copolymerized with the above monomers in such a manner that each of the copolymer contains 40 milliequivalents of sulfonic acid per 10^3 grams of polymer. The resulting copolymers are respectively dissolved in 46 % aqueous solutions of sodium thiocyanate to prepare spinning dopes whose copolymer concentrations are identical, i.e. 11 percent. As shown in Table 8, these three different spinning dopes, in various combinations of two each, are wet-spun through a composite fiber spinning apparatus shown in U.S. Pat. No. 3,182,106 into 12 % aqueous solutions of sodium thiocyanate at -3°C . in such a manner that the two components are extruded in equal amounts to form composite filaments. The resulting filaments are guided into a water bath, whereby the former are thoroughly washed, and are stretched in boiling water 9 times their initial length to obtain swollen gel fiber of a moisture content of 166, 171 and 125 %, respectively. Then, those fibers are immediately relaxed in boiling water under no tension for 10 minutes, whereby the latent spiral crimps of the fibers are developed. Then, the fibers are dried under no tension in a controlled atmosphere at a dry-bulb temperature of 110°C . and a wet-bulb temperature of 75°C .

On the other hand, comparable mono-component fibers are prepared under the same conditions as above and their irreversible swelling and in-process shrinkage are measured. The results are also summarized in Table 8.

Table 8

Intrinsic viscosity of copolymer $[\eta]$	1.0	1.0	1.4
High shrinking component	1.7	1.4	1.7
Low shrinking component			
Mono-component fiber			
Irreversible swelling			
High shrinking component	3.12	3.12	2.29
Low shrinking component	2.20	2.29	2.20
Difference ΔQ	0.92	0.83	0.09
In-process shrinkage			
High shrinking component (%)	41.0	41.0	29.3
Low shrinking component (%)	27.2	29.3	27.2
Difference ΔI	13.8	11.7	2.1
Composite fiber			
Fundamental crimp frequency (C_f)	33.5	29.4	18.3
Splitting (%)	0	0	0
Dry Strength (g/d)	3.39	2.70	3.08
Knot Strength (g/d)	2.20	2.06	2.80
Dry Elongation (%)	30.7	33.6	34.1
Knot Elongation (%)	18.5	20.9	29.4

By way of controls, when the fibers of compositions of Table 8 are treated, after the thermal stretching, in the conventional manner, that is to say, in the sequence of stretching, compacting-drying, and hot, humid relaxing treatment, there arises substantially no difference in shrinkage and, therefore, no composite fibers having spiral crimps are obtained.

EXAMPLE 9

In obtaining a copolymer of 91 % acrylonitrile, 9 % methyl acrylate and $[\eta]=1.5$, a slight amount of sodium methallylsulfonate was copolymerized with the monomers so that the sulfonic acid content would be 50 milli-equivalents per 10^3 grams of the polymer. The copolymer was dissolved in a 46 % aqueous solution of sodium thiocyanate to prepare three kinds of spinning dopes having the copolymer concentrations of 9, 11 and 13 % respectively. Two kinds of these three kinds of spinning dopes were combined as shown in Table 9 and were wet-spun into a 12 % aqueous solution of sodium thiocyanate at -3°C . by adjusting a metering pump so that two layers might be of equal amount by using the composite fiber spinning apparatus according to U.S. Pat. No. 3,182,106. The formed composite fibers were then well water-washed by being passed through a water-washing bath, and then stretched 10 times the initial length in boiling water to prepare swollen gel fibers of moisture contents of 117, 128 and 98 % respectively. Immediately thereafter the fibers were relaxed for 10 minutes in a non-tensioned state in boiling water so that spiral crimps developed and were then dried to be compacted in a non-tensioned state in an atmosphere in which the humidity had been adjusted so that the dry-bulb temperature is 110°C . and the wet-bulb temperature is 75°C .

On the other hand, the single spinning dopes were respectively singly spun under the same conditions as are mentioned above. The irreversible swellings and the process shrinkages were measured. The results are also mentioned in Table 9.

In case the fibers of the composition in Table 9 as Control 1 were thermally stretched, dried to be compacted and wet-heated to be relaxed by usual processes, no shrinkage difference was substantially pro-

duced and no self-crimped fibers having spiral crimps were obtained. Further, in Control 2, the fibers of the composition in Table 9 were practice. crimps stretched and were then dried under no tension at a temperature of 80°C. by a method of the Dawson type without being immediately relaxed. As a result, spiral crimps developed favorably but the splitting of the two layers was remarkable, further the knot strength and elongation were remarkably low, very brittle fibers were formed and they could be hardly used in practice. Further, when these fibers were wet-heated to be relaxed, the coily crimps entirely disappeared.

On the other hand, the single spinning dopes were respectively singly spun under the same conditions as are mentioned above. The irreversible swellings and the process shrinkages were measured. The results are also mentioned in Table 10.

In case the fibers of the composition in Table 10 as a control were thermally stretched and were then stretched, dried to be compacted and wet-heated to be relaxed by usual processes, no shrinkage difference was substantially produced and no self-crimped fibers having coily crimps were obtained.

Table 9

Polymer concentration in the spinning dope:		Control 2			
High shrinkage side (%)	9	9	11	9	
Low shrinkage side (%)	13	11	13	13	
Fiber from single spinning dope					
Irreversible swelling (Q)					
High shrinkage side	2.46	2.46	2.09		
Low shrinkage side	1.88	2.09	1.88		
Difference	0.58	0.37	0.21		
Process shrinkage (%)					
High shrinkage side	33.3	33.2	29.3	15.0	
Low shrinkage side	26.9	29.5	26.9	13.0	
Difference	6.3	3.9	2.4	2.0	
Spiral crimped fibers					
Fundamental crimp frequency (C _p)	27.2	17.1	12.7	16.2	
Splitting of two layers (%)	0	0	0	52	
Dry strength (g/d)	2.97	3.48	3.92	3.34	
Knot strength (g.d)	2.69	2.68	3.20	1.11	
Dry elongation (%)	35.8	43.8	36.6	19.1	
Knot elongation (%)	30.4	31.9	28.6	4.8	

EXAMPLE 10

Polymers of a composition of 95 % acrylonitrile and 5 % methyl acrylate; 97 % acrylonitrile and 3 % methyl acrylate; and 100 % acrylonitrile and $[\zeta]=1.5$ produced by using azobisisobutyronitrile as a polymerization initiator were respectively dissolved in 48 % aqueous solutions of sodium thiocyanate to prepare, for each polymer, two kinds of spinning dopes of polymer concentrations of 11 and 13 % respectively. These two spinning dopes of the same polymer of different polymer concentrations were wet-spun into a 12 % aqueous solution of sodium thiocyanate at -3°C. by adjusting a metering pump so that both layers would be of equal amount by using the composite fiber spinning apparatus according to U.S. Pat. No. 3,182,106. The formed fibers were then washed by being passed through a water-washing bath, and then stretched 10 times the length in boiling water to prepare swollen gel fibers having moisture contents of 112, 130 and 239 % respectively. The stretched fibers were immediately relaxed for 10 minutes in a non-tensioned state in boiling water so that spiral crimps were developed and were then dried to be compacted in a non-tensioned state in an atmosphere in which the humidity had been adjusted so that the dry-bulb temperature is 110°C. and the wet-bulb temperature is 75°C.

Table 10

Polymer composition (acrylonitrile/methylacrylate)		95/5	97/3	100/0
Polymer concentration in the spinning dope				
High shrinkage side (%)		11	11	11
Low shrinkage side (%)		13	13	13
Fiber from single spinning dope				
Irreversible swelling (Q)				
High shrinkage side		2.19	2.52	3.86
Low shrinkage side		2.04	2.08	2.92
Difference		0.15	0.44	0.94
Process shrinkage (%)				
High shrinkage side		25.4	29.0	37.5
Low shrinkage side		24.8	27.7	35.2
Difference		0.6	1.3	2.3
Spiral crimped fibers				
Fundamental crimp frequency (C _p)		12.6	14.9	14.6
Splitting of two layers		0	0	0

EXAMPLE 11

A copolymer ($[\zeta]=1.5$) of acrylonitrile and vinylidene chloride (93/7 by weight) was prepared with the

use of azobisisobutyronitrile as the initiator so that no sulfonate group is introduced in the resulting polymer terminal. The copolymer was dissolved in a 46% aqueous solution of sodium thiocyanate to prepare two spinning solutions having polymer concentrations of 9 % and 12 % respectively. These spinning solutions were simultaneously spun into composite fibers, which were washed with water and stretched in the same manner as in Example 9 to obtain swollen gel fibers of a moisture content of 170 %. The so stretched fibers were immediately relaxed in a non-tensioned state for 10 minutes in hot water of 80°C. to develop coil crimps and dried in a moisture-controlled atmosphere of a dry-bulb temperature of 110°C. and a wet-bulb temperature of 75°C. in a non-tensioned state. The results are shown in Table 11.

Table 11

Polymer composition (acrylonitrile/vinylidene chloride)	93/7
Polymer concentration in the spinning solution (%)	
High shrinkage side	9
Low shrinkage side	12
Fiber from single spinning solution	
Irreversible swelling (Q)	
High shrinkage side	3.24
Low shrinkage side	2.09
Difference	1.15
Process shrinkage (%)	
High shrinkage side	35.5
Low shrinkage side	24.7
Difference	10.8
E _r ⁹⁵ (g/d)	
High shrinkage side	1.38
Low shrinkage side	2.04
Coil crimped fiber	
Fundamental crimp frequency (C _f)	21.6
Elastic recovery of crimp (%)	70.6

What we claim is:

1. A method of producing an acrylic composite fiber consisting of two components arranged in layers in side-by-side relationship throughout the length of the fiber, which comprises wet-spinning two different acrylic spinning solutions to form a composite fiber, washing the composite fiber with water, stretching the composite fiber to form a swollen gel fiber having a moisture content of at least 40%, relaxing the swollen gel fiber for 5 - 20 minutes, without drying, in hot water or steam at 60° - 130°C in a non-tensioned state, and drying the relaxed fiber under correlated conditions of temperature and humidity within the graphical area defined by coordinates of wet-bulb temperature-ordinate, dry-bulb temperature-abscissa in °C of 65,135, 65,90 85,90 and 90,135, the spinning solutions being selected to provide fiber components respectively formed therefrom having a difference in degree of irreversible swelling of 0.05 - 3 so as to cause a difference in shrinkage between the fiber components.

2. A method as claimed in claim 1 wherein two different acrylonitrile polymers are employed for the respec-

tive spinning solutions, said acrylonitrile polymers being different by less than 0.5 % in acrylonitrile content, and the acrylonitrile polymer which forms the high shrinkage fiber component containing strong acidic groups in a larger amount than in the other acrylonitrile polymer by 10 - 30 milliequivalents per 10³ grams of the polymer.

3. A method as claimed in claim 2 wherein the strong acid group is a sulfonic group.

4. A method as claimed in claim 3 wherein the sulfonic group is introduced in the polymer by copolymerizing methallyl sulfonic acid or its salt with monomers forming said polymer.

5. A method as claimed in claim 1 wherein two different acrylonitrile polymers are employed for the respective solutions, said acrylonitrile polymers being different by less than 0.5 % in acrylonitrile content, the content of neutral and weak acidic hydrophilic groups in the polymer forming the high shrinkage fiber component being higher by 3 - 10 % by weight than that in the other polymer.

6. A method as claimed in claim 5 wherein the hydrophilic group is an amide group.

7. A method as claimed in claim 1 wherein an acrylonitrile content in one acrylonitrile polymer for one spinning solution is different, if any, by less than 0.5 % from that in the other acrylonitrile polymer for the other spinning solution, and the polymer content in the spinning solution forming the high shrinkage fiber component is lower by 0.3 - 5 % by weight than that in the other spinning solution forming the low shrinkage fiber component.

8. A method as claimed in claim 1 wherein two different acrylonitrile polymers are employed for the respective spinning solutions, a difference, if any, in acrylonitrile content between the polymers being less than 0.5 %, and the molecular weight (as expressed in intrinsic viscosity [η] measured in dimethylformamide at 30°C.) of the polymer forming the high shrinkage fiber component being lower by at least 0.1 than that of the other polymer forming the low shrinkage fiber component.

9. A method as claimed in claim 1 wherein two different acrylonitrile polymers are employed for the respective spinning solutions, and a difference, if any, of acrylonitrile content between the polymers is less than 0.5 %, and the acrylonitrile polymers are selected from terpolymers of acrylonitrile, vinylidene monomer and non-crystalline high molecular substance forming monomer, there being a difference in the vinylidene monomer content between the two polymers.

10. A method as claimed in claim 9 wherein the vinylidene monomer is vinylidene chloride.

11. A method as claimed in claim 9 wherein the monomer for forming the non-crystalline high molecular substance is methyl acrylate.

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