

# United States Patent

Ohki et al.

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## [54] COMPOSITE POLYACRYLONITRILE FIBER

[72] Inventors: **Makoto Ohki; Hisashi Irie; Kazuo Okamoto**, all of Osaka, Japan

[73] Assignee: **Kanegafuchi Boseki Kabushiki Kaisha**, Tokyo, Japan

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### [56] References Cited

#### UNITED STATES PATENTS

3,039,524 6/1962 Belck et al. ....161/173 X

3,330,895 7/1967 Fujita et al. ....264/171 X  
3,426,117 2/1969 Shimoda et al. ....264/171 X

*Primary Examiner*—Robert F. Burnett

*Assistant Examiner*—Linda C. Koeckert

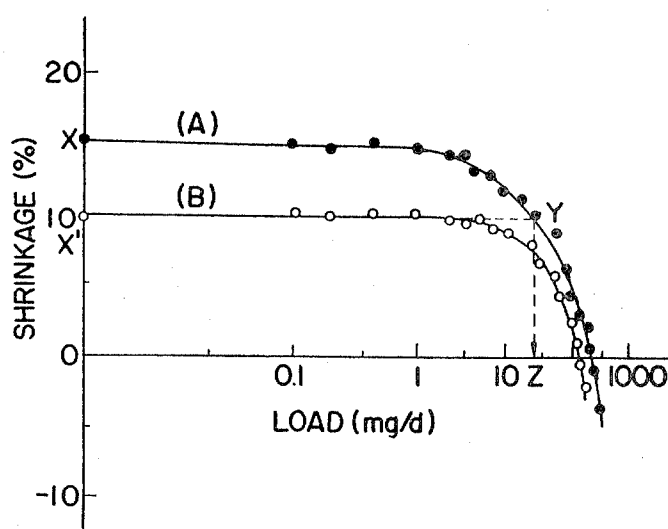
*Attorney*—Robert E. Burns and Emmanuel J. Lobato

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### ABSTRACT

A drawn composite filament consisting of two acrylic components differing in heat shrinkability eccentrically disposed along the filament axis, which is capable of developing, upon heating in relaxed condition, a uniform crimp having a high frequency, high degree of elasticity and large retention of the degree of elasticity. The higher shrinking component consists of a copolymer or terpolymer comprising 65–95 percent by weight of combined acrylonitrile and 35–5 percent by weight of a combined higher alkyl acrylate having five to 14 carbon atoms in its alkyl group, the lower shrinking component comprises acrylonitrile homopolymer, or copolymer or terpolymer containing up to 25 percent by weight of at least one combined monoethylenically unsaturated addition type monomer, and the product of the difference in shrinkability between the two components and the residual shrinking stress is at least 50.

13 Claims, 1 Drawing Figure



## COMPOSITE POLYACRYLONITRILE FIBER

This invention relates to synthetic textile fibers and particularly to composite filaments having an improved crimpability.

Numerous studies and investigations have been made, heretofore, towards the production of helically crimped composite filaments by cospinning of two or more different materials so that they form a unitary filament which contains the components in an eccentric relation over the cross section of the filaments. Thus, when two materials are used which possess substantially different physical properties, such as for example, different residual shrinkage, a crimp is brought about by the application of a suitable aftertreatment to the spun and drawn composite filaments. In such prior studies, various efforts have been directed to the selection and the combination of two materials to be cospun which are determined depending upon object and outlet of the spun composite filaments.

However, it has been pointed out that composite polyacrylonitrile fibers are in general inferior in their crimp developability due to the following facts.

Firstly, there is naturally a considerably narrow limitation in the combination of the materials to be cospun consisting of acrylonitrile polymers. Generally speaking, it is preferred for the provision of composite filaments possessing an excellent crimp developability that the difference in heat shrinkability between two materials to be conjugated be as large as possible; so that in most instances, in order to obtain a good result, there have been used two acrylonitrile polymers differing in the degree of polymerization or two spinning solutions of polyacrylonitrile having different concentrations, or sometimes, two acrylonitrile copolymers are used which differ from each other in the amount or the nature of their comonomers. However, too large a quantitative or qualitative difference between acrylonitrile polymers to be cospun causes either impairment of heat resistance or cleavage of the components of the resulting composite filaments whereby their utility is extremely reduced. Thus, it has not been easy to discover a suitable combination of spinning materials so as to satisfy the requirements of excellent heat resistivity and mutual compatibility in combination with large differences in heat shrinkability.

Secondly, acrylonitrile polymers including its homopolymer generally show an extremely small shrinking stress when shrunk by heating. Namely, in the case when heat shrinkability of component *a* is higher than that of component *b*, the composite filament develops by the application of heat treatment a spiral crimp wherein, as a matter of course, the component *a* having higher heat shrinkability locates inside of the helices. Besides, crimp characteristics of the resultant composite filament, such as elastic property and durability of crimp depend mainly upon the nature of the component *a*. Therefore, it is extremely important to select a relevant polymer for the component *a*. However, since the component having the higher heat shrinkability exhibits in general a lower thermal shrinking stress, such composite filaments often have the disadvantage that the ability to develop crimps is considerably attenuated or lacks uniformity in yarns or fabrics composed of such filaments, due in large to the fact that the filaments become compacted and lose freedom of movement in the yarn or fabric resulting in yarns or fabrics of reduced covering power or leanness, so that the best use cannot be made of the characteristics found in acrylic fibers.

The above-mentioned drawbacks are fundamental with respect to the composite polyacrylonitrile fibers and therefore necessitates prudent care with respect to the products as well as the process of their manufacture and in particular much effort is still being expended in the processes of the crimp development and dyeing thereof.

It is an object of the present invention to produce a novel composite polyacrylonitrile filament having an excellent crimp developability which will eliminate completely the drawbacks as aforementioned.

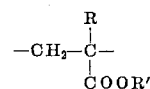
Another object is to produce a uniformly crimped composite polyacrylonitrile filament having improved crimp

characteristics such as crimp frequency, crimp elasticity and crimp durability.

Other objects will become apparent from the following description.

In accordance with the present invention, there is obtained a drawn composite filament consisting of two fiber forming acrylonitrile polymer components eccentrically disposed and adhered towards each other in a side-by-side or a sheath and core relationship throughout the entire length of the filament, wherein one of said components consists of a acrylonitrile copolymer comprising 65–95 percent by weight of combined acrylonitrile and 35–5 percent by weight of a combined higher alkyl acrylate having five to 14 carbon atoms in its alkyl group, the other component is an acrylonitrile polymer which may or may not contain said higher alkyl acrylate, the difference in the content of the higher alkyl acrylate between said two components is at least 5 percent by weight based on the polymer, the component containing a greater amount of the higher alkyl acrylate contains less combined acrylonitrile as compared with the other component, and the product of the difference in shrinkability between the two components and the residual shrinking stress as defined hereinafter is at least 50. The filament of the present invention is capable of developing throughout its entire length, upon heating at 100°C. in relaxed condition, a uniform helical crimp having a frequency of 8–50, particularly 10–40 per 25 mm. of crimped length, its degree of elasticity under a load corresponding to 50 mg. per denier of at least 75 percent, particularly at least 80 percent and a retention of the degree of elasticity under a load corresponding to 150 mg. per denier of at least 85 percent, particularly at least 90 percent based on the degree of elasticity under a load corresponding to 50 mg. per denier, and characterized by a high crimpability and crimp stability when spun into yarn and woven or knit into fabric.

For convenience, by the expression "higher alkyl acrylate" used hereinafter is meant a structural unit having the general formula,



where R is hydrogen or methyl radical and R' is a higher alkyl group having five to 14 carbon atoms.

In the manufacture of composite acrylonitrile fibers in the past, the components selected have been confined, in general, to those consisting of a copolymer or terpolymer of acrylonitrile and at least one neutral or hydrophilic  $\alpha$ ,  $\beta$ -monoethylenically unsaturated addition type comonomer such as vinylacetate, acrylic amide, acrylic acid, acrylic sulfonate, a lower alkyl acrylate, e.g., methylacrylate and methylmethacrylate, and the like. In Japanese Pat. application Publication No. 11,136/1966, highly shrinkable fibers obtained by spinning solely a copolymer comprising butylacrylate, octylvinylether, laurylvinylother, or the like have been disclosed, while in Japanese Pat. application publication No. 19,554/1968, a homogeneous emulsion polymerization of 2-ethylhexylacrylate has been disclosed. However, these disclosures do not relate to composite fibers and moreover the inventions disclosed therein are directed to objects entirely different from those of the present invention.

Suitable higher alkyl acrylates, i.e., combined acrylic acid esters of higher alcohol having five to 14 carbon atoms, include, for instance, amylacrylate, hexylacrylate, 2-ethylhexylacrylate, octylacrylate, decylacrylate, laurylacrylate, myristylacrylate, amylmethacrylate, hexylmethacrylate, octylmethacrylate, 2-ethylhexylmethacrylate, decylmethacrylate, laurylmethacrylate and derivatives thereof. In case a lower alkyl acrylate having four or less carbon atoms in its alkyl group is employed, the resultant composite fibers will not be provided with a satisfactory ability to develop crimp and desirable crimp characteristics which are the features of the

present invention or will sometimes cause a split of the components after drawing; while in case a higher alkyl acrylate, containing 15 or more carbon atoms in its alkyl group employed, its copolymer not only loses its adaptability for spinning, because of an extreme lowering of its solubility in ordinary solvents which have so far been used for dissolving polyacrylonitrile, but also results in fibers which show a remarkable deterioration of their physical or mechanical properties such as luster, tensile strength and elongation at break and the like, due to an increase in its devitrifying property. In general, acrylonitrile copolymers having a higher alkyl ester of methacrylic acid are somewhat inferior in their solubility in solvents to those having higher alkyl ester of acrylic acid and in particular, the larger the number of carbon atoms of the alkyl group, the more opaque or muddy their solutions are. However, as far as the number of carbon atoms of the alkyl group is in the range prescribed above, according to this invention, the copolymer has been found in solution to have good filterability as well as spinnability and is satisfactorily applicable as a spinning material.

Since the ability to develop crimp and crimp characteristics of composite filaments depend largely upon the nature of the component having higher heat shrinkability, which is naturally to locate inside of the helices as stated before, its physical properties are of very important significance. In order to attain the objects of this invention, the component having higher heat shrinkability should be provided with high shrinking stress, high heat durability and excellent compatibility with the other acrylonitrile polymer component having lower heat shrinkability. Such a requirement is completely met by the higher shrinking component to be applied to the composite filament of the present invention, which component consists of an acrylonitrile copolymer or terpolymer comprising 65-95 percent by weight of combined acrylonitrile and 35-5 percent by weight of a higher alkyl acrylate or further comprising a small amount of another combined  $\alpha$ ,  $\beta$ -monoethylenically unsaturated comonomer.

The polymerizable  $\alpha$ ,  $\beta$ -monoethylenically unsaturated comonomers, which are so-called dye improving agents, include acidic and basic comonomers such as p-styrenesulfonic acid, allylsulfonic acid, methallylsulfonic acid and salts thereof; vinylpyridine, vinylimidazole, vinylpyrrolidone; and the like. These comonomers may be used in an amount of up to 5 percent by weight. In consequence, the largest content of the higher alkyl acrylate can be 30-35 percent by weight based on the polymer and it is one of the advantages of the present invention that such a large amount of the higher alkyl acrylate can be introduced into the copolymer. That is to say, since any components having desired shrinkability are obtainable according to one's purpose, various composite fibers differing in the crimp characteristics in and over a wide range can be manufactured, which have never been so produced in the past, so that the composite fibers of this invention are capable of being adapted for multiple purposes and utilities of acrylonitrile polymer fibers.

The component comprising a smaller amount of combined acrylonitrile should contain the higher alkyl acrylate in a larger amount as compared with the other component comprising a larger amount of combined acrylonitrile; the difference in the content of the higher alkyl acrylate between the two components should be at least 5 percent, preferably 10 percent, by weight based on the polymer, in order to ensure a satisfactory crimp frequency of the resulting crimped fibers.

Another feature of the acrylonitrile copolymer component, to be applied to the invention, is its high-heat resistivity. When a noncrystallizable comonomer is introduced into acrylonitrile polymer, there is usually seen a marked lowering of the heat resistivity of the polymer depending upon the amount of the comonomer introduced. In fact, yarns consisting of an acrylonitrile copolymer comprising more than 15-16 percent by weight of methylacrylate have extreme shrinkage and the individual filaments in the yarns stick together entirely, on application of steam treatment at 130°C.; whereas it is surprising

that by incorporating 35 percent by weight of the higher alkyl acrylate containing a hexyl group there is no such sticking phenomenon of the resultant fibers. It may be said, in this connection, that in the above-mentioned instance, the amount of the incorporated methylacrylate is about 10 percent by mole, while that of the higher alkyl acrylate is about 14 percent by mole and therefore the superiority in heat resistivity of the component consisting of higher alkyl acrylate copolymer is clearly evidenced by the above fact.

The component having higher shrinkability, to be employed to this invention, has its merit in the ability of firmly bonding to or excellent compatibility with the other component having lower shrinkability, so that the latter acrylonitrile polymer component need not be specified from the viewpoint of mutual compatibility. This fact also facilitates the preparation of various composite fibers differing in their crimp characteristics in a wide range which is a very advantageous feature of the present invention.

Yet, it is preferred, from the viewpoint of quality with respect to composite fibers, that the component having lower shrinkability consists substantially of an acrylonitrile homopolymer or of a copolymer or terpolymer comprising at least 75 percent by weight of combined acrylonitrile and up to 25 percent by weight of at least one monoethylenically unsaturated addition type monomer combined therewith including higher alkyl acrylate. In case the acrylonitrile content is less than 75 percent by weight, the initial modulus as well as the degree of crimp elasticity of the resultant composite fibers will be lowered and consequently the so-called acrylic touch, dimensional stability and the bulkiness of the fabric made therefrom will deteriorate and therefore is not preferable.

Furthermore, the combination of the above-mentioned higher shrinking component and lower shrinking component in order to form the composite fiber of the present invention must satisfy the requirement that the product of the difference in shrinkability between the two components ( $\Delta\epsilon\%$ ) and the residual shrinking stress ( $\Delta F$  mg./denier) is at least 50, and preferably at least 100.

By the expression "residual shrinking stress" is meant a shrinking stress of the higher shrinking component, corresponding to the difference in shrinkability between the two components, or in other words, a shrinking stress which remains in the higher shrinking component upon completion of the contraction of the lower shrinking component.

The shrinkability of a component is determined by measuring the shrinkage, upon immersion in boiling water under various tensions, of a monocomponent filament made from the component polymer spun and otherwise processed under substantially the same conditions as the composite filament. More particularly, the shrinkage is measured by the following procedure.

Several samples are taken from the monocomponent filament prepared as above. One end of the sample is loaded with a weight corresponding to a 30 gram per denier and the loaded length is observed accurately at 25°C. under 65 percent R.H. After replacing the weight with another weight corresponding to 0-700 mg. per denier, the sample filament is soaked for 10 minutes in boiling water at 100°C. to shrink. The shrunk sample filament is then air-dried as being loaded for 24 hours at 25°C. under 65 percent R.H. The measurements are obtained by using a sufficient number of samples of the same monocomponent filament using in each instance a different weight in the shrinking treatment, until substantially no shrinkage is observed, due to the balance of the load and the shrinking stress. After replacing the weight for the initial weight again, the length of the dried sample filament is observed. The shrinkage is expressed by the percent loss of the original length upon shrinkage, that is, the percentage of the difference between the length before shrinking and the length after shrinking, against the former length. The shrinkages obtained by several series of measurements are plotted on a graph to draw a load-shrinkage curve from which the difference in shrinkability of the two components and the residual shrinking stress are obtained.

Referring to the drawing:

The FIGURE is a graphical representation showing the relationship between shrinkages of two components and load applied, and illustrating the difference in shrinkability and the residual shrinking stress.

In the FIGURE, curves (A) and (B) are respective plots of shrinkages of a higher shrinking component filament (A') and a lower shrinking component filament (B'). Line OX represents the shrinkability of filament (A') and line OX' represents the shrinkability of filament (B'). In the combination of filament (A') and filament (B'), line XX' represents residual shrinkability that still remains in filament (A'), after filament (B') has shrunk, i.e., the difference in shrinkability ( $\Delta\epsilon\%$ ) between the two filament components. The extension of the horizontal straight line in curve (B) intersects curve (A) at point Y and the perpendicular passing through the intersecting point Y intersects the axis of abscissa at point Z. The load (mg./denier) corresponding to the intersecting point Z is a residual shrinking stress ( $\Delta F$ ).

The ability of composite filaments to develop crimp is characterized by the interrelation between the difference in the shrinkability of two components and the residual shrinking stress. From the standpoint of practical operation, it is of greater advantage to provide composite filaments with the combination of components showing a large residual shrinking stress rather than to prepare composite filaments having much difference in shrinkability between the two components thereof. Its principal reason is that the former composite filaments develop a more stable crimp. In polyacrylonitrile crimped fibers, their liability to deform has been already substantiated as a problem awaiting solution in heat treatment such as crimp developing treatment and dyeing.

The component having higher shrinkability in the composite filament of the present invention always exhibits a higher value of residual shrinking stress compared with any components in any conventional composite polyacrylonitrile filaments having a difference in shrinkability between the two components equal to that of the composite filament of the present invention. In consequence, the composite filament of the present invention can develop a crimp excellent in its stability as compared with the conventional composite polyacrylonitrile filaments.

In this connection, the filament components should be so selected and combined that the product of the difference in shrinkability therebetween and the residual shrinking stress of the higher shrinking component may be at least 50, more preferably at least 100. In case it is less than 50, the composite filament will develop little crimp, or even if it develops, such a crimp will lack utility.

The ability to develop of the crimp having excellent stability and high frequency depends upon the above-mentioned product  $\Delta\epsilon \times \Delta F$ . However, other physical or mechanical factors such as the bending modulus, relative proportions of the components and the cross-sectional configuration of the composite filament will affect the crimp stability and crimp frequency to some extent and may involve a variation in the difference in shrinkability as well as the residual shrinking stress. With the procedures described in the examples, satisfactory results are obtained by a difference of shrinkability  $\Delta\epsilon$  of about 2.5–36, a residual shrinking stress  $\Delta F$  of about 17–43 and a product  $\Delta\epsilon \times \Delta F$  of about 65–1,200.

The process for manufacturing the composite fibers of the present invention is illustrated in the following manner.

A conventional process per se can be used for the polymerization of acrylonitrile copolymer containing a higher alkyl acrylate while can yield satisfactory results, however emulsion polymerization and solution polymerization are preferably employed due to the slight solubility in water of the higher alkyl acrylate monomer. A higher alkyl acrylate has a rather excellent ability for copolymerizing with acrylonitrile and the yield of copolymer often exceeds 95 percent depending upon the conditions of polymerization, so that the amount of unreacted monomers to be recovered are advantageously diminished. No special additives are required essential for the

polymerization, such as catalysts, emulsifier and the like, only the conventional ones are necessarily used. The polymer prepared by polymerization reaction is directly subjected to a spinning process in the case of solution polymerization, or otherwise after purifying, drying and dissolving into a solvent. The spinning solution is a 15–25 percent by weight solution of the polymer in an organic or inorganic solvent and usually has a viscosity of 100–500 poises.

In the spinning process, either a side-by-side type conjugation or eccentric sheath-core type conjugation can be adopted. The former provides better crimp characteristics to the resultant fibers. Furthermore, fibers produced in accordance with the present invention preferably contain about equal parts of the two components, although good results may be obtained with composite fibers containing at least 30 percent, more particularly at least 40 percent by weight of one component and up to 70 percent, more particularly up to 60 percent by weight of the other component. Any known spinneret for conjugate spinning may be employed for the manufacture of the composite fibers of this invention.

The spinning process can be effected by wet spinning, dry spinning or semimelt spinning. In the case of wet spinning, special precautions on coagulation conditions are required. One of the several reasons why no higher alkyl acrylates have so far been manufactured commercially, at least in the fiber industry, wherein the lower alkyl acrylates have met with such success, is their drawback such as unsatisfactory spinnability or drawability due to inadequate coagulation conditions, causing devitrification of the resultant fibers, inferiorities of luster, quality, or the like. In particular, when the solvent for the polymer composition is an organic solvent, e.g., dimethylformamide and the coagulation system comprises an aqueous solution of the same or mixture thereof, it is not a rare occurrence, though it may depend on the nature of the polymer composition to some extent, that the performance of the spinning operation becomes impossible, so that the adaptable conditions of coagulation are restricted to an extremely narrow range.

The coagulation systems well adapted for the manufacture of the composite fibers of the present invention are aqueous solutions of certain lower alcohols such as methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol, glycerine and the like; of inorganic salts such as rhodanates, calcium chloride, zinc chloride and the like; and of inorganic acids such as nitric acid, sulphuric acid and the like. Whatever the solvents in the spinning solution may be, good spinnability and fibers of superior quality are obtained according to said coagulation systems. It may be necessary to select and to adequately manage coagulation conditions so that the solvent in the spun filamentary solution may be extracted and diffused as much as possible into the coagulation bath and thereby a homogeneous coagulation may take place at an inner portion as well as a peripheral portion of the fiber. From this point of view, it is preferable for the composite fibers of the present invention to be manufactured by a dry spinning process.

After thus setting up the fiber structure, the solidified fibers are hot drawn according to a conventional manner and are dried and wound up on a tube, if required. The preferable draw ratio is in general 4–8x in the case of dry spinning, and otherwise 6–12x. The composite fiber of the present invention never causes any splitting of its components owing to their good compatibility, during or after the drawing.

The crimp development of the composite fibers may be carried out by the use of any suitable known shrinking agent. Crimp developing will ordinarily be effected by the use of hot aqueous media such as hot or boiling water, steam or hot highly humid atmosphere, or by the use of hot air or other hot gaseous or liquid media chemically inert to the polymers of the composite fibers. The crimp developing temperature is generally in the neighborhood of 100° C. but may be higher or lower, e.g., not exceeding the melting point of the lower melting polymeric component of the fiber.

Thus the obtained crimped filament possesses, throughout its entire length, a uniform and stable helical crimp having its frequency of 8-50, particularly 10-40 per 25 mm. of crimped length, its degree of elasticity under a load corresponding to 50 mg. per denier of at least 75 percent, particularly at least 80 percent and a retention of the degree of elasticity under a load corresponding to 150 mg. per denier of at least 85 percent, particularly at least 90 percent based on the degree of elasticity under a load corresponding to 50 mg. per denier.

In many applications of the continuous or staple-length crimped filaments in textile materials, sometimes relatively high tensions are applied to the fabrics and thus to the single filaments in daily use of these materials. Therefore, high crimp stability, including high tensions, which is necessary for dimensional stability of the worsted or knitted goods from these crimped filaments is very important for a practical application of the filaments.

The characteristic of the filaments of the present invention having the intense ability to crimp to developing stable and durable crimps also after the application of high tensions or high loads to the filaments makes them especially useful for many textile applications where bulky highly crimped filaments are desired and where high crimp retention under high stress is of great importance. This applies also to the crimped filaments which are cut to staple length and which are usually spun into yarns and processed according to known textile processing methods to knitted or woven goods. The staple fibers of this invention can be crimped before they are further processed or in any state of processing, for instance, after they are spun into yarns or after the woven or knitted goods are made from these yarns. Another important application comprises the processing of the continuous filaments into bulky fabrics which again can be carried out with the continuous filaments in the crimped or uncrimped state. In the latter case, the crimp can be developed after weaving or knitting the yarns obtained therefrom or in any stage of the processing. Very interesting applications of the continuous yarns are, for instance, the preparation of worsted fabrics which may be woven from the uncrimped yarns containing the potential crimp and which are crimped after weaving and finishing. These worsted fabrics have an appearance and hand very similar to those obtained from staple yarns. However, they do

not possess the disadvantages in the processing and use of these fabrics.

In the following examples, which are illustrative of the invention, percentages are by weight unless otherwise indicated. Also, in all the examples, the polymers were fed to the spinneret, in the form of their solutions at equal volumes.

The crimp frequency and the degree of elasticity under a load corresponding to 50 mg. per denier of the fibers of this invention is determined by the following test.

A 5-mg. initial weight is attached to a single end of a crimped filament when the apparent denier of the filament is less than 5, or a 10-mg. initial weight is attached when the apparent denier of the filament is 5 or more. The total number of crimps in 25 mm. of crimped length under the above-mentioned load, i.e., the crimp frequency are counted.

The filament length  $l_0$  under the above-mentioned initial weight is observed and then, after the filament has been loaded by a weight corresponding to 50 mg. per denier for 30 minutes, the loaded filament length  $l_1$  is observed. After removing the load, the filament is allowed to shrink for 2 minutes, and thereafter the crimped filament length  $l_2$  under the above-mentioned initial weight is again observed. The

degree of crimp elasticity is obtained by the following equation.

Degree of crimp elasticity

$$(\text{percent}) = \frac{l_1 - l_2}{l_1 - l_0} \times 100$$

For the determination of the degree of crimp elasticity under a load corresponding to 150 mg. per denier is made in the same manner as above except that a weight corresponding to 150 mg. per denier is employed instead of the weight corresponding to 50 mg. per denier.

#### EXAMPLE 1

Predetermined various acrylonitrile copolymers for lower shrinking components and acrylonitrile copolymers containing higher alkyl methacrylate for higher shrinking components were produced by slurry polymerization or emulsion polymerization. These polymers were dissolved in dimethyl-formamide to prepare their respective spinning solutions having a polymer concentration of 25 percent. The spinning solutions were dry spun from a spinneret containing 50 orifices 0.16 mm. in diameter, to form their respective monocomponent filament yarns. The solutions were extruded at 105° C. Preheated nitrogen gas at 235° C. was blown through the spinning cell in parallel to the running direction of spun yarn. The yarns were wound up at 250 meters per minute.

The as-spun yarns were drawn to four times their original length in boiling water. The drawn yarns were then subjected to washing in water, followed by drying at 120° C. in a dryer. The resultant yarns had a denier per filament of 3. Upon certain combinations of the obtained filaments for lower shrinkage component and those for higher shrinking component, the difference in shrinkability ( $\Delta\epsilon$ ) and the residual shrinking stress ( $\Delta F$ ) were determined, which are given in table 1 below.

On the other hand, composite filaments were produced from the combinations of two filament components in the same manner as above, except that a spinneret for side-by-side cospinning containing 50 orifices 0.16 mm. in diameter was used. The resultant composite filaments were boiled off in water at 100° C. to develop their crimps and the crimp characteristics were determined, the results of which are shown in Table 2 below.

TABLE 1

Item	Lower shrinking component	Higher shrinking component	$\Delta\epsilon$ (percent)	$\Delta F$ (mg./den.)	$\Delta\epsilon \times \Delta F$
1.....	AN <sub>84</sub> -M6 <sub>15</sub> -MAS <sub>1</sub>	AN <sub>84</sub> -M6 <sub>15</sub> -MAS <sub>1</sub>	6.4	33.2	212.5
2.....	AN <sub>91</sub> -M6 <sub>8</sub> -MAS <sub>1</sub>	AN <sub>91</sub> -M6 <sub>8</sub> -MAS <sub>1</sub>	6.3	6.8	42.8
3.....	AN <sub>93</sub> -M12 <sub>6</sub> -MAS <sub>1</sub>	AN <sub>87</sub> -M12 <sub>12</sub> -MAS <sub>1</sub>	3.8	17.4	66.1
4.....	AN <sub>95</sub> -M12 <sub>10</sub> -MAS <sub>1</sub>	AN <sub>87</sub> -M4 <sub>12</sub> -MAS <sub>1</sub>	3.9	11.2	43.6

Note (1) In tables in all examples, the abbreviations mean combined comonomers as follows:

AN—Acrylonitrile  
M6—2-ethylhexyl methacrylate  
MAS—Sodium methacrylsulfonate  
M12—Lauryl methacrylate  
2—Ethyl acrylate  
4—Butyl acrylate

Note (2) The suffixed numeral indicates a percentage of the combined comonomer.

Table 1 above is a comparative study in shrinking stress for items 1 and 2 as well as items 3 and 4 which show substantially equal difference in shrinkability. As is apparent from table 1, the residual shrinking stress of item 1 and item 3 are high, and the products of the difference in shrinkability and the residual shrinking stress ( $\Delta\epsilon \times \Delta F$ ) exceed 50. Those values are reflected in the crimp characteristics as shown in table 2 wherein both items 1' and 3' exhibit superior values in their crimp frequency, degrees of crimp elasticity and in their retention of degree of crimp elasticity, indicating that they are provided with excellent crimp characteristics.

TABLE 2

Item	Den.	Tensile strength at break (g./den.)	Elongation at break (percent)	Crimp frequency (No./25 mm.)	Degree of crimp elasticity (percent)		Retention of degree of crimp elasticity (percent)
					Under 50 mg./den. load	Under 150 mg./den. load	
1'	3.2	2.6	32	29	88	83	94.3
2'	3.0	2.8	35	4			
3'	3.0	2.4	29	19	78	76	97.4
4'	3.0	2.7	33	5			

Contrary to the foregoing, since items 2 and 4 are less than 50 in their product of the difference in shrinkability and the residual shrinking stress, due to inferiority in their residual shrinking stresses, the respective composite filaments, item 2' and item 4', manufactured from the polymers of items 2 and 4, have such low crimpability that they are not applicable for practical use.

## EXAMPLE 2

Predetermined various acrylonitrile polymers for lower shrinking components and higher shrinking components were manufactured by slurry polymerization or emulsion polymerization. These polymers were dissolved in dimethylformamide to prepare their respective spinning solutions having a polymer concentration of 20 percent. The spinning solutions were wet spun from a spinneret into isopropyl alcohol bath at 20° C. to form their respective monocomponent filament yarns. The as-spun yarns were drawn 2.5x in a 50 percent aqueous solution of isopropyl alcohol at 45° C. and further drawn 3.5x in boiling water. The drawn yarns were then subjected to washing in water, followed by 1.2x drawing at 150° C. in a dryer. The resultant yarns of 300 denier of 100 filaments were wound up at 42 meters per minute.

Upon certain combinations of the obtained filaments for lower shrinking component and those for higher shrinking component, the difference in shrinkability ( $\Delta\epsilon$ ) and the residual shrinking stress ( $\Delta F$ ) were determined, which are given in table 3 below.

On the other hand, composite filaments of 300 denier of 100 filaments were produced from the combinations of two filament components in the same manner as above except that the two spinning solutions were extruded concurrently in a side-by-side relation from the same orifices of a spinneret. The resultant composite filaments were boiled off in water at 100° C. to develop their crimps and the crimp characteristics were determined, the results of which are shown in table 4 as follows:

TABLE 3

Item	Lower shrinking component	Higher shrinking component	$\Delta\epsilon$ (percent)	$\Delta F$ (mg./den.)	$\Delta\epsilon \times \Delta F$
5	AN <sub>65</sub> -65-MAS <sub>2</sub>	AN <sub>60.5</sub> -67.5-MAS <sub>2</sub>	2.4	11.1	27
6	AN <sub>68</sub> -MAS <sub>2</sub>	AN <sub>65</sub> -65-MAS <sub>2</sub>	3.0	25.5	77
7	AN <sub>65</sub> -65-MAS <sub>2</sub>	AN <sub>67</sub> -19-MAS <sub>2</sub>	3.7	12.2	45
8	AN <sub>60.5</sub> -17.5-MAS <sub>2</sub>	AN <sub>65</sub> -VAC <sub>10</sub> -MAS <sub>2</sub>	4.2	11.3	47
9	AN <sub>68</sub> -MAS <sub>2</sub>	AN <sub>65</sub> -19-MAS <sub>2</sub>	5.0	27.1	136
10	AN <sub>68</sub> -MAS <sub>2</sub>	AN <sub>60.5</sub> -67.5-MAS <sub>2</sub>	5.4	37.6	203
11	AN <sub>65</sub> -65-MAS <sub>2</sub>	AN <sub>68</sub> -610-MAS <sub>2</sub>	5.5	21.0	116
12	AN <sub>68</sub> -MAS <sub>2</sub>	AN <sub>65</sub> -610-MAS <sub>2</sub>	8.5	42.4	360

NOTE 3.—6=2-ethylhexyl acrylate; 1=Methyl acrylate; VAc=Vinyl acetate.

TABLE 4

Item	Den.	Tensile strength at break (g./den.)	Elongation at break (percent)	Crimp frequency (No./25 mm.)	Degree of crimp elasticity (percent)		Retention of degree of crimp elasticity (percent)
					Under 50 mg./den. load	Under 150 mg./den. load	
5'	3.0	3.4	25	2			
6'	3.1	3.6	24	16	84	83	99
7'	2.8	3.2	28	6			
8'	3.0	3.5	26	5			
9'	3.4	3.5	29	(Undeterminable due to splitting of components)			
10'	2.9	3.5	26	21	84	78	93
11'	3.0	3.1	30	18	81	76	94
12'	3.0	3.3	30	28	80	77	96

In table 3 above, the difference in shrinkability ( $\Delta\epsilon$ ) increases as the item number becomes larger. Items 6, 10, 11 and 12, which are the combination applicable to the present invention show high residual shrinking stresses, the products of the difference in shrinkability and the residual shrinking stress are in excess of 50, so that the filaments made therefrom exhibit an excellent ability to shrink. In particular, in spite of the fact that item 6 shows smaller difference in its ability to shrink, as compared with items 7 and 8, the former can develop its excellent crimps due to the high residual shrinking stress of its higher shrinking component, whereas the latter can develop substantially no crimps due to inferior residual shrinking stress of their higher shrinking components and are not suitable for practical use.

Such results are clearly evidenced by the crimp characteristics given in table 4. Namely, the crimp frequency as well as the degree of crimp elasticity is large in items 6', 10', 11' and 12'. In particular, the retention of degree of crimp elasticity under a load corresponding to 150 mg. per denier which represents expediently the stability of crimp, is remarkably large in those items. On the contrary, as is apparent from the crimp frequency in table 4, both items 7' and 8' develop little satisfactory crimps. Furthermore, notwithstanding that the product of the difference in shrinkability and the residual shrinking stress is in excess of 50, the filament components in the composite filament of item 9' lack compatibility and thereby a partial delamination or splitting of the components is observed in the composite filament, so that developed crimps are not uniform throughout the entire length of the filament. Such a delamination phenomenon has been observed when measuring the tenacity and elongation of the filament on the Instron Tensile Tester and confirmed by load-elongation curves automatically recorded on a chart which show separately breakages of the respective individual components.

## EXAMPLE 3

Predetermined various acrylonitrile polymers for lower shrinking components and acrylonitrile copolymers contain-

ing higher alkyl acrylate for higher shrinking components were manufactured by slurry polymerization or emulsion polymerization. These polymers were dissolved in dimethylformamide to prepare their respective spinning solutions having a polymer concentration of 20 percent. The spinning solutions were wet spun separately from a spinneret containing orifices 0.09 mm. in diameter, into an isopropyl alcohol coagulation bath, to form their respective monocomponent filament yarns. The as-spun yarns were drawn 2x at 60° C. in a hot water bath and further drawn in boiling water. The drawn yarns were washed in water, dried at 150° C. and wound up at 38 meters per minute. The resultant yarns were of 300 denier of 100 filaments. The total draw ratio was 9x.

Upon certain combinations of the obtained filaments for lower shrinking component and those for higher shrinking component, the difference in shrinkability ( $\Delta\epsilon$ ) and the residual shrinking stress ( $\Delta F$ ) were determined, which are given in table 5 below.

On the other hand, composite filaments were produced from the combinations of two filament components in the same manner as above except that the two spinning solutions were extruded simultaneously in a side-by-side arrangement from the same orifices of a spinneret. The resultant composite filaments were boiled off in hot water at 100° C. to develop their crimps and the crimp characteristics were determined, the results of which are shown in table 6 below.

TABLE 5

Item	Lower shrinking component	Higher shrinking component	$\Delta\epsilon$ (per cent)	$\Delta F$ (mg./den.)	$\Delta\epsilon \times \Delta F$
13	AN <sub>3</sub> -MAS <sub>2</sub>	AN <sub>3</sub> -1 <sub>5</sub> -MAS <sub>2</sub>	2.3	10.9	25
14	Same as above	AN <sub>3</sub> -3 <sub>5</sub> -MAS <sub>2</sub>	2.5	16.5	41
15	do	AN <sub>3</sub> -5 <sub>5</sub> -MAS <sub>2</sub>	2.9	22.6	66
16	do	AN <sub>3</sub> -8 <sub>5</sub> -MAS <sub>2</sub>	3.3	35.7	118
17	do	AN <sub>3</sub> -10 <sub>5</sub> -MAS <sub>2</sub>	3.1	34.8	108
18	do	AN <sub>3</sub> -12 <sub>5</sub> -MAS <sub>2</sub>	3.0	30.9	93
19	do	AN <sub>3</sub> -14 <sub>5</sub> -MAS <sub>2</sub>	2.5	26.0	65
20	do	AN <sub>3</sub> -16 <sub>5</sub> -MAS <sub>2</sub>	1.8	20.1	36

NOTE 4.—3=Propyl acrylate; 5=Amyl acrylate; 8=Octyl acrylate; 10=Decyl acrylate; 12=Lauryl acrylate; 14=Myristyl acrylate; 16=Cetyl acrylate.

TABLE 6

Item	Den.	Tensile strength at break (g./den.)	Elongation at break (percent)	Crimp frequency (No./25 mm.)	Degree of crimp elasticity (percent)		Retention of degree of crimp elasticity (percent)
					Under 50 mg./den. load	Under 150 mg./den. load	
13'	3.0	3.6	27	3			
14'	3.2	3.5	25	4			
15'	3.4	3.3	24	10	85	83	98
16'	2.8	3.5	26	22	82	79	96
17'	2.7	3.7	26	20	81	79	98
18'	3.1	3.0	27	17	83	80	96
19'	3.0	3.2	25	12	81	80	99
20'	2.9	3.3	24	2			

Table 5 above shows various composite filaments wherein the lower shrinking components consist of the same polymer and the higher shrinking components consist of acrylonitrile copolymers containing 5 percent of acrylate differing in the number of carbon atoms. Such combinations as shown in items 13 and 14, indicating the use of a copolymer containing a combined lower alkyl acrylate is selected, yield a smaller difference in shrinkability and a lower residual shrinking stress as compared with the combinations which include a copolymer containing a combined higher alkyl acrylate, and accordingly the former has a product of the difference in shrinkability and the residual shrinking stress of less than 50, so that composite filaments prepared therefrom develop little crimps. Contrary to the foregoing, the combinations which include a higher shrinking component containing a higher alkyl acrylate ex-

hibit satisfactorily large values of both the difference in shrinkability and residual shrinking stress, and as is apparent from table 6, the composite filaments obtained therefrom readily develop their crimps, the crimps filaments being useful due to their high retention of degree of crimp elasticity, i.e., high stability of crimp.

The polymer component comprising, as its comonomer, an acrylate containing the higher alkyl group having 16 carbon atoms cannot provide a clear spinning solution but a slightly opaquely muddy solution having insufficient spinnability.

## EXAMPLE 4

Predetermined various acrylonitrile copolymers for lower shrinking components and higher shrinking components were manufactured by emulsion polymerization. As conducted in the foregoing example 3, these polymers were dissolved in dimethylformamide to prepare their respective spinning solutions having a polymer concentration of 20 percent. The spinning solutions were wet spun separately from a spinneret containing orifices 0.09 mm. in diameter, into a 40 percent aqueous solution of calcium chloride and solidified to form their respective monocomponent yarns. The as-spun yarns were drawn 2x at 60° C. in a 30 percent aqueous solution of calcium chloride and further drawn at 90° C. in an ethylene glycol bath. The drawn yarns were washed in water, dried at 150° C. and wound up at 37 meters per minute. The resultant

yarns were of 300 denier of 100 filaments. The total draw ratio was 8.5x.

Upon certain combinations of the obtained filaments for lower shrinking component and those for higher shrinking component, the difference in shrinkability ( $\Delta\epsilon$ ) and the residual shrinking stress ( $\Delta F$ ) were determined, and the results are set forth in table 7 below.

On the other hand, composite filament yarns of 300 denier of 100 filaments were produced from the combinations of two filament components in the same manner as above except that the two spinning solutions were extruded simultaneously in a side-by-side relation from the same orifices of a spinneret. The resultant composite filament yarns were boiled off in hot water at 100° C. to develop their crimps and the crimp characteristics were determined, which results are set forth in table 8



TABLE 7

Item	Lower shrinking component	Higher shrinking component	$\Delta\epsilon$ (percent)	$\Delta F$ (mg./den.)	$\Delta\epsilon \times \Delta F$
21.....	AN <sub>78</sub> -1 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -1 <sub>30</sub> -MAS <sub>2</sub>	(Undeterminable due to sticking)		
22.....	AN <sub>78</sub> -3 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -3 <sub>30</sub> -MAS <sub>2</sub>	(Undeterminable due to sticking)		
23.....	AN <sub>78</sub> -5 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -5 <sub>30</sub> -MAS <sub>2</sub>	30.9	20.7	640
24.....	AN <sub>78</sub> -8 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -8 <sub>30</sub> -MAS <sub>2</sub>	35.2	32.8	1155
25.....	AN <sub>78</sub> -10 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -10 <sub>30</sub> -MAS <sub>2</sub>	33.4	31.8	1062
26.....	AN <sub>78</sub> -12 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -12 <sub>30</sub> -MAS <sub>2</sub>	31.0	27.6	853
27.....	AN <sub>78</sub> -14 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -14 <sub>30</sub> -MAS <sub>2</sub>	24.9	22.5	560
28.....	AN <sub>78</sub> -16 <sub>20</sub> -MAS <sub>2</sub>	AN <sub>68</sub> -16 <sub>30</sub> -MAS <sub>2</sub>	(Not spinnable due to small solubility)		

TABLE 8

Item	Den.	Tensile strength at break (g./den.)	Elongation at break (percent)	Crimp frequency (No./25 mm.)	Degree of crimp elasticity (percent)		Retention of degree of crimp elasticity (percent)
					Under 50 mg./den. load	Under 150 mg./den. load	
21'							
22'							
23'	2.7	2.8	48	39	80	73	91
24'	3.0	2.7	45	48	78	69	88
25'	3.1	2.9	43	47	79	69	87
26'	2.8	3.2	46	43	78	70	90
27'	3.1	3.5	44	34	81	74	91

As is apparent from table 7 above, the polymer components containing a large amount of combined lower alkyl acrylate are so extremely inferior in their heat resistivity that the yarns containing such a polymer component becomes tacky in the drawing process in hot water, or in the drier, causing sticking of their individual filaments and thereby providing a stiff hand to the yarns. Moreover, the shrinkage and crimp characteristics of the composite filament yarns prepared from such a polymer component are impossible to determine. Further the polymer component comprising, as its comonomer, an acrylate containing the higher alkyl group having 16 carbon atoms provides an opaquely muddy spinning solution which has not only a rapid coagulation property but also an insufficient drawability yielding fibers of little practical utility.

On the other hand, the filaments of the present invention, which lower the shrinking component, containing a higher alkyl acrylate, are provided with an excellent ability to develop crimp and yields useful crimped filaments having superior crimp characteristics as shown in table 8.

We claim:

1. A drawn composite filament consisting of two fiber-forming acrylonitrile polymer components eccentrically disposed and adhered towards each other in a side-by-side or a sheath and core relationship throughout the entire length of the filament, wherein the first and higher shrinking component consists of an acrylonitrile copolymer comprising 65-95 percent by weight of combined acrylonitrile and 35-5 percent by weight of combined higher alkyl acrylate having five to 14 carbon atoms in its alkyl group and the second and lower shrinking component consists of an acrylonitrile polymer optionally containing said higher alkyl acrylate, the amount of said higher alkyl acrylate contained in the second component is at least 5 percent by weight less based on the polymer than that contained in the first component, the first component contains less combined acrylonitrile as compared with the second component, the weight ratio of the first component to the second component is in the range of 3:7 to 7:3, the difference in shrinkability between the two components is about 2.5-36, the residual shrinking stress is about 17-43 and the product thereof is about 65-1,200.

2. A filament as claimed in claim 1, wherein the said higher alkyl acrylate is selected from the group consisting of amylacrylate, hexylacrylate, 2-ethylhexylacrylate, octylacrylate, decylacrylate, laurylacrylate, myristylacrylate, amylmethacrylate, hexylmethacrylate, octylmethacrylate, 2-ethylhexylmethacrylate, decylmethacrylate, laurylmethacrylate and derivatives thereof.

3. A filament as claimed in claim 1, wherein said acrylonitrile copolymer further comprises a small amount of

an  $\alpha$ ,  $\beta$ -monoethylenically unsaturated comonomer selected from the group consisting of p-styrenesulfonic acid, allylsulfonic acid, methallylsulfonic acid and salts thereof; and vinylpyridine, vinylimidazole and vinylpyrrolidone.

4. A filament as claimed in claim 3, wherein the amount of an  $\alpha$ ,  $\beta$ -monoethylenically unsaturated comonomer is up to 5 percent by weight based on the polymer.

5. A filament as claimed in claim 1, wherein the difference in the content of the higher alkyl acrylate in said first and second components is at least 10 percent by weight based on the polymer.

6. A filament as claimed in claim 1, wherein the second component containing a greater amount of combined acrylonitrile is substantially composed of acrylonitrile homopolymer.

7. A filament as claimed in claim 1, wherein the second component containing a greater amount of combined acrylonitrile consists of a copolymer or terpolymer comprising at least 75 percent by weight of combined acrylonitrile and up to 25 percent by weight of at least one monoethylenically unsaturated addition type monomer combined therewith.

8. A filament as claimed in claim 7, wherein said monomer is a higher alkyl acrylate.

9. A filament as claimed in claim 1, wherein the said product of the difference in shrinkability between the two components and the residual shrinking stress is at least 100.

10. A filament as claimed in claim 1, wherein the weight ratio of the said two components is 4:6-6:4.

11. A filament as claimed in claim 1, wherein the weight ratio of the said two components is about 1:1.

12. A filament as claimed in claim 1, which is capable of developing throughout its entire length, upon the application of a heat treatment at 100° C. in relaxed condition, a uniform helical crimp having its frequency of 8-50 per 25 mm. of crimped length, its degree of elasticity under a load corresponding to 50 mg. per denier of at least 75 percent and a retention of the degree of elasticity under a load corresponding to 150 mg. per denier of at least 85 percent based on the degree of elasticity under a load corresponding to 50 mg. per denier.

13. A filament as claimed in claim 1, which is capable of developing throughout its entire length, upon the application of a heat treatment at 100° C. in relaxed condition, a uniform helical crimp having its frequency of 10-40 per 25 mm. of crimped length, its degree of elasticity under a load corresponding to 50 mg. per denier of at least 80 percent and a retention of the degree of elasticity under a load corresponding to 150 mg. per denier of at least 90 percent based on the degree of elasticity under a load corresponding to 50 mg. per denier.