United States Patent [19]

Lohwasser et al.

[11] **3,895,165**

[45] **July 15, 1975**

[54] **COMPOSITE FIBRES AND YARNS OF ACRYLONITRILE POLYMERS**

[75] Inventors: **Hermann Lohwasser; Alfred Nogaj; Dieter Brokmeier,** all of Dormagen; **Helmut Engelhard,** Leverkusen, all of Germany

[73] Assignee: **Bayer Aktiengesellschaft,** Leverkusen-Bayerwerk, Germany

[22] Filed: **Sept. 18, 1974**

[21] Appl. No.: **507,174**

[30] **Foreign Application Priority Data**

Sept. 27, 1973 Germany 2348679

[52] **U.S. Cl.** ..... **428/374;** 264/168; 264/171; 264/182; 260/79.5 C; 260/85.5 ES

[51] **Int. Cl.** **D02g 1/00;** D02g 3/00

[58] **Field of Search** ..... 161/173, 175, 172; 260/85.5 ES, 88.5; 264/168, 182, 17

[56] **References Cited**

UNITED STATES PATENTS

2,682,518	6/1954	Caldwell	260/85.5 ES X
3,515,627	6/1970	Sekiguchi et al.	161/173
3,671,619	6/1972	Fitzgerald et al.	161/173
3,719,738	3/1973	Fujii	161/173

Primary Examiner—George F. Lesmes
Assistant Examiner—Lorraine T. Kendell
Attorney, Agent, or Firm—Plumley & Tyner

[57] **ABSTRACT**

The invention relates to a spontaneously crimping composite fibre of acrylonitrile polymers in which one of the fibre-forming component has a content of copolymerized esters up to 6% by weight and another fibre-forming component a content of copolymerized esters which is from 2 to 6% by weight higher whereby at least one of the fibre-forming components contains as copolymerized ester at least 2% by weight of isobutene-diacetate and the total quantity of the copolymerized esters in one fibre-forming component does not exceed 12% by weight.

5 Claims, No Drawings

COMPOSITE FIBRES AND YARNS OF ACRYLONITRILE POLYMERS

Numerous composite fibres (bicomponent fibres) based on acrylonitrile are capable of spontaneous crimping as a result of suitable selection of the chemical composition of the fibre-forming components and, in some cases, as a result of special processes of polymerisation, solution, spinning or after-treatment. It is thought that crimping may be due, for example, the shrinkage tensions released by heat in the case of compound fibres whose components contain varying amount of neutral comonomers. Among the neutral comonomers, those preferably used on account of their dyeing properties are the commercially available acrylic ester and vinyl ester type of compounds. In fibres of this kind, however, in which crimping is due to equalisation of the shrinkage tension, the stability under thermal or hydrothermal stress is reduced, especially if higher porportions of comonomer are used in one of the polymers. This reduced stability has the effect, for example, of impairing the development of bulk when dyeing the textiles.

It has now been found that a stable crimp which extends uniformly throughout the yarn may be obtained by using composite fibres of acrylonitrile polymers which contain a substantially equivalent number of acidic groups, but in which varying proportions of acrylic ester or vinyl ester type comonomers are incorporated by polymerisation.

It is therefore an object of the invention to provide textile fibres which develop a stable and uniformly extending crimp.

Other objects will be evident from the description and the Examples.

These objects are accomplished by a spontaneously crimping composite fibre comprising at least two different acrylonitrile polymers which have substantially the same acidic group content, produced in a side-by-side arrangement of the two fibre-forming components in proportions, by weight, of from 40:60 to 60:40, one of the fibre-forming components containing up to 6%, by weight, of at least one copolymerised ester while the quantity of said copolymerised ester in the other fibre-forming component is from 2 to 6%, by weight, higher, said copolymerised ester being methyl acrylate and/or isobutene diacetate (2-methylenepropane-1,3-diacetate), under the condition that at least one of the fibreforming components contains at least 2%, by weight, isobutene diacetate and the total quantity of said copolymerised esters in one fibre-forming component does not exceed 12%, by weight.

A further object of this invention is a yarn or a textile article when containing such a fibre.

The second fibre forming component may also be produced from several different polymers provided that the mixture has the total ester content indicated above. The nature and quantity of additional copolymerised acidic dye additives in the fibre-forming component is not critical provided it is within the range of from 0.5 to 6%, by weight, and that the equivalent contents are approximately equal.

If composite fibres containing isobutene diacetate as comonomer and having the compositions indicated above are produced by a dry-spinning process in which two streams of fibre-forming polymer solutions in a solvent, such as dimethylformamide, are brought together

in spinning dies in such a manner that composite fibres are obtained in a side-by-side arrangement and these spun fibres are then treated by the conventional processes, then three-dimensionally crimped fibres are obtained which may be worked-up into yarns in conventional textile machines. When such yarns are dyed in hanks, for example, they develop excellent bulk and elasticity after drying without any thin patches or colour irregularities in the plied yarns. Once the crimp has developed in the fibre, it is not diminished by subsequent wet treatments and knitted textiles manufactured from these yarns therefore remain dimensionally stable after washing and retain their gloss which is due to the intensity of crimping.

Whereas the irreversibility of the crimp in the fibres was deliberately achieved according to the invention by choosing fibre-forming components which contain equal amounts of acidic groups, the stability of the crimp discovered in the new composite fibres containing isobutene diacetate comonomer was unexpected.

If, for example, a bicomponent fibre is spun from equal parts of copolymers of acrylonitrile with methyl acrylate and with sodium methallylsulphonate, which copolymers have the same sulphonate content but differ from each in their ester contents which are 5.6% and 9.0%, by weight, respectively, and if yarn produced from such a bicomponent fibre is hank dyed, it is found that distributed over the circumference of the hank there are strands of yarn of unequal or varying thickness and colour which prohibits the use of such yarn for fine quality knitwear. If, on the other hand, a yarn is produced under similar conditions from the following fibre-forming components:

A. 93.4% acrylonitrile, 5.6% methylacrylate, 1.0% sodium methallylsulphonate; and

B. 90.5% acrylonitrile, 8.5% isobutene diacetate, 1.0% sodium methallysulphonate,

then it is surprisingly found that the dyed yarn is very uniform in thickness, colour and elasticity and knitted goods produced from it have an attractive appearance and good wearing qualities.

Composite fibres with equally stable crimp may be obtained from a combination of acrylonitrile polymers which contain from 2 to 6%, by weight, of a vinyl or acrylic ester compound with copolymers which in addition to from 2 to 6%, by weight, of vinyl or acrylic ester compounds contain from 3to 6%, by weight, isobutenediacetate calculated so that the total quantity of ester comonomers in the last mentioned copolymer does not exceed 12%, by weight.

Lastly, composite fibres obtained from a combination of acrylonitrile polymers which contain from 2 to 6% by weight, of a vinyl or acrylic ester compound and polymer mixtures which contain a total of from 2 to 6% by weight, of a vinyl or acrylic ester and in addition from 3 to 6% by weight, of isobutene diacetate in this mixture also fulfill the purposes of this invention.

Copolymers of acrylonitrile with isobutene diacetate and optionally other copolymerisable monomers may be obtained in high yields by the process of redox polymerisation in an aqueous medium at pH values of from 2 to 7 and temperatures of from 0° to 90°C with the aid of peroxy compounds and sulphur compounds in a lower oxidation state preferably using a ratio of activator to catalyst of 5:1. Examples of suitable copolymerisable compounds include the lower vinyl and acrylic esters, such a vinyl acetate and methyl acry-

late, unsaturated sulphonic acids, such as methallylsulphonic acid or its salts, acrylic or vinyl compounds which contain neutral or basic groups, such as acrylamide, allylurethane, N-vinylpyrrolidone, and N,N-dmethylaminoethyl-methacrylate. There is no restriction to the use of particular comonomers provided they may be incorporated in the desired acrylonitrile polymers in economically acceptable yields. Copolymers containing from 3 to 30%, by weight, of isobutene diacetate were successfully prepared according to the invention.

The polymers obtained in this way were spun by a dry-spinning process from dimethylformamide solutions of a suitable concentration for spinning. Suitable designed nozzles were used so that the fibre-forming components were united side-by-side shortly before discharge from the die aperture in predetermined proportions which were identical for all fibres and were then coagulated in this permanently united form to produce filament bundles which could be drawn off. The selected ratio of fibre-forming components may be from 75:25 to 25:75, the best crimping properties in the finished fibres being obtained in the region of from 60:40 to 40:60 and most preferably about 50:50.

It is well known to one skilled in the art to produce similar composite fibres in which the distribution of components varies from fibre to fibre or to produce fibres with a sheath and core or multilayered arrangement. Furthermore, spinning of composite polyacrylonitrile fibres according to this invention is of course not restricted to the solvent referred to herein or to the dry-spinning technique. Various conventional processes are available for producing textile fibres from dry-spun goods of the type described above, from which the most suitable may be selected according to the subsequent textile processes which are to be applied to the fibres. If, for example, the fibres are to be processed in worsted spinning or cotton spinning machines, it is most suitable to produce completely shrunk fibres with fully developed crimp. If, on the other hand, the fibres are to be torn up as cable yarns in a turbostapler or converting machine, it is advantageous to prepare them in the form of bands which are in a potentially crimpable state because, in this case, the proper crimp is developed only in the end-product by steaming or dyeing. The composite fibres according to this invention may, of course, also be spun together with other completely shrunk or still shrinkable natural or synthetic fibres, and the fibrous products obtained by tow processing in suitable machines may also be worked-up in combination with other fibre products in various ways.

The yarns obtained from processing pure fibres according to this invention are distinguished by their wool-like bulk and hand, clear surface structure, high elasticity and springiness and uniformity of yarn. These qualities are not impaired by wear and repeated washing of textile fabrics produced from these yarns, and the dimensional stability of such products is very satisfactory.

The fibres according to the invention are therefore also suitable for addition to other natural or synthetic fibres in which by virtue of their own permanent crimp they substantially improve such qualities as the bulk, hand and springiness as well as the pilling properties of the finished articles.

EXAMLPES

In the following Examples, which are to further illustrate the invention without limiting it, the figures given for the polymer compositions and concentrations are percentages by weight.

The criterion adopted for determining the stability of the crimp was in all cases the uniformity of worsted yarn after it has been hank dyed at 100°C and dried at 80°C. Fibres which developed their bulk in the composite yarn without significant fluctuations in thickness or elastivity were classed as crimp stable.

EXAMPLE 1

Copolymers of the composition

A. 93.4% acrylonitrile, 5.6% methylacrylate, 1.0% sodium methallylsulphonate; and

B. 90.5% acrylonitrile, 8.5% isobutenediacetate, 1.0% sodium methallylsulphonate

were used to prepare dimethylformamide solutions with solid contents of 28.6% and 25.8% respectively. These solutions were spun in equal parts (by volume) through ring-shaped spinning nozzle with 180 apertures as side-by-side composite fibres at a draw-off rate of 250 m/min. The fibres were coagulated with hot air and wound on to spools. They had a curved "dumb-bell-shaped" cross-section and still contained 22.6% dimethylformamide.

Several spinning spools were combined and streached to 1:4.0 in boiling water and then washed. The tow obtained in this way was covered with an application of oil, dried under tension, crimped in a compression chamber and cut to a staple length of about 120 mm, and the staple fibres were shrunk by steaming and dried. The fibres at that stage still contained 0.4% dimethylformamide and after boiling and drying at 80°C they had 13.4 crimps per cm of stretched length. Their thickness was 3.0 dtex, their tensile strength 2.55 g/dtex and their elongation at break 44%.

When hank dyed, the worsted yarn (Nm 16/4) of these fibres shrunk by 9.3% and gave rise to a yarn which had a full bulk and firm hand and was completely uniform when plied.

EXAMPLE 2

Copolymers composed of

C. 91.7% acrylonitrile 7.5% isobutene diacetate, 0.8% sodium methallylsulphonate; and

D. 93.8% acrylonitrile, 5.5% methylacrylate, 0.6% sodium methallylsulphonate

were used as described in Example 1to prepare dimethylformamide solutions at concentrations of 27.5% and 28.3% respectively. The solutions were spun to composite fibres with a "dumb-bell-shaped" cross section and a residual solvent content of 17.3%. By aftertreating the fibres in a similar way as described in Example 1, except that a stretching ratio of 1:3.6 was employed, fibres with a residual dimethylformamide content of 0.8% and a crimp number (after boiling and drying) of 10.4/cm were obtained. The titre was 4.3 dtex, the tensile strength 2.34 g/dtex and the elongation at break 49%.

A worsted yarn (Nm 16/4) of these fibres had a boiling shrinkage in the raw state of 5.0%, and when hank dyed it developed an excellent bulk with a pearly appearance on the surface of the yarn and uniformity of the individual strands.

EXAMPLE 3

Equal parts, by volume, of a 27.4% solution in dimethyl formamide of a polymer

E. 94.0% acrylonitrile, 5.0% isobutenediacetate, and 1.0% sodium methallylsulpnonate;

and of the 29.4% solution of a polymer

F. 90.5% acrylonitrile 8.5% isobutenediacetate and 1.0% sodium methallysulphonate

were spun through a spinning die, as described in Example 1, to produce composite fibres with a "dumbbell-shaped" cross section and a solvent content of 17.5%. The fibres were stretched by 1:3.6 in boiling water, washed, brightened, dried, cut to a length of about 110 mm and shrunk by streaming at normal pressure. The residual solvent content was 1.4%, the crimp number, after boiling and drying, 9.9/cm the titre 3.7 dtex, the tensile strength 2.54 g/dtex and the elongation at break **46%**.

A fibre yarn of a thickness used for hand knitting (Nm 16/4) was hank dyed, and after a yarn shrinkage of 7.4% it had a bulky, pleasantly soft and elastic handle without pressure points or thickenings in the yarn.

EXAMPLE 4

Copolymers of the following compositions

G. 88.2% acrylonitrile, 5.0% isobutene diacetate, 5.8% methylacrylate, 1.0% sodium methallysulphonate; and

H. 93.4% acrylonitrile, 5.6% methylacrylate, 1.0% methacroylaminobenzene-benzene-disulphonimide;

were used as described in Example 1 to prepare 28.1% and 28.7% solutions, respectively. These solutions were spun through a spinning die with 120 apertures to produce composite fibres with a solvent content of 20.0% and a lobed cross-section. The fibres were stretched by 1:3.7 in water at 98°C, dried under tension, sprayed with dressing and shrunk by steaming in the form of a mechanically crimped tow. The residual solvent content at that stage was 0.3% and the crimp number, after boiling and drying, was 15.7/cm, The titre of the individual fibres was 2.9 dtex, the tensile strength 2.35 g/dtex and the elongation on break of 34%.

After cutting up into staple fibres, a yarn (Nm 16/4) was spun and hank dyed as described above. The yarn shrinkage was 10.6%. The yarn had high bulk and a springy elasticity and the plied yarn had a uniform thickness.

COMPARISON EXAMPLE

The experiment shows that the crimping properties of a fibre are insufficient for practical purposes if there is too little difference in the ester content between the fibre-forming components. The components used to prepare a side to side composite fibre, as described in Example **1**, were the polymers

J. 94.2% acrylonitrile, 5.0% isobutene diacetate, 0.8% sodium methallylsulphonate; and

K. 93.25% acrylonitrile, 5.75% methylacrylate, 1.0% methacroylaminobenzene-benzenedisulphonimide.

These polymers were used as 27.4% and 28.6% dimethylformamide solutions respectively. The solutions were spun in equal parts, by volume, through a spinning die of the type described above to form fibres with a "bean-shaped" cross-section and a solvent content of 14.1%. The shrunk fibres produced from these fibres by stretching by 1:4.6 still had a residual dimethylformamide content of 0.2%, a titre of 3.1 dtex, a tensile strength of 3.15 g/dtex, an elongation on break of **33%** and a crimp number after development of 5.8/cm.

When a worsted yarn (Nm 16/4) of this product was hank dyed in a single bath together with other samples of yarn it shrunk by 4.1% and had a low bulk, was marked by pressure points and had little elasticity and a poor hand.

EXAMPLE 5

In accordance with Example 1, 28.0% and 26.7% solutions of the copolymers

L. 89.0% acrylonitrile, 10.0% isobutenediacetate, 1.0% sodium methallylsulphonate; and

M. 99.4% acrylonitrile 0.6% sodium methallysulphonate,

were spun through **120** aperture dies to produce composite fibres which contained 22.0% dimethylformamide and had a "mushroon-shaped" or lobular cross-section. Further treatment was carried out as described in Example 1, to produce fibres with a residual solvent content of 1.2% and a crimp number of 16.3/cm. The titre was 3.0 dtex, the tensile strength 2.18 g/dtex and the elongation on break of 35%.

Hank dyeing resulted in an exceptionally high bulk worsted yarn (Nm 16/4) which had shrunk by 12.6% and had a high elasticity of elongation and uniform thickness in the plied thread.

EXAMPLE 6

The following polymers

N. 93.3% acrylonitrile, 5.7% methyl acrylate, 1.0% methacroylaminobenzene-benzene disulphonimide; and

O. 70.0% acrylonitrile, 30.0% isobutenediacetate,

were used to prepare a mixture of 80% (N) and 20% (O) which was spun as a 27.5% dimethylformamide solution, together with a 28.3% solution of polymer (N), through a 120 aperture die to produce a composite fibre in the manner described above. The solvent content of the spinning material was 17.0%. The fibres has a "club-shaped" profile. Staple fibres 100 mm in length were produced as described in Example 1. They had a residual solvent content of 1.5%. the titre of the fibres was 5.4 dtex, the tensile strength 2.31 g/dtex, the elongation on break of 48% and the crimping 15.4 arcs/cm.

A worsted yarn (Nm 16/4) of the fibre had a shrinkage of 9.7%. The hank dyed sample had a very high bulk, springiness and elongation elasticity and a woolly hand without pressure points or stretching points.

When side-by-side composite fibres were produced from about half and half of polymers (N) and (O), nodular cross-sections were obtained, and fibres which had received the same after-treatment had a very tight crimp which made further textile operations impossible.

EXAMPLE 7

Using polymers of the following compositions

P. 93.3% acrylonitrile, 5.7% methylacrylate, 1.0% methacroylaminobenzene-benzenedisulphonimide; and

Q. 78.5% acrylonitrile 23.0% isobutene diacetate, 1.0% sodium methallylsulphonate,

a 28.7% dimethylformamide solution of (P) was dry-spun with a 26% solution of a mixture of 75% (P) and

25% (Q) through a 120 aperture die of the type described above at a draw-off rate of 250 m/min to produce a composite fibre. The spinning fibres contained 12.5% solvent and had a "dumb-bell-shaped" cross-section.

Completely shrunk fibres with a dtex of 3.3 were produced as described in Example 3. The residual solvent content was then 0.5% and the crimp number, after boiling and drying 10.3/cm.

A fibre yarn (Nm 16/4) was hank dyed and shrunk by 13.1%. A yarn with a full hand and uniform bulk was obtained. A knitted fabric produced from this yarn was distinguished by its exceptional clarity and covering power of the stitches. The character of the fabric was unchanged after machine washing.

EXAMPLE 8

Equal parts by volume, of 28.5% dimethylformamide solutions of the fibre-forming components

R. 93.3% acrylonitrile, 5.7% methylacrylate, 1.0% methacroylaminobenzene-benzenedisulphonimide; and

S. 90.15% acrylonitrile, 9.25% isobutene diacetate, 0.6% sodium methallylsulphonate

were dry-spun through tubular dies with 240 apertures to produce fibres with a residual solvent content of 19.6% and a "bean-shaped" to trilobular cross-section. The spinning bands were stretched by 1:4.5 in boiling water, washed, brightened, dried with 20% shrinkage, crimped in compression chambers and laid off as tows with a total weight of 27 g/m. The solvent content was then 0.7%, the remaining boiling shrinkage 5.4%, the titre 3.4 dtex, the tensile strength 3.0 g/dtex, the elongation on break of 33% and the crimp number after development 4.1/cm.

This material, combined in the form of a band weighing 54 g/m was processed into a spinning band in a "Seydel" converting machine (type 633) with 30% elongation and a hotplate temperature of 180°C. After steaming under pressure, the spinning band was processed into a fine yarn (Nm 30/2). When hank dyed, this yarn again shrunk by 9.6% and had excellent bulk and elongation elasticity and worked-up into a knitted fabric with clear, uniform stitches.

When the spinning band was directly made up into a yarn of the same number without steaming, the shrinkage in the dye bath was 28.2% and resulted in an unacceptably tight, rough thread.

We claim:

1. A spontaneously crimping composite fibre comprising at least two different acrylonitrile polymers which have substantially the same acidic group content, produced in a side-by-side arrangement of the two fibre-forming components in proportions, by weight, of from 40:60 to 60:40, one of the fibre-forming components containing up to 6%, by weight, of at least one copolymerised ester while the quantity of said copolymerised ester in the other fibre-forming component is from 2 to 6%, by weight, higher, said copolymerised ester being methyl acrylate and/or isobutene diacetate (2-methylenepropane-1,3-diacetate), under the condition that at least one of the fibre-forming components contains at least 2%, by weight, isobutene diacetate and the total quantity of said copolymerised esters in one fibre-forming component does not exceed 12%, by weight.

2. The spontaneously crimping composite fibre of claim **1**, in which both fibre-forming components contain isobutene diacetate, one component containing from 2 to 6% by weight, thereof more than the other and the total isobutene diacetate content based on the one fibre-forming component, not exceeding 12%, by weight.

3. The spontaneously crimping composite fibre of claim **1**, in which one of said fibre-forming components contains from 0to 6%, by weight, methyl acrylate and the other up to 12%, by weight, isobutene diacetate, the quantitative difference in the ester content between said two components being at least 2%, by weight.

4. The spontaneously crimping composite fibre of claim **1**, in which both fibre-forming components contain from 2 to 6% methyl acrylate and one of said fibre-forming components in addition contains from 3 to 6%, by weight, isobutene diacetate.

5. A yarn or a textile article produced from the composite fibre of claim **1**.

* * * * *