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Joh et al.

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[54] **ACRYLIC FIBER AND A METHOD FOR MANUFACTURING THE SAME**

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[58] **Field of Search** ..... 260/898, 63 UY, 63 N

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[57] **ABSTRACT**

A novel acrylic fiber having enhanced hydroscopic and antistatic properties is obtained from a copolymer (A) comprising, as unit components, at least 10 percent by weight of acrylonitrile, 0.2 to 20 percent by weight of N-3-oxo-hydrocarbon-substituted acrylamide and balancing quantity of the third hydrophilic monomer.

The acrylic fiber may be prepared from a mixture of the copolymer (A) and another copolymer (B) which comprises, as a unit component, at least 85 percent by weight of acrylonitrile.

For convenience, the two carbon atoms of the main chain of the ethylene group in the R′ group are numbered from the side of the nitrogen atom. In the case the carbon atom directly combined with the nitrogen atom is named as first carbon atom and another as the second carbon atom, R′ may be selected from ethylene group and substituted ethylene groups having at least one lower alkyl group combined to the first carbon atom.

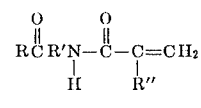
8 Claims, No Drawings

ACRYLIC FIBER AND A METHOD FOR MANUFACTURING THE SAME

The present invention relates to a novel acrylic fiber having an excellent hygroscopic property and therefore, an excellent antistatic property and to a method of manufacturing the same.

Acrylic fibers are generally provided with excellent features regarding their handling quality, dyeing property and weathering property. Owing to these characteristics, a rapid penetration of this fiber into the textile industry is recognized together with nylon and polyester fibers. There is on one hand an increasing consumers' attention towards synthetic fibers because of their excellent properties which are not found in the natural fibers but, on the other hand, it is also well-known that they are accompanied with particular drawbacks which are not found in any natural fiber. Their relatively poor hygroscopic property and antistatic property of the synthetic fibers are typical examples of such drawbacks. Similarly to nylon and polyester fibers, the acrylic fibers possess very poorer hygroscopic properties than wool, cotton and regenerated fibers. In addition to this, these synthetic fibers tend to develop static charge with ease and this undesirable tendency decreases the commercial value of the fibers when they are worn. Further, penetration of the synthetic fibers into the field of underwear is hindered considerably owing to their poorness in sweat-absorbing property. Therefore, there is an increasing demand to remove such drawbacks in the production of synthetic textile soft goods.

In order to perfectly meet this demand, the acrylic fiber of the present invention comprises a copolymer (A) comprising, as unit components, (a) at least 10 percent by weight, preferably at least 40 percent by weight, more preferably at least 85 percent by weight, of acrylonitrile, (b) 0.2 to 20 percent by weight, more preferably 0.2 to 8 percent by weight, of N-3-oxo-hydrocarbon-substituted acrylamide of formula (1):



wherein R and R'' are members selected from the group consisting of hydrogen and lower alkyl groups having not more than 10 carbon atoms, respectively, R' is a member selected from the group consisting of an ethylene group and lower alkyl-substituted ethylene groups having not more than 15 carbon atoms, (c) as the third unit, at least one copolymerizable monomer selected from the group consisting of vinyl acetate, acrylic esters, methacrylic esters, monomers having hydroxyl group, monomers having carboxyl group or its salts, monomers having solfonic acid group or its salt, monomers having amide group polyethylene glycol ester of acrylic or methacrylic acid and monomers having polyethylene glycol group in side chain thereof, and (d) another monomer capable of copolymerization with any of the above component monomer. The novel acrylic fiber having both an excellent hygroscopic and therefore, antistatic properties, is spun from a solution of the above-obtained copolymer in a suitable solvent by the conventional wet, dry or dry jet-wet spinning process.

As for the N-3-oxo-hydrocarbon-substituted acrylamide in the above-identified formula (1) the lower alkyl groups R, R'' has at most 10 carbon atoms and may include cycloalkyl group. Some examples of R, R'' are found in such groups as methyl, ethyl, propyl, isopropyl, n-butyl, pentyl, cyclohexyl, cyclopentyl, isoctyl, n-decyl and 4-ethyl-2-hexyl groups. R'' is given preferably in the form of hydrogen or methyl group. R' may be selected from an ethylene group or substituted ethylene groups in which a carbon atom directly combined with the nitrogen atom of the acrylamide has at least one lower alkyl substituent. For convenience in the later description, the two carbon atoms of the ethylene group are numbered from the side of the nitrogen atom. That is, the carbon atom directly combined to the nitrogen atom is named as the first atom and another as the second atom. With this numbering, R' is examplified as ethylene, 1-methylethylene, 1,1-dimethylethylene, 1,1,2-trimethylethylene, 1-methyl-1-ethylethylene, 1-methyl-1-isobutylethylene, 1-ethyl-1-isopropylethylene, 1,2-dimethylethylene, 1,1-diisopropylethylene, 1-n-butyl- 1-n-pentylethylene and 1-methyl 1-cyclohexylethylene.

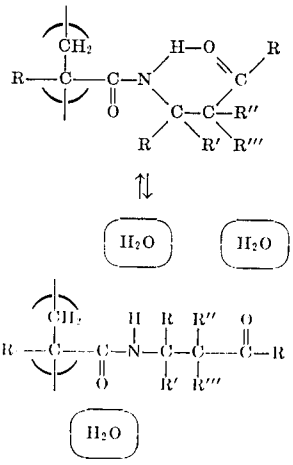
As typical examples of N-3-oxo-hydrocarbon-substituted acrylamide, there is given N-3-oxo-butyl acrylamide, N-3-oxo-1-1-methylbutyl acrylamide, N-3-oxo-1-1-dimethylbutyl acrylamide, N-3-oxo-1-methyl-1-cyclohexylbutyl acrylamide, N-3-oxo-1-1-dimethyl-2-ethylbutyl acrylamide, N-3-oxo-1,5-dimethyl-1-isopropyl-hexyl acrylamide, N-31-11-diisobutyl-2-isopropyl-5-methyl-hexyl acrylamide, N-3-oxo-1-1-dibutyl-2-n-propylheptyl acrylamide and N-3-oxo-1-methyl-butyl-α-methyl acrylamide.

Through intensive study by the inventors of the present invention, it was revealed that the copolymer of N-3-oxohydro carbon-substituted acrylamide and acrylonitrile plays a particular role regarding absorption of ambient humidity. A copolymerization of acrylonitrile with other hydrophilic monomers such as, for example, vinyl pyrrolidone, acrylic acid, methacrylic acid and vinyl pyridine does not ascertain provision of enhanced hygroscopic property. The polymers made up of one of the above-recited hydrophilic monomers such as polyvinyl pyrrolidone, polyacrylic acid, polymethacrylic acid and polyvinyl piridine are water-soluble. On the other hand, a homopolymer made up of N-3-oxo-1--dimethylbutyl acrylamide, a typical example of N-3-oxo-hydrocarbon-substituted acrylamide, is capable of swelling in water but water-insoluble. The percent hygroscopicity of the homopolymer is, although dependent upon the molecular weight thereof, about 25 percent based on the weight of the homopolymer.

In consideration of these facts, it may be supposed that the hydrophilic property of N-3-oxo-1-1-dimethyl-butyl acrylamide is poorer than that of the hydrophilic monomers making up the above-mentioned water-soluble polymers.

Unexpectedly, it was revealed by the inventors of the present invention that the copolymer of acrylonitrile and N-3-oxo-1-1-dimethyl butyl acrylamide exhibits a remarkably enriched hygroscopic property to that of the other types of acrylic copolymers. This is an epoch-making find which could never been attained on the basis of the conventional knowledge in the relevant art.

The reason for this effect is supposed to be from the fact that inner intra-molecular hydrogen bonds in the monomer are subjected to cancellation due to the presence of water. This cancellation of the hydrogen bonds causes a large deformation of the molecular structure and a superior swelling effect on the polymer molecule. The swelling effect may closely relate to the enrichment of the hygroscopic property. This cancellation of the hydrogen bond is supposed to proceed in the following manner.



In a dry condition, the N-3-oxo-hydrocarbon-substituted acrylamide units in the copolymer is formed in a six-membered ring structure due to the formation of the above-stated intra-molecular hydrogen bond but, when water is introduced into the copolymer, this hydrogen bond is broken down and the six-membered ring is opened to increase its volume. Together with this breakage of the hydrogen bond, the —C=O or —NH group is considered to be combined with the water molecules so as to further increase its volume by swelling. In conclusion, it is supposed that the high water-swelling effect of N-3-oxohydrocarbon-substituted acrylamide units in the copolymer remarkably contributes to the enrichment in the hygroscopic property of the copolymer.

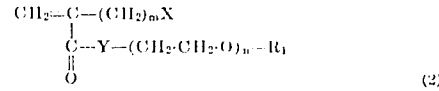
This enrichment effect in the hygroscopic property for the copolymer is further increased in its extent by including, as the third unit component monomer, such hydrophilic monomer as acrylic acid, methacrylic acid, itaconic acid and hydroxyethyl acrylic acid. This increased hygroscopic property is supposed to be caused by the combination of the hydrophilic swelling effect of N-3-oxo-hydrocarbon-substituted acrylamide with the rich hygroscopic property possessed by the hydrophilic monomer.

The above-referred third hydrophilic monomer may be copolymerizable monomer having —OH, —COOH or its salt, —SO_3H or its salt or



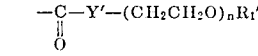
group. A typical example of such a monomer, is found in a group consisting of acrylates such as sodium acrylate, methacrylates such as sodium methacrylate, itaconic acid, hydroxyethyl acrylates, hydroxyethyl methacrylates, acrylamide, sodium vinyl benzensulfonate and N-vinyl pyrrolidone. It is a surprising find that the acrylonitrile copolymer can be provided with remarkably enriched hygroscopic property owing to the copolymerization with the above-quoted hydrophilic monomers.

In addition to the hygroscopic property, the antistatic property of the resultant copolymer is marvelously enhanced also by copolymerization of polyethyleneglycol ester of the formula (2);



(2)

wherein X is hydrogen or groups given in the form of



Y is of oxygen or —NH group; R_1 is alkyl group having 1 to 22 of carbon atoms, substituted phenyl group or non-substituted phenyl group; Y′ and R_1′ are same group as those of Y and R_1, respectively, both Y and Y′ and R_1 and R_1′ may or may not be different from each other; *m* is 0 or a positive integer from 1 to 10; *n* is a positive integer from 1 to 200; and *n*′ is positive integer from 1 to 200 and may or may not be the same as *n*.

The content ratio of the above-mentioned polyethylene-glycol ester is in a range from 0.5 to 40 percent based on the weight of the entire copolymer.

It goes without saying that the acrylic copolymer of the present invention may further be accompanied, for enhancement of the dyeing property thereof, with such fourth monomers as acid or basic monomer. Some examples of the monomers to be added for this purpose are found in a group consisting of vinylbenzene sulfonic acid, methallyl sulfonic acid, allyl sulfonic acid, sulfophenylmethacryl ether, salts of the above-recited monomers, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine and N.N-dimethylethyl acrylate.

The acrylic fiber of the present invention may be spun from a solution of a mixture which contains (1) a copolymer consisting of, as unit components, (a) at least 50 percent by weight of acrylonitrile, (b) 1 to 40 percent by weight of the above-mentioned substituted acrylamide of the formula (1) and (c) the balanced quantity of the above-recited third monomer, and (2) a copolymer containing, as unit components, at least 85 percent by weight of acrylonitrile.

In the case of the above-mentioned polyethylene glycol, the third component of the copolymer (A), is used in a range from 5 to 89 percent by weight, more preferably from 5 to 80 percent by weight, the content of acrylonitrile within the base copolymer may range from 10 to 94 percent by weight. In this case, it is preferable that the resultant content of the above-mentioned polyethylene glycol is in a range from 0.5 to 40 percent by weight, more preferably 1 to 20 percent by weight. With this situation, the desirable content of the substituted acrylamide of formula (1) in the fiber is in a range from 0.2 to 8 percent by weight.

Owing to its excellent hygroscopic property, the acrylic fibers of the present invention are suitably used for underwear. In addition to this, its excellent antistatic property prevents the clothing from undesirably sticking to the human body when worn. This is an extremely successful solution to the problem of poor hygroscopic and antistatic properties generally possessed by the conventional acrylic fibers. Supplemental application of the conventionally known methods of enriching those properties to the art of the present in-

vention further enhances the resultant properties of these kinds.

The present invention will be further illustrated in the following examples. Throughout the examples, the hydroscopic property of the fiber is presented by a difference between the content by weight of moisture absorbed on the fiber at 93 percent and 65 percent RH at 20° C.

EXAMPLE 1

An acrylonitrile copolymer was prepared by copolymerizing a mixture of 90 percent by weight of acrylonitrile, weight percent by weight of N-3-oxo-1-1-dimethyl butyl acrylamide and 3 percent by weight of sodium vinyl benzenesulfonate. The resultant copolymers had a specific viscosity of 0.17 which was determined in a solution of 0.1 g/l of the copolymer in dimethyl formamide at a temperature of 25° C. This measurement will be applied to the following examples also.

The copolymer was dissolved in dimethyl formamide so as to prepare a spinning solution of 24 percent polymer concentration by weight.

The spinning solution was subjected to the wet-spinning process in which the solution was extruded into an aqueous coagulation bath through a spinneret to form filaments. The resultant undrawn filaments were drawn at a draw ratio of 5 in boiling water while being rinsed. The drawn filaments were dried by means of a roller dryer and then dried filaments were successively subjected to relaxation under a condition of 2.3 kg/cm² steam pressure. The hygroscopic property value of the acrylic fiber thus obtained was determined as 9.1 percent. Compared with this, the hygroscopic property of the conventional acrylic fiber was determined as about 1.5 percent under similar conditions. This proves that the hygroscopic property value of the acrylic fiber of the present example was remarkably enriched owing to the application of the art of the present invention.

EXAMPLE 2

An acrylonitrile copolymer having a specific viscosity of 0.168 was prepared by copolymerizing a mixture of 93 percent by weight of acrylonitrile, 3 percent by weight of N-3-oxo-1-1-dimethyl-butyl acrylamide and 4 percent by weight of acrylic acid. A dimethyl formamide solution of the resultant copolymer was subjected to wet-spinning in the same manner as that of Example 1. The undrawn filaments were drawn at a draw ratio of 4.5 with simultaneous rinsing in a boiling water bath, dried and then relaxed under a 2.5 kg/cm² steam pressure.

The resultant acrylic fiber had a superior hygroscopic property value of 10.1 percent.

EXAMPLE 3

Dimethyl acetamide was used in dissolving acrylonitrile copolymer consisting of 93% by weight of acrylonitrile, 2.5 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 4.5 percent by weight of sodium acrylate. The obtained spinning solution of 23 percent by weight concentration was subjected to a usual wet-spinning process. After spinning, the filament was subjected to a drawing at a draw ratio of 5 in a boiling water bath and dried. The thusly obtained acrylic fibers had a hydroscopic property of 12.3 percent. A measurement of the antistatic property was applied to this acrylic fiber in the following manner. The humidity content of the specimen filament was adjusted by placing it within an environment of 20° C temperature and 50 percent relative humidity for at least 20 hours. After this conditioning, the specimen was charged with an electric voltage of 10,000 V for more than 5 seconds with 1,000 RPM rotation of the specimen. After being charged, the half value period of the charge was measured on a static-honest-meter and the result obtained is shown in the following Table 1 together with the results of other type fibers.

Table 1

specimen	Length of the half-value-period in sec before scouring	after scouring	after dyeing	after 10 times of washing using a detergent
filament of the invention	less than 1.0	14.0	15.0	25.0
conventional acrylic fiber	ditto	38.0	larger than 60	larger than 60
viscose fiber	ditto	1.2	1.4	1.3
wool	ditto	1.5	5.7	15.0

As is apparently understood from the above results, it should be noted that the acrylic fiber of the present invention can be provided with an antistatic property far better than that possessed by the conventional acrylic fibers and the degree thereof is almost similar to that characteristic of wool fibers. This excellent antistatic property can be further enriched by using a conventionally known antistatic agent. No trouble caused by the generation of electrostaticity could be recognized in the actual use of the textile product such as underwear made up of the fiber of the present invention. No considerable soiling of the product could be recognized also, and these facts endorse the conclusion that the fiber of the present invention is superior in its resistance against soiling to the conventional acrylic fibers.

EXAMPLE 4

In order to prepare a spinning solution of 18 percent by weight concentration, dimethylsulfoxide was used in dissolving an acrylonitrile copolymer of 0.162 specific viscosity consisting of 92 percent by weight of acrylonitrile, 3 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 5 percent by weight of hydroxyethyl acrylate and the obtained spinning solution was spun into filaments in a manner of the usual wet spinning process.

The obtained filament was drawn at a draw ratio of 6 within an aqueous bath of 100° C temperature containing 10 percent dimethylsulfoxide. After the subsequent rinsing process within a boiling water bath for removal of the remaining solvent in the fiber, the filament was dried. Next, the filament was annealed under a 20 atmosphere steam pressure. The hygroscopic property of thusly obtained filament was estimated as 9.6 percent.

EXAMPLE 5

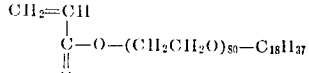
In order to obtain a spinning solution of 28 percent by weight concentration, dimethylformamide was used in dissolving an acrylonitrile copolymer of 0.160 specific viscosity and consisting of 94 percent by weight of acrylonitrile, 3 percent by weight of N-3-oxo-1-1-dimethyl-1-ethyl-butylacrylamide and 3 percent by weight of N-vinylpyrrolidone. This spinning solution was spun into acrylic filaments by a usual dry-spinning process, wherein the temperature of the spinning solution was 120° C, the flow velocity of the drying air was 0.6 mpm, the temperature in the vicinity of the spinning cell top was 240° C and in the vicinity of the spinning cell bottom was 120° C and the take-up speed of the spun filaments was 300 mpm. The obtained undrawn filaments were processed to a drawing operation at a draw ratio of 4 within a boiling water bath. After this drawing process, the drawn filaments were subjected to a free relaxation within an environment of 140° C and 25 percent relative humidity. The hygroscopic property shown by this acrylic fiber was 10.9 percent. The measurement of the antistatic property of Example 3 was applied to thusly obtained acrylic fibers and it was confirmed that the half-value period of the fiber even after washing 10 times was 10 seconds, which result endorses the provision of the excellently enhanced antistatic property by employment of the art of the present invention.

EXAMPLE 6

In order to obtain a spinning solution of 24 percent by weight concentration, an acrylonitrile copolymer of 0.172 specific viscosity was dissolved in dimethyl acetamide. The copolymer was made up of 93 percent by weight of acrylonitrile, 5 percent by weight of N-3-oxo-1-1-dibutyl-2-n-propyl-heptyl acrylamide and 2 percent by weight of methylacrylate. The acrylic fiber made from thusly prepared spinning solution by the same method as that employed in Example 1, was provided with a hygroscopic property of 8.6 percent.

EXAMPLE 7

An acrylic copolymer (A) having a specific viscosity of 0.14 was prepared from 61 percent by weight of acrylonitrile, 2 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide, 30 percent by weight of polyethylene glycol ester of acrylic acid and having the following formula:



and 7 percent by weight of vinyl acetate.

Further, another acrylic copolymer (B) having a specific viscosity of 0.17 was prepared from 95 percent by weight of acrylonitrile and 5 percent by weight of vinyl acetate.

15 parts by weight of the copolymer (A) and 85 parts by weight of the copolymer (B) were dissolved in dimethyl formamide so as to prepare a spinning solution of 21% by weight concentration. Thusly prepared spinning solution was extruded into an aqueous coagulation bath in a usual manner of wet-spinning. The undrawn filament was subjected to a drawing operation at a draw ratio of 5 within a boiling water bath.

After the rinsing and drying operations for the drawn filament, the dried filament was processed to a relaxation under a 2.3 kg/cm² steam pressure. Thusly treated filaments were converted into a knitted fabric in conventionally known manners of spinning and knitting. The fabric thusly obtained was subjected to the below-specified bleaching and washing operations. At each stage of the operations, measurement of the hygroscopic property, antistatic property, softness and resistance against soiling was applied to the specimen fabric.

(1) Bleaching of the specimen fabric was carried out under the following process conditions.

Bleaching composition:	
Sodium chlorite	2 g/l
Acetic acid	0.2 g/l
Sodium acetate	0.2 g/l
Bleaching auxiliary agent HV (*1)	1.5 g/l
Liquor ratio	1 : 50
Temperature	98° C
Time	60 min

Note: (*1) Trade name of a bleaching auxiliary agent made by Hodogaya Chemical Industry, Ltd.

(2) After the bleaching, dechlorination for the bleached specimen fabric was carried out under the following process conditions.

Acid sodium sulfite	1 g/l
Liquor ratio	1 : 50
Temperature	70° C
Time	15 min

(3) Subsequent to this dechlorination, washing of the specimen fabric was carried out under the following process conditions.

ZABU (*2)	3 g/l
Liquor ratio	1 : 50
Temperature	40° C
Time	20 min

Note: (*2) Trade name of a detergent made by Kao Soap Co.

(4) Measurement of the softness was carried out according to the known manner of organoleptic handling test and the result was classified into the following five classes.

Class 5	Remarkably soft
Class 4	Soft
Class 3	Slightly soft
Class 2	Slightly stiff (an extent characteristic similar to the conventional acrylic fibers)
Class 1	Stiff

(5) Measurement of resistance against soiling was carried out according to the below specified manner.

(a) Oily soiling test	
soiling composition:	
Carbon black	0.3 g
Cow fat	0.5 g
Fluid paraffin	1.5 g
carbon tetrachloride	400 ml
Liquor ratio	1 : 100
Temperature	room temperature
Time	2 min

After the immersion into the above-specified bath, the fabric was rinsed with water, air-dried and then the

dried specimen fabric was subjected to a measurement of whiteness using a spectrophotometer in the conventional manner.

(b) Dry soiling
soiling composition:

Carbon black	1.75 g
Clay	17.0 g
Cement	17.0 g
Silica	17.0 g

The above-mentioned soiling composition was placed within a ball mill box together with 10 specimen fabrics of 5 × 5 cm size and 30 balls. After 10 min of rotation of the mill, the excessive soiling composition being laid on the surfaces of the specimens was removed and then the specimens were subjected to measurement of whiteness in the same manner as the above-described.

The result was set forth in the following Tables 2A and 2B, wherefrom it can be well noted that the acrylic fiber of the present invention can be, when compared with the conventional acrylic fibers, provided with an excellently enriched soft handling quality, soil resistance, hygroscopic property, antistatic property and their durabilities against washing. In the following tables, results obtained relating to the conventional acrylic fibers are illustrated, also.

Table 2A

For the acrylic fibers of the present invention

	Soil-resist property				Anti-static property
	Whiteness in %			Hygro-scopic	Half-value
	Oily soiling	Dry soiling	Softness in class	property in %	period in sec
After bleaching	61	67	4 to 5	10.5	4.5
After 10 times	63	67	4 to 5	9.8	4.4

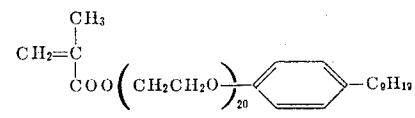
Table 2B

For the conventional acrylic fibers

	Soil-resist property				Anti-static property
	Whiteness in %			Hygro-scopic	half-value
	Oily soiling	Dry soiling	softness in class	property in %	period in sec
After bleaching	49	58	2	1.8	longer than 60
After 10 times washing	54	61	2	1.7	longer than 60

Example 8

A purified dimethyl formamide was used in dissolving a copolymer at a concentration of 28 percent, which copolymer was made up of 78 percent by weight of acrylonitrile, 7 percent of vinylacetate, 3 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 12 percent by weight of polyethylene glycol methacrylate of the following formula:



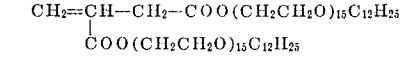
The obtained spinning solution was spun by the known dry-spinning method under the process conditions of 220° C at the nozzle ends and 200° C at the spinning cell bottom. With subsequent application of drawing, washing, oiling, drying and relaxation, an acrylic fiber of excellent hygroscopic property, antistatic property, softness and resistance against soiling could be obtained as shown in the following Table 3.

Table 3

	Soil-resist property				Anti-static property
	Whiteness in %			hygro-scopic	half-value
	Oily soiling	Dry soiling	softness in class	property in %	period in sec
After bleaching	60	63	5	10.7	6.5
After 10 times washing	62	65	5	10.4	5.1

Example 9

In order to obtain a spinning solution of 24 percent by weight concentration, 20 parts by weight of a copolymer (A) of 0.12 specific viscosity and 80 parts by weight of another copolymer (B) were uniformly mixed and dissolved with dimethylacetamide. The first named copolymer (A) was made up of 67 percent by weight of acrylonitrile, 8 percent by weight of N-3-oxo-1-methyl-butyl-α-methyl acrylamide and 25 percent by weight of polyethylene glycol of itaconic acid and having the following formula:



The second named copolymer (B) was made up of 93.5 percent by weight of acrylonitrile, 6 percent by weight of methylacrylate and 0.5 percent by weight of sodium vinylbenzene sulfonate. Thusly prepared spinning solution was extruded into an aqueous coagulation bath in a manner of wet-spinning. After subsequent drawing, washing, drying and relaxation, an acrylic fiber having such excellent functional properties as shown in the following table could be obtained.

Table 4

	Soil-resist property Whiteness in %			
	Oily soiling	dry contamination	softness in class	hygroscopic property in %
before	65	66	4 to 5	12.1

dyeing after dyeing (*3)	—	—	4 to 5	11.7

Note: (*3) The acrylic fiber was dyed with 5% Deorlene Blue 5G (trade name of a basic dye made by Ciba) based on the weight of the acrylic fiber.

EXAMPLE 10

20 parts by weight of a copolymer (A) was uniformly mixed with 80 parts by weight of another copolymer (B) so as to obtain an acrylic fiber of excellent hygroscopic property, softness and resistance against contamination in a method the same with that employed in the foregoing Example 1 and the functional property thereof is shown in the following Table 5A. The first named copolymer (A) was made up of 60% by weight of acrylonitrile, 10 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 30 percent by weight of polyethylene glycol acrylamide having the following formula:

$$CH_2=CH$$
$$|$$
$$CONH(CH_2CH_2O)_{30}C_{12}H_{25}$$

The second named copolymer (B) was made up of 94 percent by weight of acrylonitrile and 6 percent by weight of methylacrylate.

For the purpose of comparison, a uniform mixture of 20 parts by weight of a copolymer (C) with 80 parts by weight of another copolymer (D) was prepared in a manner the same with that of the foregoing specimen preparation. The copolymer (C) was made up of 63 percent by weight of acrylonitrile, 7 percent by weight of methylacrylate and 30 percent by weight of polyethylene glycol acrylamide of the above-shown formula whereas the copolymer (D) was made up of 94 percent by weight of acrylonitrile and 6 percent by weight of methylacrylate. The functional property of thusly prepared comparative fiber is also shown in the following Table 5B. From this comparison of the results, it is well-understood that the essential effect of the present invention can be brought about by use of N-3-oxo-1-1-dimethylbutyl acrylamide component.

Table 5A

For the fiber of the present example

	Soil-resist property Whiteness in %			
	Oily soiling	Dry soiling	Softness in class	Hygroscopic property in %
After bleaching	69	67	4 to 5	12.3
After 10 times washing	68	68	4 to 5	12.1

Table 5B

For the comparative specimen

	Soil-resist property Whiteness in %			
	Oily soiling	Dry soiling	softness in class	Hygroscopic property in %
After bleaching	66	63	4	5.0
After 10 times washing	63	65	4	4.7

EXAMPLE 11

A spinning solution of 24% by weight concentration was prepared by dissolving 30 parts by weight of acrylonitrile copolymer (A) of 0.170 specific viscosity and 70 parts by weight of another copolymer (B) in dimethyl acetamide. The copolymer (A) was made up of 80 percent by weight of acrylonitrile, 15 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 5 percent by weight of itaconic acid whereas the other copolymer (B) was made up of 93 percent by weight of acrylonitrile and 7 percent by weight of vinyl acetate. The obtained spinning solution was extruded into an aqueous coagulation bath according to the same method as that of Example 1. The obtained filament was drawn at a draw ratio of 5 within a boiling water bath and simultaneously cleared therein for taking-up onto a dryer roller. Subsequent to this, the dried filament was subjected to a relaxation under a 2.3 kg/cm² steam pressure. The hygroscopic property of thusly obtained acrylic fiber was found to be 11.9 percent.

EXAMPLE 12

A spinning solution of 23.5 percent by weight concentration was prepared by dissolving 40 parts by weight of acrylonitrile copolymer (A) of 0.168 specific viscosity and 60 parts by weight of acrylonitrile copolymer of 0.17 specific viscosity (B) in dimethyl acetamide. The acrylonitrile copolymer (A) was made up of 77 percent by weight of acrylonitrile, 20 percent by weight of acrylic acid and 3 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide whereas the acrylonitrile copolymer (B) was made up of 93 percent by weight of acrylonitrile and 7 percent by weight of methylacrylate. The prepared spinning solution was extruded into an aqueous coagulation bath in a manner similar to that employed in Example 1 and the obtained filament was drawn at a draw ratio of 4.5 within a boiling water bath. After drying, the filament was subjected to a relaxation treatment under a 2.5 kg/cm² steam pressure. The hygroscopic property of the obtained acrylic fiber was found to be 12.5 percent.

EXAMPLE 13

A spinning solution of 23 percent by weight concentration was prepared by dissolving 40 parts by weight of acrylonitrile copolymer (A) of 0.15 specific viscosity and 60 parts by weight of another copolymer (B) of 0.16 specific viscosity with dimethylacetamide. The acrylonitrile copolymer (A) was made up of 80 percent by weight of acrylonitrile, 5% by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 15 percent by weight of acrylic acid whereas the other copolymer (B) was made up of 94 percent by weight of acrylonitrile and 6 percent by weight of methylacrylate. The obtained spinning solution was extruded to form filament form according to the conventional wet-spinning method. The obtained filament was drawn at a draw ratio of 5 within a boiling water bath and dried. The hygroscopic property of thusly obtained acrylic fiber was 12.9 percent and the result of the measurement of the antistatic

property is shown in Table 6, wherefrom it is seen that the acrylic fiber manufactured according to the art of the present invention is provided with a durable antistatic property far superior to those possessed by the conventional acrylic fibers and that the degree thereof is very proximate to that of viscose fibers. This antistatic property can be further enriched by the combined application of the known antistatic agents. No trouble was recognized in relation to the electrostatic property of the textile products such as underwear made up of the acrylic fibers of the present invention. Further, it was confirmed that the fabric was provided with an excellent resistance to soiling.

TABLE 6

Samples	Antistatic property Half-value period in sec Original	after scouring	After dyeing	after 10 times of washing
Acrylic fiber of the invention	Less than 1.0	1.5	3.9	3.0
Conventional acrylic fiber	ditto	38.0	Larger than 60	Larger than 60
Viscose fibers	ditto	1.2	1.4	1.3
Wool	ditto	1.5	5.7	15.0

EXAMPLE 14

A spinning solution of 18 percent by weight concentration was prepared by dissolving 20 parts by weight of acrylonitrile copolymer (A) of 0.162 specific viscosity and 80 parts by weight of copolymer (B) of 0.17 specific viscosity in dimethyl sulfoxide. The acrylonitrile copolymer (A) was made up of 70 percent by weight of acrylonitrile, 15 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 15 percent by weight of hydroxyethylacrylate whereas the other copolymer (B) was made up of 97 percent by weight of acrylonitrile and 3 percent by weight of vinylacetate. The spinning solution was spun into filaments according to the usual wet-spinning method. The obtained filaments were drawn at a draw ratio of 6 within an aqueous bath of 100° C temperature and containing 10 percent of dimethylsulfoxide and rinsed within a boiling water bath for removal of the remaining solvent. After drying operation, the filaments were subjected to a relaxation process under a 2.0 atmosphere steam pressure. The hygroscopic property of thusly obtained acrylic fiber was 9.1 percent.

EXAMPLE 15

A spinning solution of 28 percent concentration was prepared by dissolving 45 parts by weight of acrylonitrile copolymer (A) of 0.16 specific viscosity and 55 parts by weight of another copolymer (B) of 0.167 specific viscosity in dimethylformamide. The acrylonitrile copolymer (A) was made up of 77 percent by weight of acrylonitrile, 3 percent by weight of N-3-oxo-1-1-dimethyl-2-ethyl-butyl acrylamide and 20 percent by weight of vinyl pyrrolidone whereas the other copolymer (B) was made up of 96 percent by weight of acrylonitrile and 4% by weight of methylacrylate. The obtained spinning solution was spun into filaments in a common dry-spinning process, wherein the temperature of the solution was 120° C, the flow velocity of the drying air was 0.6 mpm, the temperature at the top of the spinning cell was 240° C, the temperature at the bottom of the spinning cell was 120° C and the take-up speed of the spun filaments was 300 mpm. The obtained undrawn filaments were drawn at a draw ratio of 3.4 within a boiling water bath and the drawn filaments were subjected to a relaxation with no tension within an environment of 140° C temperature and 25 percent relative humidity. The hygroscopic property of the resultant acrylic fibers was 12.5 percent. Further, the antistatic property of the specimen was measured in a manner employed in Example 3 and the half-value period after washing 10 times was 2.5 sec, which result endorsed the provision of remarkably enhanced durable antistatic property.

EXAMPLE 16

A spinning solution of 24 percent by weight concentration was prepared by dissolving 30 parts by weight of acrylonitrile copolymer (A) of 0.172 specific viscosity and 70 parts by weight of another copolymer (B) of 0.17 specific viscosity in dimethyl acetamide. The acrylonitrile copolymers (A) was made up of 80 percent by weight of acrylonitrile, 15 percent by weight of methylacrylate and 5 percent by weight of N-3-oxo-1-1-dibutyl-2-n-propyl-heptyl acrylamide whereas the other copolymer (B) was made up of 97 percent by weight of acrylonitrile and 3% by weight of methylacrylate. The acrylic fiber obtained from this spinning solution by a process the same with that employed in Example 1 was provided with hygroscopic property of 11.0 percent.

EXAMPLE 17

A spinning solution of 24 percent by weight concentration was prepared by dissolving 30 parts by weight of copolymer (A) of 0.169 specific viscosity and 70 parts by weight of copolymer (B) of 0.169 specific viscosity in dimethylacetamide. The first named copolymer (A) was made up of 77 percent by weight of acrylonitrile, 10 percent by weight of acrylic acid, 10 percent by weight of sodium vinylbenzene-sulfonate and 3 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide whereas the second named copolymer (B) was made up of 93 percent by weight of acrylonitrile and 7 percent by weight of vinylacetate. The spinning solution was extruded into an aqueous coagulation bath according to the known wet-spinning process. Together with prosecution of rinsing, the filament was drawn at a draw ratio of 5 within a boiling water bath. After the drying process, the filament was subjected to relaxation under a 2.5 kg/cm² steam pressure and the obtained acrylic fiber was provided with 12.7 percent hygroscopic property. The other functional properties thereof were almost similar to those possessed by the conventional acrylic fibers.

EXAMPLE 18

A spinning solution of 24% by weight concentration was prepared by dissolving 8 parts by weight of a copolymer (A) of 0.159 specific viscosity and 92 parts by weight of another copolymer (B) of 0.169 specific

viscosity in dimethyl acetamide. The first named copolymer (A) was made up of 65 percent by weight of acrylonitrile, 5 percent by weight of vinylacetate and 30 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide, whereas the second named copolymer (B) was made up of 89 percent by weight of acrylonitrile, 6 percent by weight of vinyl acetate and 5 percent by weight of methacrylic acid. The spinning solution was then processed in the known wet-spinning method. Together with the prosecution of rinsing, the obtained filament was drawn at a draw ratio of 5 within a boiling water bath. Next, the drawn filament was dried and subjected to the relaxation treatment. The obtained acrylic fiber was provided with 13.1 percent hygroscopic property.

EXAMPLE 19

Five spinning solutions of 24 percent by weight concentration were prepared by dissolving 10 parts by weight of a member selected from five acrylonitrile copolymers (A) and 90 parts by weight of another copolymer (B) in dimethylformamide. Each acrylonitrile copolymer (A) was made up of 65 percent by weight of acrylonitrile, 10 percent by weight of methacrylic acid, 5 percent by weight of vinyl acetate and 20 percent by weight of a N-3-oxo-hydrocarbon-substituted acrylamide selected from the group shown in Table 7, whereas the other copolymer (B) was made up of 93 percent by weight of acrylonitrile and 7 percent by weight of vinylacetate and its specific viscosity was 0.17. Thusly obtained spinning solutions were spun in a manner similar to that employed in the foregoing Example 1 and the hygroscopic property of thusly obtained acrylic fibers is also shown in Table 7.

Table 7

type of N-3-oxo-hydrocarbon substituted acrylamide	hygroscopic property in %
N-3-oxo-butyl acrylamide	12.1
N-3-oxo-1-methyl-cyclehexyl butyl acrylamide	10.0
N-3-oxo-1-1-dibutyl-2-n-propylhexyl acrylamide	7.5
N-3-oxo-1-methyl-butyl-α-methyl acrylamide	9.1
N-3-oxo-1-1-dimethyl-butyl-α-butyl acrylamide	7.9

EXAMPLE 20

Six kinds of uniform mixtures each containing 15 parts by weight of a member selected from six copolymers (A) of 0.13 specific viscosity and 85 parts by weight of copolymer (B) of 0.18 specific viscosity were dissolved in dimethyl acetamide. Each first named copolymer (A) was made up of 50 percent by weight of acrylonitrile, 10 percent by weight of N-3-oxo-1-1-dimethylbutyl acrylamide and 40 percent by weight of a member selected from six polyethylene glycol esters as shown in Table 8, whereas the second named copolymer (B) was made up of 94 percent by weight of acrylonitrile and 6 percent by weight of methylacrylate. The acrylic fibers obtained from thusly prepared spinning solutions in a manner the same with that used in Example 1 were provided with excellent hygroscopic and antistatic properties such as shown in Table 8.

Table 8

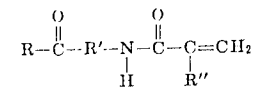
Copolymer (A) Substituents of the polyethylene glycol ester In the formula (2)					Hygroscopic property	Antistatic property
m	n	x	y	R_1	in %	Half-value period in sec after dyeing
0	50	—H	—O—	$C_{12}H_{25}$	10.1	4.5
0	100	—H	—O—	$C_{12}H_{25}$	12.3	3.9
0	30	—H	—O—	C_8H_{17}	10.9	5.0
0	30	—H	—O—	CH_3	11.8	3.8
2	15	—H	—O—	C_4H_9	9.4	9.4
4	15	—H	—O—	C_4H_9	9.0	9.6

What we claim is:

1. An acrylic fiber of enhanced hygroscopic property, which comprises a copolymer (A) comprising, as unit components,

a. at least 10 percent by weight of acrylonitrile;

b. from 0.2 to 20 percent by weight of N-3-oxo-hydrocarbon-substituted-acrylamide of the formula (1):



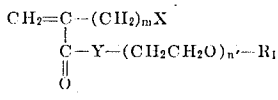
(1)

wherein R and R'' are members selected from the group consisting of hydrogen and lower alkyl groups having not more than 10 carbon atoms, respectively, and R' is a member selected from the group consisting of an ethylene group and lower alkyl-substituted ethylene groups having not more than 15 carbon atoms; and

c. at least one third copolymerizing monomer selected from the group consisting of monomers having hydroxyl group, ethylenically unsaturated monomers having carboxyl group or its salts, ethylenically unsaturated monomers having sulfonic acid group or its salts, ethylenically unsaturated monomers having amide group and polyethylene glycol esters of acrylic acid, methacrylic acid and ethylenically unsaturated monomers having a polyethylene glycol side chain, and another different copolymer (B) containing at least 85 percent by weight of acrylonitrile, said copolymer B being mixed with said copolymer (A).

2. A novel acrylic fiber as claimed in claim 1, wherein said copolymer (A) comprises, as a unit component, at least 50 percent by weight of acrylonitrile, 1 to 50 percent by weight of said substituted acrylamide of formula (1) and balancing quantity of said third monomer, and the content of said substituted acrylamide of the formula (1) in said fiber is in a range from 0.2 to 20 percent based on the weight of said fiber.

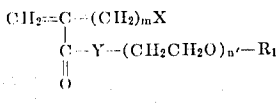
3. A novel acrylic fiber as claimed in claim 1, wherein said copolymer (A) comprises, as a unit component, (a) from 10 to 94 percent by weight of acrylonitrile, (b) from 0.2 to 20 percent by weight of said substituted acrylamide of said formula (1), and (c) from 5 to 89 percent by weight of said polyethylene glycol ester of the following formula (2),



(2)

wherein X is a member selected from the group consisting of hydrogen and groups having the formula; —C—Y'—$(CH_2CH_2O)_n$—R_1; Y is a member selected from the group consisting of oxygen and —NH group: R_1 is a member selected from the group consisting of alkyl groups having 1 to 22 carbon atoms, phenyl groups and substituted phenyl groups; Y' and R_1' are selected from the groups the same as that of Y and R_1, respectively; Y and Y' and R_1 and R_1', may or may not be different from each other; *m* is 0 or a positive integer from 1 to 10; *n* is a positive integer from 1 to 200; and *n'* is a positive integer from 1 to 200 and may or may not be the same as *n*, and the content of said substituted acrylamide of the formula (1) in said fiber is in a range from 0.2 to 8 percent based on the weight of said fiber.

4. A novel acrylic fiber as claimed in claim 1, wherein said copolymer (A) comprises, as a unit component, (a) from 10 to 94 percent by weight of acrylonitrile, (b) from 0.2 to 20 percent by weight of said substituted acrylamide of the formula (1) (c) from 5 to 80 percent by weight of said polyethylene glycol ester of the following formula (2);

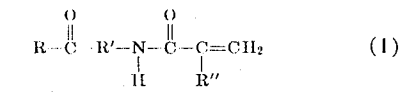


(2)

wherein X is a member selected from the group consisting of hydrogen and groups having the formula; —C—Y'—$(CH_2CH_2O)_n$—R_1; Y is a member selected from the group consisting of oxygen and —NH group: R_1 is a member selected from the group consisting of alkyl groups having 1 to 22 carbon atoms, phenyl groups and substituted phenyl groups; Y' and R_1' are selected from the groups the same as that of Y and R_1, respectively; Y and Y' and R_1 and R_1', may or may not be different from each other; *m* is 0 or a positive integer from 1 to 10; *n* is a positive integer from 1 to 200; and *n'* is a positive integer from 1 to 200 and may or may not be the same as *n*, and (d) balancing quantity of at least one member selected from said third monomers except for said polyethylene glycol esters of said formula (2) and the content of said substituted acrylamide of the formula (1) in said fiber is in a range from 0.2 to 8 percent based on the weight of said fiber.

5. A method of manufacturing acrylic fiber of enhanced hygroscopic property comprising:

1. preparing a copolymer (A) by copolymerizing a mixture of (a) at least 10 percent by weight of acrylonitrile; (b) from 0.2 to 20 percent by weight of N-3-oxo-hydrocarbon-substituted acrylamide of the formula (1):



(1)

wherein R and R' are a member selected from the group consisting of hydrogen and lower alkyl groups having not more than 10 carbon atoms; respectively and R' is a member selected from the group consisting of ethylene group and lower alkyl-substituted ethylene groups having not more than 15 carbon atoms; and (c) at least one third copolymerizing monomer selected from the group consisting of monomers having a hydroxyl group, monomers having a carboxyl group or its salts, monomers having a sulfonic acid group or its salts, monomers having an amide group and polyethylene glycol esters of acrylic acid and methacrylic acid;

2. preparing in a solvent a spinning solution containing said copolymer (A) and another different copolymer (B) containing at least 85 percent by weight acrylonitrile, and
3. extending said spinning solution into a coagulation medium to form filament.

6. A method as claimed in claim 5, wherein said copolymer (A) to be mixed comprises as unit components, at least 50 percent by weight of acrylonitrile and from 1 to 40 percent by weight of said substituted acrylamide of formula (1) and balancing quantity of said third monomer and the content of said copolymer (A) in said mixture is determined so that the content of said substituted acrylamide of formula 1) in the resultant fiber is in a range from 0.2 to 20 percent based on the weight of said resultant fiber.

7. A method as claimed in claim 5, wherein said copolymer (A) to be mixed comprises, as unit components, (a) 10 to 94 percent by weight of acrylonitrile, (b) 0.2 to 20 percent by weight of said substituted acrylamide of said formula (1), and (c) 5 to 89 percent by weight of polyethylene glycol ester, and the content of said copolymer (A) in said mixture is determined so that the content of said substituted acrylamide of the formula (1) in the resultant fiber is in a range from 0.2 to 8 percent based on the weight of said resultant fiber.

8. A method as claimed in claim 5, wherein said copolymer (A) to be mixed comprises, as unit components, (a) 10 to 94 percent by weight of acrylonitrile, (b) 0.2 to 20 percent by weight of said substituted acrylamide of the formula (1), (c) 5 to 80 percent by weight of said polyethylene glycol ester and (d) balancing quantity by weight of at least one member selected from said third monomers other than said polyethylene glycol esters, and the content of said copolymer (A) in said mixture is determined so that the content of said substituted acrylamide of the formula (1) in the resultant fiber is in a range from 0.2 to 8 percent based on the weight of said resultant fiber.

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