United States Patent

Buisson et al.

[15] **3,673,160**

[45] **June 27, 1972**

[54] PROCESS FOR PRODUCING BRILLIANT SULFONATED POLYAMIDE-IMIDE FIBERS AND SUCH FIBERS SO PRODUCED

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[22] Filed: **Feb. 2, 1971**

[21] Appl. No.: **112,083**

[30] **Foreign Application Priority Data**

Feb. 12, 1970	France	7005024
Nov. 17, 1970	France	7041462

[52] **U.S. Cl.** ....**260/78 TF,** 8/178 R, 57/140 R, 260/29.2 N, 260/30.2, 260/47 CZ, 260/47 CB, 264/184

[51] **Int. Cl.** **C08g 20/32**

[58] **Field of Search** ....260/78 TF

[56] **References Cited**

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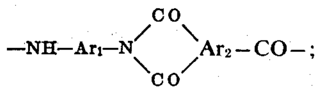
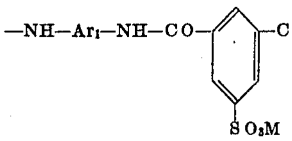
[57] **ABSTRACT**

A process for producing brilliant thermostable polyamide-imide fibers and such fibers so produced, such process comprising extruding an N-methylpyrrolidone solution of a polymer having a structure characterized by the following linkages:



B. amide linkages of the formula:



; and, optionally

C. amide linkages of the formula:

—NG—Ar_1—NH—CO—R—CO— aqueous N-methylpyrrolidone coagulating 1.5 X;

wherein Ar_1 represents a bivalent aromatic radical, Ar_2 represents a trivalent aromatic radical, R represents a bivalent aromatic, aliphatic, cycloaliphatic or arylaliphatic radical, and M represents an alkali or alkaline earth metal, linkages B representing at least 3 percent of the total of linkages A, B and C in an aqueous N-methylpryyolidone coagulating bath; drawing the extruded filaments in air at a rate of at least 1.5 ×; drying the filaments to eliminate N-methylpyrrolidone; and drying the filaments. The filaments obtained are characterized in being brilliant, homogenous, thermostable filaments.

2 Claims, No Drawings

PROCESS FOR PRODUCING BRILLIANT SULFONATED POLYAMIDE-IMIDE FIBERS AND SUCH FIBERS SO PRODUCED

The present invention relates to a process for producing brilliant thermostable polyamide-imide fibers by a wet spinning process, and to such fibers so produced; more particularly, the present invention is directed to such a process wherein polyamide-imide fibers are spun from an N-methylpyrrolidone solution, the polyamide-imide containing sulfonate groups.

Polyamide-imide fibers are well known as are processes for producing the same. For example, it has been known to produce thermostable filaments by dry spinning of polyamide-imides but, such process is disadvantageous for various reasons. Primary among these is that to produce such a dry spinning process it is difficult to remove and eliminate the solvent, making such process one which is uneconomical and unsatisfactory from an industrial standpoint. In addition, while such dry spinning technique can lead to the production of brilliant yarns of polyamide-imides, when it is desired to spin cables having a large number of strands, such dry spinning process is totally unsatisfactory, leading to the necessity for wet spinning.

Accordingly while wet spinning processes have been largely adopted, such wet spinning processes developed to date have possessed various deficiencies and disadvantages not allowing for the production of brilliant thermostable fibers.

For example, the wet spinning of polyamide-imides generally leads to the production of porous fibers and filaments and, accordingly, very dull fibers and filaments lacking the brilliance desired for commercial acceptance.

In addition to the foregoing, it is pointed out that prior to the development of the present invention it has been known to copolymerize sulfonated monomers and to introduce sulfonated linkages into polymers in order to achieve various effects. For example, French Patent 1,223,162 involves the spinning of sulfonated acrylic polymers in order to improve the homogeneity of coagulation of the acrylic fibers having the natural tendency to form voids at the time of their coagulation in wet spinning. In accordance with this French patent any sulfonic group containing monomer copolymerizable with acrylonitrile can be utilized to improve the homogeneity of coagulation and, accordingly to improve the characteristics of the fibers.

Similarly, it has been previously known to improve the dyeing affinity of various polymers, including polyamides for basic dyes by introducing sulfonated linkages into the polymer. For example, French Patent 1,548,029 relates to the introduction in the chain of an aromatic polyamide, links containing sulfonic groups. Here again, any sulfonic product which can be condensed with the aromatic diamines and diacids in the production of the polyamide is found to be suitable for improving the dyeing affinity for the polyamide.

With the foregoing background, it has now been discovered in accordance with the present invention that the foregoing disadvantages with respect to the wet spinning of polyamides-imides can be overcome, and brilliant filaments not heretofore obtainable obtained, by wet spinning the polymers from an N-methylpyrrolidone solution, the polymers containing an alkali or alkaline earth salt of dicarboxy-3,5 benzene sulfonic acid.

In connection with the foregoing, it has been surprisingly discovered that when incorporating an alkali or alkaline earth salt of dicarboxy-3,5 benzene sulfonic acid in the polyamide-imide and wet spinning the polymer from an N-methylpyrrolidone solution, it is possible to produce brilliant filaments and fibers, which brilliant filaments and fibers cannot be produced through the introduction of different sulfonic acid or sulfonate groups and cannot be produced through spinning the polymer from a different solution.

Accordingly it is a principal object of the present invention to provide a novel process for the production of brilliant thermostable polyamide-imide fibers and such fibers so produced, wherein such method eliminates the various deficiencies and disadvantages of conventional wet spinning processes.

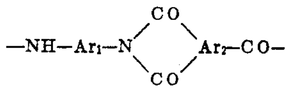
It is a further object of the present invention to provide such a process for the wet spinning of polyamide-imide fibers to produce brilliant thermostable fibers, wherein a polyamide-imide polymer containing an alkali or alkaline earth salt of dicarboxy-3,5 benzene sulfonic acid is wet spun from an N-methylpyrrolidone solution.

Still further objects and advantages of the novel process of the present invention will become more apparent from the following more detailed description thereof.

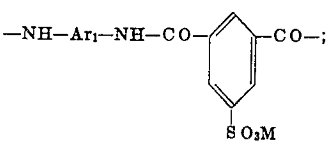
The foregoing objects and advantages of the process of the present invention are achieved by extruding from an N-methylpyrrolidone solution a polyamide-imide polymer containing an alkali or alkaline earth salt of dicarboxy-3,5 benzene sulfonic acid; drawing the filaments in air at a rate of at least 1.5 X; washing the filaments to remove N-methylpyrrolidone; and thereafter drying the filaments.

The brilliant thermostable polyamide-imide fibers are prepared by wet spinning an N-methylpyrrolidone solution of a polymer comprising:

A amide-imide linkages of the formula:



B. amide linkages of the formula:



and, optionally

C amide linkages of the formula:

$$-NH-Ar_1-NH-CO-R-CO-$$

wherein Ar_1 represents a bivalent aromatic nucleus, i.e. either a monocyclic or bicyclic aromatic nucleus; Ar_2 represents a trivalent aromatic nucleus, preferably a monocyclic aromatic nucleus; R represents a bivalent aromatic nucleus, aliphatic, cycloaliphatic or arylaliphatic radical; and M represents an alkali or alkaline earth metal. While Ar_1 represents a bivalent aromatic nucleus as set forth above, the polyamide-imide may contain structural units wherein Ar_1 represents an aliphatic or cycloaliphatic radical, although such structural units are present only in a minor proportion in the polymer structure, i.e. at least 80 percent of the Ar_1 radicals are the divalent aromatic nucleus.

In accordance with the present invention, the B linkage as described above, i.e. the linkage derived from an alkali or alkaline earth metal salt of dicarboxy-3,5 benzene sulfonic acid is present in the polymer structure in an amount of at least 3 mole percent based upon the total number of linkages A, B and C. As indicated previously, linkages c are optionally present in the polymer structure, the same generally comprising from 0 to 20 mole percent. The remaining linkages comprise linkage A.

The polymers of the present invention, hereinafter referred to as "sulfonated polyamide-imides" can be obtained by a conventional polymerization reaction. For example, the sulfonated polyamide-imide can be prepared in substantially stoichiometric proportions by polymerizing at least one aromatic diisocyanate with an acid reagent comprising at least one aromatic acid anhydride and an alkali or alkaline earth salt of dicarboxy-3,5 benzene sulfonic acid in an anhydrous polar organic solvent. Additionally the system may contain minor amounts of an aromatic, aliphatic, cycloaliphatic or arylaliphatic diacid.

The aromatic diisocyanates which can be used in the production of the sulfonated polyamide-imides can comprise any of the conventional monocyclic and bicyclic diisocyanates, including the symmetrical and unsymmetrical diisocyanates. Accordingly, suitable examples include toluylene diisocyanates, diisocyanatodiphenylmethane, diisocyanatodiphenylpropane, diisocyanatodiphenyl-ether, etc. Of the bicyclic diisocyanates, the symmetrical bicyclic diisocyanates are preferred.

In addition to the aromatic diisocyanates as indicated above, an aliphatic or cycloaliphatic diisocyanate may be added to the reaction system in a minor proportion, i.e. up to about 20 mole percent based upon the diisocyanate component. The addition of such an aliphatic or cycloaliphatic diisocyanate tends to improve certain properties of the polyamide-imide, such as the solubility of the finished product, flexibility and elasticity of the shaped articles produced therefrom.

The acid anhydride which is utilized to produce the polyamide-imide generally comprises an anhydride of a benzene tricarboxylic acid. The preferred benzene tricarboxylic acid in accordance with the present invention comprises trimellic acid, trimellitic anhydride being preferred. In addition, substituted derivatives of such benzene tricarboxylic acid anhydrides can be advantageously utilized in accordance with the present invention as long as the substituent does not interfere with the polyamide-imide forming reaction.

The dicarboxylic acids which are utilized in accordance with the present invention can be aromatic, aliphatic, or cycloaliphatic dicarboxylic acids, although aromatic dicarboxylic acids are preferred. Suitable aromatic dicarboxylic acids include for example: isophthalic, terephthalic, 4,4'-diphenyl dicarboxylic 3,3'-diphenyl dicarboxylic, 4,4-diphenylether dicarboxylic, 3,3'-diphenylether dicarboxylic, 4,4'-diphenylthioether dicarboxylic, 3,3'-diphenylthioether dicarboxylic, 4,4'-diphenylmethane dicarboxylic, 3,3'-diphenylmethane dicarboxylic, 4-4'-diphenyl-2,2-propane dicarboxylic, 3,3'-diphenyl-2,2-propane dicarboxylic, 4,4'-diphenylsulfone dicarboxylic, 3,3'-diphenylsulfone dicarboxylic, 1,4-naphthalene dicarboxylic, 1,5-naphthalene dicarboxylic, 1,6-naphthalene dicarboxylic, 2,6-naphthalene dicarboxylic,

Aliphatic dicarboxylic acids — oxalic, succinic, adipic, azelaic, sebacic, acids.

Cycloaliphatic dicarboxylic acids - 1,3-cyclohexane dicarboxylic and 1,4-cyclohexane dicarboxylic acids.

Of the foregoing, aromatic dicarboxylic acids such as terephthalic acid and isophthalic acid are preferred as are aliphatic dicarboxylic acids such as adipic acid, sebacic acid, and succinic acid. The dicarboxylic acid is generally present in the reaction system in an amount of 0–20 mole percent.

In accordance with the present invention, the B linkages, i.e. the linkages derived from an alkali or alkaline earth salt of dicarboxy-3,5 benzene sulfonic acid are present in the final polyamide-imide in an amount of at least 3 mole percent, based upon the total linkages A, B and C, preferably in an amount of 3–10 mole percent. Although greater amounts can be present where desired for particular purposes, an amount greater than about 10 mole percent is disadvantageous for economic reasons. The amount of linkages being present in the polyamide-imide varies somewhat with regard to the count of the filaments that are to be obtained. Thus, for example, good results are obtained with an amount of about 4 mole percent in the case of rather fine filaments, e.g. those with a count of less than 10 dtex at the output of the drawing in air, while an amount of about 7 mole percent provides good results for thicker filaments, e.g. those with a count approximately 40 dtex. The selection of any particular amount greater than 3 mole percent is of course easily done depending upon the final desired conditions and state of the product.

The remainder of the polyamide-imide comprises amide-imide linkages A and, optionally, amide linkages C. The amide linkages C are present in the final polyamide-imide only in a minor amount, i.e. of from 0 to about 20 mole percent. The remainder of course comprises the amide imide linkages A.

In accordance with the present invention, a solution of the polymer, preferably an N-methylpyrrolidone solution is extruded into an aqueous coagulating bath containing 30 to 75 percent by weight of N-methylpyrrolidone and, thereafter the filaments produced are drawn in air at a rate of at least 1.5 ×, generally under ambient temperature conditions. The drawn filaments are thereafter washed to eliminate the N-methylpyrrolidone and dryed by any known conventional means.

In accordance with the present invention, sulfonated copolyamides-imides can be obtained by the reaction in a polar organic solvent medium of substantially stoichiometric proportions of a diamine and a reagent comprising an acid chloride function and an anhydride function, an alkali or alkaline earth dicarboxy-3,5 benzene sulfonate dichloride and, optionally, a dichloride of an aromatic, aliphatic, cycloaliphatic or arylaliphatic dicarboxylic acid.

The polar organic solvent utilized to produce the polyamide-imide can comprise any of those conventionally utilized in such polymer production. For example, the polar organic solvent can comprise such materials as for example, dimethylformamide, dimethylacetamide, hexamethyl phosphoryltriamide, tetramethylene sulfone and preferably, N-methylpyrrolidone. In this regard if N-methylpyrrolidone is employed as the organic solvent in the production of the polyamide-imide it is generally unnecessary to eliminate the solvent prior to utilizing a solution of the polymer in the extrusion step. Accordingly if N-methylpyrrolidone is utilized as the organic solvent in the polymerization process, the solution of the sulfonated polyamide-imide directly obtained from polymerization can be utilized in the extrusion without first separation of the polymer. It is often preferable however to separate the polymer from the solution and then redissolve the polymer in N-methylpyrrolidone for extrusion so as to eliminate any byproducts which may be formed during the polycondensation reaction.

The sulfonated polyamide-imides which are utilized in accordance with the present invention are those which have an inherent viscosity greater than about 0.5 and, preferably, less than about 1.4. The inherent viscosity is measured at 25° C. with a 0.5 percent by weight solution in N-methylpyrrolidone. Preferably, in accordance with the present invention the sulfonated polyamide-imide is one having an inherent viscosity of between 0.8 and 1.2.

In accordance with the present invention the solution of the sulfonated polyamide-imide is one which has a viscosity of from about 150 to about 3,000 poises at 25° C. (measured by a Drage viscosimeter using speed II and a mobile 47.2). It is preferred in accordance with the present invention that the viscosity of the sulfonated polyamide-imide solution not exceed 1,500 poises.

In accordance with the present invention, the spinning solution normally contains the concentration of the sulfonated polyamide-imide polymer of between 10 and 30 percent by weight, preferably between 15 and 25 percent by weight. Additionally, the spinning solution can contain other various conventional adjuvants such as pigments, dulling agents, etc. The temperature of the solution at extrusion is not critical to the process of the present invention and, the same can vary within broad limits, depending upon the viscosity of the spinning solution. For example, a spinning solution having a low viscosity can easily be extruded at ordinary ambient temperatures although it is preferred to extrude high viscosity solutions at elevated temperatures, e.g. for example at 120° C. or more so as to avoid utilizing high pressures in the spinneret. Such variables however are the conventional variables utilized in spinning and extrusion processes and are not critical or peculiar to the process of the present invention.

As indicated previously, the sulfonated polyamide-imide filaments are extruded into a coagulating bath comprising an aqueous solution containing 30 to 75 percent by weight of N-methylpyrrolidone. It is preferred in accordance with the present invention that such coagulating bath contain at least 50 percent by weight of N-methylpyrrolidone since such higher concentrations allow the production of filaments having better drawability and, therefore, filaments having superior final properties.

The speed of passage of the extruded filaments in the coagulating bath can vary within broad limits and the process of the present invention is not dependent thereon. Thus the speed of passage of the filaments depends upon the N-methylpyrrolidone concentration in the coagulating bath and the distance the filaments must travel in the bath. Such passage speed in the coagulating bath generally varies between 10 to 60 meters per minute, although higher or lower speeds can be employed where desired for particular purposes. Generally, there is no advantage in spinning at lower speeds because this reduces the economic advantages of the process. On the other hand, if the passage speed of the filaments in the coagulating bath is too excessive the drawability of the filaments in air is reduced. Accordingly it is generally preferred to operate within the limits set forth above. In this respect, since the brilliance and mechanical properties for any given degree of linkages B in the starting polymer varies directly with the rate of drawing of the filaments in air, the speed of passage of the filaments in the coagulating bath should be suitably chosen taking into account both the economic advantages of the process and the qualities desired for the finished yarn.

Similarly, the length of the coagulating bath can vary within broad limits again depending upon the N-methylpyrrolidone concentration in the coagulating bath. For example, a coagulating bath of 10 centimeters is sufficient to obtain good coagulation with a bath containing less than 50 percent N-methylpyrrolidone. Similarly, there is an advantage in using lengths greater than 40 centimeters where the concentration of the N-methylpyrrolidone in the coagulating bath exceeds 65 percent. Also, it is generally preferable to increase the length of the coagulating bath when a high number of strands are spun by the same spinneret.

Similarly, the temperature of the coagulating bath is not critical to the process of the present invention and the same can be suitably chosen within wide limits. However, to achieve the best results in accordance with the present invention the coagulating bath is preferably at a temperature of between 15° and 40° C. Here again, however, higher or lower temperatures than the range set forth above can be advantageously utilized when desired for particular purposes.

As indicated previously, the coagulated filaments are drawn, in air, at a rate of at least 1.5 ×, for example, between 1.7 and 2 or more, there being no maximum to the amount of drawing except that which the filaments can withstand without breaking. In this regard, as the rate of drawing increases the brilliance of the filaments increases. Accordingly the drawing should be conducted as high as possible, the minimum being at least 1.5 ×. Again, since the drawability of the yarns increases with higher concentrations of N-methylpyrrolidone in the coagulating bath it is advantageous in accordance with the present invention to use as strong a concentration of N-methylpyrrolidone as possible so as to utilize the highest possible drawing rates to produce filaments with the greatest brilliance for a given amount of B linkages in the polymer. In addition, it should be recognized that since the brilliance of the filaments also increases with the increase in the amount of B linkages in the polymer it is also possible to increase the brilliance of the filaments and yarns in this manner and, increased brilliance can be obtained without the necessity of an extremely high rate of drawing.

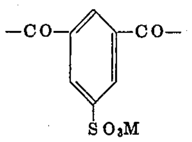
In accordance with the present invention, after the filaments are drawn the filaments are washed in order to remove any N-methylpyrrolidone which may adhere to the filaments. The filaments can be washed with water utilizing any known conventional means. Thus for example the washing can be performed in successive vats in which water circulates countercurrent or by utilizing washing rollers or any other similar means. The washed filaments are then dried by any known conventional means such as for example in a conventional dryer or on rollers. The temperature of this drying is not critical to the process of the present invention and such temperature can vary within broad limits. When the speed of drying is greater, the temperature is usually higher. It is generally advantageous to perform the drying with progressively higher temperatures, temperatures reaching and even exceeding 260° C. being applicable.

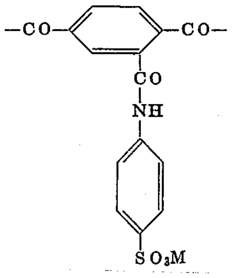
In accordance with the present invention, after drying the drawn filaments can be further drawn in a secondary drawing operation through any known conventional means. For example, this second drawing can take place in an oven by the use of plates, rollers, rollers and plates, etc., and should be conducted at a temperature of at least 300° C., temperatures up to and exceeding 420° C. being applicable. In general, the rate of this second drawing is at least 1.5×, although the rate can vary within broad limits, depending upon the qualities desired in the finished yarn. Again, it should be noted that this secondary drawing is optional in accordance with the present invention and need not be utilized to obtain a brilliant yarn as described previously.

This secondary drawing when utilized can be performed in one or more stages, continuously or intermittently with the preceding operations. Advantageously, this second drawing can be combined with drying and to accomplish this a zone of higher temperature can be utilized at the end of the drying so as to permit the secondary drawing.

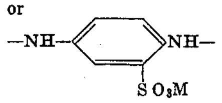
As indicated previously, the process of the present invention allows for the production of very brilliant filaments, fibers and yarns not previously obtainable by the wet spinning of polyamide-imides. In this regard, such process is dependent upon the introduction into a polyamide-imide of linkages derived from an alkali or alkaline earth salt of dicarboxy-3,5 benzene sulfonic acid in an amount of at least 3 mole percent, based upon the polyamide-imide; extruding the polymer into a coagulating bath containing 30 to 75 percent by weight of N-methylpyrrolidone; drawing the filaments in air at a rate of at least 1.5 ×; washing the drawn filaments to eliminate the N-methylpyrrolidone; drying the washed filaments by any known conventional means; and, optionally, again drawing the filaments at a rate of at least 1.5 ×. It has been discovered in accordance with the present invention that the brilliant filaments and yarns obtained through the foregoing procedure cannot be obtained utilizing a polyamide-imide without the aforementioned linkages and cannot be obtained by utilizing different coagulating baths or rates of drawings. All of these variations in the process of the present invention produce very porous and dull filaments having characteristics far inferior to the very brilliant filaments produced in accordance with the present invention.

Moreover, it has been surprisingly discovered in accordance with the present invention that if other aromatic sulfonic acid salts are introduced into the polyamide-imide chain the advantageous characteristics of the present invention and the brilliant filaments obtained thereby cannot be achieved. For example, the introduction of such linkages as:





or



previously known for introduction into aromatic polyamide chains for improved dye affinity, etc., do not lead to the advantages and effects of the present invention. Here again, the introduction of such groups or linkages merely produces dull and porous filaments.

In addition to the brilliant characteristics for the filaments produced through the process of the present invention, the filaments which are produced have excellent physical properties and are very resistant to exposure at high temperatures. Moreover, such filaments have excellent affinity for basic dyes.

The present invention will now be illustrated by references to the following examples which are presented for purposes of illustration only and are not in any way to be deemed as limiting the present invention. In such examples, unless otherwise indicated, all percentages are by weight.

In the following examples the viscosity of the solutions is measured by a Drage viscosimeter using speed II and mobile 47.2 unless otherwise indicated. The inherent viscosity is measured at 25° C. utilizing a 0.5 solution by weight of N-methylpyrrolidone.

EXAMPLE 1

A 21.3 percent solution of a sulfonated polyamide-imide is prepared in N-methylpyrrolidone by the reaction of:

diisocyanatodiphenylmethane	25 molar parts
trimellitic anhydride	24.25 molar parts
sodium dicarboxy-3,5 benzene sulfonate	0.75 molar parts

in dehydrated N-methylpyrrolidone

The viscosity at 25° C. of the solution is 2,834 poises and the inherent viscosity of the polymer is 1.25.

The solution is extruded at a speed of 10 m/min through a spinneret having 600 orifices of 0.06 mm in diameter, into a coagulating bath containing 60 percent N-methylpyrrolidone and 40 percent water. After a travel of 20 cm in the coagulating bath, the yarn exits in a gel state, and is drawn in air at ambient temperature at a rate of 1.5×. Then the drawn yarn is washed with water to remove the solvent and dried on two drying rollers at 40° and 150° C., respectively.

The yarn which is obtained through the foregoing procedure is very brilliant. The yarn has a count of 2,400 dtex, a dry tenacity of 16 g/tex and a dry elongation of 24 percent.

By way of comparison, a 21 percent polyamide-imide solution obtained by the reaction of 25 molar parts of diisocyanatodiphenyl-methane and 25 molar parts of trimellic anhydride in N-methylpyrrolidone is spun in the same manner.

The yarn which is obtained is dull, cracked and has a harsh touch.

EXAMPLE 2

A 17.3 percent solution of a sulfonated copolyamide-imide is prepared in N-methylpyrrolidone by the reaction of:

diisocyanatodiphenylmethane	100 molar parts
trimellitic anhydride	80 molar parts
terephthalic acid	3 molar parts
sodium dicarboxy-3,5 benzene sulfonate	17 molar parts

in dehydrated N-methylpyrrolidone. The concentration is then adjusted by the addition of further solvent at the end of the reaction.

A solution is obtained with a viscosity at 25° C. of 180 poises and the polymer has an inherent viscosity of 1.65.

The solution is extruded at a speed of 10 m/min through a spinneret having 64 orifices of 0.05 mm in diameter, into a coagulating bath containing 30 percent N-methylpyrrolidone and 70 percent water, the length of travel of the yarn in the coagulating bath being 20 cm. At the exit of the coagulating bath, the yarn, in a gel state, is drawn in air at ambient temperature at a rate of 1.5 ×. Then the drawn yarn is washed in water to remove the solvent and dried on a roller at 60° C.

The yarn which is obtained is very brilliant. The yarn has a count of 260 dtex/64 filaments, a dry tenacity of 9 g/tex and a dry elongation of 13 percent.

The yarn is then subjected to a second drawing at 380° C. at a rate of 6.9 ×. After this second drawing the yarn has a dry tenacity of 33 g/tex and a dry elongation of 14 percent.

EXAMPLE 3

A 20.3 percent solution of a sulfonated copolyamide-imide in N-methylpyrrolidone is prepared by the reaction of:

diisocyanatodiphenylmethane	200 molar parts
trimellitic anhydride	153.5 molar parts
terephthalic acid	38.5 molar parts
Potassium dicarboxy-3,5 benzene sulfonate	8 molar parts

in dehydrated N-methylpyrrolidone.

The viscosity at 25° C. of the solution obtained through the foregoing reaction is 458 poises and the inherent viscosity of the polymer **8** is 1.00.

The solution is extruded at a speed of 10 m/min through a spinneret having 200 orifices of 0.055 mm in diameter into the same coagulating bath as in Example 1. The yarn, in the gel state, is drawn at a rate of 2 ×and thereafter washed in water and finally dried on two rollers at 40° and 150° C., respectively.

The yarn which is obtained is very brilliant. The yarn has a count of 800 dtex/200 filaments, a dry tenacity of 17 g/tex and a dry elongation of 20 percent.

After a second drawing at 400 C. at a rate of 3.1 ×, the yarn has a count of 278 dtex/200 filaments, a dry tenacity of 33 g/tex and a dry elongation of 9 percent.

EXAMPLE 4

A 20.2 percent solution of a sulfonated copolyamide-imide is prepared by the reaction of:

diisocyanatodiphenylmethane	200 molar parts
trimellitic anhydride	153.5 molar parts
terephthalic acid	38.5 molar parts
lithium dicarboxy-3,5 benzene sulfonate	8 molar parts

in dehydrated N-methylpyrrolidone with adjustment of the concentration after the reaction.

The viscosity at 25° C. of the solution is 542 poises and the inherent viscosity of the polymer is 1.08.

The solution is extruded in the same way as in Example 3 and the yarn is then overdrawn under the same conditions.

The yarn which is obtained is very brilliant and has a count of 282 dtex/200 filaments, a dry tenacity of 36 g/tex and a dry elongation of 9 percent.

EXAMPLE 5

A 19.4 percent solution of a sulfonated polyamide-imide is prepared by the reaction of:

diisocyanatodiphenylmethane	75 molar parts
trimellitic anhydride	57.6 molar parts
terephthalic acid	14.4 molar parts
sodium dicarboxy-3,5 benzene sulfonate	3 molar parts

in dehydrated N-methylpyrrolidone, with adjustment of the concentration after the reaction.

The viscosity at 25° C. of the solution which is obtained is 413 poises and the inherent viscosity of the polymer is 1.20.

The solution is extruded at a speed of 10 m/min through a spinneret having 15,000 orifices of 0.08 mm in diameter into a coagulating bath containing 65 percent N-methylpyrrolidone and 35 percent water, the travel of the cable in the bath being 80 cm. At the exit of the bath, the cable, in the gel state, is drawn in air at ambient temperature at a rate of 1.75 ×. The cable is then washed in water countercurrent is successive washing vats and is placed without tension on a perforated endless belt of a ventilated dryer the temperature of which varies from 70° to 105° C. from one end of the dryer to the other.

The cable obtained through the above procedure is very brilliant. It has a count of 45,000 dtex/15,000 filaments, a dry tenacity of 12 g/tex and a dry elongation of 12 percent. The cable is thereafter overdrawn in an oven at 400° C. at a rate of 2 ×. The cable then has a count of 33,600 dtex, a dry tenacity of 29 g/tex, and a dry elongation of 13 percent.

EXAMPLE 6

A 12.9 solution of a sulfonated copolyamide-imide is prepared by the reaction of:

diisocyanatodiphenylether	35 molar parts
trimellitic anhydride	25.55 molar parts
terephthalic acid	7 molar parts
sodium dicarboxy-3,5 benzene sulfonate	2.45 molar parts

in dehydrated N-methylpyrrolidone.

The viscosity at 25° C. of the solution obtained by the above reaction is 720 poises and the inherent viscosity of the polymer is 1.81.

The solution is extruded at a speed of 10 m/min through a spinneret having 200 orifices of 0.055 mm in diameter into a coagulating bath containing 50 percent N-methylpyrrolidone and 50 percent water, the travel of the yarn in the bath being 20 cm. The yarn, in the gel state, is drawn at a rate of 1.8 × in air at ambient temperature, then washed and dried on two rollers, the respective temperatures of which are 40° and 150° cC.

The yarn obtained by the foregoing procedure is very brilliant. The yarn has a count of 800 dtex/200 filaments, a dry tenacity of 19 g/tex and a dry elongation of 12 percent.

After overdrawing at 400° C. at a rate of 2.6 ×, the yarn has a dry tenacity of 40 g/tex and a dry elongation of 5 percent.

EXAMPLE 7

A solution of sulfonated copolyamide-imide is prepared by the reaction in dehydrated N-methylpyrrolidone of:

diisocyanatodiphenylmethane	200 molar parts
trimellitic anhydride	157 molar parts
terephthalic acid	38 molar parts
sodium dicarboxy-3,5 benzene sulfonate	10 molar parts

The solution which is obtained has a 19.6 percent concentration and a viscosity at 25° C. of 1,500 poises. The solution is diluted to bring its concentration to 17 percent and its viscosity falls to 300 poises. The inherent viscosity of the polymer is 1.43.

The solution is extruded at a speed of 10 m/min through a spinneret having 64 orifices of 0.05 mm in diameter into a coagulating bath containing 60 percent N-methylpyrrolidone and 40 percent water, the travel of the yarn in the bath being 20 cm. Then the yarn, in the gel state, is drawn at a rate of 2 × in air, washed in water and dried on a roller at 50° C. The drawn yarn which is obtained is brilliant and silky, very soft to the touch. The yarn has a count of 280 dtex/64 filaments, a dry tenacity of 17 g/tex and a dry elongation of 30 percent. The yarn is then overdrawn at a rate of 2.3 × at 340° C. Its count is then 120 dtex, its dry tenacity 39 g/tex and its dry elongation 12 percent.

EXAMPLE 8

A 19.5 percent solution of a sulfonated copolyamide-imide is prepared by the reaction of:

diisocyanatodiphenylmethane	75 molar parts
trimellitic anhydride	57.6 molar parts
terephthalic acid	14.4 molar parts
sodium dicarboxy-3,5 benzene sulfonate	3 molar parts

in dehydrated N-methylpyrrolidone, with adjustment of the concentration after the reaction.

The viscosity at 25° C. of the solution which is obtained is 400 poises and the inherent viscosity of the polymer is 1.21.

The solution is extruded at a speed of 35 m/min through a spinneret having 64 orifices of 0.06 mm in diameter into a coagulating bath containing 52 percent N-methylpyrrolidone and 48 percent water, kept at 20° C., the travel of the yarn in the bath being 40 cm. At the exit of this bath, the yarn, in the gel state, is drawn in air at a rate of 1.94 × before its passage in several loops over a washing roller, the peripheral speed of which is 68.4 m/min. The yarn is washed countercurrent on the washing roller by demineralized water with a delivery of 170 cm^{3}min, and then passes in several loops over a drying roller. This drying roller has several different temperature levels: 40° C. at the input of the yarn and 420° C. at its output. The hot, dry yarn coming from this drying roller then undergoes a drawing of 2.17 × before being wound at a speed of 149 m/min.

The yarn which is obtained is very brilliant. The yarn has a count of 191 dtex, a dry tenacity of 30.9 g/tex and a dry elongation of 8 percent

EXAMPLE 9

A 19.5 percent solution of a sulfonated copolyamide-imide is prepared by operating in the same manner as in Example 8.

The viscosity at 25° C. of the solution which is obtained is 440 poises and the inherent viscosity of the polymer is 1.28.

The solution is extruded at a speed of 45 m/min through a spinneret having 64 orifices of 0.05 mm in diameter, into a coagulating bath containing 48 percent water and 52 percent N-methylpyrrolidone at a temperature of 20° C. At the exit of the coagulating bath, the yarn is drawn in air at a rate of 1.8 × before being sent in several loops over an ensemble of two washing rollers turning at a speed of 81 m/min. The yarn is then dried on the same drying roller as in Example 8, but the temperature of which is kept at 250° C. at the exit. The yarn then passes over a plate at 300° C. and finally is wound at a speed of 142 m/min, giving it a drawing of 1.75 ×.

The yarn which is obtained is very brilliant and has a count of 212 dtex, a dry tenacity of 28.1 g/tex, and a dry elongation of 9.4 percent.

EXAMPLE 10

A 19.8 percent solution of a sulfonated copolyamide-imide is prepared by operating in the same manner as in Example 8.

The viscosity at 25° C. of the solution which is obtained is 300 poises and the inherent viscosity of the polymer is 1.10.

The solution is extruded at a speed of 45 m/min through a spinneret having 64 orifices of 0.06 mm in diameter into a coagulating bath containing 48 percent water and 52 percent N-methylpyrrolidone at a temperature of 20° C. At the exit of this bath, the cable, in the gel state, is drawn in air at ambient temperature at a rate of 1.8 ×, before being washed on washing rollers on which it passes in a number of loops. The yarn then passes over a drying roller similar to that of Example 8, but the exit temperature of which is 360° C. and then passes over a delivery roller at a speed of 145 mm/min, giving it a drawing of 1.8 × between the drying roller and this delivery roller. The yarn then passes over a plate kept at 400°C. where it is drawn 1.4 × before being wound at a speed of 210 m/min.

The yarn which is obtained is very brilliant and presents a count of 155 dtex, a dry tenacity of 31.8 g/tex, and a dry elongation of 10.7 percent.

EXAMPLE 11

A 19.8 percent solution of a polyamide-imide is prepared by the reaction of:

diisocyanatodiphenylmethane	450 molar parts
trimellitic anhydride	360 molar parts
terephthalic acid	72 molar parts
sodium dicarboxy-3,5 benzene sulfonate	18 molar parts

in dehydrated N-methylpyrrolidone, with adjustment of the concentration after the reaction.

The viscosity at 25° C. of the solution is 325 poises and the inherent viscosity of the polymer is 1.07.

The solution is extruded at a speed of 8 m/min through four spinnerets of 10,000 orifices with a diameter of 0.055 into a coagulating bath containing 62 percent of N-methylpyrrolidone and 38 percent water, at a temperature of 27° C., the travel of the cable in the coagulating bath being 2 m. At the exit of the bath, the cable, in a gel state, is drawn at a rate of 1.8 ×. Then the cable is washed with water countercurrently in successive washing vats and is placed without tension on a perforated endless belt of a ventilated dryer, the dry temperature of which varies from 100° to 140° C. from one end of the dryer to the other and the moist temperature of which is 85° C.

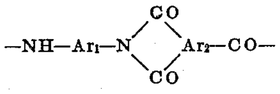
The cable which is obtained is very brilliant and has a count of 176,000 dtex/40,000 filaments, a tenacity per unit filament of 15 g/tex and an elongation of 50 percent. The cable is overdrawn in an oven at 400° C. at a rate of 2 ×. The tenacity per unit strand after overdrawing becomes 40 g/tex and its elongation: 20 percent.

While the present invention has been described primarily with regard to the foregoing specific exemplification, it should be understood that the present invention is not in any way to be deemed as limited thereto, but, rather, must be construed as broadly as any or all equivalents thereof.

What is claimed is:

1. Brilliant thermostable sulfonated polyamide-imide fibers characterized by a structural configuration consisting essentially of:

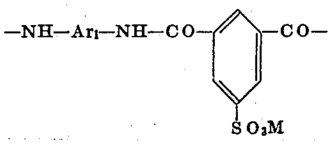
A amide-imide linkages of the formula:



$$-NH-Ar_1-N\begin{matrix}CO\\ \\ CO\end{matrix}Ar_2-CO-$$

and containing

B at least 3 mole percent of amide linkages of the formula:



and

C 0 – 20 mole percent of amide linkages of the formula:

$$-NH-Ar_1-NH-CO-R-CO-$$

wherein each Ar_1 is a radical selected from a bivalent aromatic nucleus, aliphatic or cycloaliphatic radical, at least 80 percent of the total Ar_1 radicals in the sulfonated polyamide-imide being a bivalent aromatic nucleus;

Ar_2 represents a trivalent aromatic nucleus;

R represents a bivalent aromatic nucleus, aliphatic cycloaliphatic, or arylaliphatic radical; and

M represents an alkali or alkaline earth metal.

2. The fibers of claim 1 wherein linkages B comprise 3 – 10 mole percent based on the total sulfonated polyamide-imide.

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