

United States Patent [19]

Buisson

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[54] **TEXTILE ARTICLES FOR PROTECTIVE CLOTHING**

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[58] Field of Search ... 260/32.6 NT, 78 TF, 30.4 N, 260/37 N; 264/184; 131/10, 267; 161/180

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[57] **ABSTRACT**

The present invention relates to noninflammable yarns and fibers having a base of polyamide-imide, with a high power of adsorption.

More particularly, it relates to yarns and fibers containing 8 to 35% activated carbon (referred to the quantity of dry materials), an iodine number of 100 to 500, and a specific surface of 90–300 m²/g.

The yarns in accordance with the invention are used, for example, in fabrics for protection against harmful gases, in the manufacture of cigarette filters, etc.

2 Claims, No Drawings

TEXTILE ARTICLES FOR PROTECTIVE CLOTHING

The present invention relates to novel noninflammable fibers and yarns having a base of polyamide-imide which comprise substantial quantities of activated carbon, as well as articles obtained from said yarns.

Noninflammable fibers and yarns are to be understood as yarns which have successfully passed the test published in the "American Association of Textile Chemists and Colourists" No. 34, 1966.

The present invention also concerns the process of obtaining said yarns.

It is already known from French Pat. No. 1,188,128 and its Patent of Addition 88,023 to prepare compositions of finely divided carbon black and acrylonitrile polymer whose apparent density is less than 0.400 and to spin compositions containing a high proportion of carbon black in order to obtain black fibers; however, these fibers have only a small specific surface.

It is also known from French Application No. 2,003,528 to prepare fibers or filaments having a base of copolymers of acrylonitrile and vinylidene chloride or sodium alginate containing 10 to 30% graphite, which fibers are intended for carbonization or graphitization in order to be made fireproof.

It is well known to use carbon black for the complete pigmentation of different types of polymers, but the quantity of pigment incorporated is preferably of the order of 1% and not in excess of 3% of the total quantity of the material if it is desired to be able to spin under good conditions and to obtain yarns having sufficiently good qualities to be used as such and not carbonized or graphitized.

In French Pat. No. 1,540,997 the obtaining of porous acrylic fibers has also been proposed but the specific surfaces of said fibers do not exceed 55 to 60 m²/g.

Furthermore, up to now, attempts at incorporating activated carbon in other textile substances, such as polypropylene and polyamides, have not led to the obtaining of textile articles which are both uniform and retain sufficient activity.

There have now been discovered — and this constitutes the object of the present invention — noninflammable textile yarns, fibers and articles with a base of polyamide-imide having incorporated 8 to 35% activated carbon, calculated with respect to the quantity of dry materials having an iodine number of 100 to 500 and having a specific surface of 90 to 300 m²/g.

The invention also relates to a process of obtaining noninflammable fibers having a base of polyamide-imide which comprises in succession:

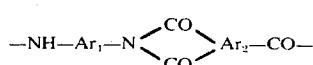
— preparing a solution of polyamide-imide in a polar organic solvent containing 8 to 35% activated carbon, referred to the weight of carbon plus polymer,

— wet-spinning said solution in a coagulating bath composed essentially of water and of solvent for the polymer,

— drawing, washing and drying the filaments in known manner,

— drying and heating in known manner.

By polyamide-imide there are understood polymers having amide-imide linkages of the formula:



and possibly amide linkages of the formula $-\text{NH}-\text{Ar}_1-\text{NH}-\text{CO}-\text{R}-\text{CO}-$ in which Ar_1 represents an aromatic divalent radical, Ar_2 represents a trivalent aromatic radical and R represents an aromatic divalent radical.

The polyamides-imides of the above formula are obtained by reacting, in a polar organic solvent, in substantially stoichiometric proportions, at least one aromatic diisocyanate and one acid reagent comprising at least one aromatic, aliphatic or cycloaliphatic acid anhydride and possibly a diacid.

Among the diisocyanates which can be used for the obtaining of these polymers mentioned may be made of monocyclic diisocyanates, such as toluylene-diisocyanates, and dicyclic diisocyanates, of preferably symmetrical nature, such as 4,4'-diisocyanato-diphenyl-methane, 4,4'-diisocyanato-diphenyl-propane and 4,4'-diisocyanato-diphenyl-ether.

As the acid anhydride, trimellitic anhydride is preferably employed. Among the diacids there are preferably employed terephthalic acid or isophthalic acid, the proportions of the diacid in the acid reagent being generally between 5 and 95 mol %, and preferably 20-80% referred to the mixture of anhydride and diacid. The polyamide-imides utilized herein are, of course, a well known class of polymers.

The activated carbon which can be used in accordance with the present invention is a form of carbon of high specific surface, and of very small particle size, of the order of a few microns, which possesses active centers and which contains other substances such as oxygen.

For the carrying out of the present invention it is generally advantageous to use an activated carbon of good iodine number and of a specific surface which is generally greater than 1000 m²/g in order to obtain the maximum effect.

In accordance with the present invention, it has surprisingly and unexpectedly been found that by the process of the present invention it is possible to incorporate up to 35% activated carbon, referred to the total weight of activated carbon plus polymer, without disturbing the spinning, and furthermore that in the yarns or fibers thus obtained, the active centers of the carbon retain the greatest part of their activity even in the finished textile articles.

The fabrics obtained from the said yarns are very useful as fabrics for protection against harmful gases and furthermore have the advantage of being noninflammable due to the very nature of the polyamides-imides.

Due to their high power of adsorption, the yarns of the present invention can also be used in the manufacture of cigarette or antipollution filters.

The adsorbent power of the yarns containing activated carbon is evaluated by "the iodine number" which represents the number of milligrams of iodine fixed per gram of dry substance.

The specific surface of the yarns is measured by the BET (Brunauer-Emmett-Teller) method which has been described in numerous publications.

For the obtaining of yarns and fibers such as described above, a solution of polyamide-imide in a polar organic solvent containing, in addition to the polymer, 8 to 35% activated carbon, referred to the total weight of polymer plus activated carbon, is extruded through

a spinneret. Above 35% activated carbon, spinning becomes impossible.

The polymer used must have an inherent viscosity of between 0.8 and 1.6 (and preferably between 0.9 and 1.4). The inherent viscosity is measured at 25°C on a 0.5 wt. % solution of polymer per volume of polar organic solvent. As organic solvent, N-methyl-pyrrolidone is preferably employed.

For the preparation of the spinning solution it is generally preferred first of all to prepare a master mix containing the solvent, the polymer and a high proportion of activated carbon.

The master mix is crushed so as to obtain good uniformity of the polymer and carbon mix and avoid agglomeration of the particles of carbon and thus permit easy spinning.

There is then added to this master mix a certain amount of solution of polymer in N-methyl-pyrrolidone. The spinning solution thus obtained is mixed immediately before the spinning and then filtered.

The spinning is effected by the wet process, which is well known to those skilled in the art, in a coagulating bath composed essentially of water and of solvent for the polymer wherein the proportion of solvent may vary between 30 and 65%, ordinarily at room temperature.

The filaments are drawn in customary fashion by any means known to those skilled in the art, for instance in air at room temperature, to the extent of generally between 1.2 × and 2.5 ×. The drawing contributes to imparting good physical and mechanical properties to the filaments without decreasing the number of active sites of the carbon, which retains its adsorbent power. The filaments are then washed with water, generally continuously, at room temperature, for instance by passage through one or more tanks or over rollers to eliminate the solvent, which is then reused.

The drying can be effected in customary fashion, for instance on rollers. It is generally preferable to dry at a temperature not above 150°C in order that the yarns may retain their full activity.

In order to permit practically complete elimination of the solvent, the filaments may undergo a heat treatment at a temperature which may vary from 200° to 220°C in a stove, or preferably a subsequent washing in known manner, for instance with a volatile organic compound such as acetone.

The following examples, in which the percentages are by weight, are given by way of illustration and not of limitation in order to illustrate the invention.

EXAMPLE 1

A solution A of a polyamide-imide is prepared by reaction of 153.6 g of trimellitic anhydride, 250 g of diisocyanato-4,4'-diphenylmethane and 33.2 g of terephthalic acid in 1310 g of N-methyl-pyrrolidone. The polymer obtained has an inherent viscosity of 1.11 and the solution has a concentration of 21% by weight of polymer.

Furthermore, there is prepared a mixture B containing 70 g of the polymer obtained above with 780 g of N-methyl-pyrrolidone and 150 g of activated carbon of particle size 3 micron, specific surface 1270 m²/g and iodine number of 1100, which has been previously crushed. The B mixture thus obtained is crushed and

there is then added to it an equal quantity of the A solution as prepared above.

After filtration through a filter, the packing of which is composed successively of longotte, cotton and flannelette in order to avoid clogging at the spinneret which has 32 orifices of a diameter of 0.20 mm, the spinning solution thus obtained is spun into a coagulating bath containing 40% water and 60% N-methyl-pyrrolidone, maintained at a temperature of 22°C.

10 The filaments drawn in air by 1.51 × are washed on rollers at a speed of 11.7 m/min. before being dried in a known manner and treated in a stove for 2½ hours at 240°C under a pressure of 5 mm Hg.

15 The noninflammable filaments which have been treated in this manner and which contain 35% activated carbon have the following properties.

20	Number	464 dtex/32 filaments
	Tensile strength	246 g
	Elongation upon rupture	11.8%
	Activated carbon in percent referred to the weight of dry substance	35%
25	Iodine number	435 (430 to 440)
	Specific surface	205 m ² /g

By way of comparison, a polypropylene containing 10% carbon black was spun by melt-spinning. The spinning is very difficult due to the clogging of the spinneret orifices. The yarn obtained has a specific surface of less than 10 m²/g.

Also by way of comparison, Example 1 of French Pat. No. 88,023/1,188,128 was reproduced. The yarn obtained contains 29% carbon black and has a specific surface of 34 m²/g.

EXAMPLE 2

An A solution of polyamide-imide in N-methyl-pyrrolidone of a polymer concentration of 21% by weight is prepared in the same manner as in Example 1.

A mixture is prepared containing 136 g of the polymer obtained above with 796 g of N-methyl-pyrrolidone and 68 g of activated carbon, of a specific surface of 1270 m²/g and an iodine number of 1100, which was previously crushed. This C mixture obtained in this manner was treated, after crushing, with an equivalent quantity of A solution to obtain a spinning solution containing 79.3% N-methyl-pyrrolidone, 17.3% polymer and 3.4% activated carbon.

55 The solution is spun into a coagulating bath composed of 40% water and 60% N-methyl-pyrrolidone at about 22°C at a speed of 8 m/min. through a spinneret having 90 apertures of 0.12 mm diameter, provided with a filter the packing of which is composed successively of longotte, cotton and flannelette. The filaments drawn in air at a rate of 2 × are washed on rollers at a speed of 16 m/min. and then dried in customary fashion at about 90°C and heat-treated under the same conditions as in Example 1.

60 The characteristics of the noninflammable yarn are as follows:

65	Number	680 dtex/90 filaments
	Dry strength g/tex	9.2
	Elongation	11%
	Activated carbon %	

-Continued	16.4
(referred to the weight of dry substance)	
Iodine number	190
Specific surface	112 m ² /g

EXAMPLE 3

There is prepared an A solution of a polyamide-imide identical to that of Example 1 and of the same concentration in N-methyl-pyrrolidone.

There are separately prepared D solutions containing 70 g of the polymer obtained above and respectively 780 g, 877.6 g, and 905.6 g of N-methyl-pyrrolidone, and activated carbon of a specific surface of 1495 m²/g and an iodine number of 1660 which has been previously crushed is added in respective quantities of 150 g, 53.4 g, and 24.4 g.

Each of these D solutions is mixed with the A solution in equal proportions.

After filtration, the spinning solutions thus obtained are extruded into a coagulating bath composed of 40% water and 60% N-methyl-pyrrolidone, maintained at room temperature, through a spinneret having 32 orifices of 0.2 mm diameter.

The filaments drawn in air to the extent of 2 X are washed with water at room temperature, then dried at a temperature of about 90°C and washed for 30 minutes with acetone.

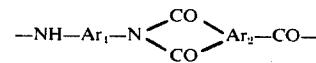
There are obtained noninflammable filaments the properties of which are set forth in the following table:

Number	364 dtex/32 filaments		
% activated carbon	35	16	8
Iodine number	500	130	110
Specific surface m ² /g	288	152	96

What is claimed is:

1. Noninflammable yarns and fibers having a base of polyamide-imide comprising 8 to 35% activated carbon, referred to the quantity of dry substance, having an iodine number of 100 to 500 and a specific surface of 90-300 m²/g.

2. Noninflammable yarns and fibers according to claim 1, wherein said polyamide-imide has amide-imide linkages of the formula



wherein Ar₁ is an aromatic divalent radical and Ar₂ is a trivalent aromatic radical.

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