Jan. 19, 1971 KAZUMASA YONESHIGE ET AL 3,556,712

METHOD OF MAKING FLAME-PROOF FIBERS

Filed May 23, 1968 2 Sheets-Sheet 1

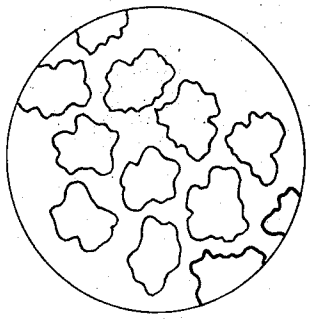


Fig. 1

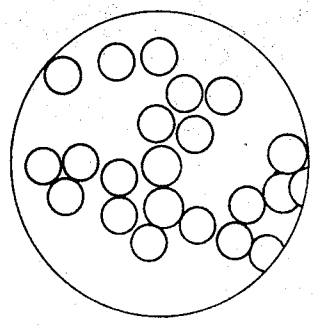


Fig. 2

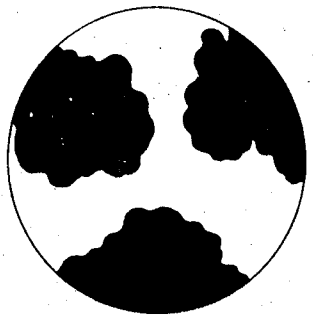


Fig. 3

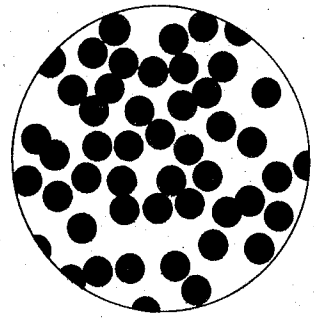


Fig. 4

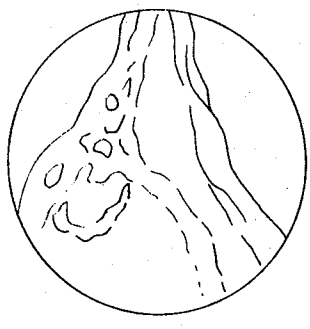


Fig. 5

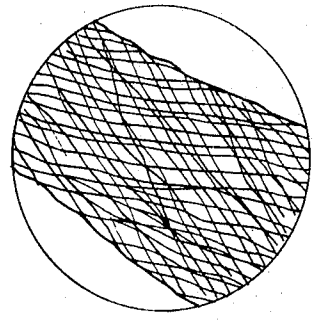


Fig 6

Kazumasa Yoneshige
Haruo Teranishi
INVENTORS

BY Wenderoth, Lind & Ponack, Attorneys

Jan. 19, 1971 KAZUMASA YONESHIGE ET AL 3,556,712

METHOD OF MAKING FLAME-PROOF FIBERS

Filed May 23, 1968 2 Sheets-Sheet 2

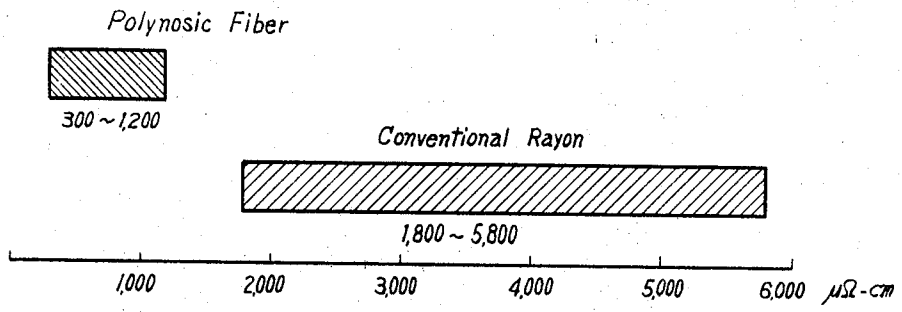


Fig. 8 Electric Resistance of Two Graphite Fibers

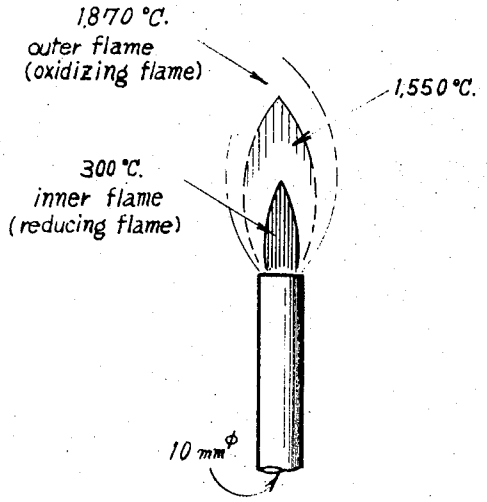


Fig. 9. Bunsen burner

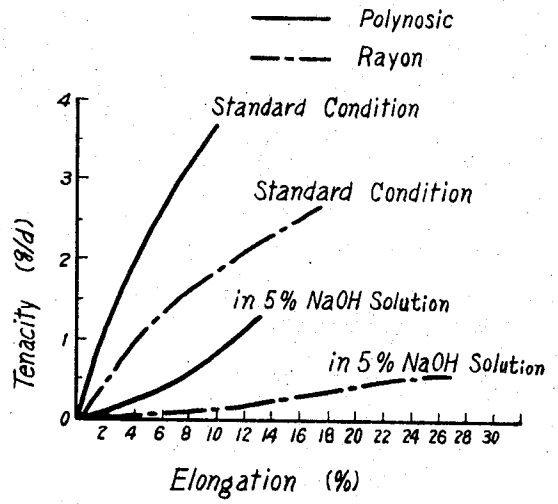


Fig. 7

Kazumasa Yoneshige
Haruo Teranishi
INVENTORS

BY Wenderoth, Lind & Ponack, Attorneys

United States Patent Office 3,556,712
Patented Jan. 19, 1971

3,556,712

METHOD OF MAKING FLAME-PROOF FIBERS

Kazumasa Yoneshige and Haruo Teranishi, Tokyo, Japan, assignors to Nippon Carbon Company, Limited, Tokyo, Japan

Filed May 23, 1968, Ser. No. 731,546
Claims priority, application Japan, June 3, 1967, 42/35,162
Int. Cl. C01b 31/07
U.S. Cl. 8—116 1 Claim

ABSTRACT OF THE DISCLOSURE

In a process for the manufacture of a high tenacity high flame-proof carbonized fiber from a cellulosic viscose rayon, a modified viscose rayon fiber having a high degree of polymerization is used as a starting cellulosic material.

This invention relates to carbon fiber, and more particularly, to a high tenacity and high flame-proof carbon fiber and to a method of making the same.

It is known that carbon fiber is produced from a regenerated cellulosic filament. This invention is directed to the method for the manufacture of a fibrous carbon product having a high tenacity as well as a flame-proofness heretofore unattainable from the regenerated cellulosic rayon as a starting fibrous stock.

Many sources of fiber have been sought for as a raw material for the production of carbon fiber. A carbon fiber is manufactured by subjecting either natural or artificial cellulosic fiber to heat treatment in an inert atmosphere; another carbon fiber is produced by the steps of spinning a molten pitch-like material, such as, waste resulting from petrochemical processing industry, and heat treating the thus obtained filament to carbonize it.

With reference to the method of making carbon fiber from a raw material selected from the group of natural cellulosic, regenerated cellulosic, acrylic, and polyvinyl alcoholic fibers, many and miscellaneous methods have been proposed: a raw fibrous stock is subjected to heat treatment under the specified conditions in connection with temperature and atmosphere to produce a known carbon fiber; the raw material is subjected to irradiation of a radioactive ray while heat treating; or it is modified by carbon black incorporated thereinto in order to improve its structure or texture.

However, it has been found that the physical properties of the carbon fiber heat treated in the manner referred above are not always satisfactory, and the tensile strength thereof barely amounts to the order of 1000–6000 kg./cm.^{2}.

In reference to the carbon fiber produced by the above process comprising the steps of providing a molten pitch-like material, such as, polyvinyl chloride resin, polyvinyl alcohol resin, and other coal or petroleum pitch, heating it to melt and remove volatile constituents therefrom so as to provide the material having a softening point and viscosity adapted for spinning, spinning it to produce a filament, and finally carbonizing it, this carbon fiber has a tenacity in the order of 3000–8000 kg./cm.^{2}. It is to be noted that the process of making carbon fiber from the pitch-like material is of a poor yield.

We have discovered that a high tenacity carbon fiber can be obtained by maintaining the theoretical structure

or texture of a raw fibrous material to be as near as possible adapted for a final fibrous carbon product, and subjecting this raw material to a known carbonizing heat treatment. In the process of this invention, the known carbonizing heat treatment which comprises subjecting the common fibrous material to heating in a non-oxidizing atmosphere can be applied in an inexpensive manner, and further the tensile strength of the carbon fiber thus produced amounts to 10,000 kg./cm.^{2}.

Research on the structure of texture of the raw fibrous material in general indicates that it consists of a cellulose molecule of low polymerization and another molecule of high polymerization. It has been found that the tenacity of fiber largely depends upon the structure of its molecule. Furthermore, it has been discovered that when a fibrous material wherein the molecules of a low degree of polymerization have been removed and its crystalline structure consists of the molecules of a high degree of polymerization oriented parallel to its filamentary axis is employed as a starting material for making carbon fiber, its tenacity is much greater than that of the carbon fiber made from the conventional fibrous material of a random amorphous structure.

While a large quantity of cellulosic stock as the starting material for making carbon fiber is now employed, no suggestion in connection with the above important requirement for the production of a high tenacity carbon fiber has been made in industry. Japan patent publication No. 13,113 (1961) entitled "Fibrous Graphite" to Ford et al., assignors to Union Carbide Corporation describes the production of graphite fiber from the cellulosic viscose rayon as a starting material, but the above insight into the inherent structure of cellulosic material is neither made nor suggested the importance of cellulosic molecules having a high degree of polymerization depending upon the property of a final fibrous carbon product. According to the teachings of the above Japan Patent Publication, when either natural or regenerated cellulosic stock is subjected to the carbonizing treatment under the known condition of temperature and atmosphere, it has been found that its tenacity is considerably reduced.

In respect of the orientation of molecules of a fibrous material, it is known that a helical arrangement of crystals which constitutes the natural cellulosic stock, e.g., cotton, results in a lower breaking strength, therefore in the formation of an unsatisfactory carbon fiber on account of an action of shear stress when it is given tension.

We, inventors, have conducted an extensive research on how to obtain a high tenacity carbon fiber, and discovered based on many experiments that the cellulosic crystalline structure influenced by the condition of production of a raw fibrous material determines considerably the property of a final product.

Based on the above discovery together with an assumption that a fibrous stock having a high degree of polymerization may result in an enhancement of property of carbon fiber, our investigation on various kinds of cellulosic rayon material has caused us to find out that the cellulosic stock having a high degree of polymerization of more than 450 as a starting material results in the production of a carbon fiber having the more improved properties than those of prior art. Besides, it is seen that the use of cellulose rayon stock having a degree of polymerization less than 450 results in the formation of a carbon fiber having a less property than desired in respect of both tenacity and flame-proofness.

It is known that the common viscose rayon is manufactured by the steps of steeping a pulp material in a solution of caustic soda to obtain alkali cellulose, pressing it to remove excess caustic soda, pulverizing it, xanthating it with carbon bisulfide to obtain cellulose sodium xanthogenate, dissolving it in a dilute solution of caustic soda to produce liquid viscose, and spinning it into a coagulating bath to produce regenerated cellulose in the form of filament. However, the common viscose rayon fiber thus produced is not always satisfactory in respect of tenacity, dimension, stability, and elastic property, hence miscellaneous processes have been proposed in order to improve the properties of rayon fiber: the first of these improved processes consists in the production of a high tenacity rayon adapted for tire cord wherein in the formation of cellulose viscose solution ageing of alkali cellulose and ripening of viscose are effected in a short period of time in order to maintain the length of cellulose molecule to be long and its degree of polymerization to be in a high level.

The term "ageing" referred above lies in the lowering of degree of polymerization of oxidizing alkali cellulose in air so as to keep its viscosity as suitable as possible, and the term "ripening" consists in keeping liquid viscose at a specified temperature for a specified period of time so as to cause chemical reaction to proceed satisfactorily. Further, with a view to arranging the cellulosic molecules to an orientation, regenerated cellulose is spun under tension or stretching. The rayon fiber made by the above spinning process compares favorably with the conventional one, and has higher tenacity and higher resistance to bending and fatigue than the rayon of prior art.

The second consists in spinning the viscose having a high degree of polymerization in a low concentration acid bath to produce a high modulus dimensionally stable modified viscose rayon staple or filament, which is in general called "polynosic" fiber, the U.S.A. registered trademark.

Briefly stated, the polynosic fiber is manufactured by the steps of maintaining the length of cellulose chain as such in making viscose therefrom, pulverizing cellulose at a relatively low temperature for a short period of time in order to prevent the lowering of degree of polymerization, omitting the known ageing step, effecting the dissolving of cellulose sodium zanthrogenate alkaline solution for a short period of time to produce a liquid viscose of high viscosity having a high degree of polymerization, and spinning the viscose in a low concentration nitric acid bath containing almost no salt while drawing slowly under tension in accordance with the degree of regeneration of cellulose. By this process it is found that the length of its cellulose molecule amounts to twice as long as that of the common rayon of prior art, and its cross section is circular as shown in FIG. 2 of the accompanying drawings. The polynosic fiber is dimensionally stable, has high tenacity, its swelling to water and alkali is small, but remains its high tenacity at the time of swelling, having more than 450 of degree of polymerization.

The third of the above improved processes consists in the method of producing a high tenacity saponified acetate rayon fiber called, "Fortisan" to Celanese Corporation of America wherein the acetate rayon fiber dry spun is drawn in steam about four times as long as its original length with the aid of its plasticity, and alkali saponified with no effect on its molecule orientation to produce a regenerated cellulose rayon fiber of high tenacity.

Our extensive experimental research on the raw fibrous material adapted for the manufacture of a high tenacity carbon fiber among the above-mentioned fibers, viz., common viscose rayon, high tenacity rayon yarn for use in tire cord, highly polymerized viscose rayon, and saponified acetate rayon has indicated us that a carbon fiber obtained from the highly polymerized rayon exhibits the most excellent property of all the fibrous materials.

Accordingly, it is an essential object of the invention

to provide a novel high tenacity high flame-proof carbon fiber.

It is another object of the invention to provide a novel high tenacity high flame-proof carbon fiber derived from the viscose rayon having a high degree of polymerization as a starting material.

It is still another object of the invention to provide a method of making a novel carbon fiber having high tenacity and high flame-proofness, and a low electric specific resistance by the steps of providing a viscose rayon having a high degree of polymerization as a starting material, and subjecting it to a carbonizing heat treatment.

These and other objects and advantages of this invention will be more completely disclosed and described in the following specification, the accompanying drawings, and the appended claims.

In the drawings:

FIG. 1 is a microscopic sectional view of a conventional viscose rayon filament magnifiying ×500.

FIG. 2 is a miscroscopic sectional view of a polynosic rayon filament magnifying ×500.

FIG. 3 is a microscopic section of a carbon fiber magnifying ×2500 produced from the rayon of FIG. 1.

FIG. 4 is a microscopic section of a carbon fiber magnifying ×500 produced from the polynosic rayon of FIG 2.

FIG. 5 is a microscopic view showing the common rayon treated in a 5% NaOH aqueous solution, and then smashed so that the cellulosic structure is broken.

FIG. 6 is a microscopic view showing the polynosic rayon treated in the 5% NaOH aqueous solution and then smashed but the cellulosic structure unchanged along the cellulosic axis.

FIG. 7 is a graphic representation showing tenacity and elongation of the common rayon and the polynosic rayon treated in the 5% NaOH aqueous solution, respectively.

FIG. 8 is a graphic representation showing electric (specific) resistances of two carbon fibers produced from common and polynosic rayons, respectively.

FIG. 9 is a sectional view of a flame of a Bunsen burner.

In general, it is known that the higher the orientation of cellulose molecule of rayon the higher its tenacity grows. However, it is found that the degree of polymerization has almost nothing to do with the tenacity of rayon filament. It has been also found that the tenacity of carbon fiber produced from various raw fibrous stock has nothing to do with the high degree of orientation, but depends upon the degree of polymerization, in other words, the higher the degree of polymerization a fibrous material has, the higher the tenacity of carbon fiber obtained therefrom becomes. This relation is shown in Table 1 listed hereinafter.

The high tenacity rayon refers to the one wherein a major proportion of a small crystal, 150 A. (angstrom) is drawn to a high orientation, about 90% while the highly polymerized viscose rayon refers to the one wherein a major proportion of a big crystal, 300 A. is drawn to a high orientation.

As described above, the raw fiber material used by this invention with a view to making a high tenacity carbon fiber is the viscose rayon having the high degree of polymerization, polynosic fiber, which will be described hereinbelow:

Polynosic fiber is a high tenacity rayon invented and developed by Tachikawa in Japan. The processes for making it are disclosed in U.S. Pats. 2,592,355; 2,732,279; 2,946,650; 2,946,782; and 3,154,614. The differences between polynosic and common rayon are as follows:

(1) The degree of polymerization of polynosic is high. While the degree of polymerization of common rayon is 200–300, polynosic is 450 or more. Some of polynosic rayon have the degree of polymerization of 600–700. Experimetally, it has as high as 900.

(2) The structure of polynosic rayon is of fibril, and

its section is circular as shown in FIG. 2 while the section of common rayon is amorphous as shown in FIG. 1.

(3) While the polynosic rayon has a plurality of continuous filamentary structure even after it was treated in the 5% NaOH aqueous solution and crushed as shown in FIG. 6, the common rayon has none of continuous filamentary structure after it was treated in the same manner (see FIG. 5).

(4) The water absorption of polynosic is low.

(5) When woven into cloth polynosic is dimensionally stable. When wet, it has no disadvantage, such as, shrinking and swelling.

(6) Polynosic has higher tenacity than that of common rayon.

Further, in the method of producing polynosic fiber, the difference between polynosic and common rayon are listed as follows:

(1) No ageing of alkali cellulose is necessary.

(2) No ripening of cellulose xanthogenate sodium is necessary.

(3) Spinning is carried out in a low concentration acid bath.

The results of comparison of carbon fibers produced from four kinds of man-made fibers, common viscose rayon, high tenacity rayon, saponified acetate fiber, and polyacrylonitrile fiber, respectively, with the carbon fiber of this invention produced from the polynosic fiber are described hereinbelow.

As clearly shown in Tables 1–5 described hereinafter, the tenacity of common viscose rayon is the lowest while those of polynosic and saponified acetate rayon are high.

As described just above, common viscose rayon has a low tenacity, because it has a low molecular weight and an insufficient crystalline orientation. As a result, a carbon fiber made from the common viscose rayon tends to have a porous structure full of inner defects so that it exhibits a very low tenacity. Further, on account of the porous structure of the carbon fiber, it tends to burn red progressively as soon as it touches a flame in air as if charcoal burns. It is combustible.

On the contrary, however, in the highly polymerized viscose rayon, polynosic fiber, its cellulose molecule has a degree of polymerization higher than at least 450, about twice as high as that of common rayon. In the course of spinning polynosic rayon, the low polymerized constituents contained therein are dissolved away into the coagulating bath, which results in the formation of polynosic fiber consisting of a dense structure of molecules.

It is seen that the filament of dense structure of molecules of polynosic is readily carbonized so that the polynosic rayon can be converted into a carbon fiber in an inexpensive manner by the known method of producing it. The carbon fiber thus made from the polynosic rayon has a dense structure, and both its tenacity and bending strength are not only far more excellent than those of conventional ones, but also it has so high flame-proof that its red burning portion never proceeds to spread itself when it is in contact with a burning flame in air.

It is to be noted in particular that the carbon fiber of this invention exhibits a flame-proofness as shown in Example 2 described hereinafter. With reference to the flame-proofness of carbon fiber, when an organic fiber heat treated to the state of organic matter wherein it is not entirely converted into carbon but shows black in appearance at a relatively low temperature of 200°–350° C. exhibits resistance to heat in touch with a burning flame, in other words, it will not burn, it is called "Flame-proof."

It is known in industry that a fiber heat treated at a temperature in the range of 300°–500° C. is called "partially carbonized" or "flame-proof," another heat treated in the range of 500°–2000° C. "carbonized" or "carbon," and the last heat treated in the range of 2000°–3000° C. "graphite."

When an organic substance is subjected to heat treatment to remove various elements, such as, hydrogen, oxygen, and nitrogen to increase its carbon content, it becomes a carbonaceous structure, and further, it is crystallized and graphitized at a high temperature above 2000° C.

It is also known today that an artificial fiber produced from acrylonitrile polymer becomes flame-proof when it is heat treated at a temperature of 200°–350° C., though the resultant carbonized fiber of acrylonitrile origin is an organic compound containing hydrogen, oxygen, nitrogen and carbon.

However, it has been impossible for the common viscose rayon to become flame-proof by a simple heat treatment. To this end, for example, U.S. Pat. 3,235,323 to Peters assignor to Minnesota Mining & Manufacturing Co., entitled "Heat-resistant Black Fibers and Fabrics Derived From Rayon" discloses that the rayon is immersed in an aqueous solution of a nitrogen compound, such as, ammonium sulfamate, diammonium hydrogen phosphate, dicyandiamide, and boric acid, then heated at a temperature of 260°–290° C. and it is given flame-proofness.

However, it is seen that the highly polymerized viscose rayon, polynosic fiber treated in accordance with this invention can be imparted flame-proof by heat treatment in the inert atmosphere with no treatment by the above nitrogen compound. This feature is attributed to the different starting material.

It is understood that the polynosic fiber of this invention heat treated at a temperature of 500°–2000° C. can be flame-proof, and even the partially carbonized polynosic fiber heat treated at a temperature of 300°–500° C. has a similar resistance to flame. On the contrary, however, carbon fibers produced from common viscose rayon, high tenacity rayon for tire cord, and saponified acetate rayon tend to burn by the flame, and their red burning portions once caught fire tend to proceed even though they are spaced from the flame away.

It is clearly seen from the following examples and tables that we provide the cellulosic carbon fiber from the polynosic material, and this cellulose carbon fiber has higher tenacity and higher flame-proofness than the carbon fibers derived from other cellulosic and acrylic artificial fibers in accordance with this invention.

Next, the test requirement of flame-proofness conducted in this invention is described hereinbelow. A test specimen of carbon fiber is introduced into the central portion of an outer oxidizing flame at a temperature of about 1500°–1600° C. of Bunsen burner (fuel: coal gas), diameter 10 mm. for 2 minutes (see FIG. 9). Then the red hot specimen is withdrawn from the flame into the air, and left quiet within a wind shield. Flame-proofness is classified into three items as follows:

(1) Good flame-proof: If test specimen turns from glowing red to dark red and then to dark gradually, it hardly lowers its tenacity.

(2) Bad flame-proof: If test specimen turns from glowing red to dark red and then to dark, but it loses its tenacity less than one-half.

(3) Not flame-proof: Instead of turning from glowing red to dark red, test specimen becomes a red ball which proceeds to spread itself and turns to ashes.

In reference to the electric specific resistance in connection with FIG. 8, it is found that a graphite fiber obtained from the polynosic by heat treating it at the temperature of 2300° C. has an electric specific resistance, 950 micro-ohm-cm. while a graphite fiber produced from the common rayon by heat treating it at the same temperature as above has 5400 micro-ohm-cm. The above polynosic and common rayon were heat treated side by side in the same heat treating furnace. They were carbonized up to the temperature of 800° C. under the carbonizing condition (from 100° to 400° C. per 5° C. per hour) described in a separate paragraph to follow, and thereafter heat treated in a Tammann furnace at 2300° C. for half an hour. The temperature was measured by an optical pyrometer. Electric specific resistance (almost equal to

electric resistance shown in FIG. 8) was measured by means of Wheatstone bridge per monofilament. U.S. Pat. 3,107,152 to Ford et al. assignors to Union Carbide Corporation discloses specific resistance, 1900–5400 micro-ohm-cm. in table at Column 5 in respect of the graphite fibers treated at 2900° C.

According to the invention, the graphite fiber heat treated at 2,300° C. from the common rayon has 1800–5800 micro-ohm-cm. while the graphite fiber heat treated at the same temperature from the polynosic 300–1200 micro-ohm-cm. as shown in FIG. 8.

In general, the carbonizing heat treatment conducted on the polynosic fiber is described:

Atmosphere: Nitrogen gas

Temperature rise:	Per hour
Room temperature–100° C.	50° C.
100°–400° C.	5° C.
400°–600° C.	25° C.
600°–800° C.	50° C.
800° C.	Hold for half an hour.

TABLE 1

	Regenerated cellulosic rayon				
	Common viscose	High tenacity rayon	High polymerized viscose	Saponified acetate	Acrylic
Fibrous stock:					
Tensile strength:					
Dry, g./d.	2.7	4.5	3.8	7.0	
Wet, g./d.	1.2	3.0	2.8	6.0	
Elongation:					
Dry, percent	24	17	9.3	6.2	
Wet, percent	35	22	10.1	6.2	
Orientation, percent	70	80	70–90	90	
Degree of polymerization	200–300	300–400	450–650	200	
Treated at 200°–350° C.:					
Flame-proof	(1)	(1)	(2)	(1)	(2)
Treated at 350°–2,000° C. (800° C.):					
Tensile strength, t./cm.²	2.6	3.6	10.3	6.5	
Knot strength, g.	0.1	0.05	0.45	0.4	
Size shrinkage, percent	30	32	30	30	
Flame-proof	(1)	(1)	(2)	(1)	
Treated at 2,000° C. or higher:					
Flame-proof	(2)	(2)	(2)	(2)	(2)
Electric specific resistance	1,800–5,800		300–1,200		

[1] No.
[2] Yes.

EXAMPLE 1

Three kinds of viscose rayon, viz common viscose rayon, high tenacity rayon for tire cord, and polynosic fiber, are heat treated in the heating schedule specified in an inert atmosphere at 800° C., respectively. In heat treating, the fibers are carbonized while they are tensioned a little so as to keep them taut.

Properties of each carbonized at 800° C. are listed in Table 2 in which the properties of carbonized fibers produced from saponified acetate rayon and polyacrylonitrile fiber, respectively, are listed for comparison. It shows that the tensile strength of the highly polymerized viscose rayon is the most excellent, the saponified acetate rayon ranks next, and the results of common viscose rayon and high tenacity rayon for tire cord are rather inferior. This tendency is clearly shown in respect of knot strength. A hard and brittle crabon fiber is produced from the high tenacity rayon having an excellent crystalline orientation while a very flexible carbon fiber is produced from the polynosic fiber having a big crystalline growth.

Further, flame-proofness of fiber in touch with a burning flame is given to the carbonized fibers of polynosic fiber and polyacrylonitrile one, but the other ones are combustible.

TABLE 2

Fiber	Cross-section of monofilament, mm.²	Dimension shrinkage, percent	Tensile strength, kg./cm.²	Knot strength, g.	Flame-proof
Polynosic (the invention)	7.8×10^{-5}	30	10,340	0.45	Yes.
High tenacity rayon for tire cord	4.5×10^{-5}	32	3,600	0.05	No.
Common viscose rayon	6.3×10^{-5}	30	2,640	0.10	No.
Saponified acetate	7.8×10^{-5}	30	6,500	0.40	No.
Acrylic	10.8×10^{-5}	2.8	8,800	0.10	Yes.

EXAMPLE 2

Two kinds of needle punch type felt, 6 mm. thick and 200 g./m.² weight, were made from the common viscose rayon and the polynosic, respectively. Two felts were heat treated at 350° C., flame-proof stage, at 800° C., carbonizing stage, and at 2500° C., graphitizing stage for a period of 30 minutes, respectively. Six test samples thus produced were subjected to the flame-proof test specified. These samples were introduced into the flame of Bunsen burner and maintained therein for a period of two minutes, and then withdrawn therefrom. The results are shown in Table 3. Test results of carbonized ones of saponified acetate rayon and polyacrylonitrile fiber are also listed for comparison. As shown in Table 3, only the polynosic is incombustible of all the products of rayon fiber heat treated up to 800° C.

TABLE 3

Fiber	Heat treated at 350° C.	Heat treated at 800° C.	Heat treated at 2,500° C.
Polynosic (the invention)	Insombustible No change after flame put out.	Incombustible. No red burning after flame put out	Incombustible. No change after flame put out.
Common viscose rayon	Combustible. Burn after flame put out.	Hardly combus tible, but burns. Red burning portion spreads gradually after flame put out.	Do.
Saponified acetate rayon	do	do	Do.
Acrylic	Incombustible. No change after flame put out.	Incombustible. No red burning after flame put out	Do.

EXAMPLE 3

A plain weave fabric, warp and weft 10 x 10 per centimeter, of double twisted yarn of count No. 20 is prepared from common viscose rayon, high tenacity rayon, polynosic fiber, and polyacrylonitrile fiber, respectively. The fabric was carbonized in a known method. The results are shown in Table 4.

TABLE 4

	Tenacity of product carbonized at 800° C. (tensile strength per cm. wide of cloth), kg.	Remaining tenacity after carbonization, percent
1. Polynosic cloth (the invention)	0.38	3.5
2. Common viscose rayon cloth	(1)	
3. High tenacity rayon cloth	1.45	9.0
4. Polyacrylonitrile cloth	1.08	6.0

[1] Lost flexibility and broke.

Remaining tenacity after carbonization is the highest for the polynosic cloth, and good for the acrylic cloth, too. The high tenacity viscose rayon cloth lost its flexibility and broke easily.

EXAMPLE 4

A round cord is made by knitting together 20 yarns each of which is spun from the count No. 10 filament prepared from common viscose rayon, polynosic fiber and acrylic fiber, respectively. The strength of each cord after carbonization is shown in Table 5 which indicates that the lowering of strength of polynosic after carbonization is the least while that of common viscose rayon is the most.

TABLE 5

	Heat treated at 350° C.		Heat treated at 800° C.	
	Tensile strength, kg.	Remaining strength, percent	Tensile strength, kg.	Remaining strength, percent
1. Polynosic cord (the invention)	22.6	16.0	12.7	9.1
2. Common viscose rayon cord			3.2	3.2
3. Acrylic cord	18.4	12.6	5.1	4.2

It is to be noted that when the above cord is carbonized at a faster rise of temperature, i.e., at the temperature of 20° C. per hour, the strength thereof after carbonization at 800° C. is lowered to 8.2 kg. In the heat treatment of the above table, the cord is carbonized from 100° to 400° C. at the temperature of 5 C. per hour.

While we have shown the best embodiment of our invention now known to us, the invention is not to be considered as limited to the exact embodiment herein shown and described, but is intended to include modifications, substitutions and equivalents within the scope of the appended claim.

We claim.

1. A method for producing a high tenacity flameproof fiber which consists essentially of heating a polynosic viscose rayon fiber having a degree of polymerization of 450 or more, to a temperature of between 200 and 350° C. in an inert atmosphere for a time sufficient to render said fiber flame proof when in contact with a flame of a Bunsen burned for a period of two minutes, and recovering said flame-proof fiber.

References Cited

UNITED STATES PATENTS

2,592,355	4/1952	Tachikawa	264—188
3,011,981	12/1961	Soltes	23—209.1X
3,179,605	4/1965	Ohsol	23—209.1X
3,294,489	12/1966	Millington et al.	23—209.1X
3,313,596	4/1967	Hogg et al.	23—209.1
3,322,489	5/1967	Moutaud et al.	8—116
3,351,696	11/1967	Drisch	264—195
3,324,216	6/1967	Inoshita et al.	264—188
3,053,775	9/1962	Abbott	252—421

EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

23—209.1