United States Patent Office 3,027,222 Patented Mar. 27, 1962

3,027,222

FIREPROOF ACRYLONITRILE COPOLYMERS

William Kenneth Wilkinson, Waynesboro, Va., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Sept. 3, 1957, Ser. No. 681,477
4 Claims. (Cl. 8—115.5)

This invention relates to fireproof organic fibers. More specifically, it relates to fireproof fibers made from copolymers of acrylonitrile.

It has been reported by Houtz (Textile Research Journal, 20, 797 [1950]) that yarns prepared from acrylonitrile homopolymer undergo a change during heating at 200° C. which results in black color and fireproof properties for the yarn. After 16 hours at this temperature, the yarns reach a condition in which they will not burn when placed in the flame of a Bunsen burner.

These yarns are, as Houtz discloses, brittle by textile standards. Because of this excessive brittleness, the Houtz procedure is necessarily limited to fabrics rather than yarns or individual fibers. Fibers heat-treated in this manner are too brittle to be spun into yarns and yarns cannot be woven or knit into fabrics. Even the heat-treated fabrics themselves are sufficiently brittle to prevent their acceptance in many applications requiring fireproof fabrics, in spite of the excellent fireproof qualities they possess.

It is an object of this invention to provide fireproof fibers that are processable on textile equipment. It is a further object to provide fireproof fibers of good abrasion resistance. It is yet another object to provide an economical process for the preparation of fireproof fibers having good textile properties. Other objects and means for accomplishing them will appear hereinafter.

In accordance with this invention there are prepared from a synthetic organic polymeric composition fireproof fibers which are sufficiently strong and flexible to be spun into textile yarns. The polymeric composition which is formed into fibers preparatory to producing the strong flexible fireproof product contains between about 85% and 99% acrylonitrile in polymer form and at least 1% of another monomer also in polymer form. It is important that the polymeric composition contain no halogens attached to any polymer chain. The strong flexible fireproof fibers of this invention are prepared by heating fibers of such a polymeric composition from a temperature lower than 20° below the stick temperature of the fibers to a temperature above about 260° C., the heating being controlled so that the temperature of the fibers rises at a rate slow enough to prevent the fibers from sticking to each other. Upon reaching a temperature above a temperature of about 260° C., heating may be continued at the same controlled rate or may be discontinued so long as the temperature of the fibers remains above about 260° C. until the fibers become fireproof.

The total time of heat-treatment required to render the fibers of this invention fireproof will usually range from about 1 to about 3 hours, depending upon the initial and maximum temperature employed. The stick temperature of the fibers must be at least 180° C. if the advantages of the invention are to be obtained, and preferably the stick temperature will be between about 230° C. and about 260° C. It is critically important also that the fibers undergoing heat-treatment be in the form of a fibrous mass having a maximum bulk density of less than about 0.2 gram per cubic centimeter. For the most uniform results, the density of the fibrous mass should be substantially uniform throughout or, at the very least, no portion of the fibrous mass should have a density greater than 0.2 gm./cc.

In carrying out the heat-treatment procedure of this

invention, the fibers are placed in a heating chamber in such a manner that the bulk density of the fibrous mass is less than about 0.2 gm./cc. Best results in terms of flexibility and strength of the product are obtained if this density is less than about 0.1 gm./cc. The fibers may be present in the form of card webs, staple batts, needle punched batts, low twist yarns, or loosely woven or loosely knit fabrics, provided that the bulk density of the material to be heated does not exceed 0.2 gm./cc.

The process of this invention is preferably applied to fibers arranged in the form of a loose batt in which fiber orientation is random, the batt being less than 10 inches in depth. Continuous filaments as well as staple fibers may be processed, but the latter are preferred as more suitable for preparing loose uniform batts of a substantially uniform density below 0.2 gm./cc. When the process is applied to continuous filaments, yarns, or fabrics, care must be taken so that adjacent filaments are not so closely associated as to create a zone having a bulk density exceeding 0.2 gm./cc. Yarns must be very loosely spun so that the maximum density of the yarn bundle does not exceed the above density limit. Fiber bundles such as, for example, tow are much easier to convert into strong flexible fireproof fibers according to this invention than are yarns or fabrics. The processing of fibrous masses containing zones with bulk densities exceeding the density maximum set forth above results in fireproof products which are non-uniform with respect to strength and flexibility, the zones with excessive density being too brittle and fragile for textile applications. The ultimate utility of such a fibrous mass will depend, of course, upon the expanse of these zones and the extent to which they dominate the strength characteristics of the fibrous product.

Fibers useful as starting materials in the process of this invention have fiber stick temperatures above 180° C. and have been oriented during their production by drawing to at least 300% of their original as-spun length. These fibers are formed from acrylonitrile polymers and polymer mixtures in which the combined acrylonitrile content is between 85% and 99% by weight. With less than 85% acrylonitrile, a fireproof structure does not necessarily form. With more than 99% of acrylonitrile, the fireproof product obtained is too brittle to be of practical value. Of particular value are those copolymers of acrylonitrile containing between 5 and 15% of other vinyl monomers, mixtures of copolymers of acrylonitrile in which the total amount of other vinyl monomers is between 5 and 15%.

Copolymers and terpolymers of acrylonitrile are preferred polymeric compositions for preparing the fibers which are heat-treated in this invention, but other acrylonitrile polymer compositions may also be used. In general, any polymer of acrylonitrile containing between about 85% and 99% acrylonitrile is useful so long as there are no halogens attached to the polymer chain and the fiber formed from the polymer has a stick temperature of at least 180° C. Exemplary monomers which may be polymerized with acrylonitrile to prepare polymers useful in this process include monoethylenically unsaturated monomers such as acrylic acid, methacrylic acid, and the corresponding amides and alkyl esters of these acids, styrene, sodium styrene sulfonate, vinyl pyridine and substituted vinyl pyridines, vinyl acetate, N-vinyl pyrrolidone, vinyl sulfonic acid, vinyl carbazole, N-phenyl maleimide, itaconic acid and its non-halogenated derivatives, and the like. Other suitable monomers are disclosed in U.S. 2,436,926 and U.S. 2,743,994.

Fibers which may be successfully heat-treated by the process of this invention may also be prepared from mixtures of polymers, which mixtures contain between about 85% and 99% acrylonitrile in polymer form and between 1% and about 15% of another monomer co-

polymerizable with acrylonitrile and also in polymer form. Thus, for example, mixtures of acrylonitrile homopolymer and poly(N-vinyl pyrrolidone) in the ratio of from about 85/15 to 99/1, or a 90/10 mixture of an acrylonitrile copolymer and acrylonitrile homopolymer, said copolymer containing 85% combined acrylonitrile and 15% combined methyl acrylate, may be successfully employed when in the form of fibers having a stick temperature of at least 180° C. Similarly, a mixture of a terpolymer of acrylonitrile with acrylonitrile homopolymer or with a polymer of a non-halogenated monoethylenically unsaturated polymerizable monomer or a mixture of an acrylonitrile terpolymer with an acrylonitrile copolymer or a mixture of acrylonitrile copolymers may be utilized so long as the total combined (in the form of polymer) acrylonitrile present in the polymeric mixture is between about 85% and 99%, the remainder being another monomer (in polymer form) copolymerizable with acrylonitrile. Obviously, it is necessary, utilizing a mixture of acrylonitrile polymers, to employ polymers which are compatible in order that useful fibers may be prepared therefrom. In any case, it is essential that the fibers utilized have a stick temperature of at least 180° C. and are free from polymers containing halogens attached to the polymer chain.

In carrying out this invention, the fibers are placed in a heating chamber at a temperature about 20° C. or more below the fiber stick temperature of the fiber to be treated. The temperature of the fibers is then raised gradually until a temperature of about 260° C. is exceeded, taking care to control the rate of temperature rise so that the fibers do not become overheated and stick to each other. Raising the fiber temperature at a rate of between about 0.3° C. and about 3° C. per minute is satisfactory, and a rate of between about 1° C. and about 2° C. per minute is preferred as providing the most desirable products in the shortest reaction time. Using a rate of from about 1° C. and about 3° C. per minute, temperatures as high as 500° may be reached without destroying the fibers, but temperatures of 300° are sufficient to fireproof any of the fibers in practical times and optimum product properties are obtained with temperatures not exceeding 280° C.

In accordance with a preferred embodiment of this invention, a fiber having a stick temperature between about 240° C. and 260° C. is heated from 220° C. to 275° C. at the uniform rate of about 1° C. per minute and maintained at 275° C. for at least 5 minutes. The product has excellent strength and flexibility properties and is fireproof.

The "stick temperature" of a fiber is measured by heating a copper block to a selected temperature and holding the fiber against the surface of the block for five minutes under a pressure of 18 grams per square centimeter. By successive tests at different block temperatures, the minimum block temperature at which the fiber does not adhere to the block at the end of the five-minute period is determined and is designated as fiber "stick temperature."

The term "fireproof" is defined as the total resistance to destruction of a material by an open flame. A "fireproof" fiber does not burn even while in contact with an open flame although it may glow.

The preferred heating medium is air. Other gas mixtures and various liquid-heating media which have an oxidizing effect may also be used but air gives completely acceptable results and is generally chosen for reasons of practicality. The apparatus used for heating is preferably chosen to give a continuous fresh supply of hot air.

The products of my invention are useful wherever fireproof fibers are desired. For example, they may be used in protective clothing to be worn by fire fighters or for those manipulating hot objects. Such protective clothing may most readily be made from non-woven felts prepared as described in the examples. The bulk of these felts gives them particularly good insulating power as compared to typical woven or knit structures. In particular, gloves, suits, boot liners, and helmet liners may be made and used. Such felt fabrics have many non-apparel uses such as in hot pads for kitchen use and in insulating blankets.

The material is also useful in operations where the ultimate need is not resistance to temperature but where a high temperature step is part of the process. For example, gaskets may be cut from the fireproof felt and impregnated with dispersions of tetrafluoroethylene polymer. The impregnated gaskets may then be heated to sufficient temperature to fuse the polytetrafluoroethylene into a continuous mass so that a fiber-reinforced polytetrafluoroethylene gasket will result. This gasket will have extreme chemical resistance and will be in the desired form because of the resistance of the fireproof fiber to changes in physical condition during the heating necessary to fuse the polymer.

For fireproof uses, the fibers are useful in other forms in addition to the above-mentioned felts. Loose fibers may be used as insulation. The fibers may be converted to spun yarns and thence to woven or knit fabrics using the usual textile procedures. These fabrics, like the felts, will be completely fireproof. The fibers may also be blended with other fibers to produce yarns and fabrics that are not completely fireproof but are considerably more flame resistant than the fibers used in the blending. For example, a yarn prepared from 50% acrylonitrile fiber and 50% of the fireproof fiber from an acrylonitrile fiber shows considerably reduced burning time over yarn from the acrylonitrile fiber alone and also shows none of the melting and dripping that is found for this material.

The fireproof fibers of this invention are particularly useful in the preparation of filters to be used for separation of solid impurities in hot gases. Bags sewn from woven fabric are most applicable for this use but in many instances the fiber may be used in other forms.

The invention will be better understood from the following examples in which parts are by weight unless otherwise specified. All temperatures are in degrees centigrade. The Stoll flex test is ASTM Test No. D1175–55T (1955 ed., Part 7, p. 179).

EXAMPLE I

A copolymer containing 94 parts of combined acrylonitrile and 6 parts of combined methyl acrylate is dissolved in dimethylformamide and converted to staple yarn by a conventional process of dry spinning, solvent extraction, drawing, crimping, and cutting. These fibers have a stick temperature of 249° C.

The staple fibers thus prepared, having a denier of 3.0 and a length of 2½ inches, are spread loosely on a tray in a forced-draft oven to form a loose batt 5.0 centimeters thick covering an area of 225 square centimeters. The layer weighs 15 grams and has a uniform density of 0.013 gram per cubic centimeter (gm./cc.). The temperature of the oven is 220° C. The temperature of the fibers is raised gradually from 220° C. to 275° C. over a period of 60 minutes and maintained at the latter temperature for 5 minutes before removal. The product is still in the form of individual staple fibers which do not stick to each other and uniformly black in color. After application of Avitex R finish (a ½% aqueous solution of a long chain fatty acid amine (C_{12}–C_{16})), the staple is carded on a conventional mechanical carding machine with no more fiber loss by fibrillation than is experienced with unheat-treated fiber of the same composition. When the heat-treated fibers are held in the flame of a Bunsen burner, they glow but do not burn. There is no after-burning or afterglow when the staple is removed from the flame and the filaments still do not stick to each other.

EXAMPLE II

Staple fibers of 3.0 denier per filament and 2.5-inch length are prepared as in Example I but using a terpolymer of 94% acrylonitrile, 5.7% methyl acrylate, and 0.3% sodium styrenesulfonate. The fiber stick temperature is 241° C. A portion of this staple is arranged in a forced-draft oven at 220° C. in such a way that 20 grams of fiber have a volume of 500 cc. and a substantially uniform density of 0.04 gm./cc. The temperature of the fibers is raised uniformly and gradually from 220° C. to 275° C. over a period of 60 minutes (less than 1°/min.) and the latter fibers temperature maintained for 10 minutes before removing the fibers. The product, when removed from the oven, is uniformly jet black in appearance and is composed of individual fibers which do not adhere to each other. These fibers have an average tenacity of 1.02 grams per denier and an average elongation of 13.9% as measured at room temperature and 65% relative humidity. When tested with a Bunsen burner as above, the staple is found to be fireproof.

A portion of the fireproof staple fibers prepared above is carded and then spun into an 880-denier yarn. Samples of this yarn are weighted with 45-gram weights and are tested for abrasion resistance using an apparatus consisting of a reciprocating bar 3 inches above a horizontal Alsimag pin, ⅛ inch in diameter. One end of the yarn strand is attached to the reciprocating bar and the strand is then caused to pass 360° around the pin, thence 180° around the portion of itself leading from the reciprocating bar to the pin and thence 90° around the pin in the direction whence it came, the free end hanging vertically and being attached to a 45-gram weight. The reciprocating motion of the bar causes the yarn to rub on the Alsimag pin and on itself. This motion is continued for a sufficient number of cycles to cut the yarn completely in two. The fireproof yarns withstand an average of 130 cycles before breaking. They withstand 23 cycles of a Stoll flex test.

For comparison, a number of fabrics prepared from polyacrylonitrile are made fireproof by heating at 255° C. for 4 hours. The fabrics include satins, twills, and basket weaves. Yarns removed from these fabrics have deniers varying from 574 and 612. Abrasion resistance, as measured by the above-described procedure, varies between 3 and 13 cycles. Thus, a tenfold improvement in this important property is realized by the use of the process of the present invention. The control product fibers withstand only 2 cycles of a Stoll flex test (30,000 denier per inch).

EXAMPLE III

A quantity of 3-denier, 3-inch staple fiber prepared from the terpolymer of Example II is carded and several layers of the card web are placed on top of each other to form a batt about 1½ inches thick with a specific gravity of about 0.003. This batt is passed through a needle loom to punch a number of the fibers into the batt in the direction of its thickness, i.e., roughly perpendicular to the top and bottom surfaces. The needling action occurs about 50 times per square inch of batt surface. After needle-punching from the top of the batt, it is turned over and run through the needle loom again to punch it from the other side. The specific gravity of the batt is increased to about 0.04 by the needling operation. The needle batt is placed in a forced-draft oven at 215° C. and the temperature of this oven is raised gradually and uniformly to 275° C. over a period of 60 minutes and is then held at this latter temperature for 5 minutes. The product removed from the oven is a black non-woven fabric with pleasing aesthetic properties. Its surface area is approximately ½ that of the needled batt placed in the oven originally. The needled fabric is pliable, strong, and tough, and can be sewn readily on a sewing machine to form fireproof garments. A glove is fabricated in which the seams are as close as 1/16 inch to the cut edges of the felt. This glove shows

many advantages over asbestos gloves commonly used for handling hot objects. Because of the flexibility of the fabric, the glove is compliant with the result that manual operations are much more readily and surely carried out than when an asbestos glove is worn. The weight of the black felt glove is only ⅙ that of the asbestos glove and yet its insulative value is found to be twice as high. The felt, like the heated staple of the previous examples, is completely fireproof. Washing the glove in a commercial washing machine for 2 hours at 165° F. does not alter the properties or appearance of the glove.

EXAMPLE IV

Using staple fibers prepared from the terpolymer of acrylonitrile, methyl acrylate, and sodium styrenesulfonate described in Example II, a series of tests is carried out to demonstrate the closeness of packing of the fibers which may be used during the heat treatment in order to obtain a useful fireproof fiber. Samples of loosely-carded staple fibers, needle-punched batts, low-twist spun yarns, and loosely-knit fabrics are placed in a forced-draft oven and heated gradually and uniformly from 220° C. to 275° C. over a period of 60 minutes and held at this latter temperature for 5 minutes. Examination of the products shows that those prepared from physical arrangements of the fibers having a uniform bulk density of less than 0.10 gram per cc. are practically indistinguishable from each other in terms of brittleness, all having excellent flexibility. The products from the samples having a uniform bulk density between 0.11 and 0.20 gm./cc. show somewhat more fibrillation during hand-carding after careful separation of individual filaments from their treated form. These samples are still sufficiently pliable, however, for the samples to be utilized in the preparation of fireproof articles. The products from original samples of bulk density about 0.20 are so brittle as to be of no practical value and in some cases are not completely fireproof.

In another series of tests, samples of the same staple fibers are placed in a forced-draft oven in different bed thicknesses, the bulk density being in all cases uniform from about 0.10 to about 0.20 gm./cc. It is found that fireproof staple of good physical properties can be obtained by heating the fibers at a slow enough rate to prevent sticking of the fibers, as above described, as long as the depth of the bed of fibers does not exceed about 10 inches.

EXAMPLE V

Samples of needle-punched batts are prepared as in Example III. One sample is placed in a forced-draft oven at 220° C. and raised gradually and uniformly to 275° C. in 60 minutes and is held at this latter temperature for 10 minutes. Other samples are placed in the oven at 275° C. and held there for 20, 40, 60, and 80 minutes, respectively. Yet another sample is placed in the oven at 250° C., raised to 275° C. over 60 minutes, and held at the latter temperature for 10 minutes. Only the sample placed in the oven at 220° C. is found to produce a pliable felt. The other samples show occasional fusing of filaments and those filaments which can be removed from the felt show low elongation (about 4%).

Still other samples are placed in the oven at 220° C. and maintained at that temperature for 10 and 20 hours. The sample removed after 10 hours is found to be incompletely fireproof. The sample removed after 20 hours is fireproof but does not show a fabric strength comparable to the felt prepared by heating gradually from 220° C. to 275° C. and then heating 5 minutes at the latter temperature.

EXAMPLE VI

Staple fibers are prepared from a number of polymers and polymer mixtures containing acrylonitrile. Compositions of these materials are given in Table I which

also gives the fiber stick temperatures. Batts of each item are prepared using hand cards and are put through various heating cycles within the limits of this invention. The staple batts all have uniform bulk densities between 0.02 and 0.05 gm./cc. All products are black and fireproof except as indicated.

In Table I, "AN" refers to acrylonitrile, "MA" is methyl acrylate, "SSS" is sodium styrenesulfonate, "MVP" is 2-methyl-5-vinyl pyridine, "VAc" is vinyl acetate, "NVP" is N-vinyl pyrrolidone, "VCl_2" is vinylidine chloride, and "VCl" is vinyl chloride. The designation "AN/MA, 94/6" refers to a copolymer containing 94% combined acrylonitrile and 6% combined methyl acrylate; "AN/MA/SSS, 94/5.7/0.3" is a terpolymer containing 94% combined acrylonitrile, 5.7% combined methyl acrylate, and 0.3% combined sodium styrenesulfonate; "50AN/50MVP//95AN/5VAc, 8//92" refers to a polymer mixture containing 8% of a copolymer consisting of 50% combined acrylonitrile and 50% combined 2-methyl-5-vinyl pyridine and 92% of a copolymer consisting of 95% combined acrylonitrile and 5% combined vinyl acetate. The other designations have corresponding connotations.

Table I

Fiber Composition	Stick Temperature, ° C.	Product Properties
Polyacrylonitrile (homopolymer)	276	brittle.
AN/MA, 94/6	249	flexible, tough.
AN/MA/SSS, 94/5.7/0.3	246	Do.
AN/SSS, 98/2	298	moderately tough, flexible.
AN/SSS, 95/5	260	flexible, tough.
AN/MVP, 96/4	250	Do.
50AN/50MVP//95AN/50VAc, 8//92	240	Do.
AN/NVP, 89/11	303	Do.
AN/VAc/MVP, 86/9/5	218	Do.
AN/acrylamide, 94/6	295	moderately tough, flexible.
AN/itaconic acid, 97/3	248	Do.
AN/NVP, 94/6	258	Do.
AN/VCl_2, 80/20	230	brittle, not fireproof.
AN/VCl, 40/60	150	brittle, fused filaments.
AN/styrene, 95/5	306	flexible, tough.

EXAMPLE VII

Staple fibers of the acrylonitrile terpolymer of Example II are heat-treated as shown in that example and carded and spun into a 1200 denier yarn using conventional textile machinery. Like all of the fiber products of this invention, yarns may be spun from these fireproof flexible fibers in the conventional woolen system. The spun yarn is then knitted on Wildman 23 inch knitting machine, Model No. FBW (manufactured by Wildman Manufacturing Co., Norristown, Pa.), at full speed (134 wales/50 courses per minute) for three minutes without a break showing that the yarn is eminently suitable for knitting.

EXAMPLE VIII

The heat-treatment procedure of Example I is carried

out on staple fibers (3.0 denier, 1½ inches long) prepared from an acrylonitrile copolymer containing 90% combined acrylonitrile and having a stick temperature of 211° C. The fiber in the form of a loose batt having a maximum bulk density of 0.05 is heated at the rate of 1° C./min. from 190° C. up to a temperature of 300° C. and removed from the heating oven. The fibers do not adhere to one another and are black, fireproof, and sufficiently strong to be spun into yarns in the woolen system.

The above procedure is repeated except that a fibrous batt with a stick temperature of 246° C. is heated at the rate of 3° per minute from 220° C. to 260° C. and maintained at 260° C. for 2.5 hours. The product fibers are strong, flexible, and fireproof and suitable for further processing on conventional textile equipment.

The claimed invention:

1. In a process for providing fireproof properties by heating fibers spun from a linear polymeric composition essentially consisting of between 85% and 99% acrylonitrile in polymer form and between 15% and 1% of other polymer copolymerized with acrylonitrile, the polymeric composition containing no halogens attached to any polymer chain, the fibers having been drawn to at least 300% of their original as-spun length; the improvement, for producing fireproof fibers which are strong and flexible enough to be spun into textile yarns, of heating said fibers in the form of a fibrous mass with a maximum bulk density of 0.2 gram per cubic centimeter, having a fiber stick temperature of at least 180° C., from a temperature lower than 20° C. below the stick temperature of the fibers at a rate of less than 3° C. per minute to a temperature between about 260° C. and about 500° C., in an oxidizing gaseous medium containing oxygen until the fibers become fireproof.

2. The process of claim 1 wherein the polymeric composition is a copolymer of acrylonitrile and a vinyl compound, and the fiber stick temperature is between about 240° C. and 306° C.

3. The process of claim 1 wherein the polymeric composition is a terpolymer of acrylonitrile, methyl acrylate and a styrene sulfonate salt.

4. The process of claim 1 wherein fibers having a stick temperature between about 240° C. and 260° C. are heated from a temperature of about 220° C. to a temperature of about 275° C. at a rate of about 1° C. per minute and maintained at about 275° C. for at least 5 minutes.

References Cited in the file of this patent

UNITED STATES PATENTS

2,799,915 Barnett ..... July 23, 1957
2,913,802 Barnett ..... Nov. 24, 1959

OTHER REFERENCES

Houtz: Textile Research Journal, November 1950, pp. 797 and 798.