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METHOD FOR PREPARING PERMANENTLY OPAQUE FIBERS

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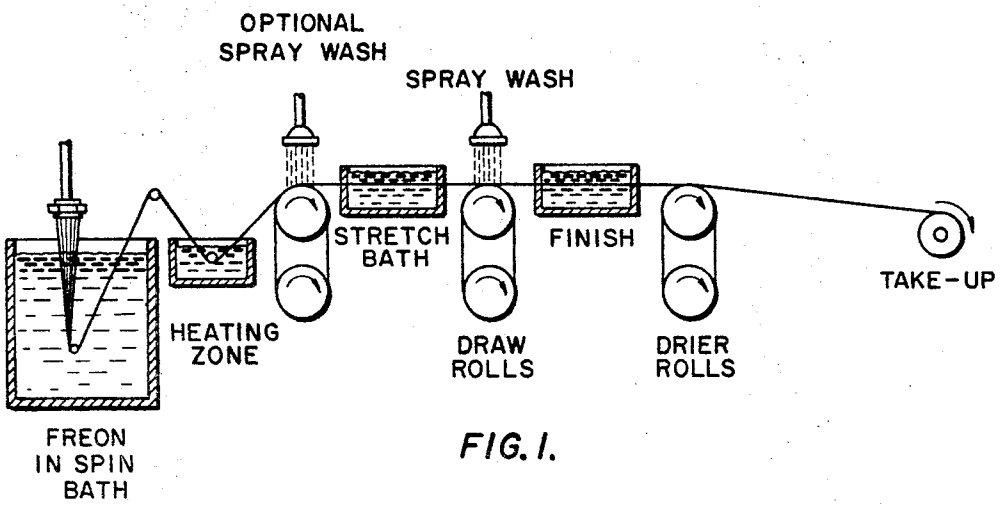


FIG. 1.

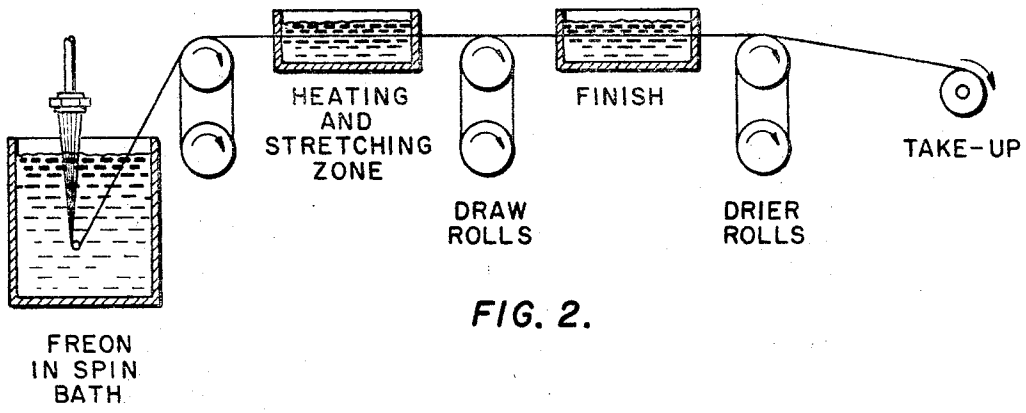


FIG. 2.

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METHOD FOR PREPARING PERMANENTLY OPAQUE FIBERS

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ABSTRACT OF THE DISCLOSURE

Smooth delustered acrylic fibers having a highly porous internal microvoid structure which is permanently sealed and not collapsed by drying have been prepared by coagulation of solution spun acrylic polymers in a coagulation bath containing volatile fluorinated aliphatic compounds dissolved therein and thereafter heating the fiber.

This invention relates to a novel process for solution spinning permanently delustered fibers.

Solution spun dull or delustered fibers of synthetic polymers are normally prepared using wet spinning techniques incorporating titanium dioxide or equivalent pigment in the polymer dope or solution prior to spinning. The dope is then extruded into a coagulating bath which comprises a liquid which is a solvent for the polymer solvent and a nonsolvent for the polymer. Coagulation of the extruded composition is effected by infusion of the coagulant and diffusion of the solvent which results in a gelled polymer structure characterized by a network or pores of varying size depending on the particular coagulant and other conditions employed. Drying of the gelled fibers results in collapse of the porous network and in cases where a pigment has been added to the polymer dope the fiber has a dull or opaque appearance. Where no pigment is employed the fibers are lustrous and silk-like in appearance.

An object of the invention is to provide a novel process for the preparation of opaque or dull fiber without using pigments.

A further object of the invention is to provide a continuous process for the preparation of dull synthetic fibers, preferably acrylic fibers or filaments, which have smooth surfaces which do not crack and become streaked and rough upon drying after preparation by wet spinning techniques.

These and other objects are accomplished by spinning solutions of polymers of acrylonitrile or other solution spun fiber-forming polymers into a coagulation bath containing dissolved therein a volatile fluorinated compound and thereafter passing the coagulated filament into a heated aqueous bath. The coagulated and heated filaments are stretched, washed and dried by conventional means to provide smooth, dull filaments of acrylonitrile polymers or other synthetic polymers having desirable properties for textile use.

The essential steps of the instant invention comprise coagulation in a bath containing a volatile fluorinated compound and thereafter heating the freshly coagulated filaments in an aqueous bath, stretching, washing and drying the heated filaments. Reference to FIGS. 1 and 2 indicate that alternate procedures may be employed. Thus, in FIG. 1 the polymer dope is spun into air for a distance of less than about 4 inches and into a coagulation bath containing a volatile fluorinated compound dissolved therein. The coagulated filament is then passed from the coagulation bath into a heated aqueous bath and on to rolls wherein the filaments are optionally washed to remove most of the remaining solvent and coagulant. The filaments according to the procedure depicted in FIG. 1

are then stretched in a hot water bath or by equivalent means and passed on the draw rolls whereupon they may be subjected to an additional washing step. Typically a finish to facilitate handling of the filaments is applied and the filaments are thereafter dried and collected in the usual manner or cut to staple as desired. Alternatively, the wet spun, coagulated filaments which are infused with the solution of coagulant and volatile fluorinated compound may be both heat-treated and stretched in a single bath as depicted in FIG. 2. In either case the provision of a volatile fluorinated compound in the coagulation bath and subsequent heat treatment in an aqueous bath provides fibers which upon drying are characterized by a sealed pore structure, low density and smooth but delustered appearance.

While fiber-forming polymers of acrylonitrile are preferred for use in the instant invention other synthetic polymers capable of forming filaments by wet spinning techniques can be employed.

The polymeric materials, which may be employed in the practice of the present invention are polyacrylonitrile, copolymers including binary and ternary polymers containing at least 80 percent by weight of acrylonitrile in the polymer molecule, or a blend comprising polyacrylonitrile or copolymers comprising acrylonitrile with from 2 to 50 percent of another polymeric material, the blend having an overall polymerized acrylonitrile content of at least 80 percent by weight. While the preferred polymers employed in the instant invention are those containing at least 80 percent of acrylonitrile, generally recognized as the fiber-forming acrylonitrile polymers, it will be understood that the invention is likewise applicable to polymers containing less than 80 percent acrylonitrile. The acrylonitrile polymers containing less than 80 percent acrylonitrile are useful in forming films, coating compositions, molding operation and lacquers.

For example, the polymer may be a copolymer of from 80 to 98 percent acrylonitrile and from 2 to 20 percent of another monomer containing the >C=C< linkage and copolymerizable with acrylonitrile. Suitable monoolefinic monomers, include acrylic, alpha-chloroacrylic and methacrylic acids; the acrylates such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromoethylene; methacrylonitrile; acrylamide and methacrylamide; alpha-chloroacrylamide, or monoalkyl substitution products thereof; methylvinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate, and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and itaconic esters; N-vinylcarbazole; vinyl furane; alkyl vinyl esters; vinyl sulfonic acid; ethylene alpha, beta-dicarboxylic acids or their anhydrides or derivatives, such as diethylcitraconate, diethylmesaconate, styrene, vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridines, for example, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, etc.; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles, such as 2-, 4-, or 5-methyl-1-vinylimidazole, and other >C=C< containing polymerizable materials.

The polymer may be a ternary or higher interpolymer, for example, products obtained by the interpolymerization of acrylonitrile and two or more of any of the monomers, other than acrylonitrile enumerated above. More specifically, and preferably the ternary polymer comprises acrylonitrile, methacrylonitrile, and 2-vinylpyridine. The ternary polymer preferably contain from 80 to 98

percent of acrylonitrile, from 1 to 10 percent of a vinylpyridine or a 1-vinylimidazole, and from 1 to 18 percent of another substance such as methacrylonitrile or vinyl chloride.

The polymer may also be a blend of a polyacrylonitrile or of a binary interpolymer of from 80 to 99 percent acrylonitrile and from 1 to 20 percent of at least one other

containing substance with from 2 to 50 percent of the weight of the blend of a copolymer of from 10 to 70 percent of acrylonitrile and from 30 to 90 percent of at least one other >C=C< containing polymerizable monomer. preferably, when the polymeric material comprises a blend, it will be a blend of a copolymer of 90 to 98 percent acrylonitrile and from 2 to 10 percent of another mono-olefinic monomer, such as vinyl acetate, which is not receptive to dyestuff, with a sufficient amount of a copolymer of from 10 to70 percent of acrylonitrile and from 30 to 90 percent of a vinyl-substituted tertiary heterocyclic amine, such as vinylpyridine or 1-vinylimidazole, to give a dyeable blend having an overall vinyl-substituted tertiary heterocyclic amine content of 2 to 10 percent based on the weight of the blend.

The polymers or polymer blends as above described are normally dissolved for wet spinning in a solvent such that a viscous solution is obtained having typically from about 10 to about 35 percent of polymer solids. The preferred solvents are highly polar organic liquids such as dimethylformamide, dimethylacetamide and dimethylsulfoxide. Other solvents which are miscible in methanol or ethanol are known and widely employed in wet spinning techniques and may be employed in the process of the instant invention.

The polymer in solution is extruded through the orifices of a spinnerette wherein the number and design of the holes is determined according to the desired objective. This invention is, of course, related to a wet spinning process which requires that the coagulation of the extruded polymer be accomplished in a liquid nonsolvent for the polymer. This objective may be accomplished by immersing the spinnerette beneath the surface of the liquid coagulant or by placing the face of the spinnerette in a position slightly above the surface of the liquid coagulant such that the filament is extruded first into air or other gaseous medium and thereafter into the liquid coagulant. In such case the distance between the spinnerette face and the surface of the coagulant is less than about 4 inches so that no appreciable coagulation occurs prior to contact with the liquid. The latter technique is a modification of wet spinning designed to provide increased spinning rates and is useful in the process of this invention.

The liquid coagulating medium may in general comprise any liquid which is a nonsolvent for the polymer, a solvent for the polymer solvent and a solvent for the volatile fluorinated compound. Various alcohols, such as methanol, ethanol and aqueous solutions of these materials may be employed. For purposes of the instant invention the coagulation path must be maintained at temperatures below the boiling point of the particular volatile fluorinated compound employed. Except for insuring the presence of substantial concentration of the fluorinated compound in the bath the temperature of the coagulation bath has not been found to constitute a critical aspect of this invention. Suitable temperatures are noted to lie up to about 30° C.

Following coagulation the gelled coagulated filaments containing dissolved fluorinated compound infused in the internal pore structure of the filaments are subjected to heat treatment to raise the temperature of the filaments above about 50° C. and preferably above 85° C. For purpose of this step passing the filaments through a hot water bath constitutes the highly preferred embodiment

of this invention because of the simplicity, economy and results. Other liquids or gaseous media may, however, be employed so long as the temperature of the filament is raised substantially above the boiling point of the volatile fluorinated compound employed in the coagulation step without effecting any appreciable drying of the filaments so treated.

Techniques for stretching, washing, applying conventional finishes and drying of wet spun synthetic filaments are well known in the art and do not constitute critical aspects of the instant invention.

The fluorinated compounds added to the spin bath are those saturated aliphatic compounds having up to four carbon atoms and at least a single fluorine atom attached to a carbon atom which are soluble in methanol or ethanol at temperatures below about 30° C. and which are volatile at temperatures at least greater than about 50° C. at atmospheric pressure. These include those compounds generally marketed as Freons and include compounds such as, CCl_3F, CCl_2F_2, $CClF_3$, $CBrF_3$, CF_4, $CHClF_2$, $CCl_2F—CClF_2$, $CClF_2—CClF_2$

These materials dissolved in the coagulant alcohol to at or near the saturation level of the coagulant at or below about 30° C. Cooling the coagulant helps maintain desirable level of the volatile flurinated compound in the bath. If desired, a mixture of more than one fluorinated compound may be employed.

EXAMPLE I

A spinning solution was prepared by disolving 500 parts by weight of a copolymer of acrylonitrile containing 7 weight percent of vinyl acetate (specific viscosity of 0.1 gms. in dimethylformamide at 25° C. was 0.15) in 1500 parts by weight of dimethylacetamide. The solution was extruded into a bath comprising 75 percent methanol and 25 percent by volume of Freon 113 ($CCl_2F—CCl_2F$). Extrusion rates of the polymer solution were controlled into two trials to provide filaments having deniers of 5.0 and 14.0 d.p.f. From the spin bath the fibers in each trial were immediately passed into a hot water bath (90°–95° C.) and onto a first godet. Dwell time in the hot water bath was about 3.25 seconds and after washing, stretching 2.88× and drying in the sequence depicted in FIG. 1 the filaments were opaque, and smooth on the surface. Microscopic examination of fiber cross-section indicated that the fibers were highly porous and uncollapsed even after drying.

EXAMPLE II

Filaments were spun under identical conditions as employed in Example I except that the hot water bath was eliminated. These filaments were essentially bright, transparent and nonporous after drying.

EXAMPLE III

The polymer solution employed in Examples I and II was extruded into a coagulation bath of methanol saturated with Freon 12 (CCl_2F_2) by sparging the Freon into the methanol from a cylinder. The bath was maintained at 25° C. Fiber from the bath was wrapped four times around the first roll and then simultaneously heat-treated and stretched 2.28× in boiling water, washed and dried in a manner depicted in FIG. II. The resulting fibers were highly porous and uncollapsed. Their appearance was dull notwithstanding a smooth surface. The fibers had a tenacity of 2.3 grams/denier and an elongation of 30 percent. Although the fibers were highly porous and of low density they were not swollen or penetrated by hot water or anisole evidencing a sealed microvoid internal structure.

The filaments or fibers prepared according to the instant invention are unique in that they possess a highly complex network of sealed micropores or microvoids which result

in a buoyant, low density fiber having a dull appearance notwithstanding a smooth surface. Moreover, the fibers of this invention are not penetrated by swelling agents such as hot water and anisole. Normally the porous network or void structure within solution spun synthetic fibers collapses upon drying. However, filiaments spun within the parameters of the process of this invention as above defined are permanently porous. Acrylonitrile fibers prepared according to the process of this invention were placed in anisole along with similarly prepared acrylonitrile fibers wherein no additive was present in the spin bath. The latter fibers became optically dissolved when anisole penetrated their pore structure. Optical disolution of the impregnated fibers results from the fact that anisole and the polymer have closely matching refractive indices. The opaque fibers of this invention were not penetrated by anisole after immersion for more than a year indicating a sealed network of pores or voids.

I claim:

1. A process for the preparation of low density, permanently opaque, synthetic fibers from a solution of fiber-forming synthetic polymers of acrylonitrile which comprises extruding a fiber-forming solution of an acrylonitrile polymer and an acrylonitrile polymer solvent into a coagulation bath maintained at a temperature below about 30° C., said coagulation bath comprising a coagulant liquid which is a non-solvent for the polymer and a solvent for the polymer solvent and a volatile fluorinated compound selected from the group consisting of CCl_3F, CCl_2F_2, $CClF_3$, $CBrF_3$, CF_4, $CHClF_2$ $CCl_2F—CClF_2$, $CClF_2—CClF_2$, CF_2 $CF_2CF_2CF_2$ to form a coagulated acrylonitrile polymer filament infused with said volatile fluorinated compound, and passing said coagulated filament to a zone heated to a temperature sufficient to volatilize said volatile fluorinated compound.

2. The process of claim 1 wherein the acrylonitrile polymer is a copolymer containing from 80 to 98 percent by weight of acrylonitrile and from 2 to 20 percent of at least one mono-olefinic monomer.

3. The process of claim 2 wherein the coagulation bath contains a nonsolvent for the polymer filament from the group consisting of methanol and ethanol.

4. The process of claim 2 wherein the polymer solution is an organic solvent.

5. The process of claim 4 wherein the organic polymer solution is selected from the group consisting of dimethylformamide, dimethylacetamide, and dimethylsulfoxide.

6. The process for the preparation of low density, permanently opaque, synthetic fibers from a solution of fiber-forming synthetic polymers of acrylonitrile dissolved in an organic solvent which comprises extruding said solution into a coagulation bath maintained at below about 30° C., said bath comprising a liquid coagulant selected from the group consisting of methanol and ethanol and a fluorinated compound selected from the group consisting of CCl_3F, CCl_2F_2, $CClF_3$ $CBrF_3$, CF_4, $CHClF_2$, $CCl_2F—CCl_2F$, $CClF_2—CClF_2$, $CF_2CF_2CF_2CF_2$ to form a coagulated acrylonitrile polymer infused with said fluorinated compound and passing said filament to a water bath heated above about 85° C., starching, washing, and drying said filament.

7. The process of claim 6 wherein the fluorinated compound is dissolved in methanol.

8. The process of claim 6 wherein the fluorinated compound is dissolved in ethanol.

9. The process of claim 6 wherein the organic solvent is dimethylacetamide.

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