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METHOD FOR PREPARING PERMANENTLY OPAQUE FIBERS

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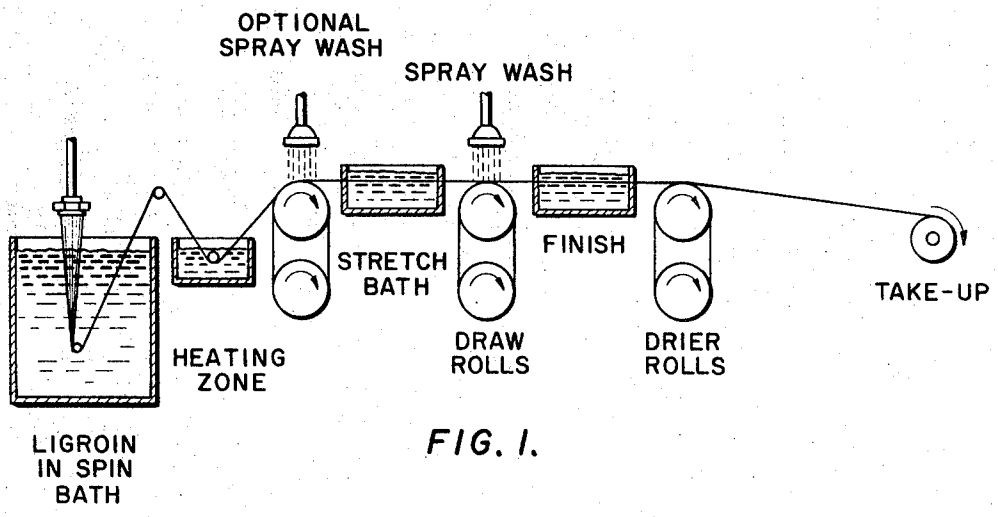


FIG. 1.

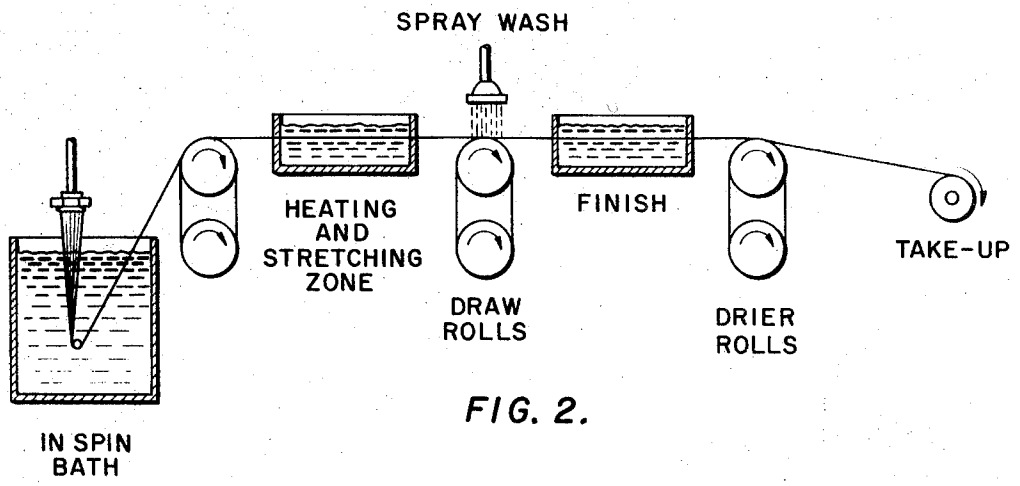


FIG. 2.

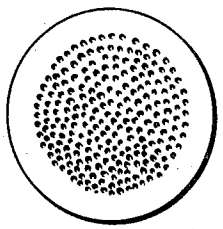


FIG. 3.

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METHOD FOR PREPARING PERMANENTLY OPAQUE FIBERS

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ABSTRACT OF THE DISCLOSURE

Method of making smooth delustered acrylic fibers having highly porous internal microvoid structures which are permanently sealed and not collapsed by drying wherein coagulation of solution spun acrylic polymer is carried out in a coagulation bath containing substantial volumes of ligroin dissolved therein and the fiber is then heated.

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

Solution spun dull or delustered fibers of synthetic polymers normally prepared using wet spinning techniques incorporate titanium dioxide or equivalent pigment in the polymer dope or solution prior to spinning. Thereafter, the dope is 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 of pores or voids 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 silk like in appearance and are designated bright by those skilled in the art.

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 petroleum ether or ligroin and thereafter passing the coagulated filament into a heated aqueous bath. The coagulated and heat filaments are stretched and dried by conventional means to provide smooth, dull filaments of acrylonitrile polymers or other synthetic polymers having desirable properties for textile use.

FIG. 1 is a schematic view of apparatus used to carry out one embodiment of the process.

FIG. 2 is a schematic view of apparatus to carry out another embodiment of the process, and

FIG. 3 is a greatly enlarged schematic cross-sectional view of a fiber showing the internal voids therein.

The essential steps of the instant invention comprise coagulation in a bath containing a volatile petroleum ether and thereafter heating the freshly coagulated filaments in an aqueous bath, stretching 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 petroleum ether 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 remaining solvent and coagulant. The filaments handled according to the procedure depicted in FIG. 1 are then stretched in a hot water bath or by equivalent means and passed on to 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 of which are infused with the solution of coagulant and petroleum ether may be both heated, treated, and stretched in a single bath as depicted in FIG. 2. In either case the provision of a volatile petroleum ether 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 apeparance.

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

The preferred 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 fluroide, vinyl bromide, vinylidene chloride, 1-chloro-1-bromoethylene; methacrylonitrile; acrylamide and methacrylamide; alpha-chloro-acrylamide; 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 vinyl pyridines, 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 of 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 polymers preferably contain from 80 to 98 percent of acrylonitrile, from 1 to 10 percent of a vinylpyridine or a 1-vinylimidazolone, 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 >C=C< 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 monoolefinic monomer, such as vinyl acetate, which is not receptive to dyestuff, with a sufficient amount of a copolymer of from 10 to 70 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 from 2 to 10 percent based on the weight of the blend.

The fiber-forming 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 solids. The preferred solvents are highly polar organic liquids such as dimethylformamide, dimethylacetamide and dimethylsulfoxide. Other polymer solvents which are miscible in ligroin 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 coagulants 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 non-solvent for the polymer, a solvent for the polymer solvent and a solvent for the volatile petroleum ether. Various alcohols, such as methanol, ethanol and aqueous solutions of the materials may be employed. Petroleum ether oriligroin having a boiling point ranging from about 20° to about 75° C. is dissolved in the coagulant in concentration of from about 40 to about 75 by volume. For purposes of the instant invention the coagulating bath should be maintained at temperatures below the boiling point of the particular ligroin fraction employed. Except for insuring the presence of substantial concentration of ligroin 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 from 10° C. up to 30° C. and

higher depending, of course, on the particular petroleum ether fraction employed.

Following coagulation the gelled coagulated filaments containing ligroin infused in the internal pore structure of the filaments are subjected to heat treatment such as to raise the temperature of the filaments above about 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 ligroin fraction employed in the coagulation step without effecting appreciable drying of the filaments so treated.

Techniques for stretching, 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.

EXAMPLE I

A spinning solution was prepared by dissolving 500 parts by weight of a copolymer of acrylonitrile containing 7 weight percent of vinyl acetate of specific viscosity 0.15 in 1500 parts by weight of dimethylacetamide. The solution was spun into a methanol coagulation bath comprising 44 volume percent of a ligroin fraction having a boiling point of 40° C. maintained at 25° C. Filaments were passed from the coagulation bath and wrapped four times around a first roll and then simultaneously heat treated and stretched 2.28× by passing the filaments from the first roll into a boiling water bath and then to draw rolls where the drawn filaments were washed with water and thereafter dried on heated rolls. The collected filaments had a denier of 8.7 per filament and possessed a smooth, dull appearance. They were porous and possessed a tenacity of 2.5 grams/denier and an elongation of 33.

EXAMPLE II

The procedure of Example I was repeated except that the coagulation bath containing methanol and 58 volume percent of ligroin boiling at 40° C. maintained at 25° C. The filament upon drying possessed a tenacity of 2.1 grams/denier and an elongation of 22% and although highly porous and very dull it possessed a smooth fiber surface.

EXAMPLE III

In contrast to filaments prepared according to Examples I and II filaments prepared by the techniques of Examples I and II wherein only 25 volume percent of the same ligroin fraction was present in the spin bath were bright and silky in appearance and then were only slight porous, even though their tensile properties were not appreciably altered.

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 bouyant, low density fiber having a dull appearance, notwithsanding a smooth surface. Normally the porous network or void structure characteristic of solution spun fibers collapses upon drying. Filaments spun within the parameters of the process of this invention as above defined are permanently porous. Acrylonitrile polymer fibers prepared by the processes of this invention were placed in anisole along with acrylonitrile polymer fibers prepared without ligroin added to the spin bath. The latter fibers became optically dissolved due to the fact that anisole and the acrylonitrile polymer have closely matching refractive indices. The optical dissolution was caused by penetration of the anisole into the collapsed pore structure of the fiber. The opaque acrylic fibers of this invention which had been dried without being collapsed were indicated to have a sealed network of pores or microvoids insofar as anisole and other liquids such as hot water could not penetrate the fiber structure and the fibers

remained permanently opaque after immersion for more than one year.

I claim:

1. A process for the preparation of low density permanently opaque synthetic fibers from a solution of acrylonitrile polymer which comprises extruding said acrylonitrile polymer and a polymer solvent into a coagulation bath comprising from about 40 volume percent to about 75 volume percent of ligroin fraction having a boiling point ranging from about 20° C. to about 75° C. dissolved in a solvent for said ligroin fraction which silvent is a nonsolvent for said synthetic polymer and a solvent for said polymer solvent, said coagulation bath being maintained below the boiling point of said ligroin fraction to form a coagulated synthetic filament infused with coagulant and passing said coagulated filament to a zone heated above the boiling point of said ligroin fraction.

2. The process of claim 1 wherein the coagulation bath contains a nonsolvent for the polymer selected from the group consisting of methanol and ethanol.

3. The process of claim 1 wherein the polymer solvent is an organic solvent.

4. The process of claim 1 wherein the organic solvent is selected from the group consisting of dimethylformamide, dimethylacetamide and dimethylsulfoxide.

5. A process for the preparation of low density, permanently opaque synthetic fibers from a solution of fiber-forming polymer of acrylonitrile dissolved in an organic solvent which comprises extruding said solution into a coagulation bath comprising from about 40 volume percent to about 75 volume percent of ligroin having a boiling point ranging from about 20° C. to about 75° C.

dissolved in a liquid selected from the group consisting of methanol and ethanol, said coagulation bath being maintained below the boiling point of said ligroin to form a coagulated acrylonitrile polymer filament infused with said ligroin and passing said filament to a water bath heated above the boiling point of said ligroin stretching, washing and drying said filament.

6. The process of claim 5 wherein the ligroin is dissolved in methanol.

7. The process of claim 5 wherein the ligroin is dissolved in ethanol.

8. The process of claim 5 wherein organic solvent is dimethylacetamide.

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