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SYNTHETIC FIBER PREPARATION

Carroll A. Hochwalt, Dayton, Ohio, assignor to
Monsanto Chemical Company, St. Louis, Mo., a
corporation of Delaware

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This invention relates to the preparation of fibers from acrylonitrile polymers by extruding a solution thereof into an aqueous medium and separating the precipitated fiber. More particularly the invention relates to a novel method for removing certain solvents from extruded fibers of acrylonitrile polymers.

Acrylonitrile polymers are well known as synthetic fiber forming materials. Similarly the methods of preparing such fibers by dissolving the acrylonitrile polymers in certain unusual solvents, extruding the solution through a suitable orifice into a medium for extracting the solvent, and recovering the fiber so precipitated, are also well known. Although many solvents have been suggested, very few of them are practicable because of their unavailability, the poor viscosity characteristics of their solutions, or the cost of recovering the solvent for reuse. Many extruded fibers are soft and plastic because of their solvent retention, and the difficulty in effecting complete elimination.

It is the primary purpose of this invention to provide a novel spinning method for preparing high tenacity fibers from acrylonitrile polymers. A further purpose is to provide a new method of removing certain solvents from the extruded solutions of acrylonitrile polymers in order to achieve a more rapid and more complete removal than is effected by methods heretofore used. A still further purpose is to provide a practicable wet spinning process in which the solvent can readily be removed from the polymer and conveniently recovered for reuse.

In copending application, Serial No. 351, filed January 2, 1948, now abandoned, by Carroll A. Hochwalt, there is described and claimed a method of spinning, utilizing butyrolactone as a solvent for polyacrylonitrile and copolymers of more than 70 percent of acrylonitrile and minor proportions of other copolymerizable monomers, such as vinyl acetate, vinylidene chloride, and methacrylonitrile. The spinning method herein described and claimed is a valuable improvement in the method of spinning these lactones.

In copending application, Serial No. 17,111, filed March 25, 1948, now abandoned, by Carroll A. Hochwalt, there is described and claimed a method of spinning acrylonitrile copolymers, particularly the copolymers of acrylonitrile, methacrylonitrile and vinyl acetate, by extruding solutions thereof in gamma-valerolactone into a medium which removes the solvent from the extruded fiber. The method herein described and claimed is a valuable improvement in the method

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of wet spinning solutions of gamma-valerolactone, because it provides an efficient and convenient method of recovering the solvent from dilute aqueous solutions thereof and reconverting it for reuse. The method of separating the gamma-valerolactone from dilute water solution is possible by means of extraction with aromatic hydrocarbons in accordance with the invention described and claimed in copending application, Serial No. 17,096, filed March 25, 1948, now Patent No. 2,503,200, by George E. Ham.

In accordance with this invention it has been found that strong fibers can be prepared efficiently from lactone solutions of acrylonitrile polymers by extruding the solutions through an orifice, or a spinnerette having a plurality of orifices, into an aqueous alkaline bath. The alkaline reagent converts the lactone to a very soluble salt of the corresponding hydroxy acid and thereby rapidly removes the lactone from the fiber. In the wet spinning processes described in the prior art, wherein the solvent diffuses from the fiber into the bath, only a solution effect is involved. Under such circumstances the greatest resistance to the diffusion is encountered at the fiber-water interface, where a saturated solution of the solvent and spin bath is found. The slow gel-formation on the fiber surface is in many cases so disturbing that the fibers become sticky and do not form true multifilaments. In the present method the lactone is decomposed the moment it contacts the alkaline bath and is thereby eliminated from the fiber surface. Accordingly, much more rapid rates of diffusion from the fiber are effected and therefore completely coagulated free splitting fibers are obtained. In many cases the freshly extruded fiber is somewhat porous and the alkaline reagents may actually enter the pores or interstices and thereby remove the lactone from the interior of the fiber.

The alkaline bath is an aqueous solution of any readily water soluble alkaline reagent, such as sodium hydroxide, potassium hydroxide, ammonia, sodium carbonate, sodium phosphate, or other water soluble salt of an alkali metal or an alkaline earth metal having an alkaline reaction in water solution. Solutions of amines or other organic bases may also be used. Since the high acrylonitrile copolymers are generally quite resistant to strong alkali solutions it is usually desirable to use sodium hydroxide, preferably in concentrations of from two to 20 percent. For more economical practice of the invention counter-current flow of the alkaline agents through the

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bath is practiced, so that the fiber almost exhausted with respect to the lactone is contacted with the strongest alkali solution, exceptionally rapid removal of the lactone thus being effected.

More rapid spinning is possible if small proportions of wetting agents are dissolved in the spin-bath. These are compounds, which contain both hydrophobic and hydrophilic radicals, are water-soluble yet do not repel the fibers. The fiber is thereby more quickly wetted by the alkali solution and more quickly freed of the solvent content. Suitable wetting agents are the common soaps, such as sodium stearate and other alkali and ammonium salts of long chain fatty acids, and mixtures thereof as obtained by the saponification of animal and vegetable oils; the soaps obtained by neutralization of rosin acids and tall oil; triethanol amine, dodecyl-methylamine, and other "amino soaps," particularly those of higher molecular weight; the sulfonated hydrocarbons, and salts thereof, such as sodium salt of sulfonated alkyl benzene; the ester salts of sulfuric acid, such as sodium lauryl sulfate; and similar compounds having affinity for both water and oils. These wetting agents are used in aqueous solution, preferably to the extent of from 0.005 to 2.0 percent by weight.

In the practice of this invention the acrylonitrile polymer is dissolved in the lactone by any convenient means. Mass polymers may be ground to finely divided state, or the form in which polymers are obtained by emulsion polymerization methods is used directly without further processing. The finely divided polymer is mixed with the lactone in any type of mixing device, such as a dough mixer or a Banbury mixer. It is advisable to heat the mixture and to stir vigorously to promote a more rapid dissolution. Generally it is also desirable to use as high a concentration as possible, but the maximum concentration is frequently limited by the molecular weight of the polymer, high molecular weight materials being less soluble. Since the high molecular weight polymers produce fibers of better physical properties it is advantageous to use a polymer with molecular weights in excess of 25,000, and with such polymers it is difficult to dissolve more than about twenty percent by weight without exceeding practicable viscosity values. Although as low as five percent of the polymer can be used in the spinning solution such concentrations are undesirable because they necessitate the removal of too much solvent from the extruded solution, thereby increasing solvent recovery costs and reducing spinning speeds by increasing the time required for coagulation. The concentration of polymer in the spinning solution will preferably be between seven and eighteen percent, but will ultimately be determined by selecting a uniform high molecular weight polymer with good fiber forming properties and dissolving it in as little lactone as is possible to form a viscous solution capable of being spun at convenient temperatures.

The fibers are spun by extruding the polymer solution through an orifice, or a spinnerette having a plurality of orifices, into the aqueous alkaline bath. The volume of solution passed through the spinnerette must be constant in order to produce a fiber of uniform size. This is best achieved by using a positively driven gear pump adapted to deliver a constant flow of solution, regardless of minor changes in viscosity and in the resistance offered by the spinnerette. It is also desirable to pass the prefiltered solution through

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one or more additional filters before the spinnerette to remove the last traces of foreign matter and particles of incompletely dissolved polymer. The polymer may be delivered to the gear pump by pressure applied by an inert gas to the solution reservoir which is heated if necessary to make the solution fluid enough to pass through the conduits. The extruding operation may be conducted at elevated temperatures but should be maintained substantially below the boiling point of the lactone to facilitate the handling of the filament. Bath temperatures of 60-90° C. have been found to accelerate coagulation.

In the practice of this invention higher fiber speeds are possible because of the rapid and efficient removal of the lactone. This benefit may also permit the use of shorter fiber baths than are usually required, however it may be necessary to wash the fiber by passing it through fresh water to eliminate all traces of the alkali. The size of the spin baths can readily be determined by the usual economic considerations, but will also depend upon the strength of the alkaline solution, the cost of recovering the lactone and the necessity for removing all traces of the alkali.

The liquor from the spin baths, which may contain up to as high as ten percent of the lactone salt is processed by neutralizing it with an acid, for example any inexpensive mineral acid, such as sulfuric or hydrochloric acid. The acid neutralizes any residual alkali and reconverts the lactone salt to the lactone. This recovery method is only practicable with the lactones which have five or six member rings, such as butyrolactone and gamma-valerolactone. The aqueous liquor containing the lactone may then be extracted with benzene, toluene, or other aromatic hydrocarbon and subsequently separated therefrom by distillation, or by merely evaporating the more volatile hydrocarbon. In this manner the costly evaporation of large quantities of water is effectively avoided.

Further details of the practice of this invention are set forth with respect to the following specific examples.

Example 1

A spinning solution was prepared by dissolving eight parts by weight of a copolymer of 84 percent by weight of acrylonitrile, 11 percent methacrylonitrile, and 5 percent vinyl acetate, and 92 parts by weight of gamma-valerolactone. This solution was extruded through a spinnerette having ten apertures, each 0.005 inch in diameter. The copolymer was extruded into an aqueous spin bath comprised of distilled water having dissolved therein 0.4 percent by weight of sodium salt of a sulfonated alkyl benzene. The spinning was conducted with a bath temperature of 80° C. and the coagulation was so slow that continuous spinning was very difficult. The spin solution caused the clogging of the spinnerette and gradually reduced the number of filaments. The fibers so produced were tacky and the individual filaments became welded into a single coarse strand. Only after extensive washing, first in water and then in alcohol, were they sufficiently freed of lactone to develop satisfactory tensile strength.

Example 2

Using the apparatus described in Example 1, and the identical copolymer solution, fibers were spun into a solution of 5.1 percent of potassium hydroxide dissolved in distilled water and con-

taining in addition 0.4 percent of the sodium salt of the sulfonated alkyl benzene as a wetting agent. Spinning operations conducted at 80° C. were uniform and uninterrupted. The continuous fiber was lead out of the alkaline spinning bath into a wash bath of distilled water at a temperature of 65° C. The fibers so produced were free of physical defects and tackiness, and were capable of being oriented by stretching. The oriented fiber had a tensile strength of 4.7 grams per denier, was soft and flexible and the individual filaments of the fiber did not cohere.

Although the invention may be practiced with any of the modifications described in the preceding specification it is obvious that other changes may be made without departing from the nature and spirit of the invention. The details set forth in the preceding specification are not to be construed as limitations upon the scope of the invention except to the extent incorporated in the following claims.

I claim:

1. A method of spinning fibers of acrylonitrile polymers which comprises dissolving the acrylonitrile polymers in a lactone to form a homogeneous solution, and extruding the said solution into an aqueous alkaline solution.

2. A method of spinning fibers of a polymer of a monomer, substances having at least 70 percent of its polymerizable content in the form of acrylonitrile, which comprises dissolving the polymer in a lactone to form a homogeneous solution and extruding the said solution into an aqueous alkaline solution.

3. A method of spinning fibers of a polymer of 75 to 97 percent of acrylonitrile, two to 18 percent of methacrylonitrile, and from one to ten percent of vinyl acetate, which comprises dissolving the polymer in a lactone to form a homogeneous solution, and extruding the said solution into a solution of a hydroxide of an alkali metal.

4. A method of spinning fibers of a polymer of 75 to 97 percent of acrylonitrile, two to 18 percent of methacrylonitrile, and from one to ten percent of vinyl acetate, which comprises dissolving the polymer in gamma-valerolactone to form a homogeneous solution, and extruding the said solution into a solution of sodium hydroxide.

5. A method of spinning fibers of a polymer of 75 to 97 percent of acrylonitrile, two to 18 percent methacrylonitrile, and from one to ten percent of vinyl acetate which comprises dissolving the polymer in butyrolactone to form a homogeneous solution, and extruding the said solution into a solution of sodium hydroxide.

6. A method of spinning fibers of polyacrylonitrile which comprises dissolving the polyacrylo-

nitrile in butyrolactone to form a homogeneous solution, and extruding the said solution into a sodium hydroxide solution.

7. In a method of spinning fibers of acrylonitrile polymers by dissolving the acrylonitrile polymers in a lactone, extruding the said solution into a coagulating bath, and recovering the fiber; the step of utilizing an aqueous alkaline solution as the coagulating bath.

8. In a method of spinning fibers of a copolymer of 75 to 97 percent acrylonitrile, two to 18 percent methacrylonitrile, and from one to ten percent vinyl acetate, by extruding a solution of said polymer and gamma-valerolactone into a coagulating bath, and removing the precipitated fiber; the step of utilizing sodium hydroxide as the coagulating bath.

9. In a method of spinning fibers of a copolymer of 75 to 97 percent acrylonitrile, two to 18 percent methacrylonitrile, and from one to ten percent vinyl acetate, by extruding a solution of said polymer in butyrolactone into a coagulating bath, and removing the precipitated fiber; the step of utilizing sodium hydroxide solution as the coagulating bath.

10. In a method of spinning fibers from polyacrylonitrile by extruding a solution of the polyacrylonitrile in butyrolactone into a coagulating bath, and recovering the precipitated fiber; the step of utilizing an aqueous solution of sodium hydroxide as the coagulating bath.

11. A method of spinning fibers of acrylonitrile polymers which comprises dissolving the acrylonitrile polymers in a lactone to form a homogeneous solution, and extruding the said solution into an aqueous alkaline solution containing dissolved therein a wetting agent.

12. A method of spinning fibers of acrylonitrile polymers which comprises dissolving the acrylonitrile polymers in a lactone to form a homogeneous solution, and extruding the said solution into an aqueous alkaline solution at a temperature in excess of 50° C.

CARROLL A. HOCHWALT.

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The following references are of record in the file of this patent:

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