

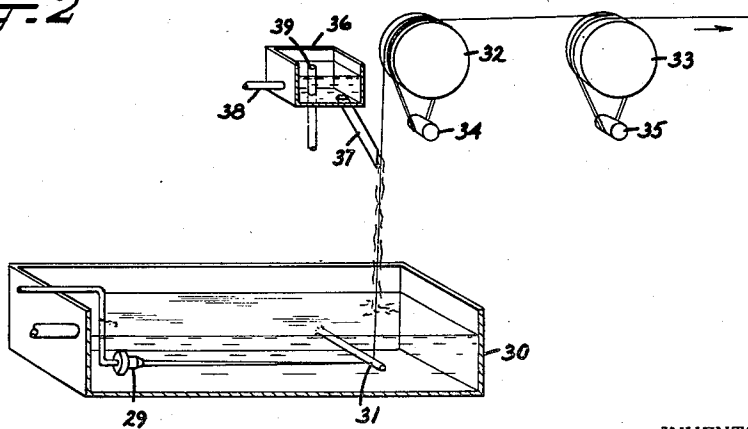
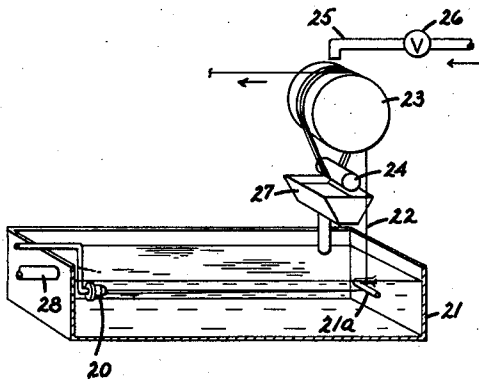
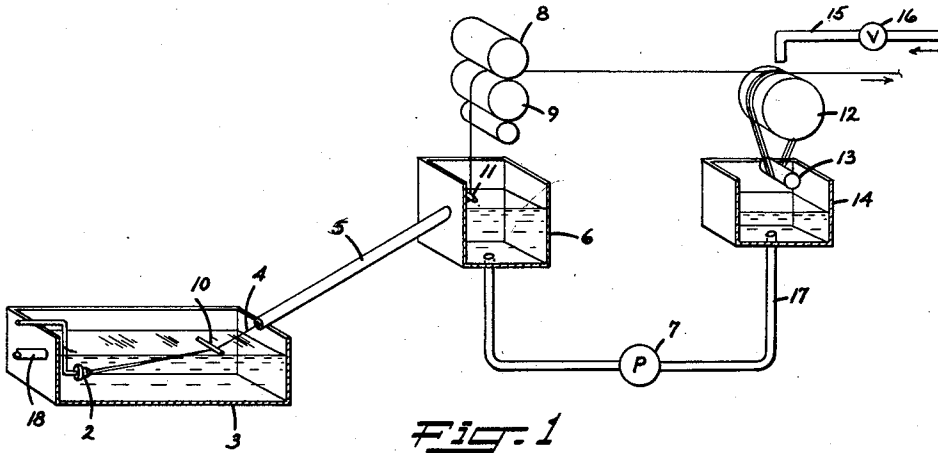
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WET SPINNING PROCESS

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WET SPINNING PROCESS

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This invention relates to improvements in the production of synthetic or artificial fibers, films, or other shaped articles by the wet-spinning or wet-forming process.

In wet-spinning or wet-forming, as conventionally practiced, a solution of the material to be shaped is extruded into a vessel containing a suitable setting liquid which is continuously or periodically withdrawn from the vessel, reconditioned, and returned to the extrusion vessel.

In making shaped articles from fiber or film-forming materials by a wet-spinning or wet-forming process in which chemical reaction is not involved, it has been found advantageous to extrude the solution into a setting medium comprising a controlled predetermined proportion of the solvent and a precipitant for the fiber-forming material which is an extractive for the extrusion solvent but chemically inert to the fiber or film-forming material. Thus, in wet-spinning fiber-forming acrylonitrile polymers, including polyacrylonitrile and certain copolymers of acrylonitrile, improved results are obtained by spinning a dimethylformamide solution of the polymer into a setting medium consisting of water and dimethylformamide in controlled predetermined proportions, as disclosed in my pending application filed November 27, 1948, Serial No. 62,413.

The present invention is concerned more particularly with wet-spinning or wet-forming processes in which a solution or dispersion of the fiber or film-forming material is extruded into a setting medium comprising the solvent and a precipitant for the fiber-forming material which precipitant extracts the solvent or dispersing agent used in the extrusion, and has as one object to automatically maintain the composition of the setting medium constant or substantially constant from the beginning to the end of the extrusion by the addition thereto of liquid obtained by washing the article with a medium comprising the precipitant.

In accordance with the invention, the solution or dispersion of fiber or film-forming material is extruded into a setting medium consisting of a predetermined proportion of the extrusion solvent or dispersing agent and a predetermined proportion of a liquid which is a precipitant for the fiber-forming material and an extractive for the extrusion solvent or dispersing agent but which is chemically inert to the fiber or film-forming material, to form the desired shaped article, the article is withdrawn from the bath and washed with the precipitant, or with a mix-

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ture of the precipitant and a minor proportion of the solvent or dispersing agent, to remove solvent or dispersing agent carried out of the bath from the fibers, and liquid from this initial washing of the article is delivered directly to the setting bath. The liquid resulting from the initial washing consists of a mixture of the extrusion solvent or dispersing agent and the precipitant, i. e., a mixture the constituents of which are the same as the constituents of the setting medium. By controlling the amount of wash liquid added to the setting bath, and the proportion of solvent or dispersing agent mixed with the precipitant in that liquid, if a mixture of the two is used for washing the article, taking into account the amount of solvent or dispersing agent introduced into the bath during the extrusion, the composition of the setting medium is automatically maintained substantially constant from the beginning to the end of the extruding operation, the composition being automatically and continuously adjusted by the introduction of the liquid from the washing step. It is unnecessary, therefore, to withdraw the bath from the vessel in which the extrusion is performed, in order to refresh it or to depend on periodic or haphazard additions to the bath for maintaining the composition constant.

By "initial washing" is meant the first washing to which the fibers are subjected after their withdrawal from the setting bath. This may also be the final washing, or the article may be subjected to one or more further washings with the precipitant if it retains residual extrusion solvent.

In some cases, extrusion solvent or dispersing agent remaining in or on the article after initial washing thereof may be removed by heating the article to volatilize the solvent or dispersing agent if the temperature of volatilization is below the temperature at which the article is damaged by heat. However, in the preferred embodiment, residual solvent or dispersing agent carried by the fibers after initial washing thereof is removed by subsequent washing and cycled for mixing with the liquid to be used in the initial washing step. The proportion of solvent or dispersing agent mixed with the precipitant in the liquid used in the initial washing step is controlled so that the solvent or dispersing agent in the liquid from the washing step plus the solvent or dispersing agent introduced in the extrusion and remaining in the setting medium after the fibers are withdrawn is sufficient to maintain the relative concentrations of solvent or dis-

persing agent and precipitant in the setting medium constant or substantially constant throughout the extrusion operation. All of the liquid from the initial washing may be added directly to the setting bath or only a controlled portion thereof may be added to the bath, depending on the amount of precipitant used to wash the fibers and the amount of precipitant and solvent required to be added to the bath to maintain the composition of the bath constant.

The method of the invention can be used for producing artificial or synthetic fibers or other shaped articles from any fiber or film-forming material which can be dissolved or dispersed and wet spun, when the shaping involves precipitation only, and the setting medium consists of a mixture of the solvent or dispersing agent for the fiber-forming material and a liquid which is a precipitant for the fiber-forming material and an extractive for the extrusion solvent or dispersing agent. Examples of suitable fiber and film-forming materials are the organic acid esters of cellulose, the fiber-forming synthetic resins, including polyamides, polyesters, fiber-forming vinyl resins, polyvinyl alcohol, and fiber-forming polymers and copolymers of acrylonitrile.

The solvent or dispersing agent selected will depend on the particular fiber or film-forming material to be spun or shaped. The precipitant which extracts the extrusion solvent or dispersing agent but which is inert to the fiber-forming or film-forming material will depend on both the fiber or film-forming material and the solvent or dispersing agent in which it is dissolved or dispersed. As examples of suitable solvents or dispersing agents may be mentioned acetone for commercial, secondary cellulose acetate and such fiber-forming vinyl resins as those resulting from the copolymerization of vinyl chloride and vinyl acetate or of vinyl chloride and acrylonitrile and containing from 40 to 55% acrylonitrile in the molecule; hot phenol or formamide for the polyamides; chloroform for the polyesters; and dimethylformamide, dimethylacetamide or dimethylpropionamide for polyacrylonitrile or acrylonitrile copolymers containing from 70 to 98% by weight of acrylonitrile in the molecule and obtained by copolymerizing acrylonitrile with one or more monoethylenically unsaturated polymerizable substances including vinyl acetate, styrene, vinyl chloride, basic vinyl monomers such as the vinyl pyridines and particularly 2-vinyl pyridine, isobutene, dimethylfumarate, methylmethacrylate, methacrylonitrile, and acrylic acid and its esters.

The solvents and dispersing agents mentioned are illustrative only and other solvents or dispersing agents may be substituted for them.

The precipitant may be any liquid which is an extractive for the extrusion solvent or dispersing agent but inert to the fiber-forming material. When water meets these essential requirements, water is the preferred precipitant for use in the setting medium and as the precipitant for use in washing the article.

A specific embodiment of the invention contemplates the production of fibers or threads from solutions or dispersions of acrylonitrile polymers, including polyacrylonitrile and copolymers containing from 70 to 98% by weight of acrylonitrile, in dimethylacetamide, by spinning the solution into a setting medium consisting of water and a controlled proportion of dimethylacetamide. In a preferred embodiment, a solution of the acrylonitrile polymer in dimethylacetamide is con-

tinuously extruded into a setting medium comprising a mixture of water and dimethylacetamide containing the dimethylacetamide in a selected proportion between 20 and 70% by volume, and the composition of the setting medium is maintained constant by washing the fibers withdrawn from the bath with water or water containing a minor proportion of dimethylacetamide, and directly adding all or a controlled amount of the liquid from the washing step into the setting bath. The conditions are selected so that the composition of the setting medium does not vary more than 2% from the predetermined volumetric proportions, and the proportion of dimethylacetamide is at least 20% by volume.

At the start of operations, under any given set of spinning conditions, the amount of liquid resulting from the washing of the fibers which must be directed into the setting bath, and the proportion of precipitant to solvent required in that liquid, to maintain the composition of the setting bath constant, can be determined by observation of the refractive index of the bath, and thereafter adjustments in the washing conditions and in the amount of wash liquid directed into the bath are generally not required, so long as the spinning conditions are not changed.

Suitable apparatus for the production of artificial or synthetic fibers or threads in accordance with the invention is illustrated in the accompanying drawing in which

Figs. 1 to 3 inclusive, are diagrammatic perspective views of various embodiments of the invention.

Referring to Fig. 1, reference numeral 2 indicates a spinneret through which a solution of the dispersion of the fiber-forming material is extruded into the setting liquid comprising a mixture of the solvent and a precipitant for the fiber-forming material, in selected proportions, contained in vessel 3. The fibers 4 are withdrawn from the bath and passed upward through tube 5 to the squeeze rolls 8, 9. The tube 5 may be of any suitable internal diameter and length and is supported in inclined relation between vessel 3 and a tank or vessel 6 with its lower end projecting into vessel 3 and its upper end communicating with vessel 6. Guides 10 and 11 are provided for guiding the filaments or yarn. Washing liquid comprising the precipitant is metered to tube 5 from vessel 6 by pump 7 and flows downward through the tube to vessel 3, countercurrently to the fibers advancing from the setting bath. Vessel 3 is provided with an overflow pipe 18 for maintaining the bath at constant level. Any liquid squeezed from the fibers between rolls 8, 9 is caught in vessel 6. The fibers are passed to a washing drum 12 on which they are wrapped, a thread displacing guide 13 being provided adjacent to the drum, and the fibers are washed on the drum with washing liquid projected against the fibers through pipe 15 provided with valve 16 and consisting of the precipitant which comprises one constituent of the setting bath, or a mixture of the precipitant and a minor proportion of the solvent. The resulting wash liquid consisting of a mixture of the precipitant and solvent is caught in the vessel 14 and cycled through pipe 17 to vessel 6. If necessary, the liquid from the washing can be diluted by addition of controlled amounts of the precipitant to vessel 14 or to vessel 6. A plurality of drums 12 and pipes 15 may be provided, the fibers being washed in successive stages whereby any residual solvent carried by the fibers after their initial

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washing in tube 5 is progressively reduced. The wash liquid obtained at these successive washing stages, and containing progressively reduced amounts of spinning solvent, may be cycled back to the previous washing stages and to vessel 6, or the liquid remaining after each washing may be cycled directly to vessel 6.

The angle of inclination of the tube with respect to vessel 3 and vessel 6, the length and diameter of the tube, and the rate at which the washing liquid is metered to the tube, as well as the concentration of solvent, if any, in the liquid used to wash the fibers, affect the efficiency of the washing. These conditions are selected so that the amount of solvent, if any, in the liquid used to wash the fibers and the amount of solvent removed from the fibers in tube 5, plus the amount of solvent which remains in the setting bath when the fibers are withdrawn after any given immersion length, is such that the relative proportions of precipitant and solvent in the setting medium are maintained substantially constant.

Referring to Fig. 2, reference numeral 20 designates a spinneret through which the solution of fiber-forming material is extruded into the setting bath contained in vessel 21 and consisting of a mixture of the solvent and a precipitant for the fiber-forming material in predetermined proportions. The fibers or threads 22 are withdrawn from the bath under guide 21a and wrapped around the drum 23 and thread displacing guide 24. Washing liquid comprising the precipitant or a mixture of the precipitant and a minor proportion of the solvent is projected against the fibers on drum 23 through pipe 25 provided with valve 26. The mixture of precipitant and solvent resulting from the washing is delivered to vessel 21 through funnel 27. The quantity of washing liquid projected against the fibers on the drum is controlled by valve 26 so that the composition of the mixture of precipitant and solvent delivered to the bath through the funnel 27 is such as to maintain the relative proportion of precipitant to solvent in the setting medium constant, taking into account the amount of solvent introduced as spinning solution and remaining in the bath after the fibers are withdrawn. Vessel 21 is provided with an overflow pipe 28 for maintaining the setting bath at constant level. A plurality of washing drums 23 and valve-controlled pipes 25 may be provided, the fibers being washed in successive stages and the mixture of precipitant and solvent or dispersing agent obtained at each washing stage being cycled to a preceding stage and ultimately to the initial washing stage.

In the embodiment illustrated in Fig. 3, the fibers formed by extruding the spinning solution through the spinneret 29 into the setting medium comprising a mixture of solvent and precipitant contained in vessel 30 are withdrawn under guide 31 and passed to the godets 32 and 33, thread-displacing guides 34 and 35 being supported adjacent to the godets. Along the path of its advance to godet 32, the filamentary bundle or yarn is washed with liquid comprising the precipitant flowing to the bath from the vessel 36 provided with the angularly disposed open-ended member or spout 37. The washing liquid is introduced to vessel 36 through conduit 38 at a rate greater than the rate at which the liquid flows from the vessel through member 37, and flows out of the vessel 36 through the overflow pipe 39 to maintain the liquid level constant.

An advantage of the present method, addi-

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tional to that of maintaining the composition of the setting bath constant by the addition thereto of liquid resulting from initial washing of the fibers, is that the spinning solvent is recovered from the setting bath, in which it is present in relatively high concentration, and does not have to be recovered from dilute mixtures obtained at later washing stages. If the fibers are subjected to one or more washings additional to the initial washing, the liquid from such washing is delivered to the initial washing stage.

In washing the fibers, the proportion of solvent, if any, admixed with the precipitant used to wash the fibers must be controlled and should not be greater than one-half the amount of solvent present in the setting medium.

The fibers may be stretched prior to, during, or after the initial washing, at temperatures which will depend on the particular fiber-forming material, and may or may not be after-stretched. For example, the freshly formed fibers of the acrylonitrile polymers may be stretched 100 to 300% at temperatures up to 100° C., or they may be stretched more than 300% at temperatures above 100° C., and such stretching may be the only stretch given the fibers, or they may be stretched up to 200 or 300% at temperatures up to 100° C., and after-stretched at temperatures above 100° C., the after-stretching being performed before or after final drying of the fibers.

In the embodiment shown in Fig. 2, drum 23 may be replaced by a thread-advancing, thread-stretching reel, so that the fibers advancing over the reel are stretched concurrently with washing thereof. In the embodiment shown in Fig. 1, the fibers may be stretched between the squeeze rolls 8, 9 and drum 12.

If the acrylonitrile polymer fibers are to be simultaneously stretched and heated to a temperature above 100° C., the godet or other stretch at a temperature up to 100° C. may be omitted, or the stretching at temperatures above 100° C. may supplement the stretch at temperatures up to 100° C. Stretching may be performed prior to initial washing of the fibers, concurrently with initial washing of the fibers, before or after drying of the washed fibers, or before or after removal of residual solvent carried by the fibers after their initial washing. In treating the acrylonitrile polymer fibers it may be preferred to reduce the residual solvent to less than 1.5% by weight prior to stretching them at temperatures above 100° C. However, the fibers can be stretched at the elevated temperatures after removal of a substantial portion of the residual solvent, or immediately after initial washing. The latter procedure may be preferred, if the filaments or yarns are destined to be reduced to discontinuous lengths. For instance, the yarns may be stretched at temperatures above 100° C. after their initial washing, and forwarded to a cutter or collected into a large multi-filament bundle such as a tow and converted directly from tow to top, the discontinuous fibers in either case being treated with a relaxing liquid, such as hot water, when water is inert to the fibers, which shrinks and curls the fibers and extracts the residual solvent.

The following examples illustrate specific embodiments of the invention.

Example I

Using the apparatus of Figure 1, filaments are formed by extruding a spinning solution comprising a homogenous mixture of dimethylacetam-

ide and 18% by weight of a copolymer containing, in the polymer molecule, 90% acrylonitrile and 10% 2-vinylpyridine by weight, through a spinneret having 44 holes each 0.004 inch in diameter, into a setting medium consisting of 67% dimethylacetamide and 33% water by volume at a temperature of 30° C. The filaments are given an immersion of 8 inches, and as the yarn is withdrawn from the bath it is washed counter-currently in tube 5 with water metered to the tube at a rate of 0.5 liter for each liter of dimethylacetamide introduced into vessel 2 as spinning solvent. The liquid from the washing step flows directly into vessel 3, whereby the composition of the setting medium is maintained substantially constant. The yarn is stretched between godets into water at 80–85° C., washed, and then dried on a revolving drum heated by steam at 20 p. s. i., and stretched as it is passed through a tube containing steam at 60 p. s. i. The yarn is twisted and permitted to shrink freely in boiling water. The yarns are dense, transparent, and do not show voids on microscopic examination. They are dyed a brilliant scarlet in a bath containing 2%, on the yarn weight, of Wool Fast Scarlet G. Conc. under usual wool-dyeing conditions.

Example II

Using the apparatus of Fig. 2, filaments are formed by extruding a spinning solution comprising a homogeneous mixture of dimethylacetamide and 18% by weight of a copolymer containing, in the polymer molecule, 90% acrylonitrile and 10% 2-vinylpyridine by weight, into a setting medium comprising 80% water and 20% dimethylacetamide, by volume, at 30° C. The filaments are given an immersion of 8 inches, and as they are withdrawn from the bath, as a yarn, they are wrapped around the drum 23 and washed with water metered from pump 25 at the rate of 4 liters for each liter of dimethylacetamide pumped into vessel 21 as spinning solvent. The yarn is stretched between godets into water at 80–85° C., washed, and dried on a revolving drum heated by steam at 20 p. s. i. Thereafter, the yarn is stretched as it is passed through a tube containing steam at 60 p. s. i. The yarns contain small voids or bubbles and are dyed to a pale pink in a bath containing 2%, on the yarn weight, of Wool Fast Scarlet G. Conc.

Since certain changes in carrying out the invention may be made without departing from its scope, it is intended that all matter contained in the foregoing description shall be interpreted as illustrative and not in a limiting sense. In the claims the terms "solvent" and "solution" are intended to include both true solvents and solutions as well as dispersing agents and dispersions or colloidal solutions or mixtures in which the fiber or film-forming material is substantially uniformly dispersed.

I claim:

1. A method of forming artificial and synthetic fibers and other shaped articles which comprises continuously extruding a solution of the material to be shaped into a setting bath comprising a mixture of the solvent and a liquid precipitant for the material, which precipitant is an extractive for the solvent, continuously withdrawing the shaped article from the setting bath to the atmosphere, continuously washing the article, as it emerges from the setting bath and above the level of the setting bath, with a stream of liquid flowing continuously and directly into the setting bath countercurrently to the article

emerging from the bath, said washing liquid consisting of the precipitant, and, at most, a minor proportion of the extrusion solvent, and continuously correlating the relative proportions of precipitant and solvent in the liquid flowing into the setting bath from the washing with the amount of solvent introduced into the bath by the solution of the material to be shaped, to thereby maintain the relative proportions of precipitant and solvent in the setting bath substantially constant from the beginning to the end of the extrusion.

2. A method as in claim 1, wherein the material to be shaped is a cellulose organic acid ester.

3. A method as in claim 1, wherein the material to be shaped is secondary cellulose acetate.

4. A method as in claim 1, wherein the material to be shaped is a synthetic resin.

5. A method as in claim 1, wherein the article is stretched simultaneously with washing thereof.

6. A method as in claim 1, wherein the material to be shaped is an acrylonitrile polymer containing, by weight in the polymer molecule, at least 70% of acrylonitrile.

7. A method as in claim 1, wherein the material to be shaped is a copolymer of acrylonitrile containing, by weight in the copolymer molecule, at least 70% of acrylonitrile.

8. A method as in claim 1, wherein the material to be shaped comprises a copolymer of acrylonitrile and a basic vinyl monomer containing, by weight in the copolymer molecule, at least 70% of acrylonitrile.

9. A method as in claim 1, wherein the material to be shaped comprises a copolymer of acrylonitrile and a vinyl pyridine containing, by weight in the copolymer molecule, at least 70% of acrylonitrile.

10. A method as in claim 1, wherein the material to be shaped comprises a copolymer of acrylonitrile and 2-vinylpyridine containing, by weight in the copolymer molecule, at least 70% of acrylonitrile.

11. A method of forming synthetic fibers and other shaped articles from an acrylonitrile polymer containing, by weight in the polymer molecule, at least 70% of acrylonitrile, which comprises continuously extruding a solution of the polymer in dimethylacetamide into a setting bath comprising a mixture of water and dimethylacetamide containing dimethylacetamide in a selected proportion between 20 and 70% by volume, continuously withdrawing the article from the setting bath to the atmosphere, continuously washing the article, as it emerges from the setting bath, and above the level of the setting bath, with a stream of water containing, at most, a minor proportion of dimethylacetamide and flowing continuously and directly into the setting bath countercurrently to the article emerging from the bath, and continuously correlating the relative proportions of water and dimethylacetamide in the liquid flowing into the bath from the washing with the amount of dimethylacetamide introduced into the bath by the polymer solution, to thereby maintain the relative proportions of water and dimethylacetamide in the setting bath substantially constant from the beginning to the end of the extrusion.

12. A method of forming synthetic fibers from an acrylonitrile polymer containing, by weight in the polymer molecule, at least 70% of acrylonitrile, which comprises continuously extruding a

solution of the polymer through a spinneret into a setting bath comprising a mixture of the solvent and a liquid precipitant for the polymer which precipitant is an extractive for the solvent, continuously withdrawing the fibers from the setting bath to a take-up device supported above the level of the setting bath, continuously washing the fibers on the take-up device with a stream of liquid consisting of the precipitant and, at most, a minor proportion of the extrusion solvent, so that the liquid flows continuously downwardly from the take-up device into the setting bath, countercurrently to the fibers advancing to the take-up device, and continuously correlating the relative proportions of precipitant and solvent in the liquid flowing into the setting bath from the washing with the amount of solvent introduced into the setting bath in the solution of the polymer, to thereby maintain the relative proportions of precipitant and solvent in the setting bath substantially constant from the beginning to the end of the extrusion.

13. A method of forming fibers from an acrylonitrile polymer containing, in the polymer molecule, at least 70% by weight of acrylonitrile, which comprises continuously extruding a solution of the polymer through a spinneret into a setting bath comprising a mixture of the solvent and a liquid precipitant for the polymer, which

precipitant is an extractive for the solvent, continuously withdrawing the fibers from the setting bath along an upwardly inclined confined path to a take-up device supported above the level of the bath, at a point beyond the bath, continuously washing the fibers advancing from the setting bath with a stream of liquid consisting of the precipitant and, at most, a minor proportion of the solvent, and flowing continuously and directly into the setting bath along the confined path and countercurrently to the fibers advancing from the bath, and continuously correlating the relative proportions of precipitant and solvent in the liquid flowing into the bath from the washing with the amount of solvent introduced into the bath with the solution of the polymer, to thereby maintain the relative proportions of precipitant and solvent in the setting bath substantially constant from the beginning to the end of the extrusion.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,236,648	Nagel et al.	Apr. 1, 1941