

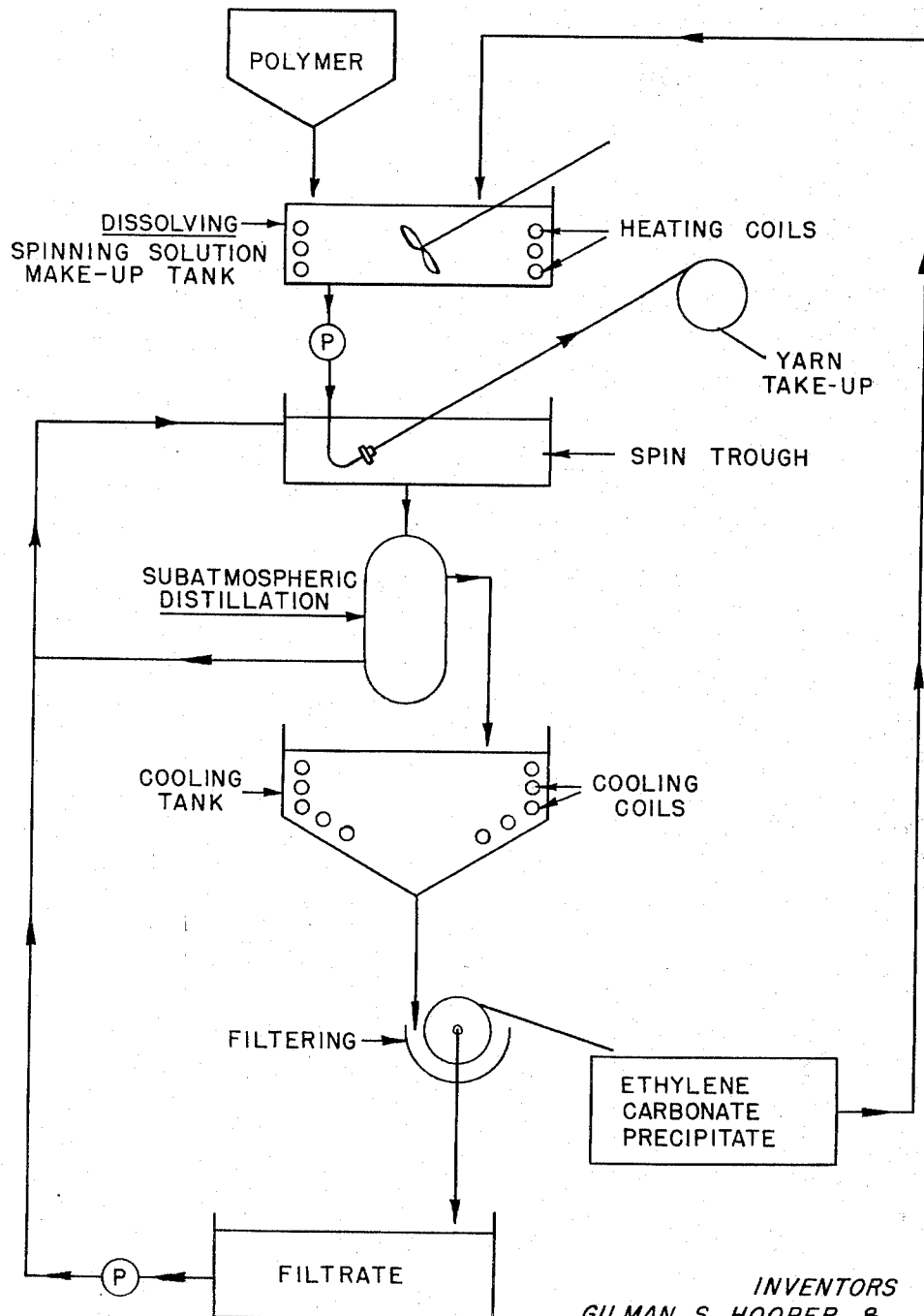
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SPINNING OF ACRYLONITRILE POLYMERS

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SPINNING OF ACRYLONITRILE POLYMERS

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This invention relates to a process for producing shaped articles such as fibers, ribbons, films, etc. by wet spinning ethylene carbonate spinning solutions of acrylonitrile polymers and copolymers. More particularly, this invention is concerned with a continuous wet-spinning process capable of being operated efficiently for prolonged periods of time without sacrificing uniformity, color or other desirable physical properties of the spun articles. More specifically, it is concerned with conducting a continuous wet-spinning process in which the ethylene carbonate solvent is continuously and efficiently recovered and re-used and the coagulating bath continuously regenerated with a minimum loss of solvent and coagulant materials.

In the wet spinning of ethylene carbonate spinning solutions of acrylonitrile polymers, there is a continuous accumulation of ethylene carbonate dissolved in the coagulating bath which, if excessive, will adversely affect not only the continuity of the spinning process but also will affect the character of the spun articles, hereinafter referred to sometimes as fibers. It is found necessary, therefore, either to continuously discard portions of the bath while continuously replenishing fresh coagulant, or, preferably, to remove and recover for re-use the excess quantities of ethylene carbonate from the used bath liquid and return the reclaimed coagulant to the coagulating bath.

With regard to the latter method of spin-bath regeneration, it has been found that fractional distillation of spin bath liquid containing ethylene carbonate cannot be accomplished completely satisfactorily in most cases even under vacuum because of one or more of the following reasons: (a) excessive decomposition of the ethylene carbonate by alcoholysis, resinification, etc. takes place during prolonged fractional distillation which substantially decreases the yield of the recovered ethylene carbonate, (b) the decomposition products which are carried over into the operating bath promote the discoloration of freshly coagulated products, particularly filamentary material, (c) such decomposition products in the bath promote further decomposition of the ethylene carbonate by alcoholysis, etc. during extrusion and coagulation in the bath.

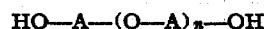
Thus, for example, if a used spinning bath liquid containing about 15% by weight ethylene carbonate and about 85% by weight glycerol is distilled in vacuum at 5–10 m. m. of mercury to fractionate out the ethylene carbonate, very little of the ethylene carbonate distills over. Instead,

an almost complete alcoholysis and breakdown takes place leading to the formation of ethylene glycol and glycidol. Losses of a similar nature but to lesser extent are experienced when fractionating ethylene carbonate from baths consisting of alkylene glycols or polyalkylene glycols such as, for example, 2-methyl-pentanediol-2,4 diethylene glycol, triethylene glycol, tetraethylene glycol, tripropylene glycol, etc.

By the process of the present invention, not only are the above difficulties in the wet spinning of ethylene carbonate solutions of acrylonitrile polymers substantially eliminated, but an efficient, continuous spinning process is provided by which fibers having desirable properties and appearance are produced with facility and efficiency.

The accompanying drawing is a schematic representation of the process conducted in accordance with the invention.

In accordance with the present invention, a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as the solvent for such polymer is wet-spun by the following process: The ethylene carbonate spinning solution is extruded into a liquid coagulating bath medium comprising ethylene carbonate and a water-soluble polyalkylene glycol having the formula

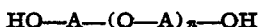


wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, or mixtures of such ether glycols. At least a portion of the used bath liquid is removed and subjected to a partial, relatively rapid distillation at a sub-atmospheric pressure without substantially any refluxing thereof thereby increasing the concentration of ethylene carbonate in the distillate. At least a portion of the distillate is cooled to precipitate the ethylene carbonate therefrom and the precipitated ethylene carbonate thereafter separated from the cooled liquid. The resulting treated liquid from which ethylene carbonate has been removed, together with the undistilled portion remaining after the partial distillation, is recycled in controlled quantities to the operating coagulating bath to regenerate the same as desired and the wet-spinning cycle repeated. Advantageously, the removed precipitate is also recycled for re-use in preparing additional polymeric spinning solutions. In general, a sufficient quantity of used bath liquid is removed for partial distillation and treatment, and a sufficient quan-

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tity of the resulting treated liquid is returned to the bath so as to maintain the operating bath at the desired ethylene carbonate concentration. Advantageously, the concentration of ethylene carbonate in the coagulating bath is maintained between about 10% and 30% by weight.

The liquid coagulating medium employed in accordance with the present invention as indicated above comprises ethylene carbonate and a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, or mixtures of such ether glycols. Particular advantages are, however, derived with the tri- and tetra-alkylene glycols. Of the above polyalkylene glycols, particularly suitable and especially advantageous are triethylene glycol, tripropylene glycol, tetraethylene glycol, and tetrapropylene glycol.

Advantageously, the coagulating medium employed should contain, exclusive of the ethylene carbonate therein, a major proportion by weight of the polyalkylene glycol compounds. Thus, the coagulating medium may contain minor quantities of other materials or impurities dissolved or suspended therein such as, for example, minor amounts of water, e. g., water due to the hygroscopicity of the polyalkylene glycols or materials present in technical grades of the coagulants desired. In general, the less the amount of such other materials in the coagulating medium, the more beneficial and advantageous are the results. Thus, particularly advantageous results are derived when the coagulating medium, exclusive of the ethylene carbonate therein, contains at least about 70% by weight of the polyalkylene glycol compound, and preferably when it consists essentially of the polyalkylene glycol compound. In general, dissolved liquid materials in the bath, other than the ethylene carbonate and the polyalkylene glycol compounds, may be tolerated in amounts up to about 20% and 25% by weight of the polyalkylene glycol coagulant without undue adverse effect upon the spinning process. In this respect, it is noteworthy that the amount of such extraneous materials in an operating coagulating bath usually will diminish after several cycles of recovery and purification of the coagulant as hereinafter described with the result that the coagulating bath liquid will usually improve in efficiency with use.

As previously stated, the portion of the used bath liquid removed for treatment is subjected to a partial, relatively rapid distillation at a sub-atmospheric pressure without substantially any refluxing thereof, i. e. without the use of any plates, packing, etc. for treating the vapors formed. By this step an increase in the concentration of ethylene carbonate in the distillate is achieved while minimizing alcoholysis losses and the formation of deleterious impurities. By a distillation of this type only part of the originally charged liquid is vaporized and condensed. The liquid is heated quickly to its boiling point and maintained at such temperature for only a brief period of time sufficient to vaporize only a portion thereof in the order of about 15% to 50%. The vapors thus formed are condensed quickly to produce, without substantially any refluxing, a single distillate which has a higher concentration of the lower boiling components, e. g. ethylene carbonate, than that of the undistilled

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portion. This type of distillation may be accomplished by what is generally referred to as flash distillation or stripping. Specifically, it usually involves piping a continuous flow of liquid past a "reducing" valve into a chamber maintained at a subatmospheric pressure, the liquid being heated to the desired temperature just prior to the "reducing" valve. The sudden drop in pressure causes a sudden "flash" distillation accompanied by a sudden drop in temperature of the undistilled liquid portion. The amount of vapor formed and condensed depends, among other things, upon the amount of heat present in the vaporizing chamber, i. e., the temperature of the liquid introduced and any heat independently supplied to the chamber. In this type of distillation, any relatively high volatile liquids, e. g. water, etc., present in the liquid undergoing distillation would pass on through the system and advantageously, would not be condensed and collected at the condensation temperatures normally employed. For example, a used bath liquid containing 20% ethylene carbonate having a boiling point of 238° C. and 80% of the applicants' polyalkylene glycols having high boiling points, when flash distilled would produce a distillate containing an increased ethylene carbonate concentration such as, for example, about 40% or 50% ethylene carbonate and above, and an undistilled portion containing an increased polyalkylene glycol concentration such as, for example, about 90% or above depending upon the particular spin bath employed. The latter undistilled portion, low in ethylene carbonate, is returned to the operating bath directly or, if desired, returned after further purification as hereinafter described. The flash distillation should be carried out at a subatmospheric pressure, for example, pressures between about 5 m. m. and 30 m. m., and at relatively low temperatures, for example, between about 100° and 140° C.

The distillate obtained in this manner is then cooled to precipitate ethylene carbonate therefrom. This precipitation is accomplished by cooling to a temperature below that at which the ethylene carbonate precipitates therefrom but above the congealing point of the polyalkylene glycol therein. Advantageously, the liquid portion may be cooled to a temperature between about 10° C. and -20° C. Since the polyalkylene glycols of this invention are very easily supercooled below their congealing temperatures, unusually low crystallization or precipitation temperatures may be employed if desired. In general, greater economies and efficiencies are effected when the upper range of precipitation temperatures, e. g., between about 5° C. and -5° C., are employed providing, of course, that satisfactory yields of precipitate are obtained. Where, however, higher yields of ethylene carbonate precipitate are desired, the lower range of cooling temperatures may be employed providing, however, that the polyalkylene glycol is not too viscous or does not congeal under the particular conditions at such lower temperatures.

The ethylene carbonate which is precipitated from the liquid portion is removed from its associated liquid by any convenient method such as, for example, by filtering or, as has been discovered, with greater advantage by centrifuging the resulting slurry to extract most of the liquid from the ethylene carbonate solids. Advantageously, the extraction of the solids may be carried out so that the solids contain less than about 15% by

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weight of the adherent liquid bath, particular advantages being derived, however, at less than about 10% and especially at less than about 5%. This may be accomplished with advantage by centrifuging the slurry sharply under a centrifugal force of more than about $200\times G$ with a cake thickness on the wall of the centrifuge between about one-fourth inch and four inches. By the expression $200\times G$ is meant 200 times the force of gravity or 200 times the force required to accelerate a body about 980 cm./sec./sec. Especial advantages, however, are derived when the centrifuging is carried out under a centrifugal force between about $500\times G$ and $2000\times G$ with a cake thickness between about one-half inch and three inches. The centrifuging time under these conditions may range between about 30 seconds and 20 minutes depending upon the size of the ethylene carbonate crystals and upon the type of filter screen employed in the centrifuge.

The separated and extracted ethylene carbonate precipitate may be reused directly to prepare additional quantities of the polymer spinning solution, or if desired, the precipitate may be additionally purified such as, for example, by one or more of the following steps: (a) washing with cold carbon tetrachloride or more advantageously with ice water, (b) recrystallization from ice water, (c) distillation under reduced pressure, or (d) treatment with decolorizing carbon. Thus, particular advantages are derived, for example, when the precipitate obtained by centrifuging the slurry is rinsed briefly with a small amount of ice water at between about 0° and 5° C. and the residual water in the precipitate flash distilled off. Even greater advantages are derived in the way of purity and color when the precipitate is distilled under vacuum prior to recycling the same for re-use in the preparation of additional polymeric spinning solution.

As previously stated, both the treated liquid above which remains behind after the removal of the ethylene carbonate precipitate from the slurry and also the undistilled liquid remaining from the flash distillation, are recycled to the operating coagulating bath in controlled quantities sufficient to maintain the operating bath at the desired concentration, e. g. an ethylene carbonate concentration between about 10% and 30% by weight. If desired, such reclaimed liquids to be recycled may, with advantage, be filtered prior to their reintroduction into the operating bath. Since a bath which is recycled and re-used repeatedly in accordance with the present process tends to discolor eventually and since impurities tend to form and accumulate therein during spinning, it is found advantageous to further treat part or all of such reclaimed liquids at intervals to remove such impurities. Thus, for example, a portion of each of such liquids may be by-passed and heated occasionally in the presence of small quantities of decolorizing carbon for about 5 to 30 minutes at 60° to 100° C. and the resulting decolorized liquids then returned to the operating bath. In addition, or in the alternative, such reclaimed liquids may occasionally be distilled under vacuum to remove solid impurities and both low and high boiling impurities accumulated therein after repeated use.

This invention will be more fully described by the following examples, although it is understood that the invention is not intended to be limited by these examples. In these examples "parts" and "percent" of materials is intended to mean parts and percent by weight.

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Example I

20 parts of polyacrylonitrile (average molecular weight about 42,000) is dissolved in 80 parts ethylene carbonate. This solution after filtering and deaerating under vacuum, is heated to 120° C. and extruded through a spinneret having 40 holes (.003 inch diameter) into a coagulating bath consisting of 80 parts triethylene glycol and 20 parts ethylene carbonate. The bath temperature is maintained at 130° C. while the coagulated filaments are drawn through the bath for 30 inches of bath travel and then collected on bobbins rotating at a peripheral speed of about 44 meters per minute. The yarn is then washed, stretched and relaxed to produce a final product which is very light colored and of uniform quality having a soft, silky feel, a denier of about 94, and a breaking tenacity of about 4.4 grams per denier and a breaking elongation of about 18%.

500 grams of bath liquid is removed from the operating bath and is subjected to a flash distillation under a pressure of about 13 m. m. while maintaining a vapor temperature between about 115° and 130° C. so as to collect a distillate comprising about 20% of the original charge. The collected distillate contains about 54% ethylene carbonate and the undistilled liquid remaining behind contains about 11% ethylene carbonate. The distilled portion is then cooled to and maintained for about two hours at 0° C. to assure sufficient precipitation (crystallization) of the ethylene carbonate. The resulting slurry is then centrifuged for 15 minutes in a perforated cylindrical basket about 5 inches in diameter and about 2 1/2 inches in height. The interior of the perforated basket is lined with a metal cloth having a 55×60 mesh twill weave. The basket is spun at about 3000 R. P. M. ($640\times G$) [$CF=0.0000142(\text{dia})^2$ (R. P. M.)², where the diameter is the diameter of the basket in inches and CF is the centrifugal force in G's; $CF=0.0000142(5 \times 3000)^2$]. The thickness of the caked precipitate is about 3/4 inch. The yield of the recovered ethylene carbonate is approximately 60% and has a purity of about 90%. The recovered ethylene carbonate is used to dissolve additional quantities of the polymer to form more spinning solution. The above filtrate, together with the undistilled liquid from the flash distillation, is returned to the bath in controlled quantities to maintain the operating bath at the above operating concentration, and the cycle is then repeated.

Example II.

The procedure of this example is the same as Example I except for the following: The operating coagulating bath consists of 78 parts triethylene glycol and 22 parts ethylene carbonate. The distillate collected from the flash distillation comprising about 20% of the original charge and containing about 60% ethylene carbonate is cooled to and maintained at 9° C. The resulting slurry is centrifuged for 15 minutes with the perforated basket spinning at about 3600 R. P. M. ($920\times G$) while employing a cake thickness of about one inch. The yield of the recovered ethylene carbonate is about 50% and has a purity of about 91%.

Example III

The procedure of this example is the same as Example I except for the following: The operating coagulating bath consists of 82 parts triethylene glycol and 18 parts ethylene carbonate. The distillate collected from the flash distillation

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comprising about 15% of of the original charge and containing about 50% ethylene carbonate is cooled to -5°C . The resulting slurry is centrifuged for 10 minutes with the basket spinning at about 3600 R. P. M. (920×G) while employing a cake thickness of about $\frac{3}{8}$ inch. The yield of the recovered ethylene carbonate is about 60% and has a purity of about 92%.

Example IV

The purity of the recovered ethylene carbonate of Examples I, II and III is improved by rinsing the resulting cake in the rotating basket with water at between about 0° and 5°C . After centrifuging for an additional period to allow for the removal of most of the water, the cake is removed from the centrifuge and the residual water removed from the cake by a flash distillation operation at about 60 m. m. pressure and at about 45°C . The purity of the resulting carbonate is about 95%.

Example V

The recovered ethylene carbonate from Examples I, II and III after the purification of Example IV is decolorized by heating to about 80°C ., adding to the resulting solution about 0.5% of decolorizing carbon (activated charcoal) and stirring for about 15 minutes. The charcoal is then filtered from the heated solution and the decolorized solution is returned for use in preparing the spinning solution. Both the filtrates and the undistilled liquids remaining from the flash distillations of Examples I, II and III are also decolorized by adding about 1% by weight decolorizing carbon to the liquid maintained at about 90°C . and stirring for about 5 minutes. The resulting carbon slurry is filtered and the filtrate is returned to the operating coagulating bath.

Example VI

The procedure of this example is the same as Example I except for the following: The portion of the operating bath removed for the recovery treatment is decolorized prior to the flash distillation step by adding to the hot liquid about 1% decolorizing carbon and stirring for about 10 minutes. The carbon is removed by filtering and the bath portion is then cooled to permit precipitation of the ethylene carbonate therefrom.

Example VII

The procedure of this example is the same as Example I except for the following: About 45 pounds of the operating bath liquid is removed, flash distilled and the collected distillate weighing about 9 pounds and containing about 55% ethylene carbonate is then cooled to 0°C . The resulting slurry is then transferred to a centrifuge similar to but larger than that of Example I and having a basket about 12 inches in diameter and about 5 inches in height. The transfer of the slurry is performed in about 2 minutes while the basket is rotated at about 1300 R. P. M. forming a cake in the basket having a thickness of about $1\frac{1}{4}$ inches. The speed of the basket is then increased to about 2750 R. P. M. (1200×G) and maintained at this speed for about one minute. The resulting filtrate is set aside for purification prior to recycling the same to the spin bath. Thereafter, the rotating cake is rinsed with about one pound of water at between 0° and 5°C ., the rinsing step being performed in about one minute. The increased speed is then con-

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tinued for another 4 minutes. The centrifuge cake is then removed and residual water flash distilled therefrom at a temperature of 45°C . at 60 m. m. pressure. Thereafter, the ethylene carbonate is distilled at 10 m. m. pressure and collected at between 110° and 125°C . The resulting distilled ethylene carbonate is a colorless product and has a purity of about 97%. This material is then used to dissolve additional quantities of polyacrylonitrile polymer to form the polymeric spinning solution employed. The filtrate obtained from the centrifuging of the cooled slurry, together with the undistilled bath liquid remaining after the flash distillation step, is heated to and maintained at 80°C . for about 15 minutes while stirring and admixing about 0.5% by weight of decolorizing carbon. The resulting mixture is then filtered to remove the carbon and the filtered liquid returned in controlled quantities to the operating bath.

Example VIII

The procedure of this example is the same as Example I except for the following: The coagulating bath consists of 77 parts tetraethylene glycol and 23 parts ethylene carbonate. A 200 gram portion of the operating bath is flash distilled at 13 m. m. pressure while maintaining a vapor temperature between about 115° and 130°C . and the distillate collected containing about 65% ethylene carbonate is then cooled to and maintained at -10°C . for about one hour. The resulting slurry is then centrifuged for 15 minutes. The yield of the recovered ethylene carbonate is approximately 65% and has a purity of about 90%.

Example IX

The procedure of this example is the same as Example I except for the following: The coagulating bath consists of 80 parts tripropylene glycol and 20 parts ethylene carbonate. A 200 gram portion of the operating bath is flash distilled at 13 m. m. pressure while maintaining a vapor temperature between about 115° and 130°C . and the distillate collected containing about 65% ethylene carbonate is then cooled to and maintained at -10°C . for about one hour. The resulting slurry is then centrifuged for 15 minutes. The yield of the recovered ethylene carbonate is about 70% and has a purity of about 91%.

Example X

The procedure of this example is the same as Example I except for the following: The coagulating bath consists of 85 parts of a technical grade of triethylene glycol and 15 parts ethylene carbonate. The bath portion is flash distilled at 10 m. m. pressure while maintaining a vapor temperature between about 110° and 125°C . and the distillate collected containing about 45% ethylene carbonate is cooled. The yield of the recovered ethylene carbonate is about 50% and has a purity of about 91%. The coagulant component in the operating bath, exclusive of the ethylene carbonate, consists of approximately 94% triethylene glycol, 3% tripropylene glycol, 1% tetraethylene glycol and 2% ethylene glycol.

Example XI

The procedure of this example is the same as Example I except for the following: The coagulating bath consists of 78 parts of a mixture of polyalkylene glycols and 22 parts ethylene carbonate. The mixture of polyalkylene glycols con-

tains approximately 75% triethylene glycol, 10% tetraethylene glycol and 15% tripropylene glycol. The bath portion is flash distilled at 10 m. m. pressure while maintaining a vapor temperature between about 110° and 125° C. and the distillate collected containing about 40% ethylene carbonate is then cooled. The yield of the recovered ethylene carbonate is about 60% and has a purity of about 90%.

Example XII

The procedure of this example is the same as Example I except that the polymer contains 95% acrylonitrile and 5% 2-vinylpyridine.

Under certain operating conditions it may be desirable and advantageous to modify or treat the used bath liquid in various ways prior to the cooling and crystallization step of the present process. Thus, for example, in order to enhance the purity and color of both the recovered ethylene carbonate and the reclaimed bath liquid, the used bath liquid removed from the operating spin bath may be either decolorized or filtered or both as in Example VI prior to the crystallization step.

Among the polymers and copolymers containing at least 80% acrylonitrile which may be employed in accordance with the process of this invention may be mentioned polyacrylonitrile and copolymers of acrylonitrile with the following monomeric compounds: vinyl esters (vinyl acetate, vinyl formate, vinyl benzoate), vinyl ethers, and vinyl ketones; acrylic acid and its esters and amides; methacrylic acid and its esters, amides, and nitrile; maleic, itaconic, fumaric, crotonic acids and their esters, amides and nitriles; allyl alcohol and its esters; styrene and nuclear substituted styrenes, e. g. chloro- and dichloro styrene; halogenated mononethylenic compounds such as vinyl chloride, vinyl fluoride, and vinylidene chloride; N-vinyl compounds such as N-vinyl pyrrolidone, N-vinyl succinimide, N-vinyl carbazole, 2- and 4-vinylpyridine; and the like.

For various purposes it may be desirable to chemically and physically modify the polymeric compositions of this invention by the presence of other materials such as, for example, pigments, dyes, plasticizers, color stabilizers, spinning agents, etc.

The acrylonitrile polymers and copolymers may be prepared by any suitable polymerization method such as, for example, the ammonium persulfate catalyzed polymerization of monomer or monomers dissolved or dispersed in water. Molecular weights of these polymers and copolymers are preferably within the range of 10,000 and 250,000, or even higher, although polymers having molecular weights between 30,000 and 150,000 may be used with particular advantage in the production of fibers.

In general, the spinning solutions may be prepared by heating a mixture of the finely divided acrylonitrile polymer or copolymer with the ethylene carbonate solvent until the polymer is dissolved. Advantageously, the spinning solution may be maintained, prior to extrusion, at temperatures between about 60° and 150° C., and preferably between about 80° and 120° C. These spinning solutions, preferably, should have a solids content between about 15% and 30% solids depending upon the molecular weight of the polymer, and preferably between about 18% and 25%.

In general, in the preparation of spinning solutions with recovered and recycled ethylene

carbonate according to the present process, it is advantageous to employ the ethylene carbonates of higher purity with the more difficultly soluble polymers and copolymers. Thus, when employing polyacrylonitrile or copolymers containing more than 95% acrylonitrile, it is preferable that the recycled ethylene carbonate contain less than about 10% by weight of the coagulating liquid and with especial advantage less than about 5%. On the other hand, with copolymers containing between about 80% and 90% acrylonitrile, the lower purity carbonates, for example, those containing between about 10% and 15% of the coagulating liquid, can be used with similar success.

The freshly coagulated materials withdrawn from the coagulating bath of the present process may be washed with an aqueous media such as water, and then stretched up to 600-1000 percent or more. The stretching may be accomplished in secondary baths containing materials similar to those suitable for use in the coagulating baths of this invention, or if desired, in other heated media such as, for example, inert liquids, vapors or gases, e. g. steam. The stretched products may be heat treated while in a relaxed condition at temperatures between about 100° and 180° C. to improve their physical properties.

We claim:

1. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium comprising ethylene carbonate and a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature below that at which the ethylene carbonate precipitates therefrom but above the congealing point of the polyalkylene glycol compound; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; separating the precipitated ethylene carbonate from the cooled liquid; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; and repeating the cycle.

2. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate therein, contains a major proportion by weight of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature below that at which the ethylene carbonate precipitates therefrom but above the congealing point of the polyalkylene glycol compound; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; separating the precipitated ethylene carbonate from the cooled liquid; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

3. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate therein, contains at least about 70% by weight of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature below that at which the ethylene carbonate precipitates therefrom but above the congealing point of the polyalkylene glycol compound; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; separating the precipitated ethylene carbonate from the cooled liquid; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

4. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate therein, consists essentially of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures

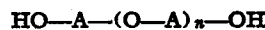
thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature below that at which the ethylene carbonate precipitates therefrom but above the congealing point of the polyhydric compound; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the cooled liquid from said precipitated ethylene carbonate until less than about 15% by weight of said liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

5. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; separating the precipitated ethylene carbonate from the cooled liquid; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

6. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene

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carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the coagulating liquid from said separated precipitated ethylene carbonate until less than about 10% by weight of said coagulating liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

7. A process according to claim 6 in which the polyalkylene glycol is a mixture of said polyalkylene glycols, triethylene glycol being present in a major proportion of said mixture.

8. A process according to claim 6 in which the polyalkylene glycol is a mixture of said polyalkylene glycols, tetraethylene glycol being present in a major proportion of said mixture.

9. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, contains at least about 70% by weight of triethylene glycol, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the coagulating liquid from said separated precipitated ethylene carbonate until less than about 10% by weight of said coagulating liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

10. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, contains at least about 70% by weight of tetraethylene glycol, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cool-

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ing at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the coagulating liquid from said separated precipitated ethylene carbonate until less than about 10% by weight of said coagulating liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

11. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer; the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, contains at least about 70% by weight of tripropylene glycol, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the coagulating liquid from said separated precipitated ethylene carbonate until less than about 10% by weight of said coagulating liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

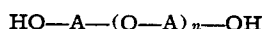
12. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, contains at least about 70% by weight of tetraethylene glycol, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the coagulating liquid from said separated precipitated ethylene carbonate until less than about 10% by weight of said coagulating liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated

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ethylene carbonate to form said spinning solution; and repeating the cycle.

13. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of triethylene glycol, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the coagulating liquid from said separated precipitated ethylene carbonate until less than about 10% by weight of said coagulating liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

14. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of a water-soluble polyalkylene glycol having the formula

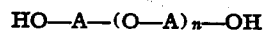


wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; extracting the coagulating liquid from said separated precipitated ethylene carbonate until less than about 5% by weight of said coagulating liquid remains in said precipitate; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said partial distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

15. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for

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said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of said distilled liquid to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; centrifuging the resulting mixture until the precipitate contains less than about 10% by weight of said cooled liquid; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said rapid distillation; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

16. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; centrifuging the resulting mixture under a centrifugal force above about 200×G; maintaining the precipitate in said centrifuge at a thickness between about one-fourth inch and four inches; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said rapid distillation; said liquids being returned in a quantity sufficient to maintain the concentration of ethylene carbonate therein between about 10% and 30% by weight; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

17. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile

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and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of triethylene glycol, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a sub-atmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquids; centrifuging the resulting mixture under a centrifugal force above about 200×G; maintaining the precipitate in said centrifuge at a thickness between about one-fourth inch and four inches; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said rapid distillation, said liquids being returned in a quantity sufficient to maintain the concentration of ethylene carbonate therein between about 10% and 30% by weight; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

18. A process according to claim 16 in which the polyalkylene glycol is a mixture of said polyalkylene glycols, triethylene glycol being present in a major proportion of said mixture.

19. In the process of producing shaped articles from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least 80% by weight of acrylonitrile and ethylene carbonate as a solvent for said polymer, the steps comprising, extruding said spinning solution into a liquid coagulating medium which, exclusive of the ethylene carbonate, consists essentially of a water-soluble polyalkylene glycol having the formula



wherein A is an alkylene group having not less than two nor more than three carbon atoms and n is an integer greater than one, and mixtures

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thereof, said coagulating medium containing between about 10% and 30% by weight of ethylene carbonate; removing at least a portion of said liquid coagulating medium; subjecting said removed portion to a partial, relatively rapid distillation at a subatmospheric pressure without substantially any refluxing thereof; cooling at least a portion of the resulting distillate to a temperature between about 10° C. and -20° C.; precipitating at least a portion of the ethylene carbonate present in said cooled liquid; centrifuging the resulting mixture under a centrifugal force between about 500×G and 2000×G; maintaining the precipitate in said centrifuge at a thickness between about one-half inch and three inches; returning to said coagulating medium at least a portion of the liquid resulting from said separation and at least a portion of the undistilled liquid remaining from said rapid distillation, said liquids being returned in a quantity sufficient to maintain the concentration of ethylene carbonate therein between about 10% and 30% by weight; rinsing said precipitate with water below about 10° C. while said precipitate is being centrifuged; dissolving additional quantities of said polymeric material with said separated ethylene carbonate to form said spinning solution; and repeating the cycle.

20. A process according to claim 19 in which the polyalkylene glycol is a mixture of said polyalkylene glycol, triethylene glycol being present in a major proportion of said mixture; and said water-rinsed ethylene carbonate precipitate being distilled under vacuum prior to dissolving additional quantities of the polymer therewith.

21. A process according to claim 20 in which said filtrate, prior its return to the coagulating medium, is treated with activated carbon.

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

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