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NOVEL COAGULATION PROCESS

Richard D. Borie, Jr., Durham, and Arthur W. Lockwood, Jr., Raleigh, N.C., assignors to Monsanto Company, a corporation of Delaware
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ABSTRACT OF THE DISCLOSURE

High density acrylic fibers have been formed from polymer solutions of dimethylacetamide, dimethylformamide and dimethylsulfoxide which were spun into coagulants composed of branched chain alkanols having 4 to 5 carbon atoms.

This invention relates to a novel process. More particularly, the invention relates to a novel method for forming filaments of polymers of acrylonitrile by coagulation of a filamentary polymer solution in certain organic solutions.

In the art of forming textile filaments from acrylonitrile polymers and polymer blends it has been recognized that the particular solvent employed to prepare the polymer in solution for extrusion and the particular coagulant system employed for coagulation of the extruded filamentary polymer solution are important factors. The most widely employed systems for industrial filament manufacture involve extrusion of a polymer dissolved in a solvent, such as dimethylacetamide, dimethylformamide, ethylene carbonate, and aqueous solution of sodium thiocyanate or the like, into a coagulation bath comprising water diluted with the same solvent used to dissolve the polymer. While these systems have been found effective, there is a need in the art for solvent-coagulation systems which can be used to improve the property balance of the filaments so produced. It has been recognized in the art that the solvent-coagulant systems above mentioned provide a rather porous filament. Moreover, it is now known that porosity, evidenced by void formation at the surface of and within the filamentary structure, decreases filament density. Studies indicate that there is a definite correlation between filament density and desirable fiber properties and that increased filament density is accompanied by a better property balance. Thus, solvent-coagulation systems are needed which provide filaments having a more dense structure and which, therefore, enhance one or more other filament properties, e.g., color, extensibility, dyeability, and abrasion resistance.

It is, therefore, an object of this invention to provide improved solvent-coagulant systems for the manufacture of filaments from polymers and polymer blends of acrylonitrile.

It is a further object of this invention to provide improved solvent-coagulation systems which provide dense filamentary acrylonitrile polymer structure having improved tensile properties without adversely affecting the desirable overall property balance of the filaments.

These and other objects are accomplished by extrusion of fiber-forming acrylonitrile polymers dissolved in a solvent selected from the group consisting of dimethylacetamide, dimethylformamide and dimethylsulfoxide into an essentially non-aqueous coagulation bath comprising a branched chain monohydric alcohol having from 4 to 5 carbon atoms. The effectiveness of this invention requires the combination of one of the several solvents mentioned with one or more of the limited class of alcohols named.

While higher molecular weight branch chained alkanols serve as useful coagulants according to the techniques as

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described herein, they lack the desirable water solubility consistent with ease of coagulant removal by conventional means in later processing steps.

The coagulation bath must contain at least forty percent by weight of alcohol and may contain up to sixty percent by weight of the solvent in which the extruded polymer is dissolved. It is known that coagulation operates under the general principle that the polymer is coagulated upon removal of the polymer solvent by the coagulant, the coagulant being a non-solvent for the polymer and a solvent for the polymer solvent. Thus, where a polymer dope comprising polymer and solvent is continuously extruded into a bath containing 100 percent of an alcohol coagulant of this invention, solvent concentration in the bath increases as the polymer component of the dope is continuously coagulated and withdrawn as filament. In the practice of this invention it has been found that polymer solvent in the coagulation bath is well tolerated up to the point where it constitutes about sixty percent by weight of the coagulation bath. Concentrations above this point render spinning rates too slow and result in filament property degradation. To avoid overly high concentrations of the polymer solvent in the coagulation bath fresh or recycled alcohol is continuously added to the bath while portions of the alcohol-solvent solution are continuously removed to an appropriate recovery system. The filament properties have not been found to be greatly altered by the polymer solvent concentration in the coagulation bath as long as the polymer solvent does not exceed sixty percent by weight of the solution. However, it has been noted that the cross-sectional shape of the fibers coagulated by the process of this invention tend to be altered by changing the polymer solvent-alcohol ratio in the coagulation bath. For practical reasons, it has been found most desirable to maintain the level of polymer solvent in the bath at between 10-30 percent by weight.

Another important limitation of the invention is that the coagulation bath must be maintained essentially non-aqueous. Studies indicate that the filamentary structure associated with this invention is very markedly deteriorated where the concentrations of water reach 10 percent by weight and above. Desirably, the system should be anhydrous. However, minor concentrations of water in the bath are well tolerated and in large scale operations the added expense of maintaining anhydrous conditions is not justified. Thus, the term non-aqueous as employed herein is not intended to preclude the presence of water in minor amounts. The water level is normally kept below five percent by weight and offers no problem in the operation of this invention.

It has been found that the benefits derived by use of alkanol coagulation as described herein are dependent on the nature of the solvent employed to prepare the polymer dope because alkanol coagulation using dopes prepared with polymer solvents such as ethylene carbonate and solutions of sodium thiocyanate, do not provide the dense filamentary structure or the spinability provided where dimethylacetamide, for example is used as the polymer solvent.

The methods by which polymer solutions or dopes are prepared and extruded in the practice of this invention are well known in the art. Spinning dopes for acrylonitrile polymers and polymer blends normally comprise from about 10 to about 30 percent by weight of polymer solids dissolved in the solvent. The spinning solutions employed in the practice of this invention may also contain minor amounts of additives such as titanium dioxide, antimony trioxide or other additives commonly incorporated into the polymer solution. The optimum concentration of polymer will, as is known, depend on the particular polymer, the solvent and the temperature at which a given system is extruded. Normally, such solutions are main-

tained and extruded at temperatures in the range of from about 20 to 150° C.

The coagulation step of this invention is preferably accomplished by wet spinning techniques wherein the spinnerette is placed beneath the surface of the coagulation bath and the polymer dope is spun directly into the coagulation bath. Spinning may also be accomplished by dry jet-wet spinning wherein the face of the spinnerette is positioned a short distance above the surface of the coagulant bath and the polymer dope is extruded into air before reaching the coagulant bath, or by mist spinning wherein the polymer dope is extruded through a coagulant mist, spray or fog of alcohol into the alcohol coagulant bath from the face of a spinnerette positioned a short distance above the surface of the coagulant bath. The wet spinning technique is generally preferred because it provides greater filament uniformity and requires fewer controls and maintenance.

The coagulant bath of this invention may be maintained at temperatures of from above 25° C. up to the boiling point of the particular alcohol employed in the bath. The optimum coagulation temperature will vary with the polymer, solvent and technique employed and may be adjusted in a given case within the limits described. When using the wet spinning techniques it has been observed that optimum filament properties consistent with desirable spinning speeds are normally found in the range of from about 30–60° C. Spinning rates and bath immersion distances may be readily correlated in a given case. Spinning speeds from 100 to 300 feet per minute have been successfully employed. Moreover, bath immersion distances from about 6 inches to 48 inches have been used. In the case of a given polymer being spun at a given denier, variables such as pumping rates and bath immersion distances may readily be determined by those skilled in the art.

The essence of this invention lies in the nature of the solution-coagulation system, insofar as the particular techniques may readily be adjusted for successfully forming fiber according to this invention.

Upon leaving the coagulation bath the filaments are conventionally washed, stretched and dried. Optional washing after stretching and application of finish compositions before drying may be conducted, if desired. Other modifications of coagulated filament treatment may be employed to satisfy the needs of a given case by means well known to those skilled in the art. For example, dyeability of the fiber will normally be enhanced by annealing or heat relaxation prior to manufacture of fabrics. The steps necessary in the formation of the polymer and after treatment of the filaments coagulated by the process of this invention are conventional and do not comprise a part of this invention.

By "acrylonitrile polymer" is meant polyacrylonitrile, copolymers, and terpolymers of acrylonitrile, and blends of polyacrylonitrile and copolymers of acrylonitrile with other polymerizable mono-olefinic materials, as well as blends of polyacrylonitrile and such copolymers with small amounts of other polymeric materials, such as polystyrene. In general, a polymer made from a monomeric mixture of which acrylonitrile is at least 70 percent by weight of the polymerizable content is useful in the practice of the present invention. Besides polyacrylonitrile, useful copolymers are those of 80 or more percent of acrylonitrile and one or more percent of other mono-olefinic monomers. Block and graft copolymers of the same general type are within the purview of the invention. Suitable other monomers include vinyl acetate, and other vinyl esters of monocarboxylic acids, vinylidene chloride, vinyl chloride and other vinyl halides, dimethyl fumarate and other dialkyl esters of fumaric acid, dimethyl maleate and other dialkyl esters of maleic acid, methyl acrylate and other alkyl esters of acrylic acid, styrene and other vinyl-substituted aromatic hydrocarbons, methyl methacrylate and other alkyl esters of methacrylic acid, vinyl-

substituted heterocyclic nitrogen ring compounds, such as the vinyl imidazoles, etc., the alkyl-substituted vinylpyridines, vinyl chloroacetate, allyl chloroacetate, methallyl chloroacetate, allyl glycidyl ether, methallyl glycidyl ether, allyl glycidyl phthalate, and the corresponding esters of other aliphatic and aromatic dicarboxylic acids, glycidyl acrylate, glycidyl methacrylate, and other mono-olefinic monomers copolymerizable with acrylonitrile.

Many of the more readily available monomers for polymerization with acrylonitrile form copolymers which are not reactive with some dyestuffs and may therefore be impossible or difficult to dye by conventional techniques. Accordingly, these non-dyeable fiber-forming copolymers may be blended with polymers or copolymers which are in themselves more dye-receptive by reason of their physical structure or by reason of the presence of functional groups chemically reactive with the dyestuff, whereby the dyestuff is permanently bonded to the polymer in a manner which lends resistance to removal thereof by the usual laundering and dry cleaning procedures. Suitable blending polymers may be polyvinylpyridine, polymers of alkyl-substituted vinylpyridine, polymers of other vinyl-substituted N-heterocyclic compounds, the copolymers of the various vinyl-substituted N-heterocyclic compounds and other copolymerizable monomers, particularly acrylonitrile.

Of particular utility are the blends formed of polyacrylonitrile or a copolymer of more than 90 percent acrylonitrile and up to 10 percent vinyl acetate, and a copolymer of vinylpyridine or an alkyl-substituted vinylpyridine and acrylonitrile, the said acrylonitrile being present in substantial proportions to provide heat and solvent resistance, and a substantial proportion of the vinylpyridine or derivatives thereof to render the blend receptive to acid dyestuffs. Of particular utility are the blends of copolymers of 90 to 98 percent acrylonitrile and 10 to 2 percent vinyl acetate and sufficient copolymer of 10 to 70 percent acrylonitrile and 90 to 30 percent vinylpyridine to produce a blended composition with a total of 2 to 10 weight percent vinylpyridine.

The polymers just described may be prepared by any conventional polymerization procedure, such as mass polymerization methods, solution polymerization methods, or aqueous emulsion methods. The polymerization is normally catalyzed by known catalysts and is carried out in equipment generally used in the art.

The following examples are given to illustrate this invention and they are not intended to limit the invention. All percentages are given by weight unless otherwise indicated.

Example I

A polymer dope was prepared by stirring 500 gms. of a copolymer comprising about 93 percent by weight of acrylonitrile and about 7 percent by weight of vinyl acetate into 1500 gms. of dimethylacetamide (DMAC) at -10° C. to form a slurry. The slurry was stirred and slowly heated up to 80° C. over a period of about 30 minutes and then stirred an additional 15 minutes to form a clear solution of polymer containing 25 percent solids.

The solution was extruded at a rate of 1.89 cc./min. through a spinnerette having 40 holes, each hole being 3.5 mils in diameter. The spinnerette was positioned beneath the surface of the coagulant in an eight liter spin bath containing 100 percent t-butyl alcohol at 41° C. The filaments were taken out of the bath to provide an immersion length of 16 inches from the spinnerette face to the bath surface. The filaments passed from the spin bath to a wash roller or godet at a velocity of 25 f.p.m. which is equivalent to the theoretical extrusion velocity of the filament. From the wash godet the filaments were continuously passed through a boiling water cascade to the stretch godet to provide a 4.0 × stretch. The filaments were subjected to a second water wash on the stretch

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godet and passed continuously to the steam heated dryer godet or rolls at 100 f.p.m. and thereafter collected on bobbins. The density of freeze dried filament samples taken after stretching was 0.91 gm./cc. The density of the filament after collapsing was 1.17 gm./cc. Comparison of filament densities before and after collapsing indicates the compact structure resulting from coagulation according to the method of this invention.

The fiber tensile properties were determined on the Scott IF-4 Tester. The fiber tenacity was 3.40 g.p.d. and elongation-to-break was 19 percent.

The appearance of the filament tow was observed to be clear upon emerging from the spin bath and after stretching. It had been earlier noted that a cloudy or opaque appearance of the filaments upon emerging from the spin bath was indicative of inferior fiber structure and density.

Example II

The method described in Example I was repeated using other coagulants and conditions as indicated.

TABLE I

Alcohol	Concentration, percent	Bath Temp., ° C.	Appearance		Tenacity (g.p.d.)	Elongation, percent	Density ¹ (g./cc.)
			Unstretched	Stretched			
n-Propyl.....	100	40	Clear.....	Cloudy.....	2.56	19	0.47
Do.....	100	73	Opaque.....	Opaque.....	2.41	19	0.39
Do.....	88	40	Cloudy.....	Cloudy.....	2.54	20	0.50
Do.....	50	60	do.....	do.....	2.33	22	0.41
I-propyl.....	100	60	do.....	do.....	2.44	21	0.45
Do.....	87	45	do.....	do.....	2.66	21	0.40
Do.....	51	55	do.....	do.....	2.56	21	0.44
n-Butyl.....	100	50	do.....	do.....	2.63	21	0.66
Do.....	88	62	do.....	Opaque.....	2.44	22	0.51
Do.....	67	56	do.....	Cloudy.....	2.64	22	0.47
I-Butyl.....	100	32	Clear.....	Clear.....	3.17	17	0.78
Do.....	100	45	do.....	do.....	3.14	20	0.71
Do.....	77	32	do.....	do.....	3.23	17	0.70
t-Butyl.....	100	41	do.....	do.....	3.40	19	0.91
Do.....	90	40	do.....	do.....	3.38	19	0.85
Do.....	80	35	do.....	do.....	3.33	17	0.85
Do.....	70	40	do.....	Cloudy.....	3.35	18	0.94
I-Amyl.....	78	57	(?).....	(?).....	3.11	21	(?)
t-Amyl.....	100	50	Clear.....	Cloudy.....	3.18	21	0.72
Do.....	63	30	do.....	Clear.....	3.09	17	0.76
Do.....	63	45	do.....	do.....	3.23	20	0.70

¹ Determined from freshly coagulated fiber samples after initial washing except for t-butyl alcohol coagulated fibers which samples were collected after stretching. All samples were freeze dried.

² Determinations not recorded.

Uncollapsed fiber densities are slightly higher before stretching than after stretching.

The results shown in the Table I indicate that filaments spun by the process of this invention are more dense, have a better appearance, and have superior tensile properties to those coagulated using other alkanols.

Example III

A polymer dope was prepared and extruded as described in Example I into a coagulation bath of 100 percent by weight of ethyl acetate at 35 and 65° C. Although ethyl acetate is a solvent for the polymer solvent and a non-solvent for the polymer and provides a means for coagulation of polymer dope, the system provided filaments having inferior tenacities of 1.38 and 1.93 g.p.d., respectively.

Example IV

Filaments spun according to the procedure in Example I were compared with filaments spun under the same conditions except that the coagulation was conducted in a water/DMAc bath (45/55). Filaments from numerous trials were evaluated and the results below indicate the range of properties exhibited by each system.

	t-Butyl alcohol	H ₂ O/DMAc
Density (g./cc.) (washed and freeze dried).....	0.70-1.03	0.40-0.60
Surface area (m. ² /g.).....	>200	75-110
Pore-diameter (Angstroms).....	<100	300-600

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In similar trials using dopes wherein the polymer was dissolved in ethylene carbonate and spun into alcoholic coagulation baths the filaments repeatedly broke at the face of the spinnerette whereas trials using dimethylformamide and dimethylsulfoxide gave results similar to those using dimethylacetamide.

We claim:

1. A method for forming a filamentary structure which comprises extruding a solution comprising a polymer of acrylonitrile and a solvent selected from the group consisting of dimethylformamide, dimethylacetamide, and dimethylsulfoxide into an essentially non-aqueous coagulation bath comprising an alcohol selected from the group consisting of tertiary butyl alcohol and tertiary amyl alcohol as the principal coagulant material and up to 60 percent by weight of a solvent corresponding to that in which the aforesaid polymer is dissolved.

2. A method according to claim 1 wherein the coagulation bath comprises up to 25 percent of the solvent.

3. A method according to claim 1 wherein the solvent is dimethylacetamide.

4. A method according to claim 1 wherein the solvent is dimethyl formamide.

5. A method according to claim 1 wherein the solvent is dimethylsulfoxide.

6. A method according to claim 1 wherein the alkanol is tertiary butyl alcohol.

7. A method according to claim 1 wherein the alkanol is tertiary amyl alcohol.

8. A method according to claim 1 wherein a copolymer comprising about 93 percent by weight of acrylonitrile and about 7 percent by weight of vinyl acetate is dissolved in dimethylacetamide and extruded into a coagulation bath comprising tertiary butyl alcohol and dimethylacetamide at about 45° C.

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JAMES A. SEIDLECK, *Primary Examiner.*

H. H. MINTZ, *Assistant Examiner.*