April 27, 1965 J. P. KNUDSEN ET AL 3,180,845

METHOD OF PREPARING VOID FREE FIBERS FROM
ACRYLONITRILE POLYMERS
Filed Oct. 20, 1961

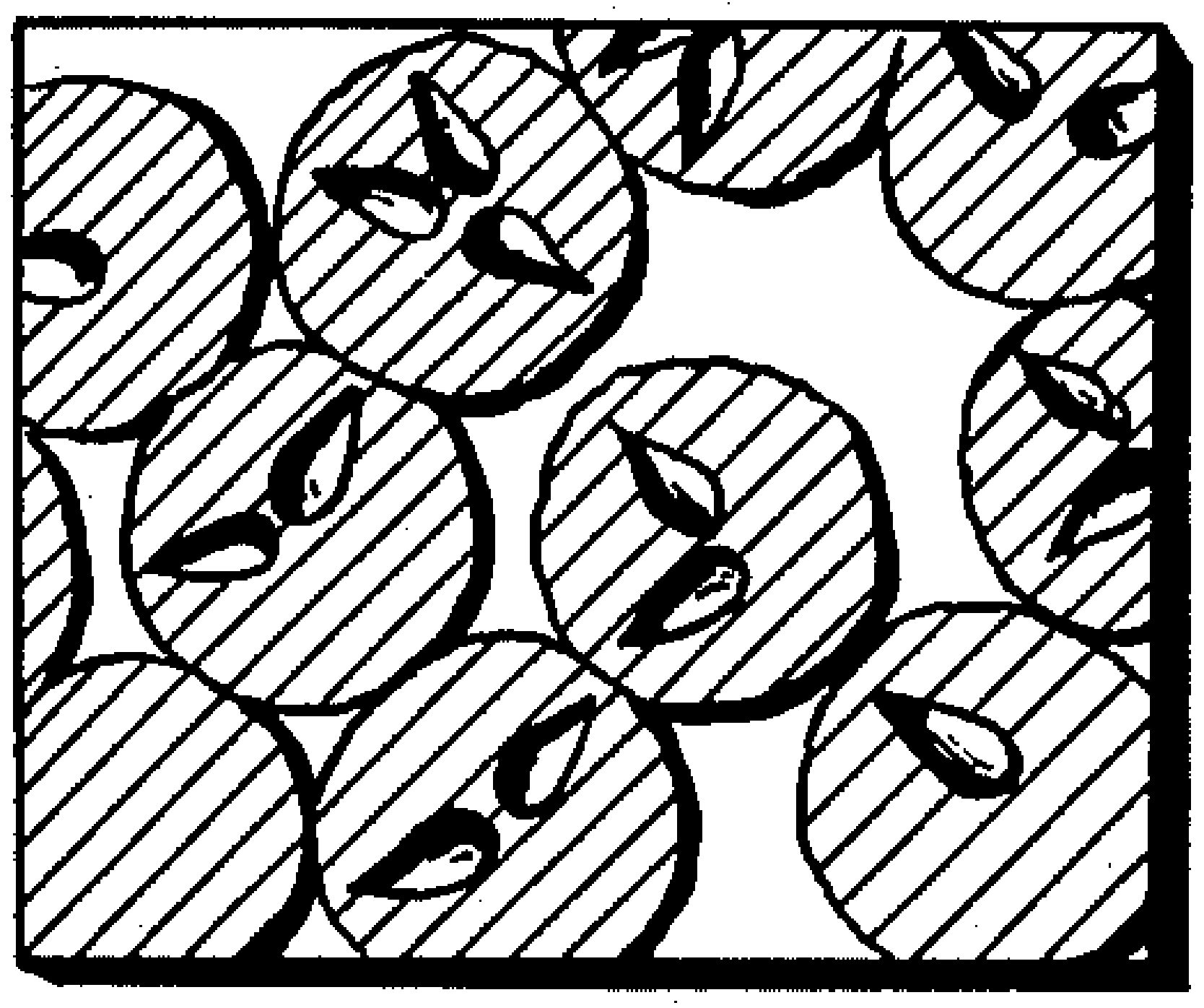

Fig. 1.

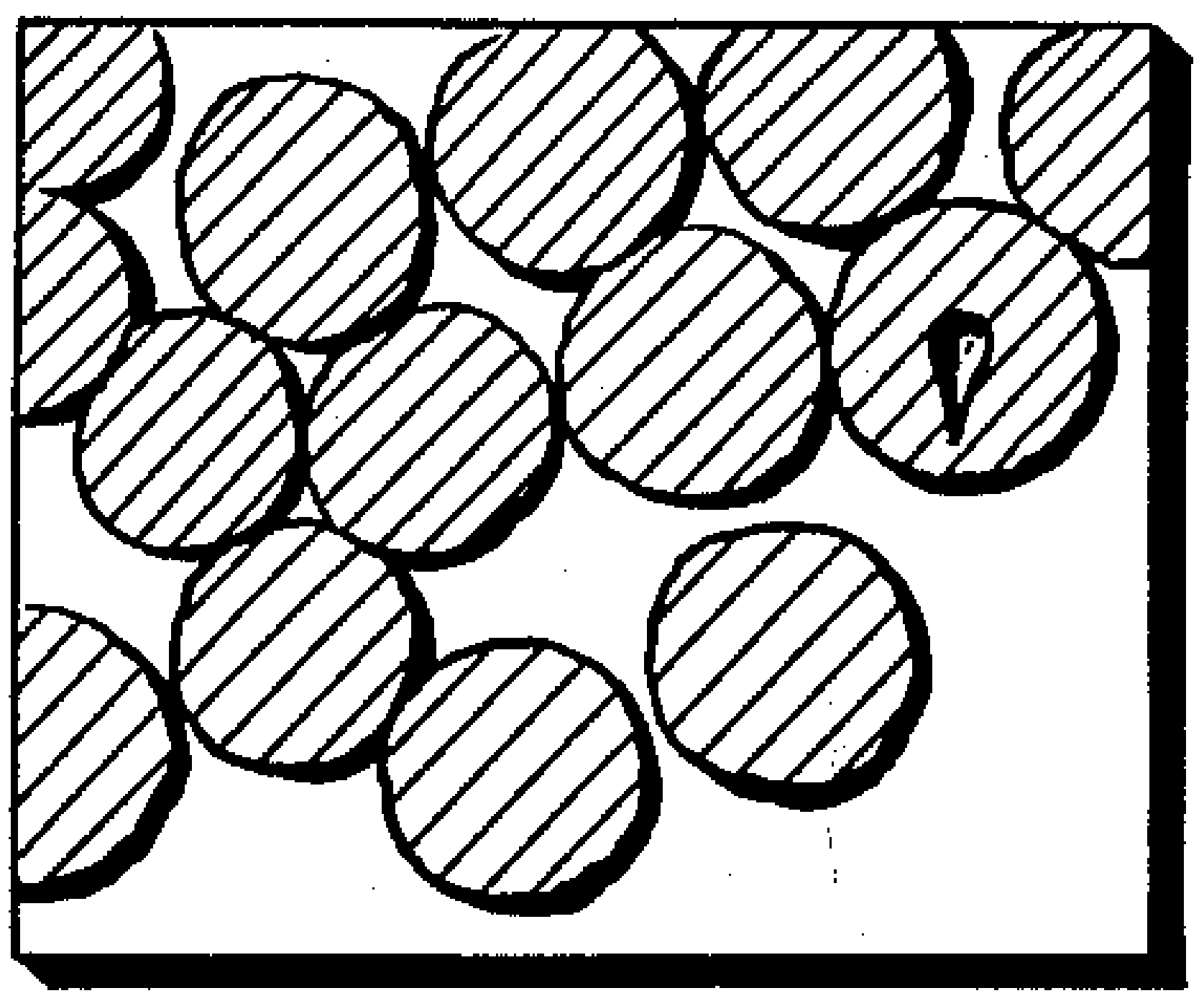

Fig. 1a.

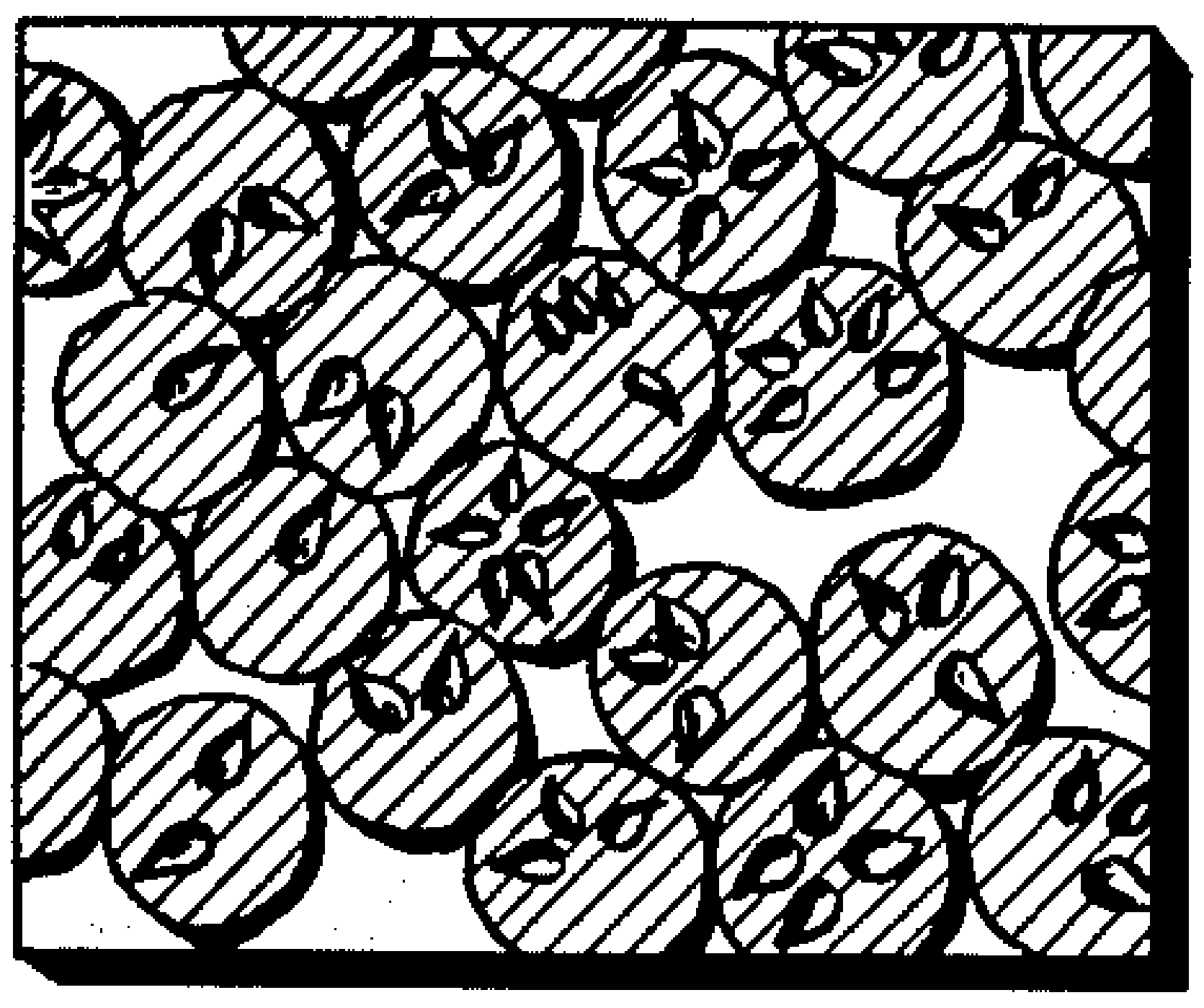

Fig. 2.

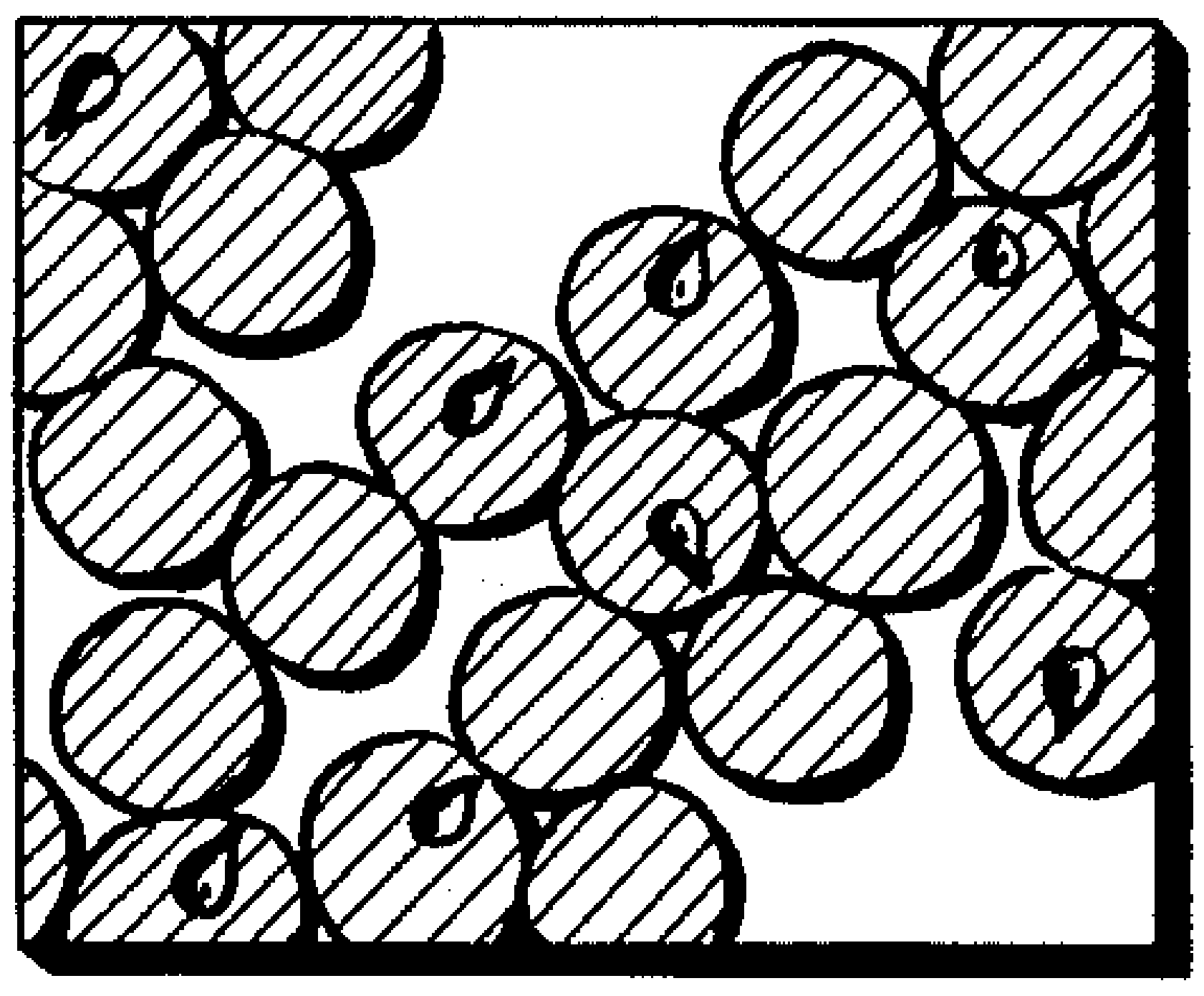

Fig. 2a.

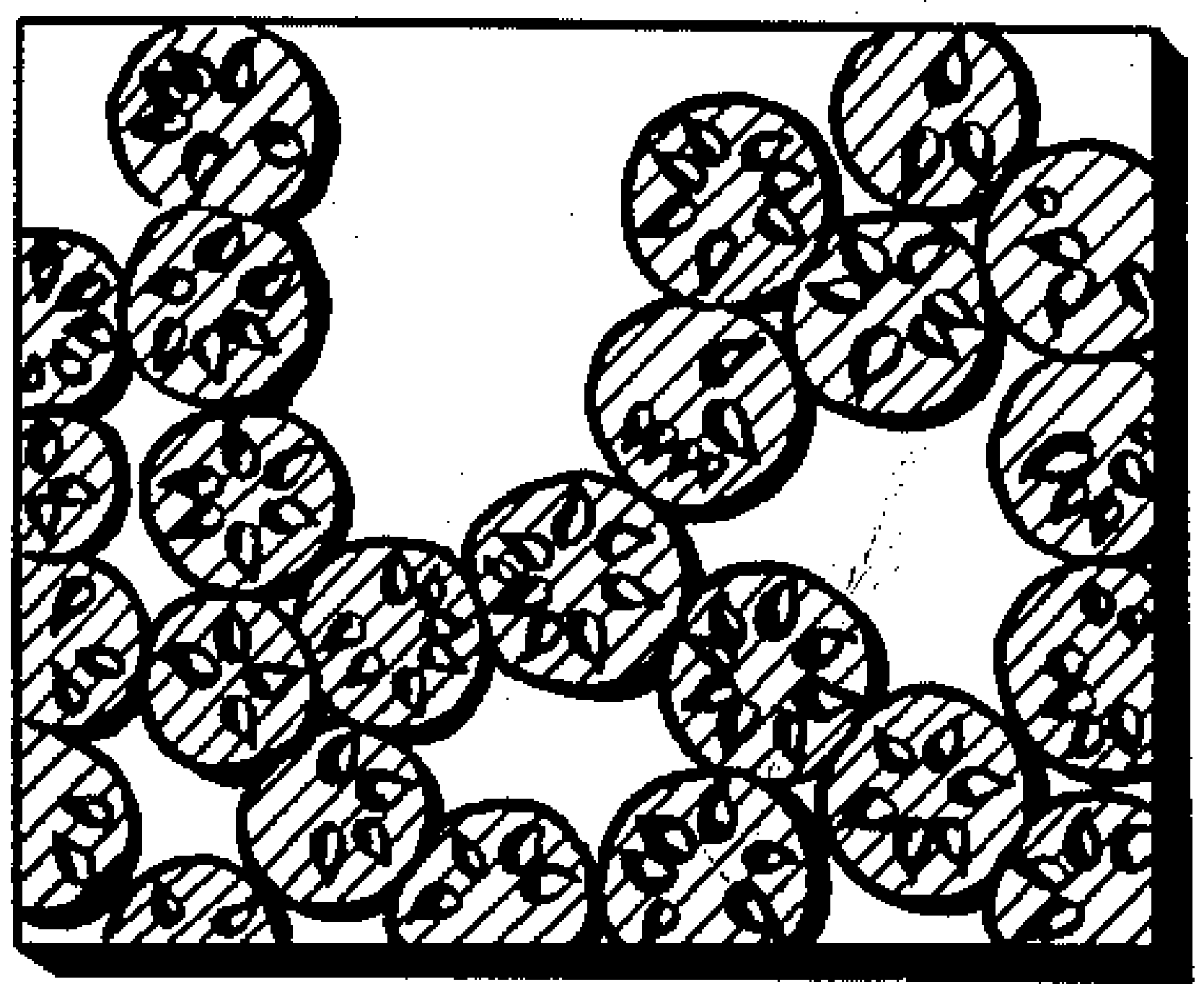

Fig. 3.

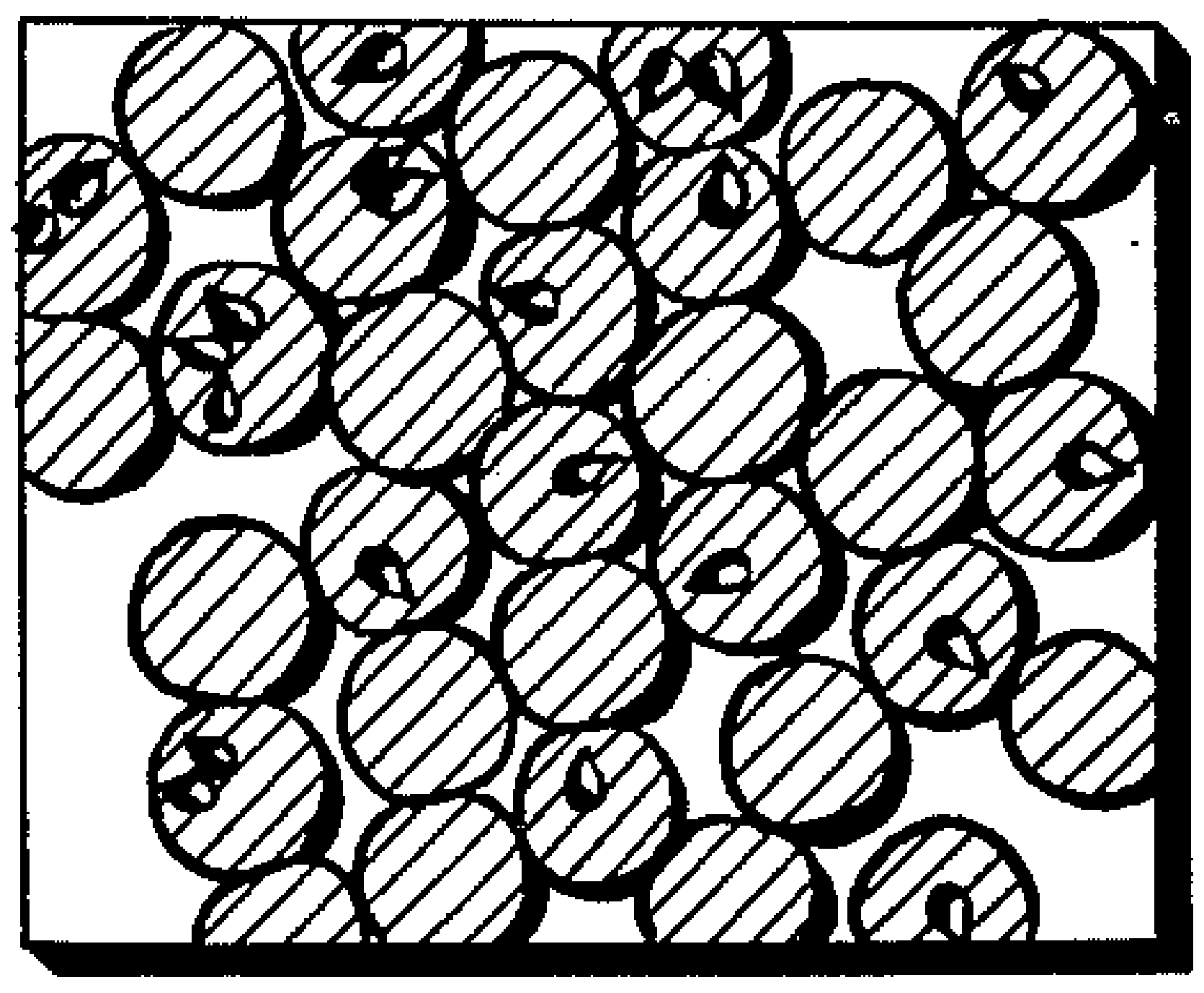

Fig. 3a.

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United States Patent Office

3,180,845
Patented Apr. 27, 1965

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METHOD OF PREPARING VOID FREE FIBERS FROM ACRYLONITRILE POLYMERS

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Filed Oct. 20, 1961, Ser. No. 146,555
13 Claims. (Cl. 260—30.8)

This invention relates to the preparation of improved fibers from acrylonitrile polymers through control of the coagulation properties of spinning solutions of these polymers. More particularly, this invention relates to the use of certain easily soluble alkylene glycol polymers compatible in solution with polyacrylonitrile to control the formation of internal voids in the fibers during coagulation.

Certain acrylonitrile polymers, copolymers, and polymer blends containing at least 80% acrylonitrile commonly used for the preparation of synthetic fibers by wet spinning yield fibers containing large numbers of internal voids when solutions of these polymers in organic solvents are coagulated in aqueous spin baths particularly at high spinning speeds. These voids appear to form at the instant of coagulation due to rapid skin formation and inward diffusion of spin bath liquors. Voids so formed persist in the fiber throughout its further processing and contribute undesirable properties such as poor abrasion resistance and reduced luster to the finished fiber.

Accordingly, it is the object of this invention to provide spinning solutions of acrylonitrile polymers which can be readily coagulated to give substantially void free fibers with improved luster and abrasion resistance. A further object of this invention is to provide a method for spinning high quality acrylonitrile fibers at increased spinning speeds. Other objects and advantages will become apparent from the description of the invention which follows hereinafter.

In general, these and other objects of the invention are accomplished by incorporating into the spinning solution a suitable small quantity of a polymer which is both compatible with the acrylonitrile polymer and also soluble or highly swellable by the coagulation medium employed. Typically, these conditions are met by incorporating in the spinning solution a suitable amount of polyethylene glycol, polypropylene glycol or polybutylene glycol. The solution may then be wet spun into a coagulation bath according to the usual well known methods, and will result in fibers of improved characteristics.

The mode of addition of the polyglycol is unimportant. That is the polyglycol may be blended with the acrylonitrile polymer during preparation of the spinning solution by any convenient means. The polymers may be dissolved sequentially in either order, or the two may be dissolved separately and the solutions mixed. However, both polymer and polyglycol must be completely and uniformly dispersed throughout the solution on order to ensure proper performance of the invention. The polymer-polyglycol solution is then extruded into a coagulation bath. The improved character of acrylonitrile fibers produced in this manner is evident by an examination of the accompanying drawings.

In the drawings,

FIGURE 1*a* shows a drawing of a mricrophotograph cross-section view of polyacrylonitrile fibers spun with 2.5% polyethylene glycol of 1,000 molecular weight in the spinning solution and subjected to a jet stretch of 1.04. Jet stretch is the rate of filament take-up divided by the extrusion rate. FIGURE 1 shows polyacrylonitrile fibers spun without polyethylene glycol and subjected to a jet stretch of 1.04. A comparison of FIGURE 1*a* and FIGURE 1 clearly shows that the occurrence of voids, the tear shaped areas which characteristically form while the filament is coagulating, is greatly reduced in FIGURE 1*a* using polyethylene glycol. FIGURES 2*a* and 2 compare polyacrylonitrile fibers spun with 2.5% polyethylene glycol of 1,000 molecular weight in the spinning solution and none respectively, to which a 2.01 jet stretch has been applied. FIGURES 3*a* and 3 show polyacrylonitrile fibers prepared with 2.5% polyethylene glycol of 1,000 molecular weight in the spinning solution and none respectively, to which a 3.10 jet stretch was applied. In all three comparisons the reduction of voids when polyethylene glycol is present in the spinning solution is clearly evident. A reduced occurrence of voids improves the abrasion resistance and other desirable qualities.

The polyglycols of this invention may be employed in an amount of from about 2 to 25 percent of the polymer by weight. The molecular weight of these polyglycols may vary from about 400 to 4,000, preferably around 600 to 2,000.

Any organic polyacrylonitrile solvent which does not undergo side reactions with the polyglcols of this invention can be used in the practice of this invention. Among the preferable solvents are N,N-dimethylacetamide, dimethylsulfoxide, ethylene carbonate, and the like.

The use of polyethylene glycol, polypropylene glycol or polybutylene glycol in accordance with the present invention, effects improvements in properties of fiber spun from all suitable solutions of acrylonitrile polymers. The invention is applicable not only to polyacrylonitrile but also to copolymers, interpolymers, and blends thereof, particularly those containing at least 80 percent by weight of polymerized or copolymerized acrylonitrile. Such polymeric materials include acrylonitrile fiber forming polymers with readily dyeable basic copolymers, the blend having an overall polymerized acrylonitrile content of at least 80 percent by weight.

For example, the polymer may be a copolymer of 80 to 98 percent of acrylonitrile and from 2 to 20 percent of another copolymerizable monoolefinic monomer. Suitable copolymerizable mono-olefinic monomers include acrylic, alpha-chloroacrylic and methacrylic acids; the acrylates, such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromoethylene, methacrylonitrile, acrylamide and methacrylamide, alpha-chloroacrylamide, or monoalkyl substitution products thereof; methyl vinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters, itaconic acid and itaconic ester; N-vinylcarbazole; vinylfuran; alkyl vinyl esters; vinyl sulfonic acid, ethylene alpha, beta-dicarboxylic acids or their anhydrides or derivatives, such as diethylcitraconate, diethylmesaconate; styrene, vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines such as the vinyl pyridines and alkyl-substituted vinylpyridines for example, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine and the like; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles, such as 2-, 4-, or 5-methyl-1-vinylimidazole, vinylpyrrolidone, vinylpiperidone, and other mono-olefinic copolymerizable monomeric materials.

The polymer can be a ternary interpolymer, for example, products obtained by the interpolymerization of acrylonitrile and two or more of any of the monomers, other than acrylonitrile, enumerated above. More specifically, and preferably, the ternary polymers containing from 80 to 98 percent of acrylonitrile, from 1 to 10 percent of a vinylpyridine or a 1-vinylimidazole, and from 1 to 18 percent of another copolymerizable mono-olefinic substance, such as methacrylonitrile, vinyl acetate, methyl methacrylate, vinyl chloride, vinylidene and the like.

The polymer can also be a blend of polyacrylonitrile or a copolymer of from 80 to 98 percent acrylonitrile and from 1 to 20 percent of at least one other mono-olefinic copolymerizable monomeric substance with from 2 to 50 percent of the weight of the blend of a copolymer of from 30 to 90 percent of a vinyl-substituted tertiary heterocyclic amine and from 10 to 70 percent of at least one other mono-olefinic copolymerizable monomer preferably, when the polymeric material comprises a blend, it will be a blend of from 80 to 99 percent of a copolymer of 80 to 98 percent acrylonitrile and from 2 to 20 percent of another mono-olefinic monomer, such as vinyl acetate, which is not receptive to dye stuff, with from 1 to 20 percent of a copolymer of from 30 to 90 percent of a vinyl-substituted tertiary heterocyclic amine such as vinylpyridine, a 1-vinylimidazole, or a vinyl lactam, and from 10 to 70 percent of acrylonitrile to give a dyeable blend having an overall vinyl-substituted tertiary heterocyclic amine content of from 2 to 10 percent based on the weight of the blend.

While the preferred polymers employed in the instant invention are those containing at least 80 percent acrylonitrile, generally recognized as the fiber-forming acrylonitrile polymers, it will be understood that the invention is likewise applicable to polymers containing less than 80 percent of acrylonitrile when such polymers are useful in forming fibers.

The polymers useful in the practice of the present invention may be prepared by any conventional polymerization procedures, such as mass polymerization methods, solution polymerization methods or aqueous emulsion procedures. If it is desired to produce shaped articles from the acrylonitrile polymer solutions of the present invention which have a modified appearance or modified properties, various agents may be added to the solutions to accomplish these effects either prior or after the addition of one of the polyglycols of this invention thereto without any ill effects thereon. Such added agents might be pigments, dyes, anti-static agents, fire-retarding agents, and the like. Solutions containing from 8 to 30 percent by weight of acrylonitrile polymers may be employed, with the preferred concentration range being from 15 to 25 percent.

The invention is further illustrated by the following examples showing the improvements obtained by adding polyethylene glycol to acrylonitrile polymer solutions. In the examples all parts and percents are by weight.

EXAMPLE I

This example involves preparing a spinning dope in the normal fashion to which polyethylene glycol (PEG) has been added. A solution was prepared by mixing 25 percent of an acrylonitrile copolymer containing 93.7 percent acrylonitrile and 6.3 percent vinyl acetate and 2.5 percent of PEG having an average molecular weight of 1,000 with N,N-dimethylacetamide and stirring at about 50° C. until a solution was formed. The solution was then spun to fiber according to normal wet spinning processes. Typical tensile properties of fibers spun from this solution and the corresponding control are tabulated below. The fibrillation measurement is comparative and such measurement is made on a fabric formed from the fibers. The degree of fibrillation is determined on a tricot knit tape and the value obtained is called a tricot rating or TR. The tape is flex abraded for 150 cycles on a "Stroll abrader" or Universal wear tester using the flexing bar with a 2 lb. tenison and ½ lb. weight on the head. Two such abrasions are made on each tape while dry and then while wet. The number of cycles until the tape breaks completely is also recorded.

Table I

	Control fiber	With 10% polyethylene glycol
Spinning speed, 350 ft./min	350	400
Denier per filament	3.33	3.10
Tenacity (grams/den.)	2.60	2.23
Elongation, percent	28	32
Dry TR	0.9	0.3
Wet TR	2.4	0.5
Dry cycles to break	767	800
Wet cycles to break	477	525

EXAMPLE II

To further define the limitations and utility of the invention a series of polymer solutions were prepared in N,N-dimethylacetamide containing 25% of the acrylonitrile polymers used in Example I and 2.5% of polyethylene glycol of varying molecular weights and spun under constant conditions into coagulating baths containing 55% N,N-dimethylacetamide and 45% water at 55° C. The resulting fibers were characterized by counting the average number of voids in a 10 micron length of unoriented fiber as well as by the tensile and abrasion tests described in Example I. The results are shown in Table II below.

Table II

Additive	Av. No. of voids/10 micron length	Denier	Ten.	Elong.	TR		Cycles to break	
					Dry	Wet	Dry	Wet
None	6	3.2	2.0	34	1.3	3.0	754	422
PEG 200	2	3.0	2.1	35	0.7	1.0	667	518
PEG 400	0.1	3.0	2.2	37	0.2	0.7	1,015	680
PEG 1,000	0.1	3.1	2.2	32	0.3	0.5	800	525
PEG 4,000	0.1	3.2	2.1	40	0.3	1.3	1,728	885
PEG 6,000	4.0	Fibers inhomogeneous and unsuitable for textile use. Additive incompatible with base polymer.						
PEG 20,000	25+							

These results clearly indicate a region of maximum efficacy in the range of 400–4,000 molecular weight for the PEG additive. They show the reduction in void number and improvement in abrasion character which marks the present invention. They also suggest the unsuitability of polymers incompatibility with the acrylonitrile polymer for the present invention.

EXAMPLE III

To further establish the requirement of polymer compatibility, spinnings were made with dopes containing 25% of the acrylonitrile polymer of Example I and 2.5% PEG 20,000, 2.5% PEG 6,000 and cellulose diacetate, all of which yield turbid inhomogeneous solutions when blended with the acrylonitrile polymers. Void counts on these fibers are given in Table III.

Table III

Additive	Dope appearance	No. of voids/10 micron length
None	Clear	6-10
PEG 6,000	Slightly turbid	4-6
PEG 20,000	Turbid	25-40
Cellulose diacetate	do	25-40

EXAMPLE IV

To study the effects of additive level on void formation during coagulation, a series of fibers were spun incorporating varying levels of PEG 1,000 into a 25% solids solution of the polymer of Example I, and the resulting dopes spun under identical conditions. Void counts on these fibers are given in the following table.

Table IV

Additive	Additive level (based on total dope wt.), percent	No. of voids per 10 micron length
None		6-10
PEG 1,000	.5	3.5
PEG 1,000	1.25	0.1
PEG 1,000	2.5	0.1

While 0.5% additive gives an improvement in void count, optimum void control requires about 1.0% additive or more.

EXAMPLE V

To study the effect of solids level on void formation spinnings were made using the polymer of Example I at 20 and 25% solids with and without 2.5% PEG 1,000 added. Results are presented in Table V.

Table V

Solids level	Additive	No. of voids/10 micron length	Den.	Ten.	Elong.	TR		Cycle to break	
						Dry	Wet	Dry	Wet
20%	None	25+	(Fiber too poor for textile evaluation)						
20%	PEG 1,000	2	3.1	2.0	43	1.0	1.7	1,138	835
25%	None	6	3.2	2.0	34	1.3	3.0	754	422
25%	PEG 1,000	0.1	3.1	2.2	32	0.3	0.5	800	525

EXAMPLE VI

To establish the lower limits additive of molecular weight useful in the practice of this invention, spinnings were made using a series of homologous materials beginning with ethylene glycol and working upward. Polymer used was the polymer of Example I at 25% solids and spinnings were conducted under identical conditions with each additive. Table VI shows the results of each additive on void formation.

Table VI

Additive	Level of additive, percent	Av. No. of voids/ 10 micron length of fiber
None		6-10
Ethylene glycol	2.5	3
Diethylene glycol	2.5	2
Triethylene glycol	2.5	2
PEG 200	2.5	2
PEG 400	2.5	0.1
PEG 1,000	2.5	0.1

These results show that while addition of even the lowest molecular weight number of the series gives some control over void formation optimum control is achieved only at molecular weights above 200.

Substantially void free fibers and filaments are also obtained when polypropylene or polybutylene glycols of suitable molecular weight are employed.

As many variations of this invention may be made without departing from the spirit and scope thereof it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A process for the production of void free fibers and filaments from acrylonitrile polymers comprising mixing an acrylonitrile polymer comprising at least 85 percent acrylonitrile, an organic solvent therefor, and from about 1 to about 25 percent based on the weight of the polymer of a polyglycol of from 1 to 4 carbon atoms and having an average molecular weight of from 400 to 4,000, stirring and thereafter extruding the resultant polyglycol polymer spinning solution through a suitable extrusion orifice to effect the formation of fibers and filaments therefrom.

2. Claim 1 wherein said polymer is polyacrylonitrile.

3. Claim 1 wherein said polymer is a copolymer comprising at least 85 percent polyacrylonitrile and up to 15 percent of a copolymerizable mono-olefinic monomer.

4. Claim 1 wherein said polymer is a blend of 80 to 99 percent of (A) a copolymer containing from 80 to 98 percent of acrylonitrile and 2 to 20 percent of a copolymerizable mono-olefinic monomer and from 1 to 20 percent of (B) a copolymer containing 10 to 70 percent of acrylonitrile and 30 to 90 percent of a vinyl substituted tertiary heterocyclic amine said blend having an overall vinyl substituted tertiary heterocyclic amine content of from 2 to 20 percent based on the weight of the blend.

5. Claim 1 wherein the solvent is N,N-dimethylacetamide.

6. Claim 1 wherein the solvent is dimethylsulfoxide.

7. Claim 1 wherein the polyglycol is polyethylene glycol.

8. Claim 1 wherein the polyglycol is polypropylene glycol.

9. Claim 1 wherein the molecular weight of the polyglycol is from 400 to 2,000.

10. Claim 1 wherein the polyglycol is polyethylene glycol of 400 molecular weight.

11. Claim 1 wherein the polyglycol is polyethylene glycol of 1,000 molecular weight.

12. Claim 1 wherein the polyglycol is polyethylene glycol of 4,000 molecular weight.

13. A process for the production of void free fibers and filaments from acrylonitrile polymers comprising mixing 25 percent by weight of an acrylonitrile polymer comprising 93.7 percent acrylonitrile and 6.3 percent vinyl acetate, 75 percent by weight of N,N-dimethylacetamide and 2.5 percent by weight of polyethylene glycol of 1,000 molecular weight, stirring and extruding the resultant polyethylene glycol polymer spinning solution through a suitable extrusion orifice to effect the formation of fibers and filaments therefrom.

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