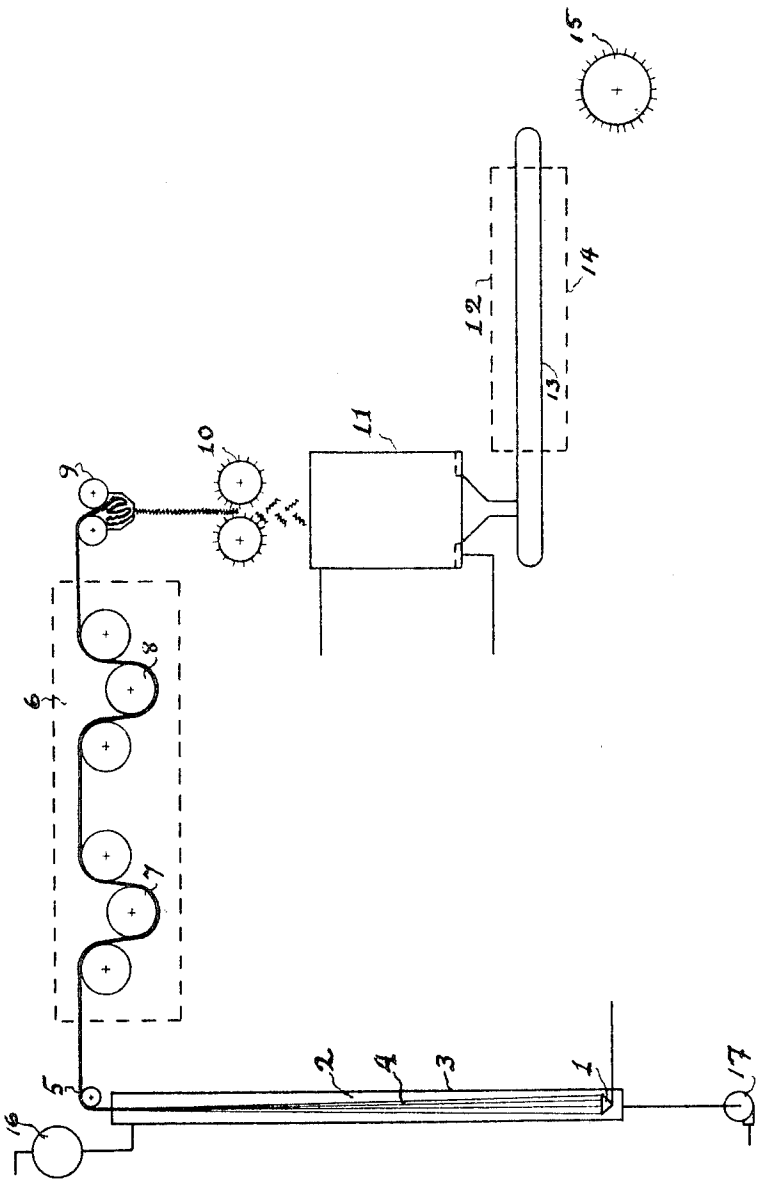
Aug. 23, 1966 O. SUNDEN ETAL 3,268,490

METHOD OF PREPARING POLYACRYLONITRILE FIBERS

Filed March 7, 1962



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United States Patent Office 3,268,490 Patented August 23, 1966

3,268,490 METHOD OF PREPARING POLYACRYLONITRILE FIBERS

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Filed Mar. 7, 1962, Ser. No. 177,957
6 Claims. (Cl. 260—78.5)

INTRODUCTION

This invention generally relates to new compositions which are particularly useful for forming filaments, yarns, fibers and films. More specifically this invention pertains to new polymer compositions which contain predominant amounts of acrylonitrile and which are cross-linked to a critically small extent so that such compositions can be wet-spun at a higher spinning rate while permitting stretching of the fiber during the coagulation step and ensuring improved properties of the product. This invention also relates to methods for preparing and using the aforesaid compositions. (The term "polymer" when used herein is intended to encompass both homopolymers and copolymers in accordance with prevailing plastic nomenclature.)

BACKGROUND

Whereas fibers containing acrylonitrile have been prepared by dry-spinning polymer solutions in heated air, in recent years the wet-spinning of such fibers has been practiced because of the more desirable properties of the products which can be obtained by wet-spinning. In wet-spinning, a viscous solution of a polymer in a polymer solvent is extruded through a spinneret into a coagulating bath wherein the polymer solvent is simultaneously released to (or extracted into) the coagulating bath as the fiber is formed. The fiber is thereafter usually stretched while still in the coagulating bath in order to orient the molecules of the fiber and to improve the extraction of the solvent.

Polymers containing 100 percent of acrylonitrile in the molecule are generally not used, since such polymers are difficult to dye by common methods. Accordingly, copolymers containing up to 30 percent of another copolymerizing unsaturated compound, such as, for example vinylacetate, methacrylonitrile, acrylates and methacrylates, unsaturated tertiary amines or unsaturated sulphonic acids and sulphones are usually employed.

The most common polymer solvents are N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, butyrolactone, ethylene carbonate and N,N-dimethylmethoxyacetamide.

A number of different coagulating liquids are known in the art. The art has also recognized that the various coagulation liquids have differing powers to coagulate insofar as acrylonitrile polymer solutions are concerned.

Among the most common coagulating liquids may be mentioned water, concentrated aqueous solutions of electrolytes, isopropanol, glycerine and aqueous solutions of the polymer solvent used. Pure water and glycerine are known to have high coagulation (i.e. solvent extracting) power, but rapid coagulation makes the formed fiber so brittle and spongy and of such low tensile strength that it cannot be appreciably stretched during coagulation without the risk of fiber rupture and impairment of the mechanical properties of the fiber.

It is also known that aromatic hydrocarbons such as benzene, toluene and cymene or hydrocarbon mixtures containing more than 50 percent aromatic hydrocarbons can be used as coagultants. Such coagulants have a somewhat lower coagulation power than pure water and glycerine and this lower coagulation power is beneficial in that it insures a gradual coagulation and makes it possible to stretch the formed fiber in the coagulation bath in order to orient the molecules and impart tensile strength. However, aromatic hydrocarbons are disadvantageous as coagulants since they are partially soluble in the polymer and cause both a certain porosity in the fiber and a loss of its abrasion resistance.

Hydrocarbon coagulants containing less than 50 percent by weight of aromatic hydrocarbons (for example hydrocarbon containing more than 50 percent by weight of aliphatic hydrocarbons—such as kerosene hydrocarbons with a boiling point of 150 to 300° C.) avoid some of the disadvantages of hydrocarbons having more than 50 percent aromatics, but they suffer from the disadvantage that they have a *very slow* coagulation rate and spinning rate owing to the very slow development of fiber strength. This slow spinning rate in effect limits the production output for any plant.

Acrylic fibers have many favorable properties in comparison with other synthetic fibers. For example acrylic fibers have a wool-like hand, warmth and comfortness. However, the acrylic fibers are less than perfect in the following four aspects:

(1) They show fibrillation (i.e. splitting of fibers into thinner fibrils during wearing);
(2) Their wrinkle recovery properties are not as good as natural wool;
(3) Their dimensional stability and pleat retention are not as good as polyester fibers;
(4) They are sensitive to soiling.

Many attempts have been made to improve the above-mentioned properties. The only known way of diminishing the tendency toward fibrillation is to decrease the orientation of the fiber—but this results in lower fiber strength. In order to improve the wrinkle recovery, the dimensional stability and the pleat retention properties it has been found necessary to use a polymer composition which has a low degree of plasticity under wearing and washing conditions—but the difficulty with this is that a fiber made from such a polymer is inferior with respect to its dyeing properties. Thus, while it has been possible to improve one or two of the above-mentioned properties, such improvement has only been possible because other valuable properties of the fiber have been sacrificed.

OBJECTS

It is therefore a primary object of this invention to provide an acrylonitrile polymer composition which can be readily spun in what have theretofore been considered as slow-acting coagulants while at the same time permitting stretching to develop better extraction of the solvent and better fiber properties.

Another object of the present invention is to improve the spinnability of the spinning dope in slow-acting coagulating baths and to improve the mechanical and physical properties—particularly at elevated temperatures—of fibers and filaments prepared from polyacrylonitrile, by using a fiber-forming completely soluble, acrylonitrile polymer which is cross-linked to a certain *low* degree.

Another object is to diminish the fibrillation tendency of the fiber. Fibers made of the polymer composition of the present invention have less tendency to fibrillate during wearing even when the fiber has a high strength. A high degree of stretching in the production of the fiber will give the higher strength of the fiber even when said polymer composition is used. The molecular orientation measured with X-ray methods, however, does not increase with the stretching at the same rate as for linear polymers and the resulting fiber will not fibrillate as much as a fiber made of a linear polymer.

Still another object of the present invention is to improve the wrinkle recovery, dimensional stability and pleat retention properties of the fiber. These properties mainly depend on the high degree of plasticity of acrylic fibers at a temperature of 35–40° C. and the humidity condition close to the skin of the human body. The composition of the polymer of the present invention contributes to improved elastic properties of the fiber and to decreased plastic properties, which result in the improvements mentioned.

Finally, an object of the invention is to produce fibers with excellent soil and stain resistance. Dry soiling is said to depend on static electricity, but in fact the surface of the fiber is more responsible for the soiling properties than the static properties. By using a slow-acting coagulant, such as one containing more than 50 percent aliphatic hydrocarbons, a very smooth and tight fiber surface is achieved without longitudinal cracks or surface porosity. Cracks and porosity are unavoidable with other synthetic fibers and they are responsible for the severe soil retention of the fibers as well as fat and wet staining. By the combination of coagulation in hydrocarbons and the polymer structure composition of the present invention it has been possible to improve the soil resistance and also the stain resistance of the fiber to a degree not previously achieved.

These and other objects and advantages will become more apparent after reading the following description and claims taken in conjunction with the drawing.

THE PRESENT INVENTION

We have found according to this invention that it is possible to produce acrylonitrile polymers of unexpected utility and novel properties composed of at least 85 molar percent of acrylonitrile units and a total of from 0 to about 15 molar percent of one or several monoethylenically unsaturated monomer units copolymerizable with acrylonitrile and cross-linked to a certain very limited degree with a cross-linking polyethylenically unsaturated monomer.

Examples of satisfactory monoethylenically unsaturated monomers would include vinyl acetate, vinyl chloride, vinylidene chloride, acrylic acid, acrylamide, methacrylonitrile, methacrylamide or an ester of acrylic acid and methacrylic acid such as methylacrylate or an unsaturated sulphonic acid. While the broad range of this monomer is 0–15 percent, a more preferred range is 2–8 or 2–10 molar percent. Of the above-mentioned monomers, we have found acrylic acid, acrylic esters and acrylic amide as well as methacrylic acid, their esters and methacrylic amide, to be the most suitable. The advantage of these latter compounds compared with the others lies in the fact that they give the fiber good dyeability, primarily with basic dyes, at concentrations as low as 2–8 molar percent in the copolymer. Furthermore, their copolymerization rates with acrylonitrile make it easy to prepare copolymers with a relatively homogeneous composition. The comonomer can be randomly distributed in the polymer, but graft and block polymers also seem to be suitable.

For improving the dyeabiilty more than one comonomer should be used, for example methylacrylate and an unsaturated sulphonic acid.

The cross-linking polyethylenically unsaturated monomer is preferably either divinyl benzene, methylenbisacrylamide, diallyl phthalate, diallylmaleate, ethylene acrylate, ethylene diacrylate or triacrylylperhydrotriazine. Methylenebisacrylamide and triacrylylperhydrotriazine may be prepared by reacting acrylonitrile and formaldehyde in the presence of sulphuric acid.

The cross-linking of the polymer may be accomplished in a number of ways. The simplest procedure is to polymerize acrylonitrile in the presence of small amounts of the polyfunctional unsaturated cross-linking compounds. It is important that the cross-linking agent is evenly distributed in the polymer. When the cross-linking is not homogeneously distributed, highly cross-linked polymer particles are obtained which do not dissolve in dimethylformamide or other common solvents for acrylonitrile polymers and which form gel-lumps or strongly swellable microgel particles, causing troublesome clogging of filters and spinnerets. The cross-linking agents named above have the advantage of solubility in acrylonitrile and/or water and therefore more readily form homogeneous cross-linked products.

Another way of obtaining cross-linked polymers is to copolymerize reactive acid or amine groups into the polymer and then react these groups with a bivalent or polyvalent base (metal) or acid. Reactions between other reactive groups may, of course, also be used for cross-linking purposes, e.g. ester formation between copolymerized acrylic acid groups and glycol etc.

The exact degree of cross-linking is quite critical to the success of the invention. The broad idea of merely cross-linking polymers or copolymers is, of course, well known. Two patents which mention cross-linking would include 2,908,659 and 2,678,924. However, these prior art patents have as their specific objective or as their inevitable result the achieving of a degree of cross-linking which renders the copolymer essentially insoluble but capable of being swollen by "solvents" under retained shape. These patents give absolutely no hint or suggestion as to the unexpected results or desirable properties which might be achieved by a very limited degree of cross-linking, particularly insofar as fiber properties and the wet-spinning of acrylonitrile copolymers is concerned. On the contrary cross-linking previously has always been regarded as deterious to the fiber forming properties of the polymer.

In accordance with this invention we have found that it is critical to have the polymer cross-linked to a degree of 0.001 to 0.3 molar percent of cross-linking units. A narrower and more preferred range is 0.005 to 0.1 molar percent. However, it is desirable to determine the optimum amount of cross-linking agent within the above-ranges depending upon the particular cross-linker being used, the polymerization process being used, the relative reaction rate of the agent with acrylonitrile, the desired properties of the final product, etc. By way of example, we carried out some experiments to determine the preferred concentrations of certain cross-linkers for one particular discontinuous emulsion polymerization process in water with water soluble catalysts. The lower limit of concentration given in the table below has been determined by the requirements of a spinning rate of 10 m./min. in aliphatic kerosene at 130° C. of a 20% solution of the polymer in dimethylformamide. The upper concentration limit has been determined by the necessity of dissolving the polymer completely in the spinning solvent and without formation of any retained swollen gel-particles. The figures are stated in moles of cross-linker used per 100 moles of acrylonitrile. The figures furthermore relate to a viscometric molecular weight of about 50,000–100,000 corresponding to a relative viscosity of 2.0–3.1 of 0.5% solutions of polymer in dimethylformamide. The preferred values of methylene bisacrylamide and triacrylohexahydrotriazine of 0.035 mole percent and 0.012 mole percent respectively refer to a molecular weight of about 70,000 corresponding to a relative viscosity of 2.5.

When calculating the primary molecular weight M, i.e.,

the molecular weight of the linear polymer chains, the formula

$$M=\frac{nr-1}{\frac{5}{m}\cdot 2\cdot 2}10^4$$

is used, where nr=relative viscosity in 0.5% solution of dimethylformamide and m=the average molecular weight of the monomer units.

Compound	Moles per 100 moles of acrylonitrile	Preferred amount for molecular weight of 70,000
Divinylbenzene	0.1–0.3	
Methylenebisacrylamide	0.02–0.06	0.035
Diallylphthalate	0.01–0.02	
Diallyl maleate	0.01–0.08	
Triacrylylhexahydrotriazine	0.005–0.02	0.012

The above given figures relate to discontinuous polymerization with laurylsulphonate as emulsifier. In a continuous process without emulsifier about two times as much cross-linker will give the most preferable result e.g. 0.03 mole of triacrylylperhydrotriazine (molecular weight of 70,000).

Methylene bisacrylamide and triacrylylperhydrotriazine are the cross-linkers giving the least complications in the copolymerization with acrylonitrile. From the figures obtained with these two cross-linkers and from other experiments we have been able to calculate as follows. The preferred degree of real cross-linking is 1 cross-linking point per 2–6 primary linear polymer molecules in the case of a tetra-functional compound (methylenebisacrylamide), corresponding to 0.02–0.06 mole percent, and 1 cross-linking-point per 3–12 primary linear polymer molecules in the case of a hexafunctional compound (triacrylylperhydrotriazine), corresponding to 0.005–0.02 mole percent. The calculated figures above refer to statistical averages counted on values of primary molecular weights obtained from viscometric determination and the amount of those poly-functional compounds which can be expected to react almost completely. This fact shows that this invention is not concerned with a fully developed insoluble net-work of cross-linked polymer molecules but is concerned with a new type of polymeric molecule consisting of two or three primary linear polymeric chains joined together at one point or nucleus by the polyfunctional compound forming a quite soluble multichain polymeric molecule with four or six linear branches of statistically the same length going out from one central nucleus (the original polyfunctional compound), each 100–1000 monomer units in length. The solvable multi-chain molecules mixed with an amount of ordinary linear chain molecules not joined together to multi-chain-molecules form the polymeric material suited for spinning to fibers in hydrocarbons with low precipitating power. For low molecular weights high amounts of cross-linker have to be used and the relationship between primary molecular weight as determined viscometrically and theoretical maximum amount Q of cross-linker in the polymer in moles percent are:

$$Q=\frac{100}{f.M/m} \text{ or } Q=\frac{0.11}{f(nr-1)}$$

where f is the number of double bonds in the cross-linker or the valency of the ions forming salt bridges. The preferred amount of cross-linker in the formed polymer is in practice between Q and Q/4. Depending on the polymerization conditions one mostly has to use an amount of cross-linker corresponding to between 2Q and Q/4 in the polymerization process.

THE POLYMER SOLVENT AND THE COAGULANT

In producing fibers by the method of the present invention several known solvents for acrylonitrile may be used, such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, ethylene carbonate, etc. The best fiber qualities are achieved when the polymer solution is extruded into a hydrocarbon coagulant in which the polymer solvent is completely soluble at the spinning temperature (80–150° C.) and only soluble to a limited degree at room temperature. We have further found that kerosene consisting essentially of aliphatic hydrocarbons and free of aromatic hydrocarbons may be used as the coagulant when dimethylformamide is used as the polymer solvent and that the spinning rate, when using a gradual coagulation bath of this kind can be considerably increased if the polymer used is cross-linked to our specified degree. A higher degree of stretching is thereby possible in the coagulation bath and greatly improved mechanical properties may be obtained in the fiber, since such spinning solutions have an elastic structure which ensures that the new-formed fiber quickly acquires a relatively high tensile strength, even if the coagulation is carried out slowly.

From cross-linked copolymers in solvents such as dimethylformamide (which show no tendency to clog the spinneret nor provoke other problems upon storing) it is possible, even at room temperature, to obtain transparent 18–20 and even 30 percent polymer solutions and even 30 percent solutions. Such polymer solutions show a suitable viscosity for the spinning process of about 10,000 cp. at 120° C., this being a suitable working temperature in this case. It may be pointed out that the cross-linked co-polymers in accordance with this invention have a softening temperature that may even be higher than the common one for non-cross-linked homopolymers, which is of advantage. The speed at which the fiber can be spun is not reduced by using a cross-linked copolymer instead of a cross-linked homopolymer. Furthermore the fibers prepared from a cross-linked polymer by wet-spinning in kerosene show much better physical properties than fibers obtained from dry-spinning of non-cross-linked polymers. To summarize, the appropriate combination of polymer cross-linking and copolymerization furnishes a new method of obtaining good solubility in solvents and spinning properties in hydrocarbon coagulants with slow coagulation power, giving as a result an acrylonitrile fiber with greatly improved properties.

The aromatic content of the kerosene must be adapted to the solvent used in order to get complete solubility of the polymer solvent in the kerosene at the spinning temperature. When using dimethylformamide aromatic-free kerosene may be chosen as the coagulation liquid for cross-linked polymers. When using dimethylsulfoxide and ethylene carbonate, however, kerosene with a certain aromatic content must be chosen in order to obtain a coagulation of sufficient strength, even in connection with our cross-linked polymer and a spinning temperature as high as 130° C. These latter solvents are very difficult to dissolve in pure aliphatic kerosene.

As stated above the composition of the hydrocarbon coagulant has to be balanced to the polymer solvent used, which means that the preferred proportion of aliphatic hydrocarbons to aromatic hydrocarbons differs for individual polymer solvents. In the following table the limits of the aromatic content in the kerosene are given for different solvents and the boiling range of the kerosene is 100–300° C., preferably 150–200° C. In this boiling range the refractive index is 1.42 for aliphatic, 1.43 for hydroaromatic and 1.49 for aromatic hydrocar-

bons. Therefore the refractive index can be used to classify the kerosene quality.

Polymer solvent	Limit of aromatic content	Preferred aromatic content
Dimethylformamide	0–50	0–20
Dimethylacetamide	0–50	0–20
Dimethylsulfoxide	40–100	60–100
Ethylene carbonate	40–100	70–100

The coagulation intensity may be regulated not only by the aromatic content of the kerosene and the temperature, but also by the content of the polymer solvent in the kerosene during the coagulation. This content will be balanced by the circulation rate of the kerosene in relation to the amount of extruded spinning solution. The lower the spinning temperature the higher the aromatic content must be chosen. The viscosity of a solution prepared in accordance with this invention may of course increase due to the cross-linking as compared to a polymer which is not cross-linked. However when using nominal molecular weights within the range of about 70,000 (determined viscometrically according to Staudinger) cross-linking in the very limited degree which we specify above will cause such a slight change of viscosity that 18–20 and even 30 percent spinning solutions can be worked up without difficulty. Viscosity problems arise, however, when the molecular weight and the cross-linking ratio are increased above that which we specify.

SPINNING AND STRETCHING

The spinning temperature should be within the range of about 80–150° C., and preferably between 100 and 140° C.

Spinning of polyacrylonitrile solutions in kerosene can be achieved by parallel or counter-flow of the coagulant. Parallel flow is easier to operate, as the coagulation power of the pure coagulant near the nozzles is then higher and the strength of the fiber is developed more rapidly. On the other hand, counter-flow of the coagulant causes somewhat slower coagulation power since the coagulant near the nozzles contains a greater amount of the polymer solvent. As stated before, the quality of the fibers formed is influenced by the coagulation power, and for that reason, a counter-flow of the coagulant gives better fiber properties than a parallel flow. It can be stated that a polymer solution (molecular weight 70,000) gave a fiber (after coagulation and stretching to 5 times its original length) with a strength of 3 g./denier and 40 percent break-elongation when a counter-flow of the coagulant was used and the dimethylformamide content was about 15 percent near the nozzles. When the same polymer solution was spun with a dimethylformamide content of 3 percent near the nozzles, the same strength of the fiber was obtained, but the elongation at break was only 25 percent. Especially when using counter-flow of the coagulant to the spinning direction the use of our cross-linked polymer has proved to be necessary. The controlled cross-linking which we specify above thereby indirectly causes a considerable improvement of the physical properties of the fiber. Spinning upwards in vertical tubes is to be preferred since the specific gravity for solvent is higher than for kerosene, and since the surface of the coagulant exposed to the atmosphere is thereby minimized.

As stated before, the fiber should get a stretch during the coagulation in such a way that the up-take-speed after the coagulation is higher (1.5–5 times higher) than the jet-velocity in the spinneret nozzles. This stretching can only be achieved with a cross-linked polymer if the spinning speed (coagulating speed) is to get in the economically preferred range of 10–50 m./min.

After coagulation is complete the spun fiber should be stretched to 3–10 times its length at 110–150° C. to achieve the desired molecular-orientation. This stretch is preferably given the fiber while still swollen in 3–15 percent residual solvent and containing 2–15 percent hydrocarbons mainly on the surface. The speed of the stretched fiber will therefore be 30–500 m./min. which is well within the scope of viscose fiber production. This after-stretch can be done directly after the coagulation without any wind up between coagulation and stretching. This is possible because the fibers coagulated in hydrocarbons under tension are not brittle but very soft and easy to handle even at high speeds, high mechanical demands and at low temperatures. If the fiber is washed free of solvent and hydrocarbons by hot water before stretching, the fiber is more difficult to handle, the stretching rate must then be decreased or the stretching temperature increased to 160–200° C. compared with 110–140° C. in the coagulated but solvent-swollen state.

The spinning of our limited cross-linked polymer in kerosene gives us a further gain in stretching the fiber directly after coagulation at a speed not heretofore achieved for a wet-spun acrylic fiber.

The stretching of the fiber can be done between rollers or groups of rollers with higher speed on the later roller or groups of rollers. The fibers are hot enough immediately after coagulation at 130° C. to be stretched but the first roller or group of rollers ought to be heated either electrically or by steam inside or by hot kerosene (coagulating bath) outside. Other heating media are, of course, also possible to use.

Our experiments have shown that a fiber coagulated in this way retains from 2 to 15 percent (an average of 5 percent) of the solvent and from 2 to 15 percent (an average of 5 percent) of other volatile compounds—mainly aromatic hydrocarbons from the kerosene. The strength of the fiber is somewhat contingent on the molecular weight of the polyacrylonitrile used, and on how much the fiber has been stretched. If the viscosimetric molecular weight of the polymer is about 70,000, and the fiber is stretched between heated rollers or in the coagulation kerosene to 5 times its original length at 130° C., its strength after spinning will be about 2.5 g./denier. The fiber will also have plastic properties, a homogeneous circular to kidney-shaped cross section, and moreover be as transparent as nylon or glass fibers.

REMOVAL OF THE SOLVENT AND COAGULANT LIQUID

After the fiber has been spun in kerosene and oriented, the residual solvent and liquid hydrocarbons should be removed, either in an alcohol or in hot water or by steaming at temperatures above 80° C. (preferably at boiling point, i.e. 100° C. at atmospheric pressure). This cannot be achieved quickly. The inner parts of a fiber have been shown to retain traces of solvent and kerosene even after 15 minutes of boiling. Such traces will not affect the mechanical properties of the yarn but may cause uneven absorption of the dye. No traces of kerosene remain in the fiber after boiling for an hour and drying.

The removal of solvent and the coagulation liquid from the fiber increases its strength from about 2.5 g./denier to about 3.0 g./denier, and its break elongation is then 40 percent.

The subsequent drying of water treated fiber is of great importance to the improvement of its structural properties, which vary with the drying conditon. If the fiber is dried at a temperature below 100° C. or preferably below 90° C., it will in the last stage of drying become more porous and rugged, more or less opaque and better able to carry moisture. If dried at temperatures above 100° C. or preferably above 120° C.—which may expediently be done over a hot metal surface—the fiber will be more translucent, vitreous and more compact. If the fiber before drying is boiled in a 10 percent aqueous salt-solution or washed in hot water thoroughly before stretching it does not turn opaque even at a low drying temperature.

A special advantage when using kerosene hydrocarbons of the kind described is that the polymer solvent and the coagulation agent are easy to separate in the spent coagulation bath by means of cooling, which results in phase separation of the polymer solvent and hydrocarbon. With admixture of a slight amount of a third component, e.g. water, the phase separation is facilitated. In this latter case, however, the separated spinning solvent phase will contain some water and must be redistilled, while the kerosene needs no redistillation is it is refined through "solvent extraction" every time it is used.

The spinning technique which can be used will be more clearly understood from the accompanying drawing illustrating diagrammatically a preferred apparatus suitable for use in producing fibers according to this invention.

Referring to the drawing the reference numeral **1** indicates a multihole spinneret through which an acrylonitrile polymer solution is extruded into a coagulating bath **2** contained in a vertical tube **3** of 3 m. height provided with a steam jacket. In its travel through the coagulating bath the yarn **4** formed by the coagulation of the polymer solution is subjected to tension directly from the spinneret by means of a positively driven up-take roller or feed wheel **5** with a peripheral speed preferably higher than the jet velocity of the solution in the spinneret. The yarn is then passed directly through a stretching device **6** comprising two groups of heated godets of different peripheral speed. The first group **7** of the heated godets has a peripheral speed of 30 m. per minute and the second group **8** a speed of 150 m. per minute. The temperature of the first group **7** of godets is preferably 140° C. and of the second group **8** between room temperature and 140° C. After the stretching device **6** the yarn is led through a crimper **8** and a cutter **10** and then to a washing and crimp-fixation device **11**. The crimper **9** and cutter **10** are of conventional type. The washing and crimp-fixation device **11** is of shaft type with inlet for steam and outlet for recovery of the polymer solvent and coagulant (not shown). The crimp fixation is achieved by treating the crimped fiber with 100–130° C steam. From the washing and crimp-fixation device **11** the washed and crimped staple fiber is dried in a drying and heat-conditioning apparatus **12** comprising an endless conveyor **13** in a heated chamber **14**. The treated staple fiber is then led through an opening device **15** to obtain the ultimate product

The drawing also illustrates one way of introducing the liquid hydrocarbon coagulant, e.g. kerosene. The coagulant liquid is stored in tank **16** and therefrom led to the upper parts of the vertical spinning tube **3**. The spent coagulating bath is led out of the tube **3** at the bottom and by a pump **17** for recovery of the polymer solvent and the coagulant for reuse.

EXAMPLES

The following examples are illustrative of preferred embodiments of the present invention. It should be understood that these examples are not intended to limit the invention and that obvious changes may be made by those skilled in the art without changing the essential characteristics and the basic concept of the invention. The parts and percentages are by weight, the temperature is room temperature and the pressure is atmospheric, unless otherwise indicated.

Example 1

A first copolymer was prepared from a mixture of 97 kg. acrylonitrile, 3 kg. acrylic acid and 120 g. methylene bisacryloamide in the following manner. The monomer mixture was gently poured during 3 hours into 400 liters of water at 50 to 55° C. containing dissolved 1 g. ammoniumpersulfate, 1.5 g. sodiumpyrosulfite and 1 g. sodiumlaurylalcoholsulfate per liter. The polymerization was continued 4 hours and a yield of 95 kg. precipitated and dried polymer was obtained. The copolymer had a molecular weight of 60,000–65,000 according to Staudinger.

Example 2

An 18 percent solution in dimethylformamide was prepared from the copolymer made in accordance with Example 1 and the solution was extruded without any preheating through a 1000 hole spinneret (hole-diameter 0.15 mm.) at a velocity of 250 ml. per minute. The spinneret was arranged in the bottom of a vertical steam-mantled tube of 3 m. length, through which an aromatic-free kerosene (boiling range 160–220° C.) with a temperature of 130° C. running from above to the bottom (counterflow). The velocity of the collecting godet in the upper part of the tube was 30 m. per minute. After said godet the fiber was still immersed in kerosene at 130° C. and the fiber was stretched 5 times its original length to another godet with a peripheral speed of 150 m. per minute. After that the fiber was allowed to relax at 130° C. in air and was then crimped and cut to staple fibers. The product was washed with boiling water containing a nonionactive soap (Berol Wasc) for 30 minutes, at pH 4, to remove 8 percent of dimethylformamide and 10 percent of kerosene, rinsed, prepared with a cationactive agent (Sapamin OC) and dried in air at 120° C. The fiber had a denier of 3.0 (measured microscopically 3.1 to 3.2), its tensile strength was 3.0 g. per denier and elongation at rupture about 40 percent. The dye receptivity to basic dyes, for example Du Pont's Basic Blue, was excellent. The amount of saturation was about 10 percent dye in the fiber. Fed into the tube at a rate of 1200 ml./min. the kerosene will contain 15 percent dimethyl formamide when passing out at the bottom. When cooled to 15° C., the precipitating bath is separated into a dimethyl formamide phase and a kerosene phase which latter is almost colorless and contains 2.5 percent of dimethyl formamide and can again be directly fed into the tube at the top. If kerosene is washed by meeting a flow of only 3 percent of water by weight of the kerosene, its dimethyl formamide content will be decreased to 0.1 percent. The dimethyl formamide phase may on the other hand be distilled to reduce its hydrocarbon contents from 5 to 1.0 percent. It is hardly practicable to separate the remaining 1 percent of hydrocarbons by distillation considering the azeotropic conditions arising during the distillation. More hydrocarbons can, however, be removed if the dimethyl formamide phase is mixed with the water previously used to wash the kerosene, and the hydrocarbon content of the dimethyl formamide can then be reduced by distillation to less than 0.1 percent.

Example 3

A copolymer prepared according to Example 1 was also dissolved in dimethylsulphoxide and spun at 130° C. in "Sangajol" kerosene from the Shell Oil Company. Other conditions were similar to those in Example 2, and the separation of solvent from kerosene followed in the same manner. "Sangajol" kerosene is a kerosene containing about 60 percent of aromatics. The yarn obtained after boiling in water and drying at 60° C. showed about the same properties as in Example 2 but was of even whiter appearance.

Example 4

A second copolymer was prepared from a mixture of 95 kg. acrylonitrile, 5 kg. methacrylate and 60 g. triacrylylhexahydrotriazine (as cross-linking agent) in the following manner. The monomer mixture was gently poured during 3 hours into 400 liters of water at 50 to 55° C containing dissolved 1 g. ammoniumpersulfate, 1.5 g. sodiumpyrosulfite and 1 g. sodiumlaurylalcoholsulfate per liter. The polymerization was continued 4 hours and a yield of 95 kg. precipitated and dried polymer was obtained. The copolymer had a molecular weight of 60,000–65,000 according to Staudinger.

Example 5

An 18 percent solution in dimethylformamide was prepared from the copolymer made in accordance with Ex-

ample 4 and the solution was extruded without any preheating through a 1000 hole spinneret (hole-diameter 0.15 mm.) at a velocity of 250 ml. per minute. The spinneret was arranged in the bottom of a vertical steam-mantled tube of 3 m. length, through which an aromatic-free kerosene (boiling range 160–220° C.) with a temperature of 130° C. was running from above to the bottom (counterflow). The velocity of the collecting godet in the upper part of the tube was 30 m. per minute. After said godet the fiber was still immersed in kerosene at 130° C. and the fiber was stretched 5 times its original length to another godet with a peripheral speed of 150 m. per minute. After that the fiber was allowed to relax at 130° C. in air and was then cut upon crimping to staple fibers. The product was washed with boiling water containing a nonionactive soap (Berol Wasc) for 30 minutes, at pH 4, to remove 8 percent of dimethylformamide and 10 percent of kerosene, rinsed, prepared with a cationactive agent (Sapamin OC) and dried in air at 120° C. The fiber had a denier of 3.0 (measured microscopically 3.1 to 3.2), its tensile strength was 3.0 g. per denier and elongation at rupture about 40 percent. The dye receptivity to basic dyes, for example Du Pont's Basic Blue, was excellent. The amount of saturation was about 8 percent dye for the methylacrylate containing fiber. Fed into the tube at a rate of 1200 ml./min. the kerosene will contain 15 percent of dimethyl formamide when passing out at the bottom. When cooled to 15° C., the precipitating bath is separated into a dimethyl formamide phase and a kerosene phase which latter is almost colorless and contains 2.5 percent of dimethyl formamide and can again be directly fed into the tube at the top. If kerosene is washed by meeting a flow of only 3 percent of water by weight of the kerosene, its dimethyl formamide content will be decreased to 0.1 percent. The dimethyl formamide phase may on the other hand be distilled to reduce its hydrocarbon contents from 5 to 1.0 percent. It is hardly practicable to separate the remaining 1 percent of hydrocarbons by distillation considering the azeotropic conditions arising during the distillation. More hydrocarbons can, however, be removed if the dimethyl formamide phase is mixed with the water previously used to wash the kerosene, and the hydrocarbon content of the dimethyl formamide can then be reduced by distillation to less than 0.1 percent.

Example 6

A copolymer prepared according to Example 4 was also dissolved in dimethylsulphoxide and spun at 130° C. in "Sangajol" kerosene from the Shell Oil Company. Other conditions were similar to those in Example 5, and the separation of solvent from kerosene followed in the same manner. "Sangajol" kerosene is a kerosene containing about 60 percent of aromatics. The yarn obtained after boiling in water and drying at 60° C. showed about the same properties as in Example 5 but was of even whiter appearance.

Example 7

A third copolymer was prepared from a mixture of 97 kg. acrylonitrile and 3 kg. of acrylic acid using the same general process outlined in Example 1, but with the exception that no cross-linking agent such as methylene bisacryloamide was used. The molecular weight of copolymer was about 58,000. A 20 percent solution of this copolymer in dimethylformamide was prepared but the solution could not be extruded and spun by following the procedure outlined in Example 2. By using a kerosene which had about 15 percent aromatics and a boiling range of about 150–210° C. (as opposed to an aromatic-free kerosene) it was possible to achieve a spinning rate (i.e. collecting velocity) of 3 m. per minute without fiber rupture. This was much lower than the spinning rate achieved in Example 1 and it is thus seen that the presence of the very small amount of cross-linking agent set forth in Example 1 made a very great difference in spinning rate.

Example 8

A fourth copolymer was prepared from a mixture of 97 kg. acrylonitrile and 3 kg. of acrylic acid using the same general process outlined in Example 1, but with the exception that the amount of cross-linking agent (methylene bisacryloamide) was increased to 0.5 molar percent. The molecular weight of the copolymer was about 75,000. This copolymer could not be satisfactorily dissolved in dimethylformamide and the resulting "solution" showed typical gel-particles. A small steel ball when dropped through a 20 percent "solution" did not descend exactly vertically but showed some irregular movements in the horizontal direction depending on big gel-particles dispersed in the continuous medium of polymer solution. In trying to spin this "solution" it was possible to start up the operation but after only a few minutes several holes of the spinneret were clogged and a spinning could not be continued.

Another polymer was prepared by exactly the same procedure with the exception that the amount of cross-linking agent was 1.0 molar percent. This polymer was so insoluble in dimethylformamide that it was not even possible to get a homogeneous 0.5 percent solution for determination of the molecular weight and it therefore could of course not be extruded and spun into filaments.

Example 9

A fifth copolymer was prepared from a mixture of 95 kg. acrylonitrile and 5 kg. of methylacrylate using the same general process outlined in Example 4, but with the exception that no cross-linking agent such as triacrylohydrotriazine was used. The molecular weight of copolymer was about 60,000–65,000. An 18 percent solution of this copolymer in dimethylformamide was prepared but the solution could not be extruded and spun by following the procedure outlined in Example 5. By using a kerosene which had about 15 percent aromatics and a boiling range of about 150–210° C. (as opposed to an aromatic-free kerosene) it was possible to achieve a spinning rate (i.e. collecting velocity) of 3 m. per minute without fiber rupture. This was much, much lower than the spinning rate achieved in Example 5 and it is thus again seen that the presence of the very small amount of cross-linking agent set forth in Example 4 made a very great difference in spinning rate.

Example 10

A sixth copolymer was prepared from a mixture of 95 kg. acrylonitrile and 5 kg. of methylacrylate using the same general process outlined in Example 4, but with the exception that the amount of cross-linking agent (triacrylohydrotriazine) was increased to 1.0 molar percent. The molecular weight of copolymer was estimated to be about 50,000 but the cloudy solution was too inhomogeneous to allow a molecular weight calculation on the basis of viscosity. This copolymer showed the same spinning trouble as did the polymer in Example 8. Examination of the spinneret after trying to start the spinning five times without practical success showed that the inside of the spinneret was covered with gel-lumps pressed against the spinneret and partly forced into the holes of the spinneret, thereby clogging same. The gel-lumps had to be removed mechanically from the spinneret as they were insoluble. In dimethylformamide they formed insoluble slime-like lumps, and these lumps did not even dissolve upon initially boiling at 153° C. but the lumps did turn more yellow and did break down into smaller lumps after heating for a number of minutes at 153° C.

This clearly demonstrates that the maximum amount of the cross-linking agent is quite critical insofar as producing a spinnable fiber is concerned.

Example 11

An emulsion of the copolymer prepared according to Example 1, but without the addition of methylenebisac-

ryloamide, was treated with 1 kg. of aluminiumsulfate at 50° C. for 30 minutes at pH 6. The copolymer was found to contain 0.04 percent aluminium after this treatment. When spinning such a copolymer according to Example 2 in kerosene containing 15 percent of aromatics the collecting velocity of 50 m. per minute could be used, or if stretched 5 times its coagulated length 250 m. per minute. Similar spinning values were obtained upon treatment with magnesium sulfate, the fiber being in this case more discolored.

FIBER PROPERTIES

Fibers made of our limited cross-linked copolymers show more valuble properties than acrylic fibers made of common linear polymers. The fiber properties at room temperature do not differ very much but the properties at elevated temperatures and wet conditions are highly improved. Below we have presented some comparable figures concerning a fiber A made of the limited cross-linked copolymer of Examples 4 and 5 and a fiber B of a linear copolymer of the same composition as of Example 4 without any cross-linking (compare Example 9).

	A	B
Tensile strength, g./den., 20° C.; 60 R.H.	3.0	2.5
Elongation at break, percent, 20° C.; 60 R.H.	35	35
Modulus, g./den., 20° C.; 60 R.H.	45	40
Tensile strength, g./den., 90° C., wet	1.3	0.5
Elongation at break, percent, 90° C., wet	60	110
Modulus, g./den., 90° C., wet	2.5	1.1
Tensile strength, g./den., 150° C., dry	0.8	0.2
Zero strength temperature, ° C.	320	210
Orientation angle according to X-ray measurement, ° C.	54	30
Crystallinity, percent	19	19
Torsional fatigue, cycles	1,000	<100
Wear strength dry, cycles	2,600	1,010
Wear strength wet, cycles	3,700	950
Soil resistance (percent residual reflectance after 10,000 steps)	98.5	78.5

The figures above illustrate the vastly improved fiber properties especially under hot-wet conditions, which are particularly important for technical textiles and for the behavior of the fiber during dyeing, drying and other hot and wet textile processes. Goods and fabrics made of fiber A show improved wrinkle recovery, improved dimensional stability and also improved pleat retention compared with fabrics made of fiber B. In practical use the soil resistance for fiber A is very remarkable, but as mentioned before this property is not only attributable on the multi-chain structure but also to the specific coagulation in hydrocarbons. It can further be emphasized that the good hot-wet properties can be found only in fibers produced from polymers cross-linked during the polymerization process. If the polymer is cross-linked by formation of salt bridges between acidic groups incorporated in the polymer, the resulting fiber shows the same bad hot-wet properties as fiber B. Only at 150° C. dry conditions does this fiber show some improved properties. The salt bridges therefore seem to be sensitive to hydrolysis by water and are inferior to cross-linking by polyunsaturated compounds in the polymerization process.

Those skilled in the chemical arts, and particularly in the art to which this invention pertains, will readily appreciate that many modifications of the basic invention set forth here are possible. For example, it is quite possible that other closely related compounds might work as well as the herein specifically described compounds and there would certainly be no invention involved in trying such closely related compounds, in view of the present broad disclosure. All of these modifications are considered to be within the scope of the present claims by virtue of the well-established "doctrine of equivalents."

This is a continuation-in-part of our prior application Serial No. 539,558 filed on October 10, 1955, and now abandoned.

We claim:

1. A fiber-forming composition of matter which is soluble in a polymer solvent selected from the group consisting of dimethylformamide, dimethylacetamide, dimethylsulfoxide, butyrolacetone, ethylene carbonate and dimethyl methoxyacetamide comprising an acrylonitrile copolymer containing at least 85 molar percent of acrylonitrile units and up to about 15 molar percent of a monoethylenically unsaturated monomer selected from the group consisting of vinyl acetate, vinyl chloride, vinylidene chloride, acrylic acid, acrylamide, methacrylonitrile, methacrylamide and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid, and cross-linked to a degree of from 0.001 to 0.3 molar percent of cross-linking units by a cross-linking agent selected from the group consisting of divinyl benzene, methylenebisacrylamide, diallylphthalate, diallylmaleate, ethylene acrylate, ethylene diacrylate and triacrylylperhydrotriazine.

2. A process for preparing a soluble acrylonitrile copolymer for the spinning of fibers, comprising reacting a mixture containing at least 85 molar percent of acrylonitrile, up to 15 molar percent of a monoethylenically unsaturated monomer selected from the group consisting of vinyl acetate, vinyl chloride, vinylidene chloride, acrylic acid, acrylamide, methacrylonitrile, methacrylamide and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid, and from 0.005 to 0.1 molar percent of a cross-linking polyethylenically unsaturated monomer selected from the group consisting of divinyl benzene, methylenebisacrylamide, diallylphthalate, diallylmaleate, ethylene acrylate, ethylene diacrylate and triacylylperhydrotriazine, in the presence of a polymerization catalyst.

3. A fiber-forming composition of matter which is soluble in a polymer solvent selected from the group consisting of dimethylformamide, dimethylacetamide,, dimethylsulfoxide, butyrolacetone, ethylene carbonate and dimethyl methoxyacetamide comprising an acrylonitrile copolymer containing at least 85 molar percent of acrylonitrile units and up to about 15 molar percent of a monoethylenically unsaturated monomer selected from the group consisting of vinyl acetate, vinyl chloride, vinylidene chloride, acrylic acid, acrylamide, methacrylonitrile, methacrylamide and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid, and cross-linked to a degree of from 0.005 to 0.10 molar percent of cross-linking units by a cross-linking agent selected from the group consisting of divinyl benzene, methylenebisacrylamide, diallylphthalate, diallylmaleate, ethylene acrylate, ethylene diacrylate and triacrylylperhydrotriazine.

4. A fiber-forming composition of matter comprising an acrylonitrile copolymer containing at least 85 molar percent of acrylonitrile units and up to about 15 molar percent of a monoethylenically unsaturated monomer and cross-linked to a degree corresponding to about 1 cross-link per 2–12 straight polymeric molecules.

5. A fiber-forming composition according to claim 4 in which the acrylonitrile polymer is cross-linked by means of a compound of the group consisting of divinyl benzene, triacrylylperhydrotriazine, methylenebisacryloamide, diallylphthalate, diallylmaleate and ethylene acrylate.

6. A fiber-forming composition according to claim 4 wherein the cross-linked acrylonitrile polymer is a copolymer of acrylonitrile and a monofunctional unsaturated monomer selected from the group consisting of vinyl acetate, vinyl chloride, vinylidene chloride, acrylamide, meth-

acrylonitrile, methacryloamide, an ester of acrylic acid and an ester of methacrylic acid.

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