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FIBER-SPINNING COMPOSITIONS

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This invention relates to a new method of preparing synthetic fibers from polymers of acrylonitrile. More particularly, the invention relates to completely miscible mixtures comprising acrylonitrile polymers and haloacetonitrile from which high tenacity fibers can be prepared by conventional extrusion procedures.

It is well-known to the prior art that polymers of acrylonitrile and especially those in which more than 85 per cent of the polymerizable content is acrylonitrile are excellent fiber-forming compositions. The conventional procedures for preparing these synthetic fibers involve the dissolution of the acrylonitrile polymer in a suitable solvent and thereafter extruding the composition through a die or spinneret, into a medium which removes the solvent and precipitates the polymer in continuous form. Although many solvents for polyacrylonitrile are known and described in the literature, most of them are costly, difficult to prepare, and sensitive to the presence of non-solvents, such as water.

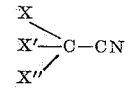
The primary purpose of this invention is to provide a new and inexpensive solvent for polyacrylonitrile and copolymers having 85 or more per cent by weight of acrylonitrile. A further purpose of this invention is to provide a new procedure for preparing synthetic fibers from acrylonitrile. A still further purpose of this invention is to provide a means for using haloacetonitrile, normally a non-solvent as a medium for spinning acrylonitrile fibers.

It has been discovered that, although neither the haloacetonitrile nor water is a solvent for acrylonitrile polymers, a mixture of the two is a very effective solvent. This is an unusual phenomenon because generally the presence of non-solvents, and water in particular, impedes any solvent action which the principal medium may have; for example, dimethylformamide well-known as an excellent solvent for acrylonitrile polymers becomes a non-solvent if it contains as little as five per cent of water. Also a solution of acrylonitrile polymer in dimethylformamide will be precipitated by the addition of very small amounts of water or other non-solvents. In the practice of this invention it has been found that mixtures of from 99 per cent to 70 per cent of the haloacetonitrile and from one per cent to 30 per cent of water are excellent solvents for the acrylonitrile polymers.

It has been found that the suitable haloacetonitriles are the halogenated acetonitriles and especially those of chlorine, fluorine, and bromine. From one to three halogens, either the same or

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different, may be present in the haloacetonitrile. The generic class of useful acetonitriles may be represented by the structural formula:



wherein X, X', and X'' each may be hydrogen or halogen, provided that at least one of the X, X', and X'' is a halogen atom. Typical haloacetonitriles are chloroacetonitrile, fluoroacetonitrile, bromoacetonitrile, dichloroacetonitrile, trichloroacetonitrile, trifluoroacetonitrile, and chlorofluoroacetonitrile.

It has been found that polymers and copolymers of acrylonitrile useful in the practice of this invention are those which are prepared by the polymerization of an olefinic monomeric substance of which at least 85 per cent of the total polymerizable monomers is acrylonitrile. These may be copolymers of 85 or more per cent of acrylonitrile and up to 15 per cent of other monomers copolymerizable therewith, for example vinyl acetate, vinylidene chloride, vinyl chloride, dialkyl fumarates, in which the alkyl radical has up to four carbon atoms, the dialkyl maleates in which the alkyl radical has up to four carbon atoms, the alkyl methacrylates and acrylates, wherein the alkyl radical has up to four carbon atoms, styrene, vinylpyridine and the alkyl substituted vinylpyridines, N-vinylimidazole, and other vinyl substituted heterocyclic nitrogen compounds, allyl chloroacetate, methallyl chloroacetate, allyl glycidyl ether, methallyl glycidyl ether, and other mono-olefinic compositions polymerizable with acrylonitrile. Of particular utility are the copolymers of acrylonitrile and olefinic monomers which contain a dye-receptive N-heterocyclic nucleus or which contains a chloroacetate, chloroacrylate, a β-chloroethyl or other active halogen containing nucleus, glycidyl radical or other groups capable of being converted into a dye-receptive group by subsequent chemical reaction, for example, a tertiary-amine, a thiourea or a 2-mercaptobenzothiazole derivative.

Another useful type of acrylonitrile polymer is that wherein the polyacrylonitrile or a copolymer of acrylonitrile and minor proportions of another polymerizable monomer is blended with a polymer of a monomer containing a dye-receptive N-heterocyclic nucleus, or other dye-receptive nucleus, or a nucleus such as chloroacetate or other active chlorine containing radical, a glycidyl radical or other radical which can be converted into dye-receptive form by subsequent

chemical reaction. The blended polymers will be comprised principally of acrylonitrile in polymeric form and sufficient of the dye-receptive radical, two to fifteen per cent of the total monomer, to enable the final blended composition to be receptive of dyestuff and adaptable to conventional dyeing procedures.

The spinning solutions are prepared from mixtures of haloacetonitrile and water by dispersing the finely divided acrylonitrile polymer or blended polymers with the solvent mixture and heating until a uniform, homogeneous mixture is obtained. In general, the solutions will contain from five to 35 per cent of polymer and the balance of the solvent mixture of a haloacetonitrile and water.

In the practice of this invention, as in the preparation of all acrylonitrile fibers, the molecular weight of the copolymer is of substantial importance. The copolymer should have a molecular weight in excess of 10,000, and preferably in excess of 25,000. These molecular weights are determined by measuring the viscosity in suitable solvents in the manner well-known to the art. It is also very desirable to use copolymers which are substantially uniform throughout, especially with respect to composition and molecular weight. These uniform copolymers enable the practice of the invention more economically by permitting the utilization of continuous uninterrupted spinning through the minimization of fiber fractures and clogging of the spinneret.

In the practice of this invention the polyacrylonitrile and copolymers of acrylonitrile are preferably used in finely divided form. Although mass polymers may be ground to desirable size and so used, emulsion or suspension polymers are preferably employed in the preparation of the spinning solutions, and the sub-divided state in which the polymer is obtained from the emulsion is used directly. The polymer is mixed with the solvent mixture and stirred until a uniform solution is formed. In some cases heating may be necessary or desirable to expedite the solution preparation. Since water is a critical component of the solvent mixture, the polymer, as obtained from the preferred aqueous dispersion polymerizations, need not be dried or even separated from the water medium. The polymer containing a substantial proportion of water may be mixed with the haloacetonitrile and the solution effected without addition of more water. It may in some circumstances be necessary to remove part of the water present, so as to utilize the optimum proportions of water and haloacetonitrile. It is often advantageous to wash the polymer with water to remove traces of polymerization reagents, monomers and other impurities, and to blend the wet polymer, recovered by decantation or filtration, with haloacetonitrile and sufficient water to produce the optimum solvent proportions. The solution preparation may be conducted in any conventional mixing machine, for example a dough mixer.

In the spinning of fibers from acrylontrile solutions in a mixture of water and haloacetonitrile, it is desirable to use a solution of as high a concentration of polymer as possible, but the maximum concentration is dependent upon the molecular weight of the polymer and the visocity characteristics of the polymer-solvent mixture. To obtain fibers of optimum physical properties, polymers of molecular weights in excess of 25,000 are used, and with such polymers it is only possible to dissolve a relatively small proportion in the haloacetonitrile-water mixtures without achieving an impracticably high viscosity. Although as little as five per cent solutions of the polymer can be used in the spinning operation, such low concentrations are undesirable because they necessitate the removal and the recovery of too much solvent from the medium into which the fiber is extruded. Dilute spinning solutions also tend to make the resultant fibers more bulky by reason of the excessive quantity of solvent removed from the inside of the fiber. Dilute polymer solutions also reduce the spinning speeds by lengthening the period of time required for coagulation of the fiber and complete removal of the residual solvent which is usually objectionable. The concentration of polymer in the spinning solution is generally between ten and twenty per cent for polymers of optimum molecular weight. Lower molecular weight polymers may be spun in solutions of as high as 35 per cent. The concentration of the polymer will ultimately be determined by considering the desired physical properties of the fiber and the desired spinning speed, the latter being a function of the concentration and the viscosity of the spinning solution. The viscosity will often depend upon the chemical composition and the molecular weight of the polymer. The optimum concentration can best be determined by selecting a uniform high molecular weight polymer having good fiber-forming properties, and dissolving it in as little of the haloacetonitrile-water mixture as is possible to form a viscous solution capable of being spun at convenient temperatures.

The spinning solution may be modified by the addition of other materials for the development of special properties in the resulant fiber. For example, finely divided titanium dioxide, or other white pigment, can be added to the spinning solution in order to reduce the lustre of the fibers prepared therefrom. Similarly, other resins may be added without impairing the homogeneity of the copolymer solution. For example, small amounts of thermoplastic resins improve the spinnability of the solution and the dyestuff affinity of the fiber. Thermosetting resins in the uncured state may also be added, and the resultant fibers subsequently cured to improve the fiber strength and elasticity. Proteins also may be added for the purpose of increasing dyestuff affinity, although slight reductions in water resistance are simultaneously developed. Additions of cellulose derivatives may also be made for developing stiffness and dyestuff affinity in the resulting fibers.

The fibers are spun by extruding the polymer solution through an orifice or a spinneret having a plurality of orifices into a medium which removes the haloacetonitrile and water. The volume rate of passage of the solution through the spinneret must be constant in order to produce a fiber of uniform size. This is best achieved by using a positively driven gear pump to deliver a constant flow of solution regardless of minor changes in viscosity and the variable resistance offered by the spinneret. It is also desirable to pass the solution, which has been filtered, into one or more additional filters before the spinneret to remove the last traces of foreign matter and particles of incompletely dissolved polymer. The polymers may be delivered to the gear pump by pressure applied by an inert gas to the solution reservoir, which is heated if necessary to make the solution fluid enough to pass through the conduits. The extruding operation may be operated

at elevated temperatures, but at temperatures not in excess of the boiling point of the haloacetonitrile-water mixture.

The medium into which the solution is extruded and which removes the solvent may be either liquid or gaseous. The method involving the use of liquids, known as wet spinning, utilizes aqueous mediums, alcohol, glycerol, methyl ethyl ketone, or other liquids in which the haloacetonitrile is at least in part soluble, but in which the copolymer is insoluble. The solutions of acrylonitrile polymers in haloacetonitrile and water mixtures are unusually adapted to dry spinning techniques in which the solution is extruded into a gaseous atmosphere at relatively high temperatures, so that the haloacetonitrile and water are evaporated from the surface of the fiber and removed in the gas stream to suitable recovery apparatus. Suitable gases are air, nitrogen, oxygen, carbon dioxide, and methane. The dry spinning method generally is operative at higher temperatures, but the maximum temperature to which the fiber can be subjected is about the boiling point of the haloacetonitrile and water mixture, since evaporation within the fiber may cause bubbles in the fiber structure. The fiber may be heated by convection from the gaseous medium or by radiation from the walls of the confining vessel. Generally a combination of both convection and radiation is involved. The use of radiation heating is more efficient and permits the operation with the wall temperature considerably in excess of the boiling point of the haloacetonitrile-water mixture.

In general the methods of both wet and dry spinning which are commercially in use are readily adaptable to spinning acrylonitrile polymer solutions in haloacetonitrile-water mixtures. Similarly, conventional automatic machinery for continuous spinning, drying the thread if necessary, and winding it upon suitable spools, can be used. As in the case of most synthetic fibers, those obtained by spinning haloacetonitrile-water solutions of acrylonitrile polymers must be oriented by stretching in order to develop the optimum physical properties. If desired part of the stretching may be accomplished in the spinning medium by drawing the fiber from the medium at a rate greater than the rate of extrusion. Both continuous and staple fibers may be produced from the described haloacetonitrile-water solutions. Oriented staple fibers may be made by stretching the continuous fiber and then cutting to the desired lengths for use in conventional textile fiber processes, either alone or in admixture with other natural or synthetic fibers. The solutions of acrylonitrile polymers in haloacetonitrile-water mixtures are also useful for the preparation of films by casting the solutions on smooth surfaces and evaporating the haloacetonitrile and water. The solutions are also useful as coating compositions.

Further details of the invention are set forth with respect to the following specific examples:

Example 1

Two parts by weight of an emulsion copolymer of 97 per cent of acrylonitrile and three per cent of vinyl acetate were dispersed in ten parts of chloroacetonitrile and ten parts of water. The resulting mixture was heated with stirring for 15 minutes at 80° C. whereby a homogeneous copolymer solution was obtained. A second supernatant liquid phase was comprised essentially of eight parts of water. Fibers and films were prepared both by precipitation of the polymer solution with alcohol and by evaporation of the solvent. A similar experiment was attempted using chloroacetonitrile without water but no solution was obtained.

Example 2

Five parts by weight of an emulsion copolymer of 95 per cent acrylonitrile and five per cent of vinyl acetate was dispersed in a mixture of 30 parts of chloroacetonitrile and ten parts of water. A homogeneous copolymer solution was prepared by heating with stirring at 70° C.

What I claim is:

1. A new composition of matter comprising a homogeneous, miscible mixture of a polymer of a monomeric mixture of which acrylonitrile is at least 85 per cent by weight of the total monomer content, homogeneously dispersed to the extent of from five to 35 per cent in a mixture of from 70 to 99 per cent of chloroacetonitrile and from one to 30 per cent of water.

2. A fiber-spinning composition comprising a homogeneous, miscible mixture of a polymer of a monomeric substance of which acrylonitrile is at least 85 per cent by weight of the total polymerized monomers and a solvent medium comprised of from one to 30 per cent of water and from 70 per cent to 99 per cent of chloroacetonitrile.

3. The composition defined by claim 1 wherein the polymer is polyacrylonitrile.

4. The composition defined by claim 1 wherein the polymer is a copolymer of from 85 per cent to 98 per cent of acrylonitrile and from two to 15 per cent of vinylpyridine.

5. The composition of claim 1 wherein the polymer is a copolymer of at least 85 per cent of acrylonitrile and up to 15 per cent of vinyl acetate.

6. The composition defined by claim 1 wherein the polymer is a blend of a polymer of at least 85 per cent of acrylonitrile and a polymer of from 30 per cent to 70 per cent of vinylpyridine.

7. The composition defined by claim 2 wherein the polymer is polyacrylonitrile.

8. The composition defined by claim 2 wherein the polymer is a copolymer of from 85 per cent to 98 per cent of acrylonitrile and from two to 15 per cent of vinylpyridine.

9. The composition defined by claim 2 wherein the polymer is a copolymer of at least 85 per cent of acrylonitrile and up to 15 per cent of vinyl acetate.

10. The composition defined by claim 2 wherein the polymer is a blend of a polymer of at least 85 per cent of acrylonitrile and a polymer of from 30 per cent to 70 per cent of vinylpyridine.

11. A new composition of matter comprising a homogeneous, miscible mixture of a polymer of a monomeric mixture of which acrylonitrile is at least 85 percent by weight of the total monomer content, homogeneously dispersed to the extent of from 5 to 35 percent in a mixture comprised of from one to 30 percent of water and from 70 to 99 percent of haloacetonitrile.

12. The composition defined by claim 11 wherein the polymer is polyacrylonitrile.

13. The composition defined by claim 11 wherein the polymer is a copolymer of from 85 to 98 percent of acrylonitrile and from two to 15 percent of vinylpyridine.

14. The composition of claim 11 wherein the polymer is a copolymer of at least 85 percent of acrylonitrile and up to 15 percent of vinyl acetate.

15. The composition defined by claim 11 wherein the polymer is a blend of a polymer of at least 85 perent of acrylonitrile and a polymer of from 30 to 70 percent of vinylpyridine.

16. A fiber-spinning composition comprising a homogeneous, miscible mixture of a polymer of a monomeric substance of which acrylonitrile is at least 85 percent by weight of the total polymerized monomers and a solvent medium com-

prised of from one to 30 percent of water and from 70 to 99 percent of haloacetonitrile.

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