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HIGH ACRYLONITRILE POLYMER SOLUTIONS CONTAINING POLYOXYALKYLENE GLYCOLS

Fred J. Lowes, Jr., 500 Crescent Drive, Midland, Mich.
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This invention relates to compositions of matter that are especially adapted for use in spinning acrylonitrile polymer synthetic textile fibers or the like structures. It relates more particularly to spinnable solutions of such polymers in concentrated aqueous salt solutions having certain polyoxyalkylene glycols dissolved therein. The invention is also concerned with shaped articles, especially filamentary structures, having increased flexibility and resistance to fibrillation and to methods for preparation of such compositions and articles.

Polyacrylonitrile and many of the fiber and film-forming copolymers of acrylonitrile may advantageously be fabricated by a wet spinning process wherein the polymer composition is extruded from compositions of the polymer in polyacrylonitrile-dissolving aqueous saline solvents, particularly aqueous solutions of zinc chloride and its saline equivalents. Such a procedure, as is well known in the art, is oftentimes referred to as salt-spinning with the fibers (or other shaped articles) obtained thereby being salt-spun. In salt-spinning, the fiber-forming, aqueous saline spinning solution or other composition of the polymer is extruded during the spinning operation into a non-polymer-dissolving coagulation liquid, or spin bath, which frequently is a solution of the same salt or salts as are in the spinning solution.

Acrylonitrile polymers (including fiber-forming copolymers), particularly polyacrylonitrile, that are salt-spun in the referred-to manner are generally formed as aquagel intermediates. Such intermediates have a water-swollen or hydrated structure prior to their being finally irreversibly dried to the desired, characteristically hydrophobic, product.

Advantageously, the aquagel structures of polyacrylonitrile and other fiber- and film-forming acrylonitrile polymers may be derived by the extrusion into and coagulation in an aqueous coagulating spin bath of a solution of the acrylonitrile polymer that is dissolved in an aqueous zinc chloride saline solvent therefor. It is usually desirable for zinc chloride to be at least the principal (if not the entire) saline solute in the aqueous saline solvent solution.

If preferred, however, various of the saline equivalents for zinc chloride may also be employed in the aqueous saline solvent medium for the spinning solution and the coagulating bath utilized. These zinc chloride equivalents, as is well known, include various of the thiocyanates (such as calcium thiocyanate) lithium bromide and the salts and salt mixtures that are "solvent" members of the so-called "lyotropic" series as are disclosed, among other places, in U.S. 2,140,921; 2,425,192; 2,648,592; 2,648,593; 2,648,646; 2,648,648; and 2,648,649.

Fabricated acrylonitrile polymer films, textile fibers and like filamentous articles derived from salt-spinning processes are generically described as being capable of lying substantially in a single plane, having at least one major dimension, and at least one minor dimension less than about 0.1 inch, said articles being characterized by having orientation of the molecules parallel to one another and to a major surface of the article. Such articles are often hard and brittle and have a tendency to fibrillate during preparation and subsequent normal usage of the shaped article.

The term "fibrillation" is used in the textile industry to indicate a type of fiber disintegration or longitudinal

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fracture generally along lines of molecular orientation. As a consequence of fibrillation the fiber or filament is longitudinally divided into segments or fibrils. Often, fibrillation may result in a frosty or whitened appearance, even of dyed fibers and fabrics.

The loss of color or change toward white is affected by several variables including the amount of division and size of fibrils produced during the processing of the spun product. Fibrils can be of such small diameters that incident light is scattered. Fibrillation of textile fibers and fabric produced therefrom appears to result from transverse forces which ultimately cause a shattering of the fiber along the lines of least resistance, namely, longitudinally. Thus, a fiber or related filamentous article having greater characteristic flexibility may often be less prone to fibrillation than a corresponding relatively less flexible article.

U.S. 2,570,200; 2,570,237; and 2,570,257 describe such useful shaped articles, filaments, films and the like, prepared by extruding certain acrylonitrile polymer masses into a liquid coagulating medium of water-soluble, liquid, aliphatic polyhydric alcohol compounds. Among such polyhydric alcohol compounds are mentioned the alkylene glycols (e.g., ethylene glycol, propylene glycol, 1,4-butylene glycol, 2-methylpentanediol-2,4) and the polyalkylene glycol ethers (e.g., diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, tetraethylene glycol, etc.) and other polyhydric alcohol compounds (e.g., glycerol, thiodiethylene glycol, etc.). None of these materials have accomplished the purposes of or are suitable for achieving the ends of the present invention.

There is still a need for a non-volatile and economically practical plasticizer to impart permanent flexibility with accompanying ease of formation and resistance to fibrillation of shaped articles produced from salt-spun acrylonitrile polymers.

Accordingly, it is the primary object of the present invention to provide compositions of matter especially adapted for use in spinning synthetic films and textile fibers or like structures comprising solutions of high acrylonitrile polymers (i.e., those at least 85 weight percent of polymerized acrylonitrile in the polymer molecule).

A further object is to provide shaped articles from the compositions of the invention which have increased flexibility and resistance to fibrillation.

A still further object is to provide a method of producing the compositions and articles of the present invention.

Other and related objects will become evident from the following specification and claims.

In accordance with the present invention, high acrylonitrile synthetic films and textile fibers having increased flexibility and resistance to fibrillation are produced from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least about 85 weight percent of acrylonitrile dissolved in an aqueous saline solvent solution, preferable where zinc chloride is the principal (if not entire) saline solute, wherein the aqueous saline solvent has additionally dispersed therein between about 5 weight percent and about 50 weight percent, preferably between about 10 percent and 20 weight percent of the acrylonitrile polymer, of certain polyoxyalkylene glycols having a molecular weight of less than about 3000, a viscosity at 100° F. ranging from about 100 to about 260 centistokes, wherein said polyoxyalkylene glycols are substantially insoluble in water.

The acrylonitrile polymer employed in practice of the present invention is, advantageously, polyacrylonitrile, although, as is readily apparent, any of the well known fiber- and film-forming copolymers thereof that contain, polymerized in the polymer molecule, at least 85 weight

percent of acrylonitrile with at least one other ethylenically unsaturated monomer that is copolymerizable with acrylonitrile may, beneficially, be utilized. The acrylonitrile polymer employed is, of course, soluble in an aqueous saline solvent for acrylonitrile which, usually, has therein at least about 50–60 weight percent of the zinc chloride or its saline equivalents. U.S. 2,776,946, among many other reference sources, set forth many of the monomers which may be copolymerized or interpolymerized with acrylonitrile to produce binary or ternary acrylonitrile copolymers that are useful in the practice of this invention.

Specific polyoxyalkylene glycols that are suitable for instant purposes include, but are not restricted to, polyoxypropylene glycols having an average molecular weight of about 2000 or so; polyoxy-1,2- or 2,3-butylene glycols having an average molecular weight of about 2000 or so; and suitably mixed polyoxyalkylene glycols wherein the polymer chains contain two or more different oxyalkylene units, either as a random sequence (heteric) or as segregated blocks (block copolymers). Ordinarily water-insoluble glycols having average molecular weights between about 1000 and 3000 are suitable.

The preparation of the polyoxyalkylene glycols useful in practice of the present invention is well known to those skilled in the art. U.S. 2,056,830 describes a method of preparing polyglycols by partial dehydration of the corresponding simple glycols in the presence of dehydration catalysts. By a "dehydration catalyst" is meant a substance which is capable of prompting splitting of water from a simple glycol, e.g. propylene glycol, with intramolecular formation of glycol ethers when such simple glycol is heated in its presence.

It has been found that to impart permanent plasticity to shaped articles produced from salt-spun acrylonitrile polymers, the polyoxyalkylene glycols to be used in the present invention must be substantially water-insoluble; this prevents excessive extraction of the glycol from the polymer during coagulation of said polymer solution in an aqueous non-polymer-dissolving medium and subsequent extraction of the polyoxyalkylene glycol from the aquagel or shaped articles produced therefrom, while water washing said aquagel or shaped article to remove residual saline material therefrom.

The polyoxyalkylene glycol used in the present invention must be present in the polymer solution in a minimum amount of about 5 weight percent based on the weight of the acrylonitrile polymer. The permissible maximum proportion depends on the particular polyoxyalkylene glycol being employed and the limit of its compatibility with the aqueous saline polymer solution, as well as the polymeric material contained therein. The maximum limit is generally about 50 weight percent, based on the weight of the acrylonitrile polymer. The amount of polyoxyalkylene glycol present in shaped articles produced from salt-spun acrylonitrile polymers is dependent

upon, and in the same ratio as, the amounts of said glycols incorporated in the spinning solution.

It has been observed that polyoxyalkylene glycols of the type here described but having a viscosity at 100° F. less than about 100 centistokes do not provide sufficient permanent flexibility to shaped articles produced from salt-spun acrylonitrile polymers. Additionally, such polyoxyalkylene glycols having a molecular weight greater than about 3000 or a viscosity at 100° F. of greater than about 260 centistokes have limited compatibility with the saline solvent solution and the polymeric materials contained therein, and, as a consequence, do not sufficiently plasticize articles produced therefrom.

The following examples, wherein all parts and percentages are to be taken by weight, illustrate the present invention but are not to be construed as limiting its scope.

EXAMPLE I

In each of a series of experiments, separate charges of about 35 grams of a solution consisting of 10 percent polyacrylonitrile, 54 percent zinc chloride, and 36 percent water, all based on the total weight of the solution, were placed in each of a number of bottles. Varying percentages of several polyoxyalkylene glycols were individually added to the individual samples with stirring until a homogeneous solution was, in each case, obtained.

The resulting samples were placed in a standard laboratory oven maintained at a temperature of about 80° C. until the mixtures were free from bubbles. Films less than about 0.10 inch thick were cast from each of the resulting solutions on "Pyrex" glass plates using a stainless steel draw-bar. The resulting films were coagulated by holding the coated plate in a stream of water at ambient temperature.

Within 1 or 2 minutes after casting, the films were detached from the glass plates and thoroughly water washed until free from zinc chloride.

The film prepared in this manner were aquagels which were each then oriented by stretching while immersed in an aqueous medium at a temperature of at least 65° C. Plasticizing was preliminarily indicated in each case when a material could be drawn with less force than required for an equivalent but untreated material (of the same cross section and with the same temperature).

Flexibility of each dried film was determined by drying sections thereof which had been drawn to 10 times their original length in a hot aqueous medium as above described. Each of the dried films was then bent over itself normal to the direction of orientation.

Rating of film flexibility was by visual inspection. Films which gave no perceptible shattering upon bending were rated "excellent," whereas films which shattered noticeably upon bending were rated "poor." Flexibility ratings for plasticized and untreated polyacrylonitrile films and corresponding physical property data and operable additive concentrations of several polyoxyalkylene glycols are set forth in the following Table I.

Table I

Polyoxyalkylene Glycol and Formula	Percent Polyoxyalkylene Glycol, Based On Polymer Weight	Description Of Polyoxyalkylene Glycol	Average Molecular Weight	Viscosity, Centistokes, 100° F.	Solubility, g./100 g. Water at 25° C.	Flexibility Of Dried Film
None						Poor.
Polyoxypropylene glycol $\text{HO}(\text{C}_3\text{H}_6\text{O})_n\text{C}_3\text{H}_6\text{OH}$	5	Viscous Liquid	2,000	164	0.1	Excellent.
Polyoxypropylene glycol $\text{HO}(\text{C}_3\text{H}_6\text{O})_n\text{C}_3\text{H}_6\text{OH}$	10	do	2,000	164	0.1	Do.
Polyoxypropylene glycol $\text{HO}(\text{C}_3\text{H}_6\text{O})_n\text{C}_3\text{H}_6\text{OH}$	50	do	2,000	164	0.1	Do.
Polyoxybutylene glycol $\text{HO}(\text{C}_4\text{H}_8\text{O})_n\text{C}_4\text{H}_8\text{OH}$	5	do	2,000	258	0.1	Do.
Polyoxybutylene glycol $\text{HO}(\text{C}_4\text{H}_8\text{O})_n\text{C}_4\text{H}_8\text{OH}$	10	do	2,000	258	0.1	Do.
Polyoxypropylene glycol $\text{HO}(\text{C}_3\text{H}_6\text{O})_n\text{C}_3\text{H}_6\text{OH}$	5	do	400	35.2	∞	Poor.
Polyoxypropylene glycol $\text{HO}(\text{C}_3\text{H}_6\text{O})_n\text{C}_3\text{H}_6\text{OH}$	50	do	400	35.2	∞	Do.
Polyoxypropylene glycol $\text{HO}(\text{C}_3\text{H}_6\text{O})_n\text{C}_3\text{H}_6\text{OH}$	5	do	4,000	545	0.1	Do.
Polyoxyethylene glycol $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{OH}$	5	do	200	20	∞	Do.
Polyoxyethylene glycol $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{OH}$	50	do	200	20	∞	Do.
Polyoxyethylene glycol $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{OH}$	5	do	600	72	∞	Do.
Polyoxyethylene glycol $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{OH}$	50	do	600	72	∞	Do.
Polyoxyethylene glycol $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{OH}$	10	Wax-like Solid	2,000	Solid	∞	Do.
Polyoxyethylene glycol $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{OH}$	50	do	2,000	Solid	∞	Do.

EXAMPLE II

In each of a series of additional experiments, fibers were individually cast from each of the spinning solutions described in Example I.

In each experiment the spinning solutions were individually extruded through a spinnerette having about 300 orifices (each orifice having a diameter of about 3 mils), into an aqueous non-polymer dissolving zinc chloride coagulating bath. The aquagels formed therein were then individually spun into a multiple filament aquagel tow and collected on a magnesium bar covered with aluminum foil and the resulting individual aquagel tows water washed until substantially free of zinc chloride.

There was thereby obtained a series of aquagel filament tows containing about 1 part water for each part of polymer therein. These aquagel filament tows were oriented by being stretched to a length of about 10 to 12 times their original extruded length and allowed to air dry at normal room temperatures.

Each filament tow was then finally irreversibly dried for about 5 minutes at about 140° C. and tested for resistance to fibrillation.

Each of the resulting fibrous materials were combed out flat; and cemented at each end of a glass slide. Each of the glass slides were fastened to the pan of a "Welsh" triple-beam laboratory balance. The "Welsh" balance was mounted on a milling vice, by means of which each fiber sample was traversed under a vibrating ball in a test of fibrillation resistance.

In each of the tests five passes of the tool were made at right angles to the fiber axis (about 1/8 inch apart) under loads of 1, 4, 16, 64 and 128 grams, respectively. Rating of fibrillation resistance was by visual and microscopic inspection.

Fibers which gave no perceptible fibrillation at 64 grams or more were rated "excellent." Those which fibrillate noticeably at 16 grams or less were rated "fair to poor."

All of the non-plasticized polyacrylonitrile fibers fibrillated noticeably under a load of 16 grams and, consequently, had a fibrillation rating of "fair to poor." Polyacrylonitrile fibers containing the polyoxypropylene glycol as described herein fibrillated only slightly under loads of 64 to 128 grams and, consequently, had a fibrillation rating of "excellent."

Similar desirable plasticizing efficiency and resistance to fibrillation is obtained using any concentration between about 5 percent to 50 weight percent of polymer weight of polyoxybutylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 258 centistokes (such glycol being a viscous liquid which is less than about 0.1 percent soluble in water at 25° C.).

On the other hand, polyoxypropylene glycols having a viscosity at 100° F. of less than about 100 centistokes and polyoxyethylene glycols having a molecular weight ranging from about 200 to 2000 and corresponding viscosities at 100° F. of more than about 20 centistokes to that of a solid material, are insufficiently insoluble in water and are not useful for the present invention. Poxypoxypropylene glycols that have an average molecular weight greater than about 3000 and a corresponding viscosity at 100° F. greater than about 260 centistokes are insufficiently compatible with most acrylonitrile polymers of interest to be useful for the present invention.

Similar good results are obtained when fiber- and film-forming acrylonitrile polymers containing at least 85 weight percent of polymerized acrylonitrile and up to 15 weight percent of one or more of such copolymerizable materials as vinyl chloride, vinyl acetate, methyl and other alkyl acrylates or methacrylates, the vinyl pyridines, allyl alcohol and many others well known to those skilled in the art are admixed with the polyoxyalkylene glycols suitable for use in practice of the present invention.

What is claimed is:

1. Composition comprising a spinnable dispersion of:

(1) a fiber-forming acrylonitrile polymer, which polymer contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomer that is copolymerizable with acrylonitrile, (2) an aqueous saline solvent for polyacrylonitrile, said solvent having additionally dissolved therein, (3) between about 5 and 50 weight percent based on said fiber forming polymer weight of a substantially water-insoluble polyoxyalkylene glycol having an average molecular weight less than about 3000 and a viscosity at 100° F. between about 100 to 260 centistokes.

2. The composition of claim 1, wherein said polyoxyalkylene glycol is polyoxypropylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 164 centistokes.

3. The composition of claim 1, wherein said polyoxyalkylene glycol is polyoxybutylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 258 centistokes.

4. The composition of claim 1, wherein said acrylonitrile polymer is polyacrylonitrile.

5. The composition of claim 1, wherein said aqueous saline solvent is a solution of zinc chloride.

6. In the process of producing articles from a spinning solution of: (1) a fiber-forming acrylonitrile polymer, which polymer contains in the polymer molecule at least about 85 weight percent of acrylonitrile, with any balance being another monoethylenically unsaturated monomer that is copolymerizable with acrylonitrile, and which polymer is dissolved as a spinnable composition in an aqueous saline solvent for said fiber-forming polymer: the step of dissolving in said spinning solution between about 5 and 50 weight percent, based on the polymer weight in said spinning solution, of a substantially water-insoluble polyoxyalkylene glycol having an average molecular weight less than about 3000 and a viscosity at 100° F. between about 100 to 260 centistokes.

7. The process of claim 6, wherein said polyoxyalkylene glycol is polyoxypropylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 164 centistokes.

8. The process of claim 6, wherein said polyoxyalkylene glycol is polyoxybutylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 258 centistokes.

9. The process of claim 6, wherein said acrylonitrile polymer is polyacrylonitrile.

10. The process of claim 6, wherein said aqueous saline solvent is a solution of zinc chloride.

11. A flexible polymeric article of manufacture capable of lying substantially in a single plane, having at least one major dimension, and at least one minor dimension less than about 0.1 inch, comprised of: (1) an acrylonitrile polymer which contains in the polymer molecule at least about 85 weight percent of acrylonitrile, with any balance being another monoethylenically unsaturated monomer that is copolymerizable with acrylonitrile, and (2) between about 5 to 50 weight percent, based on acrylonitrile polymer weight, of a substantially water-insoluble polyoxyalkylene glycol having an average molecular weight less than about 3000 and a viscosity at 100° F. between about 100 to 260 centistokes.

12. The article of claim 11, wherein said polyoxyalkylene glycol is polyoxypropylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 164 centistokes.

13. The article of claim 11, wherein said polyoxyalkylene glycol is polyoxybutylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 258 centistokes.

14. The article of claim 11, wherein said acrylonitrile polymer is polyacrylonitrile.

15. The article of claim 11, wherein said article is a flexible filamentary structure.

16. The article of claim 11, wherein said article is a flexible film.

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