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HIGH ACRYLONITRILE POLYMER SOLUTIONS CONTAINING A MIXTURE OF MONOCHLORINATED ORTHOPHENYLPHENOLS

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This application is a continuation-in-part of copending application Serial No. 177,216, filed March 5, 1962, now abandoned.

This invention relates to compositions of matter that are especially adapted for use in spinning acrylonitrile polymer synthetic textile fibers or the like structures having long-lasting bacteriostatic properties. It relates more particularly to spinnable solutions of such polymers in concentrated aqueous salt solutions having minor but effective amounts of a bacteriostatic agent composed of a mixture of 6-chloro-2-phenylphenol and 4-chloro-2-phenylphenol dissolved therein. The invention is also concerned with shaped articles especially filamentary structures, having bacteriostatic properties, and to a process for preparing such compositions, and articles.

The word "solution" is used herein in the connotation commonly employed in the acrylonitrile polymer spinning art.

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 aquegel structures of polyacrylonitrile and other fiber and film-forming acrylonitrile polymers may be derived by the extrusion of a solution of the acrylonitrile polymer that is dissolved in an aqueous zinc chloride saline solvent therefore into an coagulation in an aqueous coagulating spin bath. 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.

Fibers produced from acryonitrile polymers have excellent physical properties but do not have the inherent

ability to inhibit the growth of bacteria. The textile industry is particularly interested in a fibrous material useful for the production of blankets, carpeting and the like, which has the desirable properties of polyacrylonitrile or fiber-forming copolymers containing at least 85 weight percent of acrylonitrile in the polymer molecule and in addition has the ability to inhibit the growth of bacteria and to destroy existing bacteria. It is also highly desirable to prepare heat-shrinkable, flexible films useful for bottle closures and the like applications which have long-lasting bacteriostatic properties.

Fabricated acrylonitrile polymer film, 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 axis of the article.

The foregoing statement of the problem has referred to fibers and films, and the invention will be illustrated with respect to fibers. The problem is more general, however, and applies to the defined compositions in the forms of sheets, tubes, rods and molded articles as well as films, fibers and other filaments.

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 of high acrylonitrile polymers (i.e. those having at least 85 weight percent of polymerized acrylonitrile in the polymer molecule) having long-lasting bacteriostatic properties.

A further object is to provide shaped articles from the compositions of the present invention which have long-lasting bacteriostatic properties.

A still further object is to provide a process 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 films and textile fibers having long-lasting bacteriostatic properties are produced from a polymeric spinning solution comprising (1) an acrylontrile polymer containing in the polymer molecule at least about 85 weight percent of acrylonitrile, said polymer dissolved in an aqueous saline solvent solution, preferably where zinc chloride is the principal (if not entire) saline solute, and (2) dissolved therein at least about 5 weight percent, based on said fiber-forming polymer weight of a bacteriostatic agent composed of a mixture of 6-chloro-2-phenylphenol and 4-chloro-2-phenylphenol as described herein.

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 zinc chloride or its saline equivalents, U.S. 2,776,946, among many other reference sources, exemplifies 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 the invention.

The bacteriostatic agent which is useful for the purpose of the present invention as commonly prepared is composed of predominent amounts, usually about 80 weight percent, of 6-chloro-2-phenylphenol with the re-

mainder being 4-chloro-2-phenylphenol. Other ratios of the above isomers may also be used.

The bacteriostatic agent as defined herein is a readily available material, the preparation of which is well known to those skilled in the art.

The above defined bacteriostatic agent which is suitable for the present invention is compatible with the acrylonitrile polymers defined herein when incorporated in said polymers by the process of the present invention.

It has also been found that the bacteriostatic agent herein described must be present in the polymer solution in a minimum amount of about 5 weight percent based on the weight of the acrylonitrile polymer if the objectives of the invention are to be attained. The permissible maximum proportion depends on the limit of its compatibility with the aqueous saline solution, as well as the polymeric material contained therein. The maximum limit is generally about 20 weight percent, based on the weight of the acrylonitrile polymer.

The amount of bacteriostatic agent present in shaped articles produced from salt-spun acrylonitrile polymers is dependent upon, and approximately in the same ratio as, the amounts of said bacteriostatic agent incorporated in the spinning solution.

The bacteriostatic agent of the present invention may be suitably admixed with the polymeric spinning solution by stirring at room temperature.

It has been found that the bacteriostatic agent useful for the instant invention is compatible with the acrylonitrile polymers defined herein when used in the prescribed amounts, and, is substantially water-insoluble. The above combination of desirable properties prevents excessive extraction of the bacteriostatic agent from the polymer during coagulation of the polymer solution in an aqueous non-polymer-dissolving saline medium, and during subsequent water washing of the resulting aquagel and shaped article produced therefrom.

Shaped articles produced from acrylonitrile polymers by the process of the present invention do not significantly lose their bacteriostatic properties even after repeated laundering.

It will be appreciately by those skilled in the art that various other materials can be added to the compositions of the present invention. Such materials include, for example, plasticizers, lubricants, dye assistants, dyes and pigments.

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

EXAMPLE 1

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 separately placed in individual glass bottles. Thereafter, to one of the solutions was added, with stirring, 10 weight percent of an isomeric mixture composed of about 80 weight percent 6-chloro-2-phenylphenol and about 20 weight percent of 4-chloro-2-phenylphenol. To another solution, for purpose of comparison, was added, with stirring, 10 weight percent of 2,4,5-trichlorophenol, and to yet another solution was added 10 weight percent of o-phenylphenol. Each of the samples was then placed in a standard laboratory oven maintained at a temperature of about 80° C. until each of such samples was free from bubbles.

Each of the bubble-free spinning solutions was then 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 individually formed therein were separately spun into a multiple filament aquagel tow and collected, and the resulting aquagel tows water washed until substantially free of zinc chloride.

There were thereby separately obtained individual aquagel filament tows containing about 1 part water for each part of polymer therein. The aquagel filament tows were then each separately 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.

The filament tows were then finally irreversibly dried for about 5 minutes at about 140° C.

Each dried filament tow was then individually placed on the surface of a nutrient agar contained in a conventionally-used Petri dish or plate, which agar had been previously inoculated with *Staphylococcus aureus* by smearing the surface of the nutrient agar with a swab from a broth culture of *Staphylococcus aureus*. The dishes were then set aside for incubation at a temperature between about 30° C. and 37° C. After incubation, the plates were examined to determine the extent of control of the growth of the organisms of *Staphlococcus aureus*. Examination of the plates supporting the filament tows containing the mixture of 6-chloro-2-phenylphenol and 4-chloro-2-phenylphenol showed a zone of about 1 mm. immediately surrounding said tows which was free of the growth of the organisms of *Staphylococcus aureus*. Examination of a series of plates supporting individual filament tows containing the following known bacteriostatic agents: 2,4,5-trichlorophenol and o-phenylphenol showed that in all instances, a heavy outgrowth of colonies of *Staphylococcus aureus* was present in the zone immediately surrounding said tows.

The unexpected effectiveness of the bacterio-static agent of the present invention, when utilized in combination with a fiber and film forming acrylonitrile polymer as herein described, is illustrated by the following tests wherein the bacteriostatic properties of each of the above referred to compounds were individually determined. In such

Table I

Organism Tested	Bacteriostatic Agent		Appearance of Agar Media Following Incubation
	Type	Conc. p.p.m.	
Staphylococcus aureus	None		Heavily overgrown.
	2,4,5-Trichlorophenol	10	Heavily overgrown.
	2,4,5-Trichlorophenol	50	Essentially free of growth.
	Mixture of 6-chloro and 4-chloro-2-phenylphenols.	10	Heavily overgrown.
	Mixture of 6-chloro and 4-chloro-2-phenylphenols.	50	Essentially free of growth.
	o-Phenylphenol	50	Essentially free of growth.
Salmonella typhosa	None		Heavily overgrown.
	2,4,5-Trichlorophenol	50	Essentially free of growth.
	Mixture of 6-chloro and 4-chloro-2-phenylphenols.	50	Heavily overgrown.
	Mixture of 6-chloro and 4-chloro-2-phenylphenols.	100	Essentially free of growth.
	o-Phenylphenol	100	Essentially free of growth.
Aerobacter aerogenes	None		Heavily overgrown.
	2,4,5-Trichlorophenol	50	Essentially free of growth.
	Mixture of 6-chloro and 4-chloro-2-phenylphenols.	50	Heavily overgrown.

tests, the materials evaluated were individually dispersed in nutrient agar to prepare individual Petri dishes of agar medium containing from about 10 to 100 parts per million by weight of one of said compounds. The surfaces of these dishes were inoculated with one of several organisms as hereinafter identified by smearing the surfaces with a swab from a broth culture of such organism. At the same time, Petri dishes containing untreated agar media were similarly inoculated from the same broth culture, the dishes were set aside for incubation at a temperature of 30° C., for 72 hours. After incubation, the plates were examined to determine the control of the growth of the organism. Examination of the treated plates provided the data appearing in the above Table I.

It will be seen by reference to the data of Table I that the comparative materials, as specifically identified therein, are generally at least as effective as bacteriostats per se as the bacteriostatic agent employed for the purposes of the present invention.

Similar good results as specifically set forth herein are obtained by utilization of from about 5 to 20 weight percent of polymer weight of a bacteriostatic agent composed of a mixture of 6-chloro-2-phenylphenol and 4-chloro-2 phenylphenol, as contemplated by the present invention.

In addition, 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 prescribed amounts of the bacteriostatic agent of the present invention.

What is claimed is:

1. Bacteriostatic composition comprising a spinnable solution of: (1) a fiber-forming acrylonitrile polymer which contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomeric material that is copolymerizable with acrylonitrile, (2) an aqueous saline solvent for polyacrylonitrile; said solvent having additionally dissolved therein (3) at least about 5 weight percent based on said fiber-forming polymer weight of a bacteriostatic agent composed of predominant amounts of 6-chloro-2-phenylphenol with the remainder being 4-chloro-2-phenylphenol.

2. The composition of claim **1**, wherein the bacteriostatic agent is composed of about 80 weight percent of 6-chloro-2-phenylphenol and about 20 weight percent 4-chloro-2-phenylphenol.

3. The composition of claim **1**, wherein the bacteriostatic agent is present in amounts between about 5 and 20 weight percent based on the weight of said fiber-forming polymer.

4. The composition of claim **1**, wherein said fiber-forming 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 bacteriostatic articles from a spinning solution of a fiber-forming acrylonitrile polymer which contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomeric material that is copolymerizable with acrylonitrile, 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 at least about 5 weight percent, based on the weight of said fiber-forming polymer in said spinning solution, of a bacteriostatic agent composed of predominant amounts of 6-chloro-2-phenylphenol with the remainder being 4-chloro-2-phenylphenol.

7. The process of claim **6**, wherein the bacteriostatic agent is composed of about 80 weight percent of 6-chloro-2-phenylphenol and about 20 weight percent of 4-chloro-2-phenylphenol.

8. The process of claim **6**, wherein the bacteriostatic agent is present in amounts between about 5 and 20 weight percent based on the weight of said fiber-forming polymer.

9. The process of claim **6**, wherein said fiber-forming polymer is polyacrylonitrile.

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

11. A polymeric filament having bacteriostatic properties comprised of (1) a fiber-forming acrylonitrile polymer which contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomeric material that is copolymerizable with acrylonitrile, (2) dispersed throughout at least about 5 weight percent based on said fiber-forming polymer weight of a bacteriostatic agent composed of predominant amounts of 6-chloro-2-phenylphenol with the remainder being 4-chloro-2-phenylphenol.

12. The filament of claim **11**, wherein the bacteriostatic agent is composed of about 80 weight percent of 6-chloro-2-phenylphenol and about 20 weight percent of 4-chloro-2-phenylphenol.

13. The filament of claim **11**, wherein the bacteriostatic agent is present in amounts between about 5 and 20 weight percent based on the weight of said fiber-forming polymer.

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