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## PREPARATION OF STABLE DISPERSIONS OF FINELY DIVIDED HALOGEN-CONTAINING VINYL POLYMERS

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4 Claims

### ABSTRACT OF THE DISCLOSURE

An aqueous solution of a strong electrolyte having evenly dispersed therethrough finely divided halogen-containing vinyl polymer, said halogen-containing vinyl polymer having been prepared by emulsion polymerization of a vinyl halide and/or a vinylidene halide followed by washing with a water soluble alcohol until the emulsifier used during polymerization process is separated from the particulate halogen-containing vinyl polymer particles.

This invention relates to the provision of aqueous spinning dopes for fibers of acrylonitrile. More particularly it relates to such aqueous spinning dopes having evenly dispersed therethrough a finely divided halogen-containing vinyl polymer such as poly(vinyl chloride), poly(vinylidene chloride) poly(vinyl bromide) or poly(vinylidene bromide). It relates further to fibers prepared from the foregoing spinning dopes. Still further, it relates to the provision of such finely divided vinyl halide or vinylidene halide polymers in a form which is capable of forming stable dispersions in aqueous electrolytes.

As used in this application, the expression "halogen-containing vinyl polymers" is intended to include homopolymers and copolymers of vinyl chloride, vinyl bromide, vinylidene chloride and vinylidene bromide.

It is well known that fibers of acrylonitrile can be made flame resistant by the presence in the fiber of a compound of antimony and another compound to act as a source of chlorine or bromine. Many compounds capable of acting as the chlorine or bromine source are known. The choice of which of these compounds to employ in any given situation depends on various factors. One of these factors is the solvent which is used to form the spinning dope, since not all sources of chlorine or bromine are compatible with all available spinning solvents. For example, there are both inorganic and organic solvents which can be used for polyacrylonitrile dopes. Some chlorine or bromine compounds can be used in spinning dopes based on organic solvents, but not in spinning dopes based on inorganic solvents. Thus, halogen-containing vinyl polymers are a group of materials which are soluble in spinning dopes based on organic solvents, but neither soluble nor homogeneously dispersible in inorganic solvents. Thus, when it is attempted to disperse finely divided halogen-containing vinyl polymers throughout an inorganic spinning dope, the particles, instead of forming an even dispersion, tend to coalesce and form agglomerates. These agglomerates make the spinning dope totally impractical to use and they indicate a non-homogeneous system, which upon being forced through a spinnerette used in the fiber-making process causes plugging of the fine orifices in the spinnerettes. In general, these non-homogeneous spinning dopes result in the preparation of inferior and commercially unacceptable fibers. Prior to the present invention, when fibers of acrylonitrile were prepared from aqueous spinning dopes, there was no practical means of homogeneously incorporating finely di-

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vided halogen-containing vinyl polymers for flame retardation purposes.

It is an object of the present invention to provide a means for homogeneously dispersing finely divided halogen-containing vinyl polymers in aqueous spinning dopes used for the preparation of fibers of acrylonitrile. It is a further object of this invention to provide fibers prepared from such aqueous spinning dopes. It is still another object of this invention to provide finely divided halogen-containing vinyl polymers which are capable of forming stable dispersions in aqueous electrolytic substrates. It is still another object of the present invention to provide fibers of acrylonitrile containing evenly dispersed halogen-containing vinyl polymer and an antimony compound, which fibers have improved flame retardancy, good luster and good physical properties. Other objects will be apparent from the ensuing description of the present invention.

In accordance with the present invention, it has been discovered that particulate halogen-containing vinyl polymers derived from known emulsion polymerization processes can be made to form stable dispersions in aqueous electrolytes if, before being admixed with the electrolyte, the halogen-containing vinyl polymers are first washed free of residual emulsifier with an alcohol. The washed, finely divided halogen-containing vinyl polymers are capable of forming stable dispersions in aqueous electrolytes. Advantageously, after a long period of standing, if the dispersed polymer particles settle, they can be redispersed by mild agitation.

The halogen-containing vinyl polymers which are particularly deficient in their ability to form dispersions in aqueous electrolytes are those homopolymers and copolymers produced by the emulsion polymerization of vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene bromide monomers or mixtures thereof. Such polymerization procedures involve dispersing the monomer by means of an emulsifying agent such as lauryl sulfate salt in an aqueous system containing a peroxide catalyst, e.g., potassium persulfate. A buffering agent is normally added to control the pH. The emulsion polymerization process yields small spherical particles of the desired polymer. The product obtained as a dispersion of the polymer in an aqueous medium is commercially available as a latex or as a dried product. Drying is normally accomplished by "spray-drying" procedures. Although it is not intended to limit the present invention to theoretical considerations, it is believed that agglomeration of particles of commercially available halogen-containing vinyl polymers on contact with aqueous electrolyte is due to the presence of emulsifier in the final polymeric composition and that the deleterious effect of the emulsifier is overcome by the washing action of the alcohol in removing the emulsifier from the polymeric composition.

Among the alcohols which are useful in the present invention as washing agents are alkanols such as methanol, ethanol, propanol and hexanol; and glycols such as ethylene glycol, propylene glycol and triethylene glycol and glycerols such as glycerol.

In its simplest form, the practice of the present invention involves merely mixing the commercially available finely divided halogen-containing vinyl polymer with alcohol in the proper proportions, agitating the mixture and separating the alcohol containing the emulsifier either by filtration or centrifugation. Normally, between about 50 and 400 parts of alcohol should be used for each part of the halogen-containing vinyl polymer. The addition of alcohol to the crude halogen-containing vinyl polymer may initially lead to agglomeration of the polymer particles, but after one or more washes with alcohol, the agglomerates disappear. The washed halogen-containing vinyl polymer can with advantage be dispersed in a wide

variety of aqueous electrolytic solutions. The resulting dispersion is free of curdling and remains stable for long periods of time. If the mixture stands for a long period and some settling does result, this can be corrected by simple agitation.

One very important application of the dispersions of the present invention is in the preparation of flame-retardant fibers from polymers of acrylonitrile. One of the commonest flame-retarding agents for such fibers is a mixture of a halogen compound and antimony oxide or another antimony compound. While halogen-containing compounds are flame-retardants by themselves, their usefulness increases considerably when they are used in conjunction with an antimony compound. When a spinning dope is prepared by dissolving a polymer of acrylonitrile in an aqueous electrolyte and admixing the dispersible halogen-containing vinyl polymer of this invention along therewith, the resulting composition can be fed through conventional spinnerettes to produce fibers which have good physical properties. Addition of the antimony compound results in improved flame-retardancy.

The antimony compound for improved flame-retardancy can be dispersed in the spinning dope by conventional means. The final fiber product should contain a sufficient amount of antimony to impart the desired flame retardance. In general, about 0.002 to 0.025 part of antimony per part of acrylonitrile fiber should be used. However, it is preferred for reasons of economy and effectiveness to have 0.004 to 0.008 part of antimony per part of fiber. The antimony compounds which are useful in the present invention are those which have been heretofore conventionally used in preparation of flame-retardant compositions. Such compounds include antimony trioxide, triphenyl stilbene, antimony tartrate and sodium antimonate. The most commonly used antimony compound is antimony trioxide, sometimes called "antimony oxide."

In addition, phosphorus compounds are useful as synergists, examples being tribenzyl phosphine oxide, tricresyl phosphate and tri-2-ethylhexyl phosphate.

By "polymer of acrylonitrile" is meant a polymer composition which contains an average of at least about 70% acrylonitrile in the polymer molecules. When acrylonitrile is not homopolymerized, the remainder of the polymer molecules may contain an average of up to about 30% of another ethylenically unsaturated material as is well known in the art. Illustrative of these other compounds which may be copolymerized with acrylonitrile to form polymers which can be used in the practice of the present invention are those which may be found, for example, in U.S. Patent 3,104,938, issued Sept. 24, 1963, and U.S. Patent 3,040,008, issued June 19, 1962, and in the various other U.S. patents mentioned therein.

It has been found that the dispersible halogen-containing vinyl polymer particles of the present invention are very effectively dispersible in aqueous electrolytes which are solvents for polymers of acrylonitrile. Among such electrolytes are aqueous sodium thiocyanates in which the concentration of the salt is about 30-60%, aqueous zinc chloride in which the concentration of zinc chloride is at least about 60% and aqueous nitric acid in which the concentration of nitric acid is at least about 70%.

In addition to being used for the preparation of acrylonitrile fibers, the dispersible finely divided halogen-containing vinyl polymers of the present invention can also be added to other organic polymeric materials which are preparable from aqueous solutions or suspensions. Among such other materials are paper, acetate and rayon. The dispersible halogen-containing vinyl polymers of this invention can be homogeneously dispersed in paper pulp compositions which can then be conventionally formed into paper sheets. They can also be added to rayon and acetate spinning solutions by dispersing the spray-dried resin by any conventional means into the respective spinning dopes. When any of the foregoing compositions containing the dispersible halogen-containing vinyl poly-

mer of this invention are cast, spun, molded or milled into a shaped article whether it be film, fiber or molded object, the halogen-containing vinyl polymer is found to be homogeneously distributed throughout the final product. When an antimony compound such as is described above is also dispersed in the aqueous electrolyte, the resulting shaped article is found to have good flame retardancy.

The ability of the halogen-containing vinyl polymers of the present invention to form stable dispersions is of special importance, however, in fiber-making applications, such as in the preparation of fibers from polymers of acrylonitrile. Agglomerates of the halogen-containing vinyl polymer, if they are present in the spinning solution, can very easily plug the small orifices of the spinnerette used in the fiber-making process. Moreover, uniformity in the spinning solution is extremely critical since the fiber is of such small cross-section that even small imperfections in the spinning composition can have a significant impact on the strength of the whole fiber.

Halogen-containing vinyl polymers, as obtained from conventional emulsion polymerization processes, are normally found to have an average particle size of less than about 5.0 microns, and all such materials can be used to form stable dispersions in accordance with the present invention. For fiber-making processes, it is preferable to use finely divided halogen-containing vinyl polymer products having an average particle size of less than about 2.0 microns since such products form the most stable dispersions in aqueous electrolytes and are most easily fed through the spinnerette orifices.

The following examples are presented to further illustrate the present invention.

#### EXAMPLE 1

A mixture of 200 g. of a vinyl chloride copolymer (prepared by emulsion polymerization of a mixture of vinyl chloride and vinyl acetate and then spray-dried) and 750 ml. of ethyl alcohol was stirred in a Waring Blendor for several minutes. The resin was centrifuged to the bottom and the liquor containing some of the surfactant originally present in the resin was decanted off. The resin was again washed with another 750 ml. of ethyl alcohol; the mixture was centrifuged; the liquor was decanted off; and there was obtained 323 g. of surfactant-free resin, wet with ethyl alcohol.

This resin, as supplied, had some large agglomerate particles. In order to break up these agglomerates, the wet resin was mixed with 750 g. of aqueous 45% sodium thiocyanate. Since this resin, as supplied, contained some large agglomerates, 250 g. of Ottawa sand were added and the mixture was shaken in a paint shaker for 3-5 hours. The sand was filtered off through a fine screen, giving a filtrate containing the very finely dispersed polymer particles free of agglomeration in the presence of aqueous sodium thiocyanate.

In order to show that this material could be spun into fibers, the dispersion was then added to a solution of acrylic polymer in aqueous sodium thiocyanate. This mixture, which was also free of agglomeration, was spun into fine lustrous yarns.

The foregoing technique is equally well applicable to other vinyl chloride polymers and copolymers and to vinylidene chloride polymers and copolymers which are prepared by emulsion polymerization. In all cases, removal of the surfactant used during the emulsion polymerization process gives finely divided polymers which are dispersible in strong aqueous electrolytic solutions.

Other alcohols, such as methyl and isopropyl alcohol, can be used in the procedure of Example 1 with equivalent results.

#### EXAMPLE 2

An experiment was performed to show the importance of washing the emulsifier from the vinyl chloride poly-

mer before the polymer could be dispersed in an aqueous electrolyte.

100 g. of the vinyl chloride polymer described in Example 1 were added to 400 g. of 45% aqueous sodium thiocyanate solution. The vinyl chloride polymer was not washed with alcohol prior to being added to the aqueous electrolyte. The mixture was shaken in a paint shaker with Ottawa sand for 6 hours. The sand was filtered off. Very little resin came through into the filtrate; the major portion of the resin remained behind on the filtration screen with the sand in large agglomerates. The resin was unsuitable for spinning into fibers since the agglomerates could not be passed into the fine orifices of the spinnerette.

#### EXAMPLE 3

This example shows the applicability of the present invention to poly(vinyl chloride) latices prepared by emulsion polymerization techniques.

To 150 g. of a vinylidene chloride latex containing 50% solids (the latex having been obtained by the emulsion polymerization of vinylidene chloride and vinyl chloride) were added 200 g. of methyl alcohol. The mixture was stirred in a Waring Blendor. There was immediate coagulation of the latex. The alcohol was decanted and the washing was repeated with 200 g. of methyl alcohol. The mixture was centrifuged and then decanted off, and there was obtained particulate resin essentially free of the polymerization surfactant. The resin was dispersed with Ottawa sand in a 45% aqueous sodium thiocyanate solution by vigorous agitation in a paint shaker. Filtration of the mixture gave a filtrate containing the finely dispersed resin in an aqueous sodium thiocyanate solution. This dispersion was free of agglomerates.

In order to show the use of this dispersion for preparing acrylonitrile fibers, the dispersion was added to an aqueous sodium thiocyanate acrylic spinning dope. After thorough mixing, the dope was spun into semi-bright yarns.

#### EXAMPLE 4

A quantity of commercially available spray-dried poly(vinyl chloride) resin was washed with ethanol as described in Example 1 by shaking violently in the presence of sand, isolating the resin from the sand and collecting said resin as a sludge by centrifugation. The sludge, representing 11.0 g. of resin (dry basis) was stirred into 1,000 g. of an 11.2% solution of a copolymer of 89.2% acrylonitrile and 10.8% methyl methacrylate, in 45%

aqueous sodium thiocyanate. A homogeneous dispersion was obtained which was filtered and extruded through the holes of a spinnerette into a 10% aqueous sodium thiocyanate solution, causing the acrylic copolymer containing the finely divided resin to form a filamentary gel which was washed free of solvent, stretched in water at 95° C. dried at 115° C. and treated in a relaxed state in steam under pressure at 130° C. Chlorine analysis of the fiber indicated the fiber contained 8.5% resin based on fiber weight or 87% of the theoretical amount added.

Example 4 therefore shows that by practice of the present invention, very fine dispersions are maintained with the result that little of the resin is lost during filtration of the spinning dope or other processing steps.

I claim:

1. An aqueous solution of a strong electrolyte which is a solvent for polymers of acrylonitrile having evenly dispersed therethrough finely divided halogen-containing vinyl polymer, said halogen-containing vinyl polymer having been prepared by emulsion polymerization of a vinyl halide and/or a vinylidene halide followed by washing with a water soluble alcohol until the emulsifier used during polymerization process is separated from the particulate halogen-containing vinyl polymer particles.

2. The solution of claim 1 wherein the electrolyte is aqueous sodium thiocyanate containing at least 30% by weight of the thiocyanate.

3. The solution of claim 1 having as an additional component a polymer of acrylonitrile dissolved therein.

4. An aqueous solution of claim 1 wherein the electrolyte is aqueous sodium thiocyanate, said aqueous solution having dissolved therein a polymer of acrylonitrile, said solution being suitable for use as a spinning dope for the preparation of fibers of acrylonitrile polymers.

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