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MILD ALKALINE OXIDATION TREATMENT OF POLYACRYLONITRILE FIBERS OR FILMS TO IMPROVE FLEXIBILITY AND DYEABILITY

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No Drawing. Continuation-in-part of application Ser. No. 292,771, July 3, 1963, which is a continuation-in-part of application Ser. No. 113,117, May 29, 1961. This application June 25, 1965, Ser. No. 467,112
Int. Cl. D06m 3/18
U.S. Cl. 8—115.4 4 Claims

ABSTRACT OF THE DISCLOSURE

The treatment or articles of polyacrylonitrile with an aqueous solution of alkali metal hydroxide and alkali-metal hypochlorite to improve flexibility, resistance to fibrillation and dyeability.

This application is a continuation-in-part of copending application Ser. No. 292,771, now abandoned, filed July 3, 1963, which is in turn a continuation-in-part of application Ser. No. 113,117, filed May 29, 1961, now United States Patent No. 3,127,233.

This invention relates to a method for treating polymeric articles such as fibers or films consisting essentially of polyacrylonitrile. More particularly, it relates to a simple, easily controlled treatment of salt spun polyacrylonitrile articles with an aqueous alkaline mild oxidizing agent to improve the flexibility and subsequent resistance to fibrillation, as well as the dyeability thereof.

It is well known that polyacrylonitrile may advantageously be fabricated by a wet spinning process wherein the polymer is extruded 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.

Homopolymers of acrylonitrile that are salt-spun in the referred to manner are generally formed initially 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 structure of polyacrylonitrile 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 such 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 fracture generally along the 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 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 loss prone to fibrillation than a corresponding relatively less flexible article.

It is further well known that homopolymeric acrylonitrile is highly hydrophobic, and that fibers made therefrom are less easily dyed than most other fibers, whether natural or synthetic.

It would be desirable, therefore, to provide a simple treatment capable of producing more flexible and less hydrophobic articles such as filaments and films, having large surface area relative to thickness (or diameter), which are composed of polyacrylonitrile. It is the principle object of this invention to provide such a treatment.

The treatment of the present invention, whereby the foregoing and related objects are attained, is a method in which a normally hydrophobic polyacrylonitrile article, such as a fiber or film, is subjected to alkaline hydrolysis with resultant formation of carboxylic acid groups along the polymer chain without accompanying polymer discoloration resulting from such hydrolysis.

More particularly, the method comprises (1) immersing such article in a bath of a liquid aqueous alkaline mild oxidizing agent composed essentially of (a) from about 0.2 to 10 percent of an alkali metal hydroxide and (b) from about 1.5 to 10 percent of a hypochlorite, wherein such bath is continuously maintained at a pH of greater than 7 and wherein the article is immersed in the bath for a time inversely related to the temperature, varying from about 3 to 5 minutes near the boiling temperature to from about 1 to about 4 hours at room temperature, and at least for a time sufficient to provide an article which when washed and dried, exhibits swelling in water.

The treatment may be applied to any article made of polyacrylonitrile, but is of special benefit to those thin articles such as fibers and films.

The aqueous alkaline mild oxidizing agent useful in the invention should ordinarily, and for greatest utility of the treated product, be substantially free from discoloring metal ions, especially those colored polyvalent metal ions which might form chelates with and become bound to the polymer. The most economical agents to use have as the only metal ions present, the colorless alkali metal or alkaline earth metal ions. The alkalinity of the aqueous oxidizing agents is preferably provided by sodium or potassium hydroxide. The oxidizer is a hypochlorite, illustratively sodium hypochlorite or calcium hypochlorite or hypochlorite-chloride. The concentration of alkali in the

treating solution should not be significantly over 2.5 Normal, as much higher concentrations lead to different results. Concentrations of sodium hydroxide or of patassium hydroxide in the treating solution ranging from about 0.2 percent to about 10 percent, by weight are quite satisfactory. The concentration of hypochlorite used as the mild oxidizer is conveniently in the range from about 1.5 percent to 10 percent of the weight of solution.

While the invention is not limited to the treatment of foils, fibers and similarly thin, flexible articles, it finds particular advantage with such materials. It is applicable to such articles regardless of the manner in which they were prepared. Thus, films or sheets may be treated which were produced by molding or extrusion, or by being cast from solution or emulsion, or by being coagulated from solution by contact with a non-solvent for the polymer which is miscible with the solvent. Similarly, fibers and filaments may be treated which have been wet spun or dry spun from organic solvents or have been wet spun from known, aqueous strong salt solutions and thus coagulated as filamentary aquagel, as is known in the art. When films or filaments are first formed as an aquagel, the present treatment may be applied while the gel condition is retained, or it may be applied after the article has been so thoroughly dried as irreversibly to destroy the aquagel condition.

In one illustration of the practice of this invention, an alkaline hypochlorite solution was prepared by dissolving 100 grams of NaOH in water, diluting to one liter, and bubbling chlorine into the solution until the weight had increased by 71 grams. The resulting solution contained about one gram mole of NaOCl and about 0.5 gram mole of free NaOH per liter.

Several samples of polyacrylonitrile aquagel, 0.01 inch thick, were immersed in the alkaline hypochlorite solution for periods of between 1 and 24 hours, and then removed from the treating solution, rinsed with water, and dried to destroy the aquagel condition. The dried samples were then immersed in water and their wet flexibility was evaluated qualitatively. Each sample was then subjected to a standard dyeing procedure, using Irgalan Blue Gl, an acid dye (Colour Index Acid Blue 166), and the color yields were compared, as were the depths of penetration of the dye.

Other samples of the same polymer aquagel were immersed in the alkaline hypochlorite solution for periods of 0.5 to 2 hours at 35° C.; 0.5 hour at 50° C.; 0.1 to 0.25 hour at 70° C.; and 0.05 to 0.1 hour at 90° C. The samples were removed from the treating solution, washed, dried irreversibly, and subjected to dyeing as described above. In each case, the treated product, after exposure as reported above, and when washed and dried, was found to have highly desirable wet flexibility, was free from undesirable discoloration and was more receptive to dyes than is the normal hydrophobic polyacrylonitrile.

In addition to the benefits previously mentioned, the polymeric products treated in accordance with the invention have less tendency to undergo undesirable fibrillation and to acquire and retain charges of static electricity, than do similar but untreated hydrophobic polyacrylonitrile articles.

I claim:

1. The method which comprises (1) immersing a normally hydrophobic article consisting essentially of polyacrylonitrile in a bath of a liquid aqueous alkaline mild oxidizing agent composed essentially of (a) from about 0.2 to 10 percent of an alkali metal hydroxide and (b) from about 1.5 to 10 percent of an alkali metal hypochlorite, said bath being continuously maintained at a pH greater than 7 and said articles being immersed in said bath for a time inversely related to the temperature, vary from about 3 to 5 minutes near the boiling temperature to from 1 to about 4 hours at room temperature, but at least for a time sufficient to provide an article which when washed and dried exhibits swelling in water, and (2) washing the article to remove the alkaline agent.

2. The method claimed in claim **1**, wherein said normally hydrophobic article is a thin, flexible article from the class consisting of foils and filaments.

3. The method claimed in claim **2**, wherein the article immersed in the alkaline oxidizing medium is in the aquagel condition at the time of treatment.

4. The method claimed in claim **1**, wherein said alkali metal hydroxide is sodium hydroxide and said alkali metal hypochlorite is sodium hypochlorite.

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