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PROCESS OF DYEING ACRYLONITRILE FIBERS WITH ACID DYES USING ZINC CHLORIDE

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This invention relates to a method of modifying acrylonitrile polymeric structures. More specifically the invention relates to a method of improving the dye absorption capacity of fibers, films, or other structures, fabricated from high acrylonitrile polymers.

Polyacrylonitrile and copolymers of 80 or more percent by weight of acrylonitrile and up to 20 percent of a comonomer are conventionally fabricated into fibers and films by dissolving the polymer in suitable solvents and extruding the viscous solution through suitable dies or spinnerets. The extruded solution is passed into a medium which removes the solvent and causes the polymer to be precipitated in a solid continuous form. If the medium into which the solution is extruded is water, or other liquid in which the solvent is miscible, the process is known as a "wet" method. The "dry" method, where coagulation is effected in air or other gaseous atmosphere, produces fiber of better knot strength, higher bulk density, and softness than spinning into water. Moreover, solvent recovery is simpler when the "dry" method is used. Although the methods hereinafter described may be utilized in treating films, rods or other extruded shapes, the most important application is in the treatment of threads, yarns and fabrics, categorically referred to in the following specification as "fibers."

The fiber forming acrylonitrile polymers are polyacrylonitrile and copolymers of 80 percent or more by weight of acrylonitrile and up to 20 percent of methacrylonitrile, vinyl acetate, vinylidine chloride, methyl acrylate or other alkyl acrylate, methyl methacrylate or other alkyl methacrylate, ethyl fumarate, ethyl maleate, or other alkyl esters of fumaric and maleic acids, styrene, vinyl chloride, or other olefinic monomers capable of forming copolymers with acrylonitrile. Such polymers are insoluble in all common solvents, have good tensile strengths, low moisture absorption, high elasticity and other properties which are desirable in synthetic fibers.

Although acrylonitrile polymer fibers which are wet spun can be dyed without serious difficulty, the dry spun fibers are difficult or impossible to dye by conventional procedures. This inherent deficiency greatly restricts the utility of fibers, and the fabrics made therefrom. Accordingly, the fundamental purpose of this application is to provide a means of improving the dye affinity of the acrylonitrile polymers. A further purpose is to provide a useful general purpose fiber from a dry spun acrylonitrile polymer.

It has been found that dry spun fibers of acrylo-

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nitrile polymers, which have very little or no dye affinity, may be converted into dye susceptible fibers by contacting them with aqueous solutions of zinc chloride. Since it is known that concentrated zinc chloride solutions will completely dissolve the fiber, at elevated temperatures, it is necessary to adjust the concentration of zinc chloride, the temperature of the solution, and the period of contact so as to avoid undue depreciation of the desired fiber properties. The nature of the action involved is not fully understood, since contact under comparable conditions with other known solvents, for example aqueous lithium bromide, will not produce the same effect. Although the effect is probably a surface action, it is not a permanent alteration. A fiber, after sufficient contact with zinc chloride solutions to improve the dye accepting characteristics, will retain these characteristics after all of the zinc chloride is washed out, as long as the fiber remains moist. However, if the fiber is dried the surface regains its original condition and is no longer dye receptive. Accordingly, no permanent easily recognized physical change of the fiber surface takes place.

A wide range of operating conditions are practicable, for example concentrations from 45 percent zinc chloride to saturation (81% at 25° C.; 86% at 100° C.), temperatures from 5° C. to 100° C., and periods of time ranging from a few seconds to 60 minutes or more. The effect of varying these conditions may readily be determined by one skilled in the dyeing art. Similarly, one skilled in the prior art may select conditions to suit the individual requirements of the article being dyed, the equipment to be used and the facilities available. Some concentrations of zinc chloride, for example in excess of sixty percent are undesirable at temperatures above 60° C., because of the short duration of time required for proper treatment, this being particularly true of fiber of small denier, and fabrics prepared therefrom. The optimum conditions are 30 to 60° C., and zinc chloride concentrations of 50 to 70 percent, whereby substantial variations in color intensity can be secured by variation of contact time within ranges readily controlled, so as to insure reproducibility of desirable results and to avoid fiber injury.

Because of the unknown nature of the phenomena and the absence of a readily detectable change in the fibers it is sometimes difficult to determine the point at which the fiber treatment is adequate for the desired dye effect. In general the treatment should be long enough to per-

mit the desired dye operation, without the sacrifice of physical properties. Through the use of a pre-determined zinc chloride concentration and a pre-determined temperature, within the above described optimum ranges, the period of time required for maximum dye effect without deterioration of fiber properties may readily be determined by an examination of the fiber or fabric. Once the optimum conditions are established continued operation under controlled conditions will insure excellent dyeing characteristics without loss of desirable physical properties. The optimum conditions will vary with the contour of the polymer structure, the molecular weight of the polymer and the chemical composition of the polymer, and accordingly, the operating conditions must be determined for each fiber or fabric to be treated.

The modified surface after treatment with zinc chloride solutions is receptive to a wide variety of dyestuffs, including acid dyes, basic dyes, direct dyes, acetate dyes, and sulfur dyes. Accordingly, a wide variety of colors and color shades may be obtained by conventional dyeing techniques. As described above, the dye operation must be performed while the fiber is still moist with the zinc chloride solution or with the wash water which has removed the zinc chloride solution. The zinc chloride treatment and the dyeing steps may be conducted as separate operations with or without an intervening washing step. If desired the zinc chloride treatment may be effected in the dyeing bath, in which case it is necessary to use dyes which are sufficiently soluble in the concentrated zinc chloride solution. This latter method of simultaneously pre-treating and dyeing the fiber is particularly useful because of improved wash fastness of the resulting fibers or fabrics. It will be readily apparent that under these conditions conventional dye procedures are readily adaptable to the dyeing of acrylonitrile fiber and fabrics prepared therefrom.

Although this fiber treatment method is primarily useful in developing dye affinity in dry spun acrylonitrile polymer fibers, it is also useful in improving the normal dye affinity of wet spun acrylonitrile polymer fibers. In the treatment of wet spun fibers less rigorous conditions of treatment are required. Accordingly, lower concentrations of zinc chloride, lower temperatures of treatment or shorter periods of time may be used to develop the same optimum dyeing characteristics.

Further details of the practice of this invention are set forth with respect to the following specific examples.

Example 1

Cast films, five mils in thickness, of a copolymer of 97 percent by weight of acrylonitrile and three percent vinyl acetate were prepared, and after treating the samples with various concentrations of aqueous zinc chloride solutions for various periods of time at 60° C., the samples were dyed by immersion in a dye bath for one hour at 60° C., and thereafter washed with water for one hour. The dye bath used in these experiments was comprised of 1250 cc. of water, two grams of acetic acid, ten grams of sodium chloride and one gram of a dye concentrate known and sold commercially as "Acid Green CC, Extra Conc." (C. I. 666). The following table describes qualitatively the appearance of the films after dyeing and washing, describes the variation in color intensity with the concentration of zinc chloride in the treating bath and the duration of time of contact with the treating bath.

Concentration	Intensity of Color		
	Time, Minutes, 2	Time, Minutes, 5	Time, Minutes, 60
40	None	None	None.
45	do	do	Medium.
50	Light	Medium	
60	Dark	Very Dark	

Example 2

Three pieces of knitted fabric prepared from a dry spun fiber of a copolymer of 97 percent acrylonitrile and three percent vinyl acetate were immersed in a 60 percent zinc chloride solution at 30° C. for two seconds, fifteen minutes, and two minutes. The samples were immediately washed in a stream of water for one hour and then immersed in a dye bath containing one gram of "Acid Green CC Extra Conc.," two grams of acetic acid, ten grams of sodium chloride and 1250 grams of water. An untreated piece of the same fabric was used as a control. All samples remained in the dye bath for one hour at 60° C. After washing the dyed samples for one hour it was found that the intensity of color increased progressively with the length of pretreatment, whereas practically no dye pickup took place on the untreated fabric.

Example 3

Using the technique described in the preceding experiment, samples of cloth were pre-treated for thirty seconds and two minutes, except that "Xylene Fast Red P" was used as the dye. Excellent deep shades of red were obtained with the pre-treated samples, whereas an untreated piece of fabric used as a control absorbed practically no dye.

Example 4

The procedure of Example 2 was repeated except that a dye bath of 450 grams of water, 3.5 grams of sodium chloride and 0.5 gram of "Trisulfon Brown B Conc." (C. I. 561) was used. The treated fabrics took the dye well and resulted in deep brown colorations, whereas an untreated control sample was substantially unaffected.

Example 5

The experiments of the preceding three examples were repeated using a conventional dye bath involving "Indo Carbon CLGS," "Victoria Green WB," and "Nacelan Scarlet WB." In each case bright intense shades of color were developed on the pretreated fabrics, whereas little or no color was absorbed on the untreated fabrics.

Example 6

A piece of knitted fabric of a dry spun fiber of a copolymer of 97 percent acrylonitrile and three percent vinyl acetate was simultaneously treated and dyed by immersion for two minutes at 30° C. in a dye bath containing 100 grams of 60 percent zinc chloride solution, one gram of "Acid Green CC Extra Conc.," two grams of acetic acid and ten grams of sodium chloride. After dyeing the fabric was washed thoroughly with water. The resulting fabric developed intense green color which had wash fastness superior to a similar sample treated with zinc chloride solution and dyed in separate operations.

Example 7

A ten filament, 168 denier yarn prepared by dry spinning a copolymer of 97 percent acrylonitrile and three percent vinyl acetate was treated by immersing it in a solution of 60 percent aqueous zinc chloride for two minutes at 30° C. The treated yarn was found to have a tenacity of 2.12 grams per denier, an elongation of 24 percent, and boil shrinkage of 6.65 percent. Untreated pieces of the same yarn had a tenacity of 2.15 grams per denier, an elongation of 17 percent, and boil shrinkage of 6.15 percent. The treated sample was found to dye readily in conventional dye formulations, whereas the untreated fabric could not be dyed.

The invention is defined by the following claims.

We claim:

1. A method of dyeing a fiber of a polymer of a monomeric composition of which at least 80% by weight is acrylonitrile, which comprises treating the fiber with an aqueous solution of at least 45% zinc chloride at 5° to 100° C. for a period of 0.5 to 60 minutes, contacting the fiber to an aqueous dye bath of an acid dyestuff, and drying the dyed fiber.

2. A method of dyeing a fiber of a polymer of a monomeric composition of which acrylonitrile is at least 80% by weight of the polymerizable content, which comprises contacting the fiber with an aqueous solution of at least 45% zinc chloride at 5° to 100° C. for a period of 0.5 to 60 minutes, washing the treated fiber with water, contacting the wet fiber with an aqueous dye bath of an acid dyestuff, and drying the dyed fiber.

3. A method of dyeing a fiber of a polymer of a monomeric composition of which at least 80% by weight is acrylonitrile, which comprises contacting the dry fiber with an aqueous solution of at least 45% zinc chloride having dissolved therein an acid dyestuff at 5° to 100° C. for a period of 0.5 to 60 minutes, and drying the dyed fiber.

4. A method of dyeing a fiber of a monomeric composition of which acrylonitrile is at least 80% by weight of the polymerizable content, which comprises contacting the fiber with an aqueous solution of from 50 to 70% by weight of zinc chloride for a period of 0.5 to 60 minutes at a temperature between 20° C. and 90° C., washing the fiber with water, contacting the wet fiber with an aqueous dye bath of an acid dyestuff, and drying the dyed fiber.

5. A method of dyeing a fiber of 80 to 99% by weight of acrylonitrile and one to 20% of vinyl acetate, which comprises contacting the fiber with an aqueous solution of at least 45% zinc chloride at 5° to 100° C. for a period of 0.5 to 60 minutes, washing the fiber with water, contacting the wet fiber with an aqueous dye bath of an acid dyestuff, and drying the dyed fiber.

6. A method of dyeing a fiber of 80 to 99% by weight of acrylonitrile and one to 20% of vinyl acetate, which comprises contacting the fiber with an aqueous solution of from 50 to 70% by weight of zinc chloride at a temperature between 20° C. and 90° C. for a period of 0.5 to 60 minutes, washing the fiber with water, contacting the wet fiber with an aqueous dye bath of an acid dyestuff, and drying the dyed fiber.

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