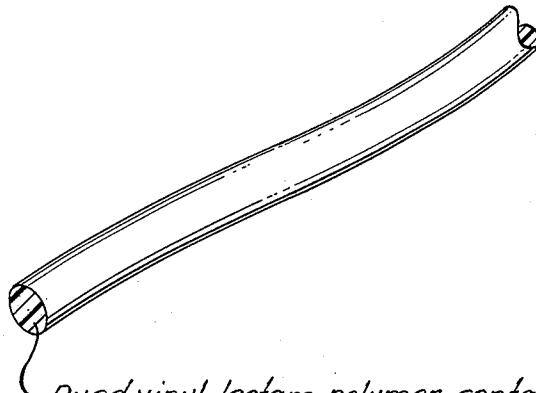


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COLOR FAST SYNTHETIC TEXTILE FIBERS FROM VINYL LACTAM
POLYMER-CONTAINING ACRYLONITRILE POLYMERS
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*Dyed vinyl lactam polymer-containing
acrylonitrile polymer synthetic textile
fiber product stabilized with copper
ion after-dyeing treatment.*

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COLOR FAST SYNTHETIC TEXTILE FIBERS FROM VINYL LACTAM POLYMER-CONTAINING ACRYLONITRILE POLYMERS

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This invention relates to the provision of color fast vinyl lactam polymer-containing acrylonitrile polymer synthetic textile fibers and the like that have been dyed with certain types of dyestuffs and rendered stable to the deleterious effects of light while in a colored condition.

Certain vinyl lactam polymers, particularly polyvinylpyrrolidone, are exceptionally well adapted for employment as dye-assisting adjuvants in shaped acrylonitrile polymer articles, particularly polyacrylonitrile fibers and the like, including filaments, yarns, films and related structures. For convenience, the various shaped articles that may be fabricated from synthetic, linear, fiber-forming acrylonitrile polymers will hereinafter be illustrated with fibers that are manufactured with such compositions. A great general improvement in dyeability with almost all of the available dyestuffs and coloring agents may be secured when vinyl lactam polymers, particularly polyvinylpyrrolidone, are incorporated in acrylonitrile polymer synthetic textile fibers. Despite this, certain difficulties may also attend such practice when it is desired to impart coloration to the fibers by means of many direct, acid (including acid-pretreated) and chrome types of dyestuffs.

By way of illustration, when vinyl lactam polymer-containing acrylonitrile polymer fibers are dyed with many of the direct, acid and chrome dyestuffs, the colored synthetic fiber product has a tendency to be unstable upon exposure to light so that they may definitely and noticeably fade in a most undesirable manner. This is notwithstanding the fact that good color yields and intense depths of shade may be initially achieved with such dyestuffs on vinyl lactam polymer-containing acrylonitrile polymer fibers and that such varieties of dyestuffs are normally quite color stable on exposure to light when they have been applied to the varieties of fibers for which they were originally designed and intended to be utilized upon.

This failure to be light fast when colored with direct, acid and chrome dyestuffs, as is apparent, tends to limit the otherwise generally utile characteristics of vinyl lactam polymer-containing acrylonitrile polymer synthetic fibers from employment as textile materials that are intended to be colored by such dyestuffs to avoid the obviously undesirable consequences that might accrue. It would be advantageous to overcome this deficiency in such fibers.

Therefore, it is principally the objective of the present invention to provide light stabilized vinyl lactam polymer-containing acrylic fibers and the like dyed with either direct, acid or chrome dyestuffs that would be substantially free from tendencies to fade upon exposure to light, including ultra violet light, in the course of their useful lives as textile materials. Other objectives and advantages ancillary to the principal objective that may be realized by practice of the present invention are manifest in the ensuing description and specification.

In accordance with the present invention, vinyl lactam polymer-containing acrylic fibers that have been dyed with a dyestuff selected from the group consisting of

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direct, acid and chrome dyestuffs may be rendered stable to light and resistant to fading from the initially obtained coloration by a treatment which comprises subjecting them after they have been dyed to an aqueous solution of cuprous ions, preferably obtained from cupric ions (as from copper sulfate) that have been converted to cuprous ions by the action of hydroxyl amine sulfate or an equivalent reducing agent for cupric ions. Beneficially, the treatment is conducted immediately subsequent to the dyeing operation. Advantageously, the aqueous solution of copper ions that is employed for the treatment contains a quantity of the ions that is equivalent to that which is obtained in an aqueous solution of copper sulfate containing from about 0.5 to 8 percent by weight, based on the weight of the fibers, of dissolved salt, and, more advantageously, from about 0.5 to 5 percent on the weight of the fibers of the dissolved salt in treating baths wherein the weight ratio of bath-to-fiber may respectively range from about 5:1 to about 100:1. Thus, the treating solution advantageously may be made up by the addition of from about 0.005 to 1.6 and, more advantageously, from about 0.005 to 1.0 gram of copper sulfate to each 100 grams of treating solution being prepared. Of course, when other copper ion-providing salts are utilized, their gravimetric proportions will vary from the indicated values for copper sulfate in accordance with the copper equivalent weight of the particular copper salt that is employed. The same ranges of weight concentrations in solution may advantageously be employed for a hydroxyl amine sulfate reducing agent and, in a similar manner, when other reducing agents for cupric ions are utilized, proportions of them that are equivalent in reducing activity to such concentrations of hydroxyl amine sulfate are usually advantageous. In many instances it may be suitable to employ an approximately equal weight percentage of copper sulfate and hydroxyl amine sulfate in the treating solution. Frequently, vinyl lactam polymer-containing acrylonitrile polymer synthetic textile fibers that have been imbued with light shades of coloration from direct, acid or chrome dyestuffs may be suitably stabilized against light fading when the concentration of reagents in the treating solution is at or towards the lower extremity of the indicated ranges. Darker hues may often be better stabilized with more concentrated treating solutions.

The treatment may be conducted for periods of at least one-half hour at temperatures from about 70° C. to the boil. Oftentimes, however, ebullient temperatures, or temperatures of at least about 95° C. are better adapted for its accomplishment. A treating solution bath-to-fiber weight ratio in the neighborhood of 30:1 may frequently be found satisfactory although variations from this may also often be suitable. Direct, acid or chrome dyed vinyl lactam polymer-containing acrylic fibers that have been treated in accordance with the present invention have a vastly augmented fastness to light. Frequently a two-fold or greater improvement (when expressed as a function of the time period under a given light exposure that is required to produce a visually discernible fading) may be realized in comparison with untreated fibers of the same type that have been dyed with the same varieties of dyestuffs. A dyed vinyl lactam polymer-containing acrylonitrile polymer synthetic textile fiber that is stabilized against fading upon exposure to light by treatment in accordance with the present invention is schematically represented, in an exaggerated perspective, in the accompanying drawing.

Although copper sulfate (CuSO_4) is, as has been indicated, a preferred source of copper ions, other copper salts may also be utilized for such purpose including copper acetate, copper chloride and the like. Likewise, such reducing agents as sodium sulfoxylate-formaldehyde, me-

tallic elemental copper, mixtures of sodium bisulfite with glyoxal and the like may also be employed in the practice of the invention, despite the great desirability of hydroxyl amine sulfate for such application. No special dyeing technique or procedure for the direct, acid or chrome dyestuffs is necessary when it is intended to stabilize the colored vinyl lactam polymer-containing acrylonitrile polymer fiber by practice of the invention. The usual and conventional techniques that are commonly employed in the art may be used on the fibers prior to the stabilizing treatment.

Advantageously, the vinyl lactam polymer-containing acrylonitrile polymer fiber that may be dyed with direct, acid or chrome dyestuffs and aftertreated for light fastness according to the present invention is derived from a fiber-forming acrylonitrile polymer that contains at least about 85 percent by weight of acrylonitrile polymerized in the polymer molecule and in which there is intimately incorporated a minor proportion of the vinyl lactam polymer as a dye-assisting adjuvant. More advantageously, the synthetic fiber is derived from polyacrylonitrile. While polyvinylpyrrolidone may be incorporated with particular benefit as a dye-assisting adjuvant in acrylonitrile polymer fibers, other vinyl lactam polymers may also be satisfactorily utilized for such purposes. These include various dye-receptive copolymers of vinyl pyrrolidone and polymers and copolymers of other vinyl lactams including vinyl caprolactam. When vinyl lactam copolymers are utilized, it is frequently desirable to employ those that contain at least about 60 or even 80 percent by weight of the vinyl lactam monomer polymerized in the copolymer molecule.

Generally, it is beneficial for a vinyl lactam polymer-containing acrylonitrile polymer synthetic textile fiber to contain up to 20 percent by weight of a dye-receptive vinyl lactam polymer in intimate physical incorporation in the acrylonitrile polymer. It may frequently be of greatest advantage when between about 6 and 12 percent by weight of the vinyl lactam polymer, particularly polyvinylpyrrolidone, is incorporated in the acrylonitrile polymer, particularly polyacrylonitrile, based on the dry weight of the associated polymers. While vinyl lactam polymer-containing acrylonitrile polymer synthetic textile fibers of the indicated variety may be literally referred to as acrylic fibers for purposes of broad generic classification, it is generally preferred, when brevity is a requirement, to characterize them as being "nitrile alloy" fibers in order to clearly distinguish them from the conventional prototype acrylic fibers that are known to the art.

Various techniques and procedures may be invoked for providing a vinyl lactam polymer-containing acrylonitrile polymer fiber of the indicated variety. For example, the vinyl lactam polymer may be uniformly incorporated in the desired quantity in a fiber-forming acrylonitrile polymer composition prior to spinning it into fibers in order to prepare the desired dye-receptive synthetic fiber product. Advantageously, however, the vinyl lactam polymer-containing acrylonitrile polymer fiber may be a wet spun product in which the vinyl lactam polymer is intimately incorporated by impregnation of the dye-assisting adjuvant from an aqueous solution thereof while the acrylonitrile polymer in the fiber is in a swollen or gel condition. Thus, a fiber-forming polymer of acrylonitrile such as polyacrylonitrile may be prepared as a spinning solution by dissolving it in a suitable solvent, such as an aqueous 60 percent by weight zinc chloride solution, and extruded in solution into a coagulating bath therefor to initially form an aquagel filamentary structure in which the vinyl lactam polymer may conveniently be incorporated by subjecting the aquagel structure to treatment with an impregnating solution of the dye-assisting adjuvant. Such an impregnating treatment may often be suitably performed by passing the aquagel through an aqueous treating bath of dissolved vinyl lactam polymer prior to drying the aquagel to a dehydrated condition.

The invention will be further illustrated in and by the following examples wherein, unless otherwise indicated, all parts and percentages are to be taken by weight. In each of the examples the vinyl lactam polymer-containing acrylic fiber consisted of 5-run polyacrylonitrile yarn in which there was intimately incorporated about 10 percent by weight, on the dry weight of the fiber, of polyvinylpyrrolidone as a dye-assisting adjuvant.

Example I

About 5 grams of scoured polyvinylpyrrolidone-containing polyacrylonitrile fiber was given a 2 percent dyeing of Benzo Azurine GA (C.I. 502), a direct dye, by initially setting the dyebath at 50° C., immersing the fiber in the dyebath, bringing the dyebath to the boil over a 20 minute period, adding 30 percent, on the weight of the fiber, of sodium chloride to the dyebath over a 15 minute period, and continuing the dyeing at the boil for a 2 hour period. The resulting fiber, which was deep and level dyed, was then given a cold rinse with water before being immersed in about 150 milliliters of a treating bath consisting of 5 percent of copper sulfate and 2.5 percent of hydroxyl amine sulfate, both based on the weight of the fiber. After placing the dyed fiber in the treating solution, the temperature was rapidly raised to about 95° C. and the dyebath was synthetically maintained for a 30 minute period. The dyed and treated fiber was then removed from the treating solution, rinsed thoroughly with cold water and dried. It had excellent light stability and was extremely color-fast upon exposure to light. For example, when the dyed and treated fiber was tested under exposure to ultra violet light in a standard Atlas "Fadeometer," a noticeable color fade did not occur until after expiration of a 20 hour period. In comparison, a similarly dyed but untreated fiber of the same type faded after only 5 hours of exposure in the "Fadeometer."

Example II

The procedure of Example I was essentially repeated with the same type of fiber excepting that the fiber was given a 6 percent dyeing with Nyliton Black B (Ciba). Similar excellent results were achieved. The treated fiber, which had accepted the dyestuff in good yield to a deep, level black, was colorfast during a 60 hour "Fadeometer" exposure.

Example III

In substantially identical repetitions of the procedures of Example I with different dyestuffs and slight variations in the concentrations of the reagents in the stabilizing treatment solutions, the color fastness of a number of dyed vinyl lactam polymer-containing acrylonitrile polymer synthetic textile fiber samples was enhanced to a degree commensurate with that illustrated in the preceding examples. The following tabulation lists and identifies some of the dyestuffs employed for the color stabilized acrylic fibers that were prepared. It also includes the nature of the dyeing with each dye and the weight concentrations, all based on the weight of the fiber, of the copper sulfate (CS) and hydroxyl amine sulfate (HAS) reagents that were in the particular treating solutions employed for stabilizing the dyed fibers.

Acid dyestuffs:

- 1.4 percent Calcocid Green B conc.—C.I. 5; 3.2 percent CS+3.2 percent HAS
- 2 percent Supramine Green BL—No C.I. or Pr.; 3.2 percent CS+3.2 percent HAS
- 1.4 percent Alizarine Fast Green CG ex. conc.—C.I. 1078; 3.2 percent CS+3.2 percent HAS
- 2 percent Alizarine Sapphire Blue 2G—Pr. 10; 3.2 percent CS+3.2 percent HAS
- 2 percent Calcocid Alizarine Blue Sky—C.I. 1088; 3.2 percent CS+3.2 percent HAS
- 6 percent Sulphon Black NB—No C.I. or Pr.; 5 percent CS+5 percent HAS

Direct dyes:

- 2 percent Cuprofix Rubine BL—Pr. 491; 4 percent CS+4 percent HAS
- 2 percent Diazo Fast Blue 2RW—C.I. 317; 4 percent CS+4 percent HAS
- 1 percent Direct Brilliant Sky Blue 6B ex. conc.—C.I. 518; 4 percent CS+4 percent HAS
- 5 percent Direct Black E ex. conc.—C.I. 581; 5 percent CS+5 percent HAS
- 2 percent Diamine Brown MBA—C.I. 420; 4 percent CS+4 percent HAS

Chrome dyestuffs:

- 1.4 percent Anthranol Chrome Red GL conc.—Pr. 135; 3 percent CS+3 percent HAS
- 2 percent Omega Chrome Red B—C.I. 652; 3 percent CS+3 percent HAS
- 2 percent Chrome Fast Orange 3 RL A CF—Pr. 247; 3 percent CS+3 percent HAS
- 2 percent Chrome Blue 2R—Pr. 7; 2 percent CS+2 percent HAS
- 2 percent Alizarine Light Grey 2BLW—Pr. 206; 2 percent CS+2 percent HAS

Those skilled in the art will readily recognize and appreciate that the treatment of the present invention differs in both substance and essence from certain diverse copper ion treatments that are known in connection with other of the conventional prototype acrylic and other synthetic fibers to either directly assist in chemically attaching a dyestuff that otherwise would not become associated with the polymer in the fiber or for causing a metallizing effect of an already attached dyestuff in the fiber. As has been indicated and as it is intended to be construed herein and in the hereto-appended claims, the term "acid dyestuffs" is meant to comprehend and to include within its generic purview the types of acid dyestuffs that are sometimes referred to and characterized as being "acid-premetallized" dyes.

What is claimed is:

1. Process of rendering color-fast a dyed synthetic textile fiber that is comprised of (a) a fiber of an intimate alloy composition of (1) a fiber-forming acrylonitrile polymer that contains in the polymer molecule about 85 weight percent of acrylonitrile and (2) a minor proportion of up to about 20 weight percent, based on the weight of the dry fiber, of a vinyl lactam polymer, said fiber being colored with (b) a dyestuff attached thereto selected from the group of dyestuffs consisting of direct, acid and chrome types of dyes, which process comprises treating said dyed fiber, for at least about half an hour at a temperature of from about 70° C. to the boil with an aqueous treating solution at a bath-to-fiber weight ratio between about 5:1 and 100:1, respectively, said treating solution containing (A) an amount of cupric copper ion equivalent to that which is obtained with between about 0.5 and 8 percent by weight, based on the weight of the fiber, of copper sulfate (CuSO_4), and (B) an amount of a reducing agent for cupric copper ions that is equivalent in activity to an aqueous solution of from 0.5 to 8 percent by weight, based

on the weight of the fiber, of hydroxyl amine sulfate to render fast-to-light the color in said dyed fiber.

2. As an article of manufacture, a colored and color fast-to-light synthetic textile fiber obtained as the product of the process of claim 1.

3. Process of manufacturing a color-fast synthetic textile fiber that is comprised of an intimate alloy composition of (1) a fiber-forming acrylonitrile polymer that contains in the polymer molecule at least about 85 weight percent of acrylonitrile and (2) a minor proportion of up to about 20 weight percent, based on the weight of the dry fiber, of a vinyl lactam polymer, which process comprises first dyeing said synthetic textile fiber with a dyestuff selected from the group consisting of direct, acid and chrome types of dyes and subsequently treating said dyed fiber, for at least about half an hour at a temperature between about 70° C. and the boil, with an aqueous treating solution at a bath-to-fiber weight ratio between about 5:1 and 100:1, respectively, said treating solution containing (A) between about 0.5 and 8 percent by weight of copper sulfate (CuSO_4) and (B) between about 0.5 and 8 percent by weight of hydroxyl amine sulfate, both based on the weight of the fiber, to render fast-to-light the color in said dyed fiber.

4. The process of claim 3, the after-dyeing treatment being conducted at a temperature between about 95° C. and the boil.

5. The process of claim 3, wherein the after-dyeing treatment is conducted in an aqueous treating solution containing separate amounts of between about 0.5 and 5 percent by weight of the copper sulfate and the hydroxyl amine sulfate, both based on the weight of the fiber.

6. The process of claim 3, wherein about equal weights of copper sulfate and hydroxyl amine sulfate are contained in the aqueous treating solution employed after said dyeing.

7. The process of claim 3, wherein the treating bath-to-fiber weight ratio that is utilized in the after-dyeing treatment is in the neighborhood of 30:1.

8. The process of claim 3, wherein said synthetic textile fiber is comprised of polyacrylonitrile in which there is intimately incorporated an amount between about 6 and 12 percent by weight, based on the weight of dry fiber, of polyvinylpyrrolidone as a dye-assisting adjuvant.

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