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STABILIZED BLEACHED POLYACRYLONITRILE ARTICLES

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This invention relates to the preparation of bleached yarns and fabrics comprising polyacrylonitrile and is particularly concerned with the preparation of such articles which do not discolor upon prolonged exposure to ultra-violet light.

Fibrous structures prepared from polyacrylonitrile monofilaments, multifilaments, and staple have highly desirable physical properties but do not possess that degree of freedom from color which is required by the exacting standards of the textile industry. Moreover, the customary method utilized in the textile art for the bleaching of color from filaments, fibers, and the like do not effect the desired elimination of color from polyacrylonitrile structures. The slightly yellow to tan color present in polyacrylonitrile articles occurs either during polymerization or processing of the polymer prior to or during shaping of the polymer to the desired form and may be caused by prolonged treatment of the polymer at high temperature, for example, 100° C. and above.

Means for preparing substantially white polyacrylonitrile structures by bleaching said structures are described in Scheiderbauer U. S. 2,432,447 and Richards U. S. 2,432,448. The bleached polyacrylonitrile structures are, however, not stable to the effect of ultra-violet light. In fact, after two hours exposure to ultra-violet light the bleached polyacrylonitrile shaped articles discolor rapidly. This disadvantage naturally limits the commercial utility of polyacrylonitrile structures.

Accordingly, it is an object of this invention to produce color-free, that is, substantially white, acrylonitrile polymer filaments, fibers, yarns and fabrics which are stable to the effect of ultra-violet light. It is a further object of this invention to provide stabilized color-free polyacrylonitrile articles without substantially impairing the physical properties of the product. Other objects will become obvious in the discussion of the invention which follows.

The objects of this invention are accomplished, in general, by means of a process which comprises bleaching the fibrous polyacrylonitrile structure with an aqueous bleaching solution containing available chlorine and subsequently impregnating the fibrous structure with a phosphorous acid derivative selected from the group consisting of hypophosphorous acid, alkyl phosphites and aryl phosphites and then heating the impregnated structure. By this process the objectionable coloring present in the yarn is removed by the bleaching treatment, and the resulting bleached structure is stabilized against discoloration upon exposure to ultra-violet light with no substantial impairment of the desired physical properties of the fibrous structure.

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The invention will be described most particularly with reference to yarn and fabric composed of continuous filaments but it will be understood that this is merely by way of illustration, since the invention may be also applied to staple fibers, monofils, artificial straw, hollow pellicles such as tubing, and other industrial products composed of polyacrylonitrile. The following examples in which parts, percentages, and proportions are by weight unless otherwise specified, and which are intended to be illustrative instead of limitative, set forth preferred forms of the invention.

Example I

Woven fabric prepared from polyacrylonitrile yarn was treated at 97° C. and at atmospheric pressure with an aqueous solution of calcium hypochlorite containing 0.25% available chlorine, the solution having been made to a pH of 2.0 by the addition of sulfuric acid. This bleaching action was allowed to take place for 20 minutes, after which the fabric sample was rinsed in warm water for a short time to remove excess bleach from the fabric. When exposed to ultra-violet light in a Fadeometer for two hours, this bleached, white fabric discolors. A sample of the bleached polyacrylonitrile fabric was treated with a solution consisting of 50% glycerine and 50% aqueous hypophosphorous acid. After removing the excess liquid the fabric sample was given a 15 minute treatment with steam under 15 pounds pressure. The resulting stabilized bleached fabric did not discolor after 100 hours exposure to ultra-violet light in the Fadeometer. Laundering of this stabilized bleached fabric did not destroy its stability to ultra-violet light. In addition, the physical properties of the fabric were not impaired by this bleaching and stabilizing treatment.

Example II

A skein of undrawn polyacrylonitrile yarn prepared by a dry-spinning process was treated at 80° C. and at atmospheric pressure for 10 minutes with an aqueous solution of calcium hypochlorite containing 0.25% available chlorine and made to a pH of 7. After a warm water rinse, the resulting white yarn was treated with 50% aqueous hypophosphorous acid and steamed under 15 pounds pressure for 15 minutes. The

stabilized bleached yarn did not discolor after 50 hours exposure to ultra-violet light in a Fadeometer. Without the stabilizing treatment with hypophosphorous acid, the bleached yarn discolored after two hours in the Fadeometer.

Example III

A sample of knitted fabric prepared from drawn polyacrylonitrile yarn was treated at 97° C. and at atmospheric pressure for 5 minutes with an aqueous calcium hypochlorite solution containing 0.125% available chlorine and made to a pH of 1 with sulfuric acid. After rinsing with warm water, the resulting white fabric was treated with a solution containing 50% glycerol and 50% triallyl phosphite. After removing the excess liquid, the sample was steamed for 15 minutes at 15 pounds pressure. The stabilized bleached fabric did not discolor after 75 hours exposure to ultra-violet light in a Fadeometer. An unstabilized bleached sample darkened after two hours exposure to the ultra-violet light.

Example IV

A skein of undrawn polyacrylonitrile yarn was treated at 97° C. and at atmospheric pressure for 30 minutes with an aqueous solution of Chloramine B (sodium N-chlorobenzenesulfonamide) containing 0.27% available chlorine, made to a pH of 2 by the addition of sulfuric acid. The resulting bleached yarn was rinsed in warm water to remove excess bleach. A sample of this yarn darkened after two hours exposure to ultra-violet light. The remainder of the yarn was treated with 100% triallyl phosphite and steamed for 15 minutes under 15 pounds pressure. The stabilized bleached yarn did not discolor after 75 hours exposure to ultra-violet light in the Fadeometer. Laundering did not destroy the stability of the stabilized bleached yarn to the action of ultra-violet light. The bleaching treatment with Chloramine B did not impair the physical properties of the polyacrylonitrile yarn.

Example V

A skein of undrawn polyacrylonitrile yarn was treated for 15 minutes at 95° C. and at atmospheric pressure with an aqueous solution of Chloramine B containing 0.13% available chlorine, made to a pH of 4 by the addition of sulfuric acid. The white yarn after rinsing was treated with a solution containing 50% glycerol and 50% tributyl phosphite and steamed for 15 minutes under 15 pounds pressure. The bleached stabilized yarn showed no signs of discoloring after 50 hours exposure to ultra-violet light.

Example VI

A skein of undrawn polyacrylonitrile yarn was treated at 80° C. and at atmospheric pressure for 10 minutes with chlorine water containing 0.24% available chlorine at a pH of 2.0. The bleached yarn was rinsed several times in warm water. This yarn discolored after two hours exposure to ultra-violet light. A sample of the yarn bleached with chlorine water was treated with a solution containing 20% acetic anhydride and 80% of 50% aqueous hypophosphorous acid. After removal of excess liquid, the sample was steamed for 15 minutes under 15 pounds pressure. The resulting stabilized bleached yarn showed no signs of discoloring after 100 hours exposure to ultra-violet light. The bleaching with chlorine water did not impair the physical properties of the yarn.

The effective bleaching agent used in the process of this invention is any solution containing available chlorine and since water is used, it is an aqueous solution containing hypochlorous acid. The hypochlorous acid solution may readily be prepared by dissolving a material such as chlorine, sodium hypochlorite or calcium hypochlorite or other soluble hypochlorites in water and acidifying with a mineral acid such as hydrochloric or sulfuric acid to a pH of 7.0 or less, preferably 2.0 to 5.0. Other materials which react with water in acid medium to form hypochlorous acid can be used as well. Examples of such compounds are Chloramine B (sodium N-chlorobenzenesulfonamide) and Chloramine T (sodium N-chlorotoluenesulfonamide). Peculiarly, stabilization cannot be effected using the stabilizers of this invention on articles bleached with agents other than active chlorine compounds, as, for example, articles bleached with peroxide. There is a cooperative action between the bleaching treatment and stabilizing treatment of this invention which leads to light fast articles.

The aqueous hypochlorous acid solutions used in accordance with the present invention will contain 0.05% to 1.0% available chlorine and preferably 0.1% to 0.5% with the most preferred concentration being in the neighborhood of 0.25%. The term "available chlorine" signifies the chlorine present as hypochlorous acid. An excess of mineral acid added to the hypochlorite solution does no harm and the pH can be lower than 2.0 or even close to 0.0, if desired.

The temperature for the bleaching treatment should be within the range 80°–150° C. and preferably 90°–100° C. with the pressure being sufficiently high to maintain the treating solution liquid. The time of treatment will be short and preferably 30 minutes or less but will depend on the temperature and available chlorine concentration. Since bleaching to satisfactory whiteness can be obtained in times as short as 5 minutes at temperatures less than 100° C., there is nothing to be gained by carrying out the bleaching treatment under pressure.

The bleaching treatment of this invention may be applied to the yarn after the removal of the solvent when the yarn is dry spun, or after drying when the yarn is wet spun, before collection of the yarn. On the other hand, drawn yarn and fabrics prepared therefrom may be bleached readily as shown by Examples I and III.

While the bleaching process described in this invention is effective of itself in producing a white polyacrylonitrile yarn, the bleached product will discolor upon exposure to ultra-violet light. Accordingly, in order to extend the outdoor uses of this high strength white yarn it is necessary to stabilize it against discoloration by ultra-violet rays. Of the numerous classes of chemical compounds that were tested as stabilizers for this purpose, only hypophosphorous acid and alkyl phosphites were found to be acceptable.

The stabilizers may be applied in various ways. The bleached fabric or skein of yarn may be suspended in a boiling aqueous solution or dispersion of the stabilizer. To aid in penetration of the fiber, compounds such as, glycerol, acetic anhydride phenol and m-cresol may be added to the stabilizer solutions as vehicles. The most effective technique has been that described in the examples. The bleached fabric or skein of yarn is effectively padded with the stabilizer liquor by a dipping process and the stabilizer is driven into the fiber by means of the pressure steaming treatment. The amount of stabilizer

picked up by the fibers by these various techniques is sufficient to stabilize the bleached structures against rapid discoloration in the presence of ultra-violet light. Usually, 2 parts of the bleached article is dipped in 5 parts of the stabilizer in 70 parts of vehicle. The fabric is removed and excess liquid is allowed to drain off. The amount of stabilizer in the final product is relatively small. The stabilizing agent may be hypophosphorous acid or derivatives thereof among the alkyl phosphites. In general, any mono-, di-, or trialkyl phosphite will work. For example, in addition to those mentioned in the examples, tributyl-, triethyl-, diethyl-, trimethyl-, diphenyl-, di-o-tolyl-, monoamyl-, monocyclohexyl phosphites or the like may be employed. If the stabilizer used produces hypophosphorous acid during the stabilizing treatment, it will function in the process of this invention.

The step of stabilization is similar to pad-steaming dye techniques. The stabilizer is padded onto the bleached article usually at room temperature and the padded article is then heated to effect penetration of the stabilizer into the article. This impregnation is essential to successful stabilization. In the heating step any convenient heating means may be used but it is preferred to use hot water or steam. Steam under pressure is advantageous in that greater penetration of the stabilizer is effected. The time and temperature ranges may be from water at the boil to water or steam under pressure up to about 20 p. s. i. At the lower temperatures, longer times are required. At 97° C. about 2 hours are required whereas at higher temperatures much shorter times may be used, as is shown in the examples. The temperatures used in the heat impregnation step may be 130° C. or higher. Generally, temperatures of about 100° C. to about 125° C. are used.

By the process of the present invention, polyacrylonitrile fabrics, yarns, filaments, fibers, films, monofilaments, artificial straw, hollow tubing and other structures can be bleached to a satisfactory colorless or white character without deleterious action on the structure. The bleached polyacrylonitrile structures are effectively stabilized against discoloration by ultra-violet light. The stabilized bleached polyacrylonitrile structures, except for improved color, exhibit substantially the same physical characteristics as the unbleached structures. Laundering of these structures does not destroy the effect of the stabilization treatment. In addition, these bleached structures yield brighter shades upon dyeing than do the corresponding unbleached structures.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

I claim:

1. A process for stabilizing a polyacrylonitrile article against discoloration by light which comprises bleaching the said article with a bleaching agent containing available chlorine; impregnating the resultant bleached article with a phosphorous acid compound selected from the group consisting of hypophosphorous acid and organic phosphites; and heating the resultant impregnated article.

2. A process in accordance with claim 1 in which the said bleaching agent is hypochlorous acid.

3. A process in accordance with claim 1 in which the said phosphorous acid compound is hypophosphorous acid.

4. A process in accordance with claim 1 in which the said bleaching agent is hypochlorous acid and the said phosphorous acid compound is hypophosphorous acid.

5. A process in accordance with claim 1 in which the phosphorous acid compound is a trialkylphosphite.

6. A process in accordance with claim 1 in which the bleaching agent contains 0.05% to 1.0% available chlorine.

7. A process in accordance with claim 1 in which the bleaching medium has a pH of from 2.0 to 5.0

8. A process in accordance with claim 1 in which the heating is done with steam at a temperature of about 100° C. to about 125° C.

9. A process is accordance with claim 1 in which the phosphorous acid compound is triallyl phosphite.

10. A process in accordance with claim 1 in which the phosphorous acid compound is tributyl phosphite.

11. A process in accordance with claim 1 in which the phosphorous acid compound is a dialkyl phosphite.

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