This invention relates to the treatment of cellulose esters to improve the resistance of dyings thereon to the deleterious effect of chlorine and to said dyed cellulose esters having improved resistance to chlorine. The invention is particularly directed to dyed cellulose acetate textile materials the colors of which have been rendered resistant to chlorine attack as exemplified in swimwear upon exposure to chlorinated swimming pool water.

It is recognized in the art that dyed cellulose acetate textile materials, even though dyed with dyestuffs which yield dyings thereon having excellent fastness to light, gas, and washing, for example, nevertheless discolor or fade upon exposure to aqueous reactive chlorine in concentrations such as are used to disinfect swimming and bathing pools. Consequently the textile trade has long sought for means for rendering the colored cellulose ester fabrics employed in bathing suits resistant to chlorinated swimming pool fading.

After extensive investigation I have discovered a procedure whereby such discoloration or fading may be obviated or greatly minimized as will be set forth in detail hereinafter.

It is an object of my invention to provide a dyed cellulose ester which is resistant to the action of reactive chlorine in concentrations such as are used to disinfect water in bathing pools. Another object of my invention is the production of dyed cellulose ester textile materials containing a chlorine fading inhibitor which has an affinity for said cellulose ester textile material and which does not discolor or cause fading when exposed to light and aqueous reactive chlorine. A further object of my invention is the production of dyed cellulose ester textile materials containing a chlorine fading inhibitor which are suitable for bathing suits and which have good resistance to chlorine fading and good fastness to water bleeding. A particular object of my invention is to provide dyed cellulose acetate textile materials which have good resistance to chlorine fading and good fastness to water bleeding.

By cellulose esters I contemplate cellulose alkyl carboxylic acid esters having two to four carbon atoms in the acid groups thereof; such esters include, for example, both hydrolyzed and unhydrolyzed cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate-propionate, and cellulose acetate-butyrate.

I have discovered that the color of dyed cellulose ester textile materials which have been dyed with dyestuffs which are not normally fast to the action of aqueous reactive chlorine solutions may be rendered fast thereto by incorporating in said cellulose ester textile materials 2,2-bis(p-hydroxyphenol) propane having the formula:

The presence of the 2,2-bis(p-hydroxyphenol) propane in the dyed cellulose ester textile material greatly improves the resistance of the dyeing to the deleterious effect of chlorine.

The 2,2-bis(p-hydroxyphenol) propane (also known as 4,4'-isopropylidene diphenol) inhibiting agent may be incorporated in the cellulose ester in any desired and convenient manner. For example, it may be incorporated into a solution of the cellulose ester before such solution is formed into a shaped article such as a filament or fiber; or the inhibiting agent may be applied to the cellulose ester textile material in fiber, filament, or fabric form, for example, either before dyeing or during the dyeing operation. Preferably, however, the 2,2-bis(p-hydroxyphenol) propane is applied after dyeing.

The 2,2-bis(p-hydroxyphenol) propane inhibiting agent may be applied to the dyed cellulose ester textile material in the form of a solution in a solvent, such as ethyl alcohol or methyl alcohol, which does not have an undesirable solvent action on the cellulose ester material.

The 2,2-bis(p-hydroxyphenol) propane inhibiting agent may also be applied to the dyed cellulose ester textile material in the form of a stable aqueous dispersion. A suitable aqueous paste dispersion can be prepared by ball milling an aqueous suspension of Bisphenol A (4,4'-isopropylidene diphenol), glycerine and Marasperse N (a sodium lignosulfonate), as follows: 50 pounds of the Bisphenol A, 5 pounds of glycerine, 5 pounds of Marasperse N and 40 pounds of water are added to a 30-gallon ball mill and milled until a 10-gm sample filtered through a Raves Angel No. 20 filter paper left a clear filtrate of less than 0.001% total soluble chlorides in the homogenous paste is discharged into resin lined steel containers for use. (Bisphenol A and Marasperse N are trademarks of Monsanto Chemical Company and the Marathon Corporation, respectively.)

The inhibiting agent may also be directly applied to the material undergoing treatment as an aqueous suspension which has been prepared by grinding the Bisphenol A to a paste in the presence of a sulfitated oil, Turkey red oil, soap, octyl glyceryl sulfate, sodium lignosulfonate, or other suitable dispersing agents, then dispersing this resulting paste in water.

The amount of 2,2-bis(p-hydroxyphenol) propane inhibiting agent incorporated into the cellulose ester textile material preferably ranges from 1% to 10% by weight of the cellulose ester. Thus, for example, when the inhibitor is applied in a padding operation, the pick-up of the padding roll should be adjusted so that sufficient inhibiting solution is retained in the cellulose ester textile material being treated to give 1% to 10% of the inhibiting agent based on the weight of the cellulose ester textile material.

My invention is described more particularly with reference to cellulose acetate. However, the invention is applicable to any of the other cellulose esters disclosed hereinafter.

Many inhibitors have a tendency to discolor in aqueous reactive chlorine solutions. However, the 2,2-bis(p-hydroxyphenol) propane employed in my invention exhibits no such tendency but demonstrates a very high inhibiting activity as shown by the following examples which illustrate my invention.

Example 1

A cellulose acetate fabric which had been dyed a light blue shade with 1,5-dihydroxy-8-nitro-4-aminoanthraquinone was padded with a solution which had been prepared by dissolving 30 parts by weight of 2,2-bis(p-hydroxyphenol) propane in 30 parts of aqueous 33% sodium hydroxide and 40 parts of methanol. The pad rolls were adjusted to an 80% to 100% pick-up at 100° F. to 120° F. After padding and drying, the fabric retained 2.5% to 3.0% of the 2,2-bis(p-hydroxyphenol) propane. The resulting fabric had a greatly improved resistance to aqueous reactive chlorine fading as evidenced by appreciable fading after it had been given an AATCC test No. 63-1957 for chlorinated pool water. It also
showed no fading when given a Jantzen test using 5 p.p.m. of chlorine in an aqueous solution with a 1:100 liquor ratio at room temperature with agitation for four hours. An undyed cellulose acetate fabric, treated in the aforementioned manner, also exhibited improved resistance to aqueous chlorine fading when subsequently dyed with 1,5-dihydroxy-8-nitro-4-aminoanthraquinone and tested.

**Example II**

Similar results were obtained when Example I was repeated, using 40 parts of ethanol in place of methanol.

**Example III**

A cellulose acetate fabric was inhibited during dyeing (in a single step operation) using a dye bath (Jig or dyebeck) containing 6% finely dispersed 2,2-bis(p-hydroxyphenyl)propene, 2% 1,8-dihydroxy-5-amino-4(4'-
β-hydroxyethylanilino)anthraquinone, 1% sodium hexametaphosphate, 1% of an anionic surfactant such as Ige-20

pon T-33, all based upon the weight of the fabric. One gallon of methanol was then added to the dye bath per 100 gallons of dye liquor at 120° F. The dye bath temperature was raised to 180° F. in one hour and the fabric rinsed with water and dried. When given the AATCC test No. 63–1957 or Jantzen test, the fabric showed little or no fading.

**Example IV**

Example III was repeated except that an equal volume of ethanol was used in place of methanol. The resulting dyed fabric shows little or no fading when given the AATCC test No. 63–1957 or the Jantzen test.

**Example V**

A cellulose acetate fabric dyed to a 1% dyeing with the violet dye 1,4-diaminoanthraquinone was after-treated in a fresh bath containing 5% of finely dispersed 2,2-bis(p-hydroxyphenol)propene based upon the weight of the fabric and one gallon of methanol per 100 gallons of water. The fabric was treated at 140° F. and dried without rinsing. The resulting fabric had greatly improved resistance to aqueous reactive chlorine fading as was shown by an appreciable fading when tested according to AATCC test No. 63–1957 or the Jantzen test.

**Example VI**

Example V was repeated except that an equal volume of ethanol was used in place of methanol. Similar improved resistance to chlorine attack was noted.

**Example VII**

Example V was repeated using undyed cellulose acetate fibers. When made into fabric and dyed with 1,4-diaminoanthraquinone (1% by weight of the fabric) the violet dyeing obtained also had good resistance to chlorine fading. Generally similar results are obtained using any of the other anthraquinone dyestuffs disclosed herein in place of 1,4-diaminoanthraquinone.

The dyes which are most benefited by my invention are the anthraquinone blue and violet types such as 1,4-diaminoanthraquinone (violet), 1,4-diamino-5-nitroanthraquinone (violet), 1,4-dimethylaminoanthraquinone (violet), 1,5-dihydroxy-8-nitro-4-aminoanthraquinone (blue), 1,8-dihydroxy-5-nitro-4-(4'-6-
β-hydroxyethylanilino)-anthraquinone, 4-(4'-6-
β-hydroxyethylanilino)-5-nitro-8-dihydroxyanthraquinone. Additional dyes, whose dyeings on cellulose esters can be made more resistant to chlorine fading in accordance with my invention, include those of U.S. Patents 2,641,602; 2,651,641 and 2,777,863. When the nitro group present in the anthraquinone compounds of these patents is reduced to an amino group the resultant dyes give dyeings on cellulose esters, such as cellulose acetate which have improved fastness to water bleeding. The reduction can be conveniently carried out by refluxing the dye compound with sodium sulfide in the presence of water as a diluent medium. The dyeings on cellulose esters obtained with these latter compounds also can be made more resistant to chlorine fading when treated with 2,2-bis(p-hydroxyphenyl)propene in aqueous solution with the present invention.

The anthraquinone compounds disclosed herein are illustrative and not limitative of the dye compounds whose dyeings on cellulose esters can be made more resistant to chlorine fading by treatment with 2,2-bis(p-hydroxyphenyl)propene. The anthraquinone compounds disclosed are water insoluble dispersed dyestuff.

I have found the preferred range of my inhibiting agent to be from 1% to 10% based upon the weight of the cellulose ester undergoing treatment. Where the 2,2-bis(p-hydroxyphenyl)propene inhibiting agent is milled for use in the practice of my invention, the particle size is preferably reduced to within a range of from 1/2 to 20 microns for optimum results.

My invention is utilizable within, but is not limited to, the usual range of chlorine concentration employed in swimming pool water and which generally runs about 5 p.p.m. in this country and as much as 10 p.p.m. abroad. Cellulose esters other than methanol and the ethanol which can be used in applying the 2,2-bis(p-hydroxyphenyl)propene to the cellulose ester textile materials include, for example, n-propyl alcohol, cyclohexanol, methyl Cellosolve, phenyl Cellosolve, methyl ether, and diethylene glycol alcohol.

The aforementioned Jantzen test for color fastness to chlorinated swimming pool water utilizes a completely closed system made up of a large reservoir, two exposure chambers, and a pump to lift the water back to the reservoir. To the reservoir containing 20,000 ml of water at a pH of 7.0 is added 2 ml of 5% sodium hypochlorite, laboratory reagent grade. This gives an available chlorine content of 5 p.p.m. The charged solution is then tested with a chlorine comparator to confirm the concentration. Four pieces of fabric weighing a total of ten grams are placed in each exposure chamber, making an aggregate sample of 20 grams. The system is sealed and the chlorinated water circulated for four hours at room temperature. The amount of available chlorine within the system will decrease during the test to an extent which is proportionate to the amount of color reduction taking place in the fabric. At the end of the four-hour period, the samples are removed and air dried at room temperature. The results of the test are comparable to 20 hours' actual use which, in turn, approximates an average season's use by a consumer.

The Ciba Company, Inc., has also published another method for determining fastness properties of dyes in chlorinated water. While their test employs an available chlorine concentration of 20 p.p.m. and a liquor ration of 1:100 for four hours at room temperature, that test and the Jantzen test show fairly good correlation with each other and also with actual swimming pool use. However, the AATCC test No. 63–1957 has been indicated by some persons working in this field to not correlate with actual swimming pool use as well as the other two tests.

Although my invention has been described in detail with reference to preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and as defined by the attached claims.

I claim:

1. A cellulose alkyl carboxylic acid ester having two to four carbon atoms in the acid groups thereof textile material having incorporated therein 2,2-bis(p-hydroxyphenyl)propenes.

2. A cellulose alkyl carboxylic acid ester having two to four carbon atoms in the acid groups thereof textile material having incorporated therein 1% to 10% by weight of said textile material of 2,2-bis(p-hydroxyphenyl)propene.
3. A cellulose acetate textile material having incorporated therein 2,2-bis(p-hydroxyphenol) propane.

4. A cellulose acetate textile material having incorporated therein 1% to 10% by weight of said textile material of 2,2-bis(p-hydroxyphenol) propane.

5. A cellulose alkyl carboxylic acid ester having two to four carbon atoms in the acid groups thereof textile material dyed with a water-insoluble disperse anthraquinone dyestuff normally tending to fade upon exposure to aqueous reactive chlorine and having incorporated therein 2,2-bis(p-hydroxyphenol) propane in an amount sufficient to resist color change normally occurring on exposure to aqueous reactive chlorine.

6. A cellulose alkyl carboxylic acid ester having two to four carbon atoms in the acid groups thereof textile material dyed with a water-insoluble disperse anthraquinone dyestuff normally tending to fade upon exposure to aqueous reactive chlorine and having incorporated therein 1% to 10% by weight of said textile material of 2,2-bis(p-hydroxyphenol) propane.

7. A cellulose acetate textile material dyed with a water-insoluble disperse anthraquinone dyestuff normally tending to fade upon exposure to aqueous reactive chlorine and having incorporated therein 2,2-bis(p-hydroxyphenol) propane in an amount sufficient to resist color change normally occurring on exposure to aqueous reactive chlorine.

8. A cellulose acetate textile material dyed with a water-insoluble disperse anthraquinone dyestuff normally tending to fade upon exposure to aqueous reactive chlorine and having incorporated therein 1% to 10% by weight of said textile material of 2,2-bis(p-hydroxyphenol) propane.

9. A textile material in accordance with claim 1 wherein the 2,2-bis(p-hydroxyphenol) propane has a particle size ranging from 0.5 micron to 20 microns.

10. A textile material in accordance with claim 2 wherein the 2,2-bis(p-hydroxyphenol) propane has a particle size ranging from 0.5 micron to 20 microns.

11. A process for rendering an undyed cellulose acetate textile material resistant to chlorine fading when subsequently dyed with a water-insoluble disperse anthraquinone dyestuff normally tending to fade upon exposure to aqueous reactive chlorine which comprises incorporating 1% to 10% by weight of said textile material of 2,2-bis(p-hydroxyphenol) propane therein.

12. A process for rendering a cellulose acetate textile material dyed with a water-insoluble disperse anthraquinone dyestuff normally tending to fade upon exposure to aqueous reactive chlorine resistant to chlorine fading which comprises incorporating 1% to 10% by weight of said textile material of 2,2-bis(p-hydroxyphenol) propane therein.

13. A process for rendering a cellulose alkyl carboxylic acid ester having two to four carbon atoms in the acid groups thereof textile material dyed with a water-insoluble disperse anthraquinone dyestuff normally tending to fade upon exposure to aqueous reactive chlorine resistant to chlorine fading which comprises incorporating 1% to 10% by weight of said textile material of 2,2-bis(p-hydroxyphenol) propane therein.

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