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OPTICALLY BLEACHED FIBROUS MATERIAL

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13 Claims. (Cl. 117—33.5)

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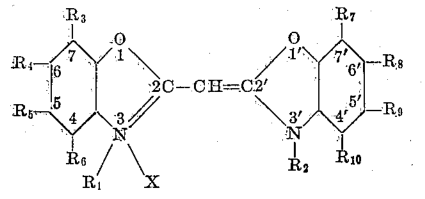
This application is a continuation-in-part of our application No. 137,673, filed January 9, 1950, and now Patent No. 2,620,282.

This invention relates to a process for the improvement of synthetic fibrous materials having a basis of organic derivatives of cellulose. Within this term is to be understood textile materials in the form of filaments, threads, yarns, woven or knitted fabrics, made of cellulose esters such as cellulose acetate, cellulose propionate, cellulose butyrate and mixed cellulose esters as, for instance, cellulose acetate-butyrate and cellulose acetate-propionate, or cellulose ethers such as ethyl cellulose and benzyl cellulose. Also included are synthetic fibrous materials made of any of the foregoing types of cellulose derivatives not in textile form, e. g. compacted synthetic fibres.

According to the present invention a process for improving synthetic fibrous materials having a basis of organic derivatives of cellulose and particularly for improving textiles made of cellulose acetate, comprises applying thereto a small quantity of a compound of the general formula:



wherein R_1 and R_2 are alkyl or oxyalkyl groups, and R_3 to R_{10} may be hydrogen atoms, or any of them may represent substituted groups such as alkyl, alkoxy, amino and substituted amino groups, or halogen atoms, and X is an acid radicle, which compound is colourless in ethyl alcoholic solution. By the term "colourless in ethyl alcoholic solution" is meant that a solution of the compound in ethyl alcohol has an absorption maximum not greater than 4000 Å.

The preferred compounds according to this invention are those in which the absorption maximum is below 3900 Å and of these the compound in which some of R_3 to R_{10} represent lower alkyl or alkoxy groups and the remainder are hydrogen atoms are preferred. The nature of the acid radicle X appears to be of little importance apart from its effect on the solubility of the compounds. It may be halide or sulphate, but from the practical standpoint the p-toluene sulphonates are generally preferred as these have usually a satisfactory degree of solubility in water.

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The following are examples of specific compounds which may be employed according to the present invention:

(1) 3,3'-dimethyl oxacyanine iodide, M. Pt. 317° C. decomp., the corresponding methosulphate, M. Pt. 323° C. decomp.
(2) 3-methyl-3'-ethyl oxacyanine iodide, M. Pt. 301° C. decomp.
(3) 3:3':6:6'-tetramethyl oxacyanine iodide, M. Pt. 317° C. decomp.
(4) 3:3':5:5':6:6'-hexamethyl oxacyanine bromide, M. Pt. 322° C. decomp., the corresponding methosulphate, M. Pt. 313° C. decomp. and the corresponding p-toluene sulphonate, M. Pt. 320° C. decomp.
(5) 3:3'-diethyl-5:6-dimethyl oxacyanine iodide, M. Pt. 292° C. decomp.
(6) 3:3'-diethyl-5:6:5':6'-tetramethyl oxacyanine iodide, M. Pt. 311° C. decomp.
(7) 3:3'-diethyl-6:6'-dimethyl oxacyanine iodide, M. Pt. 306° C. decomp.
(8) 3:3'-dimethyl-5:5'-dichlor oxacyanine p-toluene sulphonate (M. Pt. above 300° C.).
(9) 3:3':5:5'-tetramethyl oxacyanine bromide (M. Pt. 298° C. with decomp.).
(10) 3:3':5:5':6-pentamethyl oxacyanine p-toluene sulphonate (M. P. 280° C. with decomp.).
(11) 3:3':5:6-tetramethyl oxacyanine p-toluene sulphonate (M. Pt. 314° C. with decomp.).
(12) 3:3'-dimethyl-5-acetamino oxacyanine p-toluene sulphonate (M. Pt. 283° C. with decomp.).
(13) 3:3'-dimethyl 5-bromoxacyanine p-toluene sulphonate (M. Pt. 298° C. with decomp.).
(14) 3.3'.5.5'-tetramethyl oxacyanine p-toluene sulphonate, M. Pt. 269° C. decomp.
(15) 3.3'- dimethyl - 5.5'-dimethoxy-oxacyanine p-toluene sulphonate, M. Pt. 285° C. with decomp.
(16) 3.3'-dimethyl-5-methoxy-5'-methyl oxacyanine p-toluene sulphonate, M. Pt. 255° C. with decomp.

The compounds of the foregoing general formula may be prepared by condensing a quaternary salt of an appropriate 2-methyl benzoxazole with a quaternary salt of an appropriate 2-alkylthio benzoxazole in the presence of a base such as pyridine.

The compounds of the foregoing general formula which are colourless, white or pale yellow have been found to possess a strong fluorescence in daylight and a slightly less fluorescence in incandescent electric or similar light, and on application to cellulose derivative fibrous materials they impart such fluorescence to them. The fluorencence varies in colour between violet, pale blue and deep blue. The effect of applying these compounds to the fibrous materials is to impart a degree of brilliance to them which is attractive and useful. Applied to materials which are allegedly white, but of which the whiteness has a slight tinge of yellow or brown, the compounds serve to "kill" the yellow or brown tinge so that the apparent whiteness of the materials is very appreciably enhanced. This application of the materials is of especial importance, and the present invention is therefore particularly concerned with the application of the compounds to such "off-white" fibrous cellulose derivative materials. Applied to dyed cellulose derivative textile materials the compounds have the effect of improving the apparent purity of the colour.

The compounds of the present invention, being salts of organic bases, are more or less readily soluble according to their constitution in polar organic solvents such as lower alcohols, esters and ketones and are sufficiently soluble in water to permit their application to cellulose derivative fibrous materials from aqueous solution. In aqueous solution they exhibit a remarkably non-selective affinity to the various types of fibres referred to above so that they can be applied from very dilute solution without the aid of auxiliary agents and without having to be dispersed in finely divided form.

Very small quantities of the compounds are sufficient to achieve the desired improvement in the cellulose derivative fibrous materials. Thus treatment of the materials with one of the said compounds, in water or an organic solvent, at a solution concentration of 1 part in 1000 to 1 part in 1,000,000 is usually satisfactory. In such aqueous concentration they are taken up readily on fibres having a cellulose ester basis, e. g. cellulose acetate.

Optical bleaching agents or "brightening" agents which function by virtue of their inherent fluorescence are already known for application to fibrous materials. However, the previously known materials, where they have been applicable from aqueous solution, have had a restricted application to such materials as wool and cellulose fibres, and have been virtually useless for application to cellulose ester materials.

It is one of the principal features of the present invention that it provides for the first time optical bleaching agents which can be taken up from aqueous solution on to fibrous materials having a basis of cellulose esters, and yields by such treatment products which are not only satisfactorily brightened but of which the brightening effect is satisfactorily fast both to light and to washing.

The fact that the compounds of the present invention can be taken up from aqueous solution on to cellulose ester fibres is the more surprising when it is appreciated that the commercial dyeing of these fibres in deep colours can only be satisfactorily achieved by the use of finely dispersed azo dyestuffs. For this reason these fibres could, up to now, only be satisfactorily brightened by the use of fine aqueous dispersions of water-insoluble blue-fluorescing brightening agents. In contrast, the compounds of the present invention can be applied by a much simpler process and they yield products which are not only satisfactorily brightened and which have good fastness to washing, but which have, in particular, a degree of light-fastness greater than that hitherto obtained by the use of any of the usual brightening agents.

Because of their special properties, the compounds of the present invention fill a long-standing gap in the field of the optical bleaching of textiles. Their practical value in the field of treating cellulose ester fibres is remarkable and unexpected, and they present the additional practical advantage that they can be applied to mixed fibres, e. g. mixed fabrics of acetate silk with other synthetic or natural textile fibres.

The effectiveness of the compounds of this invention varies to some extent, and of those listed above the compounds found most useful are numbers 14, 15 and 16 which have a sufficiently good solubility in water to make their application from that medium a sound commercial practice.

The compounds of this invention may be applied to cellulose derivative fibrous materials at any stage in the manufacture of such materials. Thus in the production of artificial filaments or fibres by the extrusion of cellulose ester compositions, the oxacyanine compounds of this invention may be incorporated in such compositions before extrusion so that they are uniformly dispersed throughout the products.

Alternatively the cellulose derivative fibrous materials may be treated with solutions of the compounds at any stage in the manufacture of the fibrous materials. Thus in the treatment of cellulose derivative textile materials the compounds may be included in any of the liquids commonly employed for dyeing, dressing and the like.

The following examples serve to illustrate the invention but are not to be regarded as limiting it in any way:

Example 1

20 gm. of acetate silk skein are introduced at 50° C. into a dyebath containing 0.01 gm. 3:3′:5:5′:6:6′-hexamethyloxacyanine p-toluene sulphonate in 1000 cc. water. The temperature is raised during 15 minutes to 80° C. and kept at this temperature for a further 15 minutes. The skein is then rinsed with cold water and dried. The yarn so obtained exhibits in daylight a very good brightening effect which is characterised by good light fastness and fastness to washing.

Example 2

30 gm. of a satin cloth prepared from acetate silk as warp and viscose crepe as weft are introduced at 40° C. into a dyebath which contains 0.01 gm. of 3:3′:5:6-tetramethyloxacyanate p-toluene sulphonate and 1 gm. Glauber salts dissolved in 1000 cc. water. The dyebath is warmed during 15 minutes to 70° C. and then maintained at this temperature for a further 15 minutes. The cloth is then rinsed with cold water and dried. The treated material viewed in daylight appears uniformly brightened.

Example 3

20 gm. of acetate silk skein are introduced at 50° C. into a dyebath containing 0.01 gm. 3:3′:5:5′-tetramethyloxacyanine p-toluene sulphonate in 1000 cc. of water. The temperature is raised during 15 minutes to 80° C. and kept at this temperature for a further 15 minutes. The skein is then rinsed with cold water and dried. The yarn so obtained exhibits a very good brightened effect in daylight which is characterised by good light fastness and fastness to washing.

Example 4

30 gm. of a satin cloth prepared from acetate silk as warp and viscose crepe as weft are introduced at 40° C. into a dyebath which contains 0.0025 gm. of 3:3′-dimethyl-5:5′-dimethoxy-oxacyanine p-toluene sulphonate and 1 gm. of Glauber salts dissolved in 1000 cc. of water. The dyebath is warmed during 15 minutes to 70° C. and then maintained at this temperature for a further 15 minutes. The cloth is then rinsed with cold water and dried. The treated material viewed in daylight appears uniformly brightened.

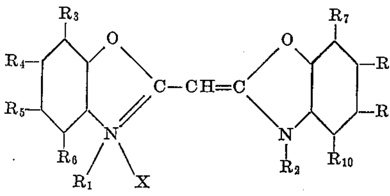
Example 5

20 gm. of acetate silk skein are introduced at 50° C. into a dyebath containing 0.005 gm. 3:3′-dimethyl-5-methoxy-5′-methyloxacyanine p-toluene sulphonate in 1000 cc. of water. The temperature is raised during 15 minutes to 80° C. and kept at this temperature for a further 15 minutes. The skein is then rinsed with cold water and dried. The yarn so obtained exhibits a very good brightened effect in daylight which is characterised by good light fastness and fastness to washing.

Though these examples refer to only five specific compounds, it is to be understood that any others of the compounds listed above may be substituted therefor with results which differ only in degree.

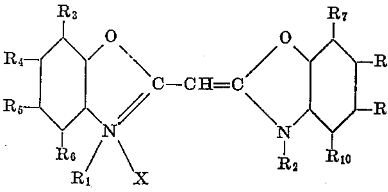
What we claim is:

1. Fibrous materials comprising fibres of organic derivatives of cellulose having adsorbed thereto a compound of the general formula:



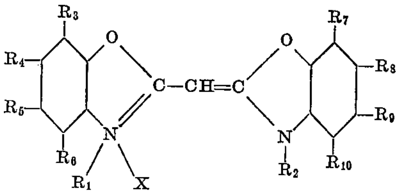
where R_1 and R_2 are selected from the class consisting of alkyl and oxyalkyl groups and R_3 to R_{10} inclusive are selected from the class consisting of hydrogen atoms, halogen atoms and alkyl, alkoxy, amino and substituted amino groups, and X is an acid radicle, which compound is colourless in ethyl alcoholic solution.

2. Fibrous materials comprising fibres of organic derivatives of cellulose having adsorbed thereto a compound of the general formula:



where R_1 and R_2 are selected from the class consisting of alkyl and oxyalkyl groups and R_3 to R_{10} inclusive are selected from the class consisting of hydrogen atoms, halogen atoms and alkyl, alkoxy, amino and substituted amino groups, and X is an acid radicle, which compound in ethyl alcoholic solution has an absorption maximum below 3900 Å.

3. Cellulose acetate fabrics having adsorbed thereto a very small quantity of a compound of the general formula:



where R_1 and R_2 are selected from the class consisting of alkyl and oxyalkyl groups and R_3 to R_{10} inclusive are selected from the class consisting of hydrogen atoms, halogen atoms and alkyl, alkoxy, amino and substituted amino groups, and X is an acid radicle, which compound is colourless in ethyl alcoholic solution.

4. Fibrous materials comprising cellulose ester fibres having adsorbed thereto an oxacyanine salt of which the benzene nuclei contain as sole substituents at most 2 lower alkyl groups.

5. Fibrous materials comprising cellulose ester fibres having adsorbed thereto an oxacyanine salt of which the benzene nuclei contain as sole substituents at most 2 methyl groups.

6. Fibrous materials comprising cellulose ester fibres having adsorbed thereto an oxacyanine salt of which the benzene nuclei contain as sole substituents at most one lower alkyl group and at most one lower alkoxy group.

7. Fibrous materials comprising cellulose ester fibres having adsorbed thereto an oxacyanine salt of which the benzene nuclei contain as sole substituents at most one methyl group and at most one methoxy group.

8. Fibrous materials of organic derivatives of cellulose having adsorbed thereto 3.3′.5.5′-tetramethyl oxacyanine p-toluene sulphonate.

9. Fibrous materials of organic derivatives of cellulose having adsorbed thereto 3.3′-dimethyl-5.5′-dimethoxy-oxacyanine p-toluene sulphonate.

10. Fibrous materials of organic derivatives of cellulose having adsorbed thereto 3.3′-dimethyl-5-methoxy-5′-methyl oxacyanine p-toluene sulphonate.

11. Cellulose acetate fibrous materials having adsorbed thereto 3.3′.5.5′-tetramethyl oxacyanine p-toluene sulphonate.

12. Cellulose acetate fibrous materials having adsorbed thereto 3.3′-dimethyl-5.5′-dimethoxy-oxacyanine p-toluene sulphonate.

13. Cellulose acetate fibrous materials having adsorbed thereto 3.3′-dimethyl-5-methoxy-5′-methyl oxacyanine p-toluene sulphonate.

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