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OPTICAL BLEACH

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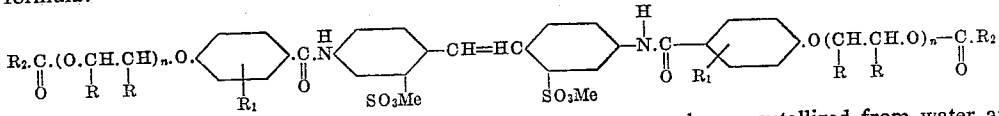
This invention relates to optical bleaches, i. e. compounds that exhibit a blue fluorescence when exposed to ultra-violet light and are adapted to be applied to textile fabrics to whiten them. More particularly the invention relates to a novel stilbene derivative which is effective as an optical bleach and to textile fabrics having this stilbene derivative applied thereto.

It has been known for many years that certain stilbene derivatives exhibit a strong blue fluorescence upon exposure to ultra-violet light and that they also show a strong affinity for cellulosic materials. These properties may be utilized to compensate for the yellowish tinge or cast frequently exhibited by cellulosic materials such as cellulosic textiles. Thus if the stilbene derivatives are applied to such a textile material it compensates for the yellowish tinge of the material to produce a whitening effect. While numerous compounds have been described which accomplish this general purpose these compounds have had one serious disadvantage. It is the usual practice to apply such optical bleaches as a part of the operation of laundering textile materials and hence additional quantities of the optical bleaching agent are applied each time the textile material is laundered. As a result of such repeated applications, the optical bleaching agents tend to accumulate on the textiles and may be the cause of a dull gray discoloration.

I have now found that it is possible to prepare stilbene derivatives which share the useful properties of the prior stilbene derivatives in that they show a strong blue fluorescence and have good affinity for cellulosic materials at about 50° C., but which differ from the prior derivatives in that they can be partially stripped from the textile material at higher temperatures, i. e. temperatures of the order of 100° C. In the laundering of textile materials it is customary to boil the textiles in a soda-containing aqueous bath and the nature of the present group of compounds is such that under these conditions a chemical reaction occurs which increases the solubility of the optical bleaching agent and at least partially removes it from the textile material. Hence a continuing accumulation of the optical bleaching agent on the textile with its concomitant gray discoloration of the textile material is avoided. The compounds of the present invention may be represented by the general formula:



wherein R is selected from the group consisting of hydrogen and alkyl radicals; R_1 is selected from the group consisting of alkyl, oxalkyl and alkoxy radicals; R_2 is selected from the group consisting of alkyl, aryl, hydroaromatic and heterocyclic radicals; Me is selected from the group consisting of hydrogen, monovalent metals and the ammonium radicals; and n is a small positive integer. The alkyl radicals in the above formula may be,

for example, methyl, ethyl, propyl, chlormethyl or higher alkyl radicals; the aryl radicals may be, for example, phenyl, methoxyphenyl, ethoxyphenyl, methylphenyl or other substituted phenyl radicals; the hydroaromatic radical may be for example, the cyclohexyl radical; and the heterocyclic radical may be, for example, the pyridyl radical. In general these new compounds may be conveniently prepared by treating a p-hydroxybenzoic acid ester with one or several mols of ethylene oxide or other agent for introducing oxalkoxy groups into the compound such as propylene oxide, dialkylethylene oxides or ethylene chlorhydrin. Thereafter, the carboxy ester is saponified to obtain the corresponding free oxalkoxybenzoic acid. The free hydroxyl group of oxalkoxy side chain is then esterified with the anhydride or acid halide of an aliphatic, aromatic, aromatic-aliphatic or heterocyclic carbonic acid. The acids used in this step of the process may have further substituents such as alkoxy or ester groups. The p-acyloxethoxybenzoic acid thus formed is then converted into the corresponding benzoic acid halide using for example thionylchloride or the halides of phosphorus, and condensed with a water soluble salt of 4,4'-diaminostilbene-2,2'-disulfonic acid to form a compound of the type defined in the general formula given above.

It has been found that when compounds of this type are heated in an aqueous solution of sodium carbonate or the like, the terminal ester groups are saponified and the free hydroxyl groups of the alkoxy side chains increase the solubility of the compound. Thus if a textile fabric having compounds of this type applied thereto is boiled with a hot aqueous alkali solution, a considerable part or all of the compound is removed therefrom and accumulation of the optical bleach on the fabric is avoided. After the fabric has been removed from the alkaline solution and rinsed, a further controlled quantity of the bleach can be applied thereto in the manner described below.

In order to point out more fully the nature of the present invention, there are given below several illustrative examples of methods of making and applying specific compounds falling within the formula given above. It is of course to be understood that these examples are illustrative only and that numerous changes may be made in the reagents used as well as in the proportions and operating conditions without departing from the spirit of the invention.

Example I

152 parts of para-hydroxybenzoic acid methylester are heated to 130–140° C. Then 0.5 part of sodium is added and dissolved in the molten ester. 48 parts by weight of ethylene oxide are then introduced at the given temperature. The reaction product, which has a Vaseline-like consistency is then cooled to about 80–90° C. and subsequently saponified by heating under reflux with an aqueous alkali solution. The resulting solution is filtered and the para-oxethoxybenzoic acid precipitated by adding dilute hydrochloric acid. The resulting white precipitate may be recrystallized from water and the recrystallized product has a melting point of 175–177° C.

40 parts of the p-oxethoxybenzoic acid are dissolved in 120 parts of acetic anhydride and a few drops of concentrated sulfuric acid are added. After slightly warming on a water bath the reaction starts and the mixture becomes clear. Heating is continued under reflux for about 30 minutes. On cooling, most of the reaction product

will crystallize. The crystals are filtered off and the filtrate, which contains unreacted acetic anhydride, is diluted with cold water, yielding a second crop of crystals. The reaction product, p-acetoxethoxybenzoic acid, is then dried and the dried product has a melting point of 169–170° C.

18 parts of the p-acetoxethoxybenzoic acid as thus prepared are mixed with 50 parts by volume of pure thionylchloride and the mixture refluxed for about one hour, yielding a clear solution. The excess of thionylchloride is then removed by distillation. The residue, an almost colorless, viscous liquid, crystallizes upon cooling and has a melting point of 63–64° C. and a boiling point at 0.3 mm. of 136–138° C.

12 parts of the sodium salt of 4,4'-diaminostilbene-2,2'-disulfonic acid are dissolved in 70 parts of water. To this solution are added 6 parts of soda dissolved in 15 parts of water and 65 parts of acetone. The reaction mixture is then cooled to about 15–20° C. While the reaction mixture is being continuously stirred and cooled, a solution of 18 parts of p-acetoxethoxybenzoyl chloride in 18 parts of acetone is run in at a rate which permits the temperature of the reaction mixture to be held at 15–20° C. After addition of the acid chloride-acetone solution, stirring is continued for 30 minutes and the reaction mixture diluted with 50 parts of water and stirred for another 30 minutes. The reaction must always be maintained on the alkaline side by adding, if necessary, further small amounts of soda solution.

The resulting product, the sodium salt of 4,4'-bis-(p-acetoxethoxybenzoylamino) - stilbene - 2,2' - disulfonic acid is filtered off, washed with a small amount of cold water and dried. It is a light yellow powder, which is soluble in water and shows a good affinity for cellulosic material.

Example II

The procedure of Example I is followed except that benzoylchloride is substituted for the acetic anhydride to produce the p-benzoyloxethoxybenzoyl derivative of the diamino stilbenedisulfonic acid. Like the compound of Example I this product is soluble in water and shows a good affinity for cellulosic materials. The stilbene derivative is conveniently applied to the textile material from an aqueous solution and either a batch or continuous process can be used for its application. The concentration of the treating solution and other conditions are preferably so adjusted as to deposit on the goods from 0.02 to 0.08% of the stilbene derivative based on the dry weight of the goods. Illustrative methods of applying the stilbene derivative are given below.

Example III

An aqueous bath is prepared by dissolving 1 gram of the stilbene derivative of Example I and 150 grams of Glauber's salt in 30 liters of water. It is evident that the concentration of stilbene in this bath is only about 0.003% by weight. The bath is heated to 50° C. and

1 kilogram of cotton textile goods is immersed in the bath and treated therein at 50° C. for 20–30 minutes after which the goods are removed, rinsed in water and dried. The goods show a strong whitening effect. When this textile material is subsequently boiled in a bath containing soda or an equivalent washing agent, saponification of the ester groups in the side chain of the stilbene derivative occurs, thus increasing the solubility of the compound and partially removing it from the textile goods.

It has been found that when cotton goods are treated as described in this example substantially all of the stilbene derivative is absorbed on the goods so that the goods have approximately 0.08% by weight of the stilbene derivative thereon and the remaining treating bath is substantially depleted with respect to the stilbene derivative. Hence further quantities of the stilbene derivative must be added to the bath if additional quantities of the textile material are to be treated to produce a satisfactory whitening effect.

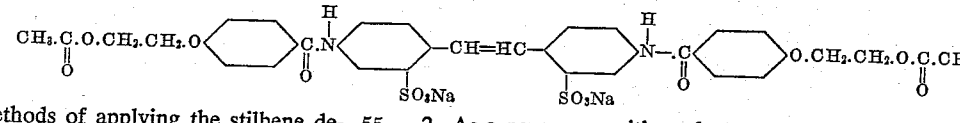
Example IV

An aqueous bath is prepared comprising a solution of the stilbene derivative containing 0.1 gram of the stilbene derivative per liter of water and the bath is heated to maintain it at 50° C. A continuous web of cotton fabric is passed through the bath at a rate that is sufficiently slow to permit the desired quantity of stilbene to be absorbed thereon and the fabric is then rinsed and dried in accordance with the usual procedures for the continuous handling of textile fabrics. Further quantities of the stilbene derivatives are added to the bath either continuously or intermittently to maintain the stilbene concentration at about 0.01% by weight. By this procedure the stilbene derivative can be continuously applied to the fabric to produce the desired whitening effect thereon.

From the foregoing description it is evident that the present invention provides a novel group of optical bleaching or brightening agents for textile materials characterized by the fact that they can be removed from the textile materials by hot alkaline solutions. Hence these compounds are removed from the fabric during conventional laundering operations, after which a further controlled quantity of the brightening agent can be applied. Thus a continuing accumulation of the brightening agent on the textile material to produce a gray discoloration is avoided.

I claim:

1. As a new composition of matter, a compound having the formula:



2. As a new composition of matter an alkali metal salt of a 4,4'-bis-(p-acyloxethoxybenzoylamino)-stilbene-2,2'-disulfonic acid.

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