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FLUORESCENT AGENTS

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4 Claims. (Cl. 260—507)

This invention relates to novel hydroxy alkyl derivatives of 4,4'-diaminostilbene sulfonic and carboxylic acids and acylated derivatives thereof which contain a free amino group.

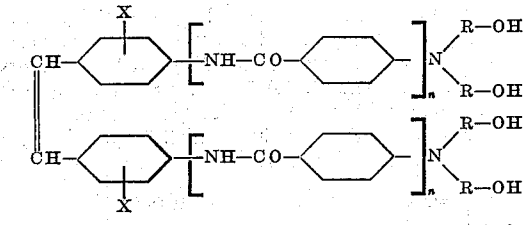
It is well known that cellulosic materials such as paper, cotton textiles and the like have a rather slight yellowish hue which, particularly in the case of textile materials, is apt to become more pronounced when the material is subjected to repeated launderings and use. Accordingly, it has long been the practice to treat many white cotton textiles, when they are washed, with a bluing substance, such as ultramarine. It has been found that the slight blue coloration thus imparted to the material compensates for the yellowish tint or similar off-white shade of the material so that it appears whiter; such bluing operations, however, result in the absorption of a measurable portion of the total visible light falling upon the treated material and, accordingly, the treated material has a slightly dull appearance. It has recently been proposed to treat paper or cotton textiles and similar cellulosic materials with agents which, while themselves colorless, fluoresce in the blue range of the spectrum so that in daylight or other light, which includes ultra violet radiation, the fluorescence of the treating agent compensates for the slight yellowish tint or similar off-white shade, the blue being complementary to yellow. Such fluorescent agents only absorb a negligible portion of the visible light falling on the material and, accordingly, as a result of the fluorescence the treated material is much brighter as well as whiter in appearance.

While a wide variety of fluorescent agents have been suggested for treatment of fibrous materials, it has been found that for the treatment of cellulosic materials, either paper or textiles, the use of fluorescent agents which are substantive to cellulose is preferable since by the use of substantive fluorescent agents a whitening or brightening effect which is resistant to laundering is obtained. Such substantive fluorescent agents have been applied to the material to be treated therewith either in a separate treating operation, or advantageously a small amount of the fluorescent agent may be incorporated in the soap or other detergent used for washing the textiles, and when the textile is washed with a detergent containing a fluorescent brightening agent, a small amount is picked up by the material so that after drying the material appears much whiter and brighter than untreated materials. These fluorescent brightening agents are also useful in treating textile materials which are to be, or have been dyed or printed with discharge paste. The whites of the materials so printed with pastes containing brightening agents are much whiter than is otherwise the case. While numerous fluorescent leaching or brightening agents have heretofore been suggested, including diaminostilbene sulfonic and carboxylic acids and certain acylated derivatives thereof, only a few of them have been satisfactory, particularly for use by incorporation in soap or other detergents. In order to be satisfactory for use as a brightening agent to be incorporated with soap or similar detergents, the fluorescent material which is employed should be itself colorless, or nearly so, and may not stain the material. It is necessary that it have a true bluish fluorescence with no tendency toward imparting visible yellow tints to the treated fabric. It must

also have a proper degree of substantivity towards the materials as too small a degree of substantivity renders it valueless as it would be removed in any rinse waters, and too high a degree of substantivity results in a gradual build-up of fluorescent agent on material during repeated launderings resulting in off-color shades. The fluorescent agent must be stable to light and not discolor on exposure. It must also be stable to hypo-chlorite treatment and not discolor under such treatment, and, in addition, it must fluoresce over a fairly wide pH differential, including both alkali and acid.

I have discovered that the hydroxy alkyl derivatives of diaminostilbene sulfonic and carboxylic acids and their acylated derivatives, which may be obtained by treating diaminostilbene sulfonic or carboxylic acids or their acylated derivatives which still contain a free amino group, with an alkylene oxide, usually ethylene oxide, although propylene or butylene oxide may be employed if desired, are decidedly superior in all the properties mentioned above to known fluorescing agents of this type which have not been so treated.

The novel hydroxy alkyl derivatives of diaminostilbene sulfonic acid and its acylated derivatives which still contain a free amino group may be represented by the following general formula:

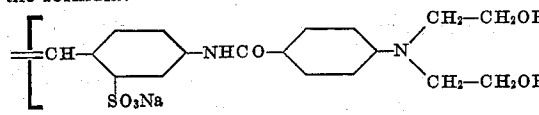


wherein *n* stands for an integer of from 0 to 4, inclusive, X represents a sulfonic or carboxylic acid group and the R in each case represents an alkylene group having 2 to 4 carbon atoms. As examples of diaminostilbene sulfonic and carboxylic acids which may be employed in producing the novel compounds of this invention may be mentioned 4,4'-diamino-2,2'-stilbenedisulfonic acid, 4,4'-diamino-3,3'-stilbenedisulfonic acid, 4,4'-diamino-2,2',6,6'-stilbenetetrasulfonic acid, 4,4'-diamino-2,2'-stilbenedicarboxylic acid or 4,4'-diamino-3,3'-stilbenedicarboxylic acid. All of these acids yield products having substantially similar properties. The 4,4'-diamino-2,2'-stilbenedisulfonic acid is generally used and therefore the present invention will be described with particular reference to its use.

The details of the present invention may be most readily described by first considering several typical examples of novel compounds of this invention and their process of preparation. In these examples the parts are by weight.

Example I

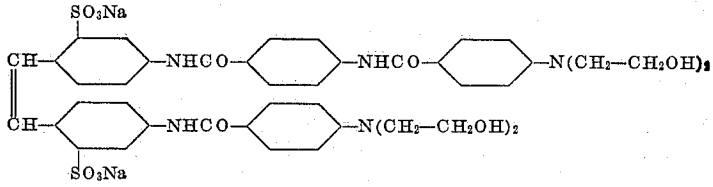
One hundred and forty-eight parts by weight of sodium 4,4'-bis(p-aminobenzamido)-2,2'-stilbenedisulfonate and 600 parts by weight of water were heated in an autoclave with 45 parts by weight of ethylene oxide until 60° C. was reached. The reaction mass was held at 60–70° C. for four hours and then gradually cooled to 25° C. during a twelve hour period. The precipitated product was filtered from the liquor and dried. Yield: 120 parts by weight of product which is principally a compound of the formula:



The pure compound may be obtained by a recrystallization from water.

Example II

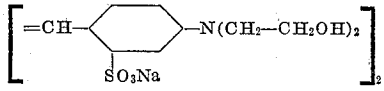
Forty parts by weight of sodium 4-[p-(p-aminobenzamido)benzamido] - 4'-(p-aminobenzamido)-2,2'-stilbenedisulfonate, 300 parts by weight of water, 2 parts by weight of 20° Bé. hydrochloric acid and 45 parts by weight of ethylene oxide were heated in an autoclave for 5 hours at 75–80° C. after which the mass was allowed to cool to 25° C. by stirring 8–10 hours. Five hundred parts by weight of water and 100 parts by weight of salt were added and the mass stirred at 20–25° C. for 10–15 hours until crystallization was completed. The product was filtered from the mother liquor and dried at 100° C. in vacuum. Yield: 65 parts by weight of product which is principally a compound having the formula:



The pure compound may be obtained by a recrystallization from water.

Example III

One hundred and eighty-five parts by weight of 4,4'-diamino-2,2'-stilbenedisulfonic acid was slurried with 600 parts by weight of water. The pH was adjusted to approximately 6.5 by the addition of caustic soda solution and the mixture treated in an autoclave with 105 parts by weight of ethylene oxide. The temperature was raised to 75° C. and maintained at 75–80° C. for four hours. The mixture was cooled to 20–25° C. while stirring overnight and then filtered. The dried paste amounted to 197 parts by weight of product which is principally a compound having the formula:



The pure compound may be obtained by a recrystallization from water.

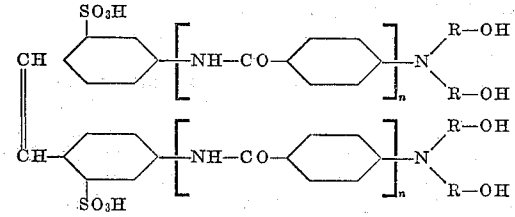
The foregoing examples are illustrative of preferred fluorescent agents embodied in the present invention and their method of manufacture. It will be understood, however, that these materials may be modified as previously indicated. Thus, in place of the 4,4'-diamino-2,2'-stilbenedisulfonic acid which was employed in these examples, other diaminostilbene sulfonic or carboxylic acids of the type previously indicated may be used. It will also be understood that in place of ethylene oxide which was employed in the specific examples, other alkylene oxides, i. e., propylene oxide or one of the isomeric butylene oxides may be employed if desired.

It will be apparent that in the foregoing examples the novel products of the present invention were obtained in the form of their sodium salts. However, the potassium salts have substantially similar properties and it will be apparent that they can be obtained by using the potassium salt of the acylated (or unacylated) diaminostilbenedisulfonate in the syntheses described in the foregoing examples and substituting potassium chloride for sodium chloride in the salting out operation where required. The free acids may be obtained by acidification of the sodium or potassium salts while other salts such as ammonium, hydroxyalkylamine salts and the like may be obtained by the neutralization of the free acids. Where spirit soluble products are desired, i. e., in brightening of lacquers, etc., the higher alkyl or cycloalkylamine salts of the free acids such as the cyclohexylamine salts may be produced by methods known in the art. The alkaline earth metal salts such as the barium and calcium salts, which may be obtained from the free acid or by double decomposition of the sodium or potassium salts, are of interest for the brightening of photographic prints.

The thus-obtained fluorescent agents are valuable additives to soap and other detergents as brightening agents for cellulosic materials to be washed therewith. They may also be applied to cellulosic materials, either textiles or paper, by means of a separate treating process in order to substantially brighten the treated material.

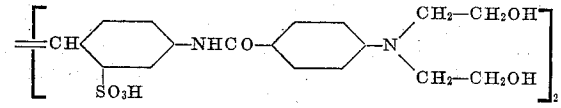
I claim:

1. Fluorescent agents selected from the group consisting of compounds of the formula

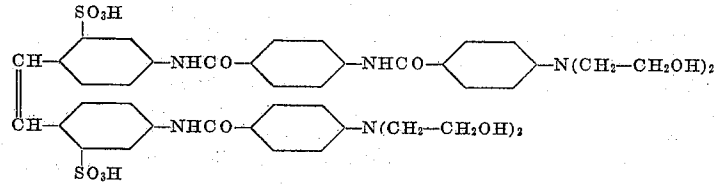


wherein *n* represents an integer of from 0 to 4, inclusive, the R in each case represents an alkylene grouping having 2 to 4 carbon atoms and salts of such compounds.

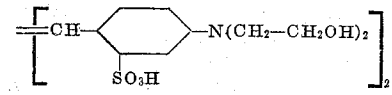
2. Fluorescent agents which in the form of their free acids have the formula



3. Fluorescent agents which in the form of their free acids have the formula



4. Fluorescent agents which in the form of their free acids have the formula



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