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DIAMINOFLUORENE DERIVATIVES

Dale R. Eberhart, Middlesex, and Nena K. Barabutes, New Brunswick, N. J., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

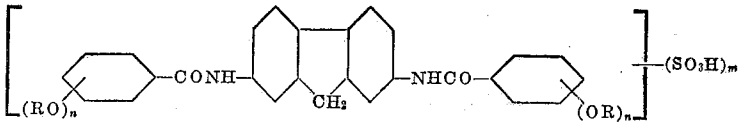
No Drawing. Application July 11, 1952, Serial No. 298,460

8 Claims. (Cl. 260—507)

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This invention is concerned with optical bleaching and brightening, and especially, with new derivatives of fluorene distinguished by their remarkable utility for this purpose. More specifically, the invention relates to water-soluble derivatives of acylated 2,7-diaminofluorene having a reddish-blue fluorescence, and their use.

In particular, the invention utilizes a novel group of compounds which may be represented by the formula:



in which R is a lower alkyl radical and *m* and *n* are positive integers smaller than three. These compounds are sulfonic acids which may be conveniently isolated and used in the form of their ammonium or metallic salts; these salts are therefore also included in the present invention as obvious chemical equivalents of the free acids.

It has been discovered that these compounds possess the properties of affinity, strength, stability, substantivity, and fluorescent hue, which are necessary for successful application as fluorescent brightening agents, to restore a pure white shade to cellulose materials which have developed the typical yellowish cast with age. These compounds effectively neutralize this yellowness, even when applied from very minute concentrations. On the other hand, they can be applied from relatively concentrated solution when it is desired to produce greatly enhanced whiteness and brilliance of discharge effects. The application of these agents may be carried out in a separate rinse bath; or they may be used in conjunction with the soaping operation; or the agents may be incorporated in the soap and marketed in that form to enhance the cleansing and whitening action of the soap; or they may be used in any manner known to the trade. The present compounds have a surprising solubility in water which is a distinct advantage over many competitive brighteners. Indeed, solubility of these fluorescent derivatives is such that they may be added to liquid soaps and bleaches without causing haze or sedimenation.

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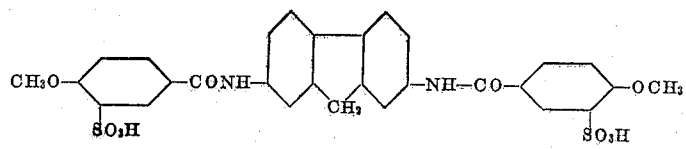
These compounds also possess valuable properties other than as bleaching or whitening agents. For example, they enhance the color effect of many different dyes and pigments. They may be used in a preliminary treatment of the fabric, applied with other dyes, or applied as an after treatment.

Utilization of the compounds of this invention is not limited to treatment of textile fabrics. They may also be beneficially used in the manufacture of paper and felt products and in making transparent or translucent sheets or pellicles of cellulose of other origin. Their usefulness extends also the mutually compatible varnishes, plastic coatings and white or colored plastic shapes.

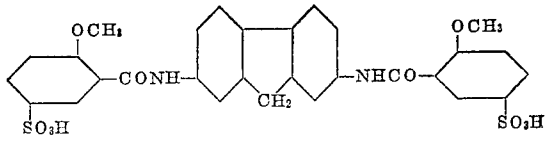
The compounds of the present invention are prepared by a variety of methods. The sulfonic acid groups may be present either in the fluorene or in the acyl nuclei, and may be introduced either before or after the step of acylating the 2,7-diaminofluorene derivative.

For example, 2,7-diaminofluorene may be sulfonated, and the resulting sulfonic acids acylated with such alkoxy substituted benzoic acids as anisic acid, p-propoxybenzoic acid, 2,4-dimethoxybenzoic acid, 2,4-diethoxybenzoic acid, p-butoxybenzoic acid, 2,5-dimethoxybenzoic acid, and the like. Or, if desired, 2,7-diaminofluorene itself may first be acylated and the product then sulfonated. In this case, the sulfonic acid groups will generally be found in the acyl radical.

Compounds of the latter type can be prepared by another variation of the present invention, in which 2,7-diaminofluorene is acylated by an alkoxybenzoic acid already substituted by a sulfonic acid group. Suitable acids of this type include 3-sulfo-4-methoxybenzoic acid (Beil. 11, 414) and 5-sulfo-2-methoxybenzoic acid (Beil. Supplement II, vol. 11, p. 233) which react with 2,7-diaminofluorene to form compounds of the formula:



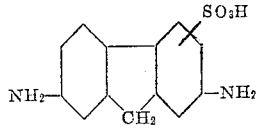
and



respectively. The products are readily isolated by methods known to the art.

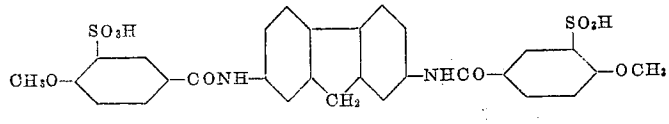
The present invention is further illustrated in the following examples. Parts are by weight unless otherwise specified.

Example 1



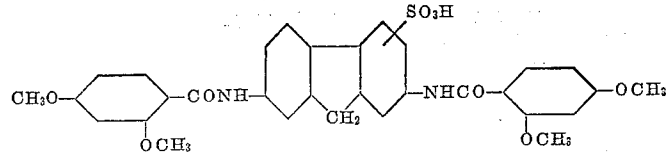
2,7-diaminofluorene is converted to the sulfate by dissolving in alcohol and adding concentrated sulfuric acid. The resulting precipitate is filtered and dried. Twelve parts of the sulfate thus prepared is added to 138 parts of 7% oleum and warmed to 45–50° C. for 10 minutes. The mixture is then drowned in ice and filtered. The product is washed with alcohol and dried.

Example 2



To a mixture of 98 parts of pyridine and 7.9 parts of thionyl chloride is added at room temperature, 16.6 parts of 3-sulfo-4-methoxybenzoic acid and 5.39 parts of 2,7-diaminofluorene dihydrochloride. After a brief period of refluxing, 3.3 parts of thionyl chloride and 2.5 parts of 3-sulfo-4-methoxybenzoic acid is added. The reaction is completed under reflux. The mixture is drowned in sodium carbonate solution, freed of solvent by steam distillation, cooled to room temperature, and filtered. The product is washed with salt solution and dried at 100° C. If desired, it may be recrystallized from dilute alcohol. 3.7 g. of this compound will completely dissolve in 100 cc. of water at 100° C.

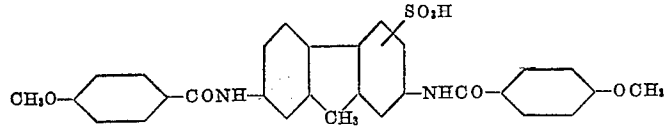
Example 3



A mixture of 19.5 parts of thionyl chloride, 9 parts of benzene, and 10.2 parts of 2,4-dimethoxybenzoic acid is warmed at 50° C. until reaction is complete, excess thionyl chloride then being removed by distillation. The resulting solution is gradually added at room temperature to a slurry of 5 parts of the above prepared 2,7-diaminofluorenesulfonic acid in 98 parts of pyridine. Reaction is completed under reflux, as

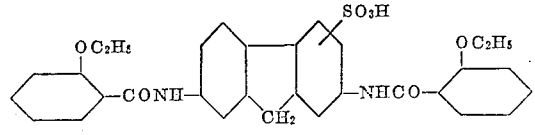
indicated by the disappearance of a test for free amino groups. The mixture is then drowned in dilute sodium carbonate solution, freed of solvent by steam distillation, cooled to room temperature, and filtered. The product may be recrystallized, if desired, from dilute ethanol. A quantitative yield of the product is obtained by washing the filtrate with salt solution and drying at 100° C.

Example 4



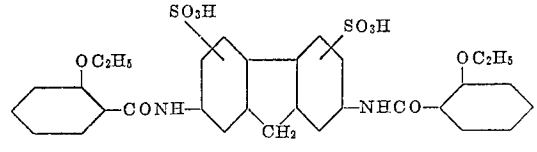
A slurry of 3.6 parts of 2,7-diaminofluorenesulfonic acid and 5.1 parts of anisoyl chloride in 98 parts of pyridine is refluxed until the reaction is complete. The mixture is then drowned in dilute sodium carbonate solution, freed of solvent by steam distillation, salted with sodium chloride, cooled, and filtered. The product is washed with dilute salt solution, and dried at 100° C.

Example 5



A mixture of 3.6 parts of 2,7-diaminofluorenesulfonic acid and 5.55 parts of o-ethoxybenzoyl chloride in 98 parts of dry pyridine are refluxed until reaction is complete. The product may be isolated as described in the preceding example.

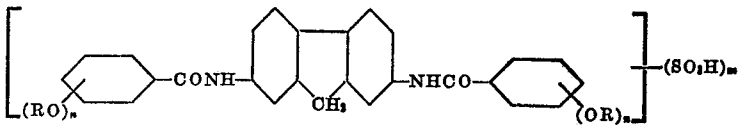
Example 6



A product of better water-solubility is prepared by a procedure similar to that of Example 5, from 4.6 parts of 2,7-diaminofluorene disulfonic acid and 5.55 parts of o-ethoxybenzoyl chloride in 98 parts of dry pyridine. 2,7-diaminofluorene disulfonic acid may be prepared by the method of Example 1 by heating the oleum reaction mixture to a higher temperature for a longer time.

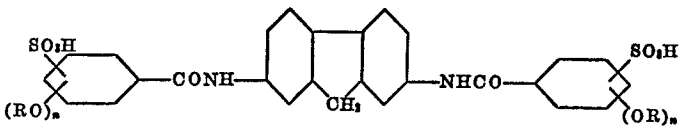
We claim:

1. A compound selected from the group consisting of those having the formula:



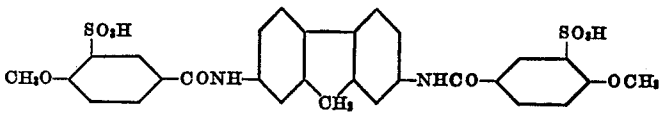
in which R is a lower alkyl radical and m and n are positive integers smaller than three; and their salts.

2. A compound of the formula:

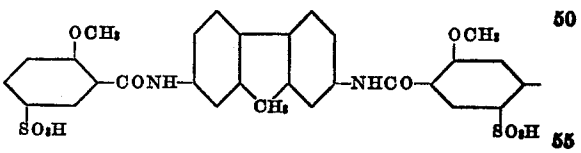


in which R is a lower alkyl radical and n is a positive integer smaller than three.

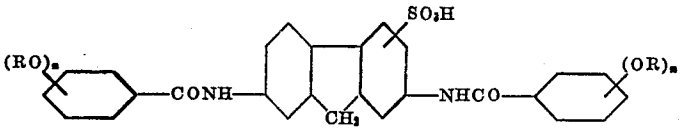
3. A compound of the formula:



4. A compound of the formula:

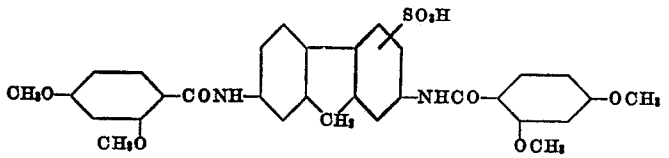


5. A compound of the formula:

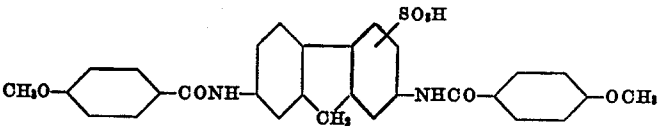


in which R is a lower alkyl radical and n is a positive integer smaller than three.

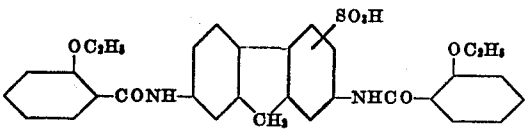
6. A compound of the formula:



7. A compound of the formula:



8. A compound of the formula:



DALE R. EBERHART.
NENA K. BARABUTES.

No references cited.