United States Patent Office

2,704,286

Patented Mar. 15, 1955

2,704,286

FLUORESCENT WHITENING AGENTS

Arthur A. Baum, New Castle County, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application May 7, 1954, Serial No. 428,374

8 Claims. (Cl. 260—304)

This invention relates to the production of novel organic compounds which are useful as whitening agents for fibrous material such as textiles or paper. It is an object of this invention to produce compounds of the above general nature which are characterized by a bluish-green fluorescence and by good bleach fastness. Additional objects and achievements of this invention will appear as the description proceeds.

The art of whitening or brightening textile fiber and paper is of relatively recent development. It has been found that fibrous materials which normally have a dull, yellowish cast when in the white, unbleached state, become whiter and brighter if treated with agents which fluoresce under ultraviolet light. Presumably the action of the ultraviolet rays present in ordinary daylight is sufficient to exite these agents upon the fiber to emit fluorescence which overcomes the undesirable tinge of color in the unbleached fiber.

Customarily agents which give a blue fluorescence are employed. Many consumers, however, prefer agents which give a greenish-blue fluorescence.

Another very important demand developed by the trade is bleach fastness. Inasmuch as the aforementioned fluorescent agents are generally incorporated into soap and synthetic detergents, which are packaged and marketed for household use, and inasmuch as in household practice laundered articles are often subjected to bleaching with various agents, for instance hypochlorites, it is essential that the fluorescent transferred from the detergent to the fiber shall not be destroyed by the action of bleach.

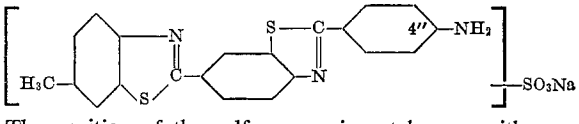
In addition to the above two primary qualifications a practical whitening agent should have good light-fastness, should be capable of being synthesized economically from readily available materials, and should have sufficient fluorescent power (often referred to as "tinctorial strength") to give the desired effect at a minimum cost. It must also have affinity for cellulosic fiber and should have sufficient solubility in water to be applicable from an aqueous bath.

Now according to my invention new chemical compounds are synthesized which have good affinity for cellulosic fibers and produce thereon a desirable greenish blue fluorescence, fast to bleach. My novel compounds may be defined by the general formula



wherein R is the 4''-radical of a compound of the group consisting of primuline and primuline base, while Q represents the 1,2-radical of a naphthalene compound of the group consisting of mono- and di-sulfo naphthalenes, the components which yield R and Q being so chosen that the resulting compound has not less than 2 sulfo groups.

Primuline and primuline base are defined in Rowe's Colour Index (1924) under color No. 812. Primuline is the mono sulfonated condensation product of p-toluidine and sulfur, chiefly



The position of the sulfo group is not known with certainty.

Primuline base is the same compound but without

the sulfo group. When primuline base is selected for R, a naphthalene component having two sulfo groups is chosen for Q.

My novel compounds may be synthesized by diazotizing primuline or primuline base, coupling the diazo compound (in acid medium) to an amino naphthalene mono- or disulfonic acid which has the amino group in position 1 or 2 and a hydrogen atom in the adjacent position of the pair mentioned, and converting the o-aminoazo dye thus obtained into a triazole by oxidation in known manner, for instance by heating the same in an aqueous solution of cupric ammonium sulfate or of alkaline hypochlorite until the color of the intermediate disazo dye has disappeared. The product is then recovered in the desired physical or chemical form, for instance in the form of its sodium, potassium or ammonium salt.

If it is found that the aqueous reaction mass, prior to salting out of the final product, contains residual color, the latter may be destroyed by treating the reaction mass with dilute hypochlorite solution or with a decolorizing charcoal.

As typical coupling components useable in the above process may be mentioned:

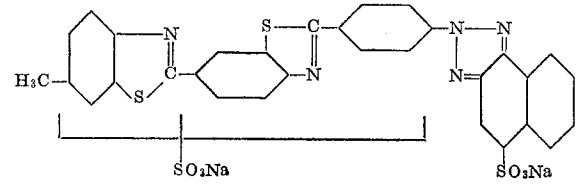
1-aminonaphthalene-4-sulfonic acid (naphthionic acid);
1-aminonaphthalene-5-sulfonic acid (Laurent's acid);
1-aminonaphthalene-4,6-disulfonic acid;
1-aminonaphthalene-4,7-disulfonic acid;
1-aminonaphthalene-4,8-disulfonic acid;
1-aminonaphthalene-5,8-disulfonic acid;
2-aminonaphthalene-4-sulfonic acid;
2-aminonaphthalene-6-sulfonic acid (Broenner's acid);
2-aminonaphthalene-3,6-disulfonic acid (amino-R acid);
2-aminonaphthalene-4,8-disulfonic acid;
2-aminonaphthalene-5,7-disulfonic acid (amino-J-acid); and
2-aminonaphthalene-6,8-disulfonic acid (amino-G-acid).

Without limiting this invention, the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

Example 1

A suspension of 33.3 parts (0.07 mol) of primuline (C. I. 812) in 1000 parts of water was diazotized at 0 to 5° C., by means of sodium nitrite and an excess of hydrochloric acid. A solution of 14.7 parts (0.06 mol) of sodium naphthionate in 430 parts of water was added. The mixture was stirred 16 hours at room temperature and then made alkaline to Brilliant Yellow paper using sodium hydroxide solution. The ortho-aminoazo dye was then salted out and filtered off.

The wet dye cake thus prepared was placed in 1600 parts water followed by additions of 300 parts of 28% ammonia and a solution of 50 parts of $CuSO_4.5H_2O$ in 100 parts of water. After refluxing for 5 hours, 20 parts of an aqueous solution containing 8 parts of sodium hydroxide were added and the mass was boiled for 1 hour and filtered hot. The hot filtrate was agitated for 30 minutes with 40 parts of a 12% solution of sodium hypochlorite, then treated with charcoal and filtered. The resulting filtrate was stirred with 20% of its weight of sodium chloride, cooled, filtered and dried. The dry material was medium brown in hue and dissolved in water with a bluish-green fluorescence. The absorption maximum of this compound in aqueous solution is located at 370 millimicrons. The product is believed to have the formula,



Example 2

The procedure of Example 1 was repeated except that the oxidation of the intermediate ortho-aminoazo dye was effected by heating the same at 80° C., for 6 hours with

an alkaline solution of sodium hypochlorite into which additional sodium hypochlorite was fed at a rate sufficient to maintain a positive test to starch-iodide paper.

After clarification of the solution with charcoal the product was recovered by salting out, filtering and drying.

Example 3

The procedure was the same as in Example 1, except that in lieu of 14.7 parts of sodium naphthionate in 430 parts of water, 22.3 parts of Broenner's acid (0.10 mol) in 900 parts of water were employed. Also after addition of sodium hydroxide at the end of the oxidation step, the mass was boiled for 3.5 hours in lieu of 1 hour. The product was recovered in the same manner as in Example 1. The compound was brown in hue and dissolved in water with a bluish-green fluorescence. Its absorption maximum in aqueous solution is located at 369 millimicrons.

A similar compound is obtained when the orthoaminoazo dye of this example is oxidized to the naphthotriazole with hypochlorite according to the process of Example 2.

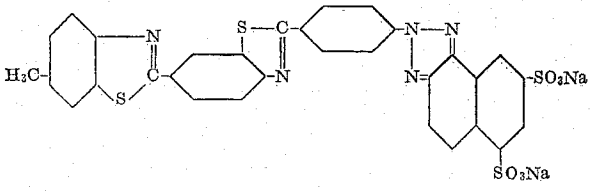
Example 4

The procedure was the same as in Example 1, except that in lieu of 14.7 parts of sodium naphthionate in 430 parts of water, 24.2 parts (0.08 mol) of amino J-acid in 530 parts of water were employed. The oxidation mass was boiled for 5 hours in lieu of 1 hour. The dry product obtained was brown in hue and its bluish-green fluorescent solution in water gave an absorption maximum located at 370 millimicrons.

Example 5

A suspension of 37.3 parts (0.10 mol) of primuline base (C. I. 812) in 700 parts of water was diazotized at 0 to 5° C., by means of sodium nitrite and an excess of hydrochloric acid. A solution of 33.3 parts (0.11 mol) of 2-aminonaphthalene-5,7-disulfonic acid in 600 parts of water was added. The mixture was buffered by addition of soduim acetate to neutrality on Congo red paper and stirred 16 hours at room temperature. The coupling mass was made alkaline to Brilliant Yellow paper, using sodium hydroxide, salted with 130 parts sodium chloride, and the ortho-aminoazo dye was filtered off.

The wet dye cake in 2000 parts of water was oxidized with 50 parts $CuSO_4.5H_2O$ and 300 parts of 28% ammonia by refluxing for 4 hours. Thereafter 24 parts of sodium hydroxide were added, the mass was boiled 1 hour and filtered while hot. The hot filtrate was agitated for a few minutes with 40 parts of a 12% solution of sodium hypochlorite, then salted with 1200 parts of potassium carbonate, filtered and dried. The dry product is yellow in hue and its bluish-green fluorescent solution in water exhibits an absorption maximum located at 364 millimicrons. It is believed to have the formula



Similar compounds may likewise be obtained by employing as coupling component, in any of the above examples, 2-amino-naphthalene 4,8-disulfonic acid, 2-aminonaphthalene-6,8-disulfonic acid, 2-aminonaphthalene-3,6-disulfonic acid; also the 1-aminonaphthalene-4,6-, 4,7-, 4,8- and 5,8-disulfonic acids.

The compounds of the aforegoing examples are suitable for incorporation into soap or synthetic detergents, and endow a fluorescent or whitening effect to cotton fabric laundered with such soap or detergent. Fabrics washed with such detergents were subjected to tests to determine the bleach fastness of the fluorescent effect and found to be highly satisfactory in this respect.

Tests for light-fastness, substantivity and wash-fastness were also carried out, and showed my novel compounds to compare favorably in respect to these qualities with the best fluorescents which are now on the market.

The compounds given in the above examples have been isolated as the sodium salts of the sufonic acids. By using potassium hydroxide and potassium salts in lieu of sodium hydroxide and sodium salts, throughout, the products may be obtained as potassium sulfonates. Isolation as the free sulfonic acids can be effected by acidification of the condensation mass, and the products thus obtained may be reacted with ammonium hydroxide or any suitable organic or inorganic base, to yield the corresponding salt.

In addition to producing a whitening effect upon textile material, my novel compounds may also be used for whitening paper and for various other purposes where fluorescence or absorption of ultraviolet light is desirable, for instance to achieve fluorescent effects in costumes or stage settings, to achieve novel effects on photographic paper, as ultraviolet filters when impregnated on cellulosic films which are used for wrapping materials, etc.

I claim as my invention:

1. A compound of the general formula



wherein R is the 4''-radical of a compound of the group consisting of primuline and primuline base, Q represents a sulfonated naphthalene radical which has no other substituents and which is attached to the above shown N-atoms in its 1,2-positions, the total number of sulfo groups in the compound being not less than 2 and not greater than 3.

2. A compound as in claim 1, wherein R designates the 4''-radical of primuline while Q designates the 1,2-radical of naphthionic acid.

3. A compound as in claim 1, wherein R designates the 4''-radical of primuline while Q designates the 1,2-radical of 2-aminonaphthalene-6-sulfonic acid.

4. A compound as in claim 1, wherein R designates the 4''-radical of primuline while Q designates the 1,2-radical of 2-aminonaphthalene-5,7-disulfonic acid.

5. A compound as in claim 1, wherein R designates the 4''-radical of primuline base while Q designates the 1,2-radical of 2-aminonaphthalene-5,7-disulfonic acid.

6. The process of producing a fluorescence agent for textile fiber, which comprises diazotizing a compound of the group consisting of primuline and primuline base, coupling the diazo compound in an acid medium to a sulfonated naphthylamine wherein the amino group is located in one of the 1,2-positions while the second of said positions is unsubstituted, and oxidizing the resulting ortho-aminoazo compound to the corresponding triazole.

7. A process as in claim 6, the oxidation being effected by heating the ortho-aminoazo compound in an aqueous solution of cupric ammonium sulfate.

8. A process as in claim 6, the oxidation being effected by heating the ortho-aminoazo compound in an aqueous solution of an alkaline hypochlorite.

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