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FLUORESCENT WHITENING AGENTS

Mario Francesco Sartori, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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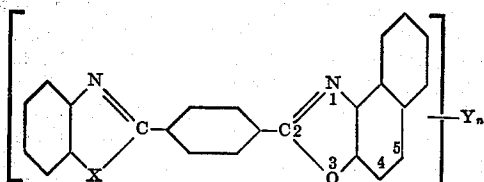
This invention relates to the production of novel organic compounds which are useful as whitening agents for various fibrous materials, including cellulosic fibers and nylon. It is an object of this invention to produce compounds of the above general nature, but which are characterized further by bleach fastness and by correct shade of fluorescence. 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 excite these agents upon the fiber to emit fluorescence which overcomes the undesirable tinge of color in the unbleached fiber. Best results are obtained when the shade of fluorescence is complementary to that of the unbleached fiber, so that the colors will cancel out each other. Since the most common off-white shade of unbleached cellulosic and nylon fibers is yellowish, the most desirable shade in a fluorescent is blue.

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 removed or destroyed by the action of bleach. Unfortunately, most of the fluorescent agents now on the market, and having the desirable blue shade, are weak in respect to this qualification of bleach resistance.

In addition to the above two primary qualifications, an agent for the purposes of this invention 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 should also have affinity for the fibers to which it is applied, and should be capable of being dispersed readily in water in the concentrations that would normally be used in the treatment of nylon or cellulosic fibers.

Now according to my invention new chemical compounds are synthesized which satisfy to an excellent degree all the foregoing qualifications. The novel compounds of this invention may be defined by the general formula

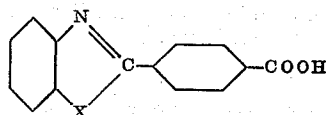


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wherein X stands for O, S or NH; Y represents a sulfo group, and n is zero or one.

According to accepted nomenclature, they may be named collectively as 2-[p-(2-benzazoly)phenyl]-naphth[1,2]oxazoles and their monosulfo derivatives.

These compounds may be synthesized by condensing the corresponding p-2-benzazoly)-benzoic acid of formula



with 1-amino-2-naphthol or a monosulfo-derivative thereof by the aid of an acid halogenating agent, such as phosphorus oxychloride, phosphorus trichloride or thionyl chloride, in a suitable liquid medium and at moderate temperature, say 70 to 125° C., to form an intermediate condensation product, presumably an ortho-hydroxy amide, and then ring-closing the latter into a naphthoxazole compound, by heating at a higher temperature, say in the vicinity of 180 to 220° C. As suitable liquid medium, a high-boiling, inert organic solvent is recommended, for instance trichlorobenzene, diphenyl ether, or alpha- or beta-methyl naphthalene. For the amide formation step, inert organic liquids of somewhat lower boiling point are also suitable, for instance pyridine.

The monosulfonated product may be prepared by sulfonating the product obtained as above from 1-amino-2-naphthol, or by starting initially with a monosulfonated 1-amino-2-naphthol. Sulfonation of the condensed product is readily achieved by treating the same with sulfuric acid monohydrate, at room temperature.

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

EXAMPLE 1

2-[p-(2-benzimidazoly)phenyl]-naphth[1,2]oxazole

A suspension of 2.6 parts of p-(2-benzimidazoly)-benzoic acid (Ann. 205, 118), 2 parts of 1-amino-2-naphthol hydrochloride and 1.8 parts of phosphoryl chloride in 30 parts of trichlorobenzene was heated at 125° C. for 1 hour and then at 200° C. for 5 hours.

After cooling to room temperature, the precipitate was filtered off and washed with petroleum ether. The gray filter cake was slurried at 50° C. with an excess of 5% sodium carbonate aqueous solution, filtered hot, washed and dried. Cream-colored crystals of M. P. 292° C. were obtained. The absorption maximum of this compound in dimethylformamide is located at 364 millimicrons.

Analysis.—Calc. for $C_{24}H_{15}ON_3$: C, 79.5; H, 4.1; N, 11.6. Found: C, 79.6; H, 4.1; N, 12.3.

EXAMPLE 2

2-[p-(2-benzimidazoly)phenyl]-naphth[1,2]oxazole sodium sulfonate

5 parts of the product prepared in Example 1 were dissolved in 50 parts of sulfuric acid monohydrate and stirred at room temperature. When a test portion of the sulfonation mixture dissolved to give a clear solution in dilute sodium carbonate, the reaction mixture was poured into 500 parts of iced water. The precipitate was filtered off and washed. The yellow filter cake was dispersed in water, the dispersion was made alkaline with sodium carbonate to form a solution and the product was finally precipitated by adding sodium chloride.

The pale yellowish precipitate was filtered off, washed

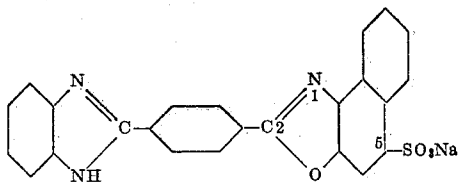
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with 10% sodium chloride solution and dried. The product dissolves in water to give a solution having a strong blue fluorescence. The absorption maximum of the compound in dimethylformamide is located at 365 millimicrons.

EXAMPLE 3

2-[p-(2-benzimidazolyl)phenyl]-naphth[1,2]oxazole-5-sodium sulfonate

A suspension of 2.6 parts of p-(2-benzimidazolyl)benzoic acid, 2.4 parts of 1-amino-2-hydroxy-4-naphthalene-sulfonic acid and 1.7 parts of phosphoryl chloride in 20 parts of pyridine was heated at 70° C. for 1 hour and then at 110° C. for 3 hours. After cooling to room temperature, the mixture was drowned in water, made acid to Congo red with hydrochloric acid and filtered. The filter cake (o-hydroxy-amide) was first washed with cold water, then with ethyl alcohol and dried. The crude product thus obtained was slurried in 30 parts of trichlorobenzene and heated at 200° C. for 8 hours. After cooling to room temperature the precipitated product was filtered off, washed with petroleum ether, dissolved in dimethylformamide, and then reprecipitated by adding an equal weight of an aqueous, 10% salt solution. The product has the formula:



The water solution of this compound exhibits a strong blue fluorescence. The absorption maximum of this compound in dimethylformamide is located at 365 millimicrons.

EXAMPLE 4

2-[p-(2-benzothiazolyl)phenyl]-naphth[1,2]oxazole

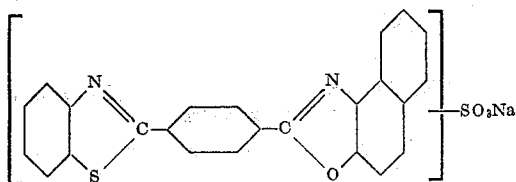
A mixture of 4.5 parts of p-(2-benzothiazolyl)benzoic acid (Chem. News, 124, 393), 3 parts of 1-amino-2-naphthol hydrochloride and 2.8 parts of phosphoryl chloride was condensed following the method described in Example 1 for the preparation of the analogous benzimidazole derivative. Cream colored crystals of M. P. 256° C. were obtained.

Analysis.—Calc. for $C_{24}H_{14}N_2SO$: C, 74.2; H, 3.6; N, 7.4; S, 8.3. Found: C, 75.2; H, 3.4; N, 7; S, 8.

The absorption maximum of this compound in dimethylformamide is located at 368 millimicrons.

EXAMPLE 5

Upon sulfonation of the product of Example 4 by the method described in Example 2, 2-[p-(2-benzothiazolyl)-phenyl]-naphth[1,2]oxazole sodium sulfonate was obtained. It is a pale yellowish powder, soluble in dilute sodium carbonate, and having the formula



The aqueous solution of the sodium salt of this acid fluoresces blue, and its absorption maximum is located at 370 millimicrons.

EXAMPLE 6

2-[p-(2-benzoxazolyl)phenyl]-naphth[1,2]oxazole

A suspension of 2.6 parts of p-(2-benzoxazolyl)benzoic acid (prepared as described below), 2 parts of 1-amino-2-naphthol hydrochloride and 1.7 parts of phosphoryl

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chloride was condensed following the procedure described in Example 1. Pale yellowish crystals of M. P. 320–325° C. were obtained.

Analysis.—Calc. for $C_{24}H_{14}O_2N_2$: C, 79.2; H, 3.85; N, 7.7. Found: C, 79.8; H, 3.9; N, 7.4.

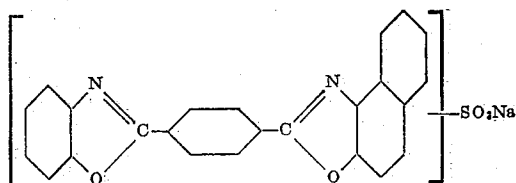
The initial p-(2-benzoxazolyl)benzoic acid was prepared as follows: A suspension of 20 parts of methylhydrogen terephthalate and 11 parts of orthoaminophenol in 110 parts of trichlorobenzene was heated at 80° C. for 3 hours and at 200° C. for 16 hours. After cooling to room temperature the reaction mass was filtered and washed with petroleum ether. The filter cake was slurried in 500 parts of water containing an excess of sodium carbonate, the slurry was boiled for 5 minutes and filtered hot. After clarification with activated carbon the filtrate was made acid with acetic acid. The white precipitate was filtered off, washed at 50° C. with ethanol and dried. A white powder of M. P. above 300° C. was obtained.

EXAMPLE 7

2-[p-(2-benzoxazolyl)phenyl]-naphth[1,2]oxazole sodium sulfonate

3 parts of the product obtained in Example 6 were treated with 50 parts of sulfuric acid monohydrate according to the procedure of Example 2 above. A pale yellow powder was obtained whose aqueous solution fluoresces blue. Its absorption maximum is located at 365 millimicrons.

The product has the formula:



EXAMPLE 8

2-[p-(2-benzoxazolyl)phenyl]-naphth[1,2]oxazole-5-sodium sulfonate

5.3 parts of 2-(p-benzoxazolyl)benzoic acid were condensed with 4.8 parts of 1-amino-2-hydroxy-4-naphthalene-sulfonic acid and 3.4 parts of phosphoryl chloride in pyridine, ring-closed and purified according to the procedure described in Example 3.

A yellowish powder, completely soluble in dilute sodium carbonate solution was obtained. The water solution of the sodium salt of this compound exhibits bluish fluorescence.

The novel products of the foregoing several examples were tested for whitening power and bleach resistance by the same tests as described in my copending application Serial No. 333,016, filed January 23, 1953 (Patent No. 2,715,632, issued August 16, 1955), and found to be satisfactory in both respects. The fluorescence imparted to a sample of cotton fabric by the novel agents was retained in full (essentially 100%) in the bleach-fastness test.

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 fluorescent dyes which are now on the market.

The monosulfonated products are useful for cotton fiber. The unsulfonated ones can be used both on cotton and on nylon.

The compounds given in the above examples have been isolated as the sodium salts of the sulfonic 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 or paper, my novel compounds may also be used 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 group consisting of 2-[p-(2-benzimidazolyl)phenyl]-naphth[1,2]oxazole, 2-[p-(2-benzothiazolyl)phenyl]-naphth[1,2]oxazole, 2-[p-(2-benzoxazolyl)phenyl]-naphth[1,2]oxazole and their 15 monosulfo derivatives.

2. 2-[p-(2-benzimidazolyl)phenyl]-naphth[1,2]oxazole.

3. The 5-sodium-sulfonate of 2-[p-(2-benzimidazolyl)phenyl]-naphth[1,2]oxazole.

4. A sodium monosulfonate of 2-[p-(2-benzothiazolyl)phenyl]-naphth[1,2]oxazole.

5. A sodium monosulfonate of 2-[p-(2-benzoxazolyl)phenyl]-naphth[1,2]oxazole.

5 6. The process of producing a fluorescent agent which comprises condensing a carboxylic acid of the group consisting of p-(2-benzimidazolyl)benzoic acid, p-(2-benzothiazolyl)benzoic acid, and p-(2-benzoxazolyl)benzoic acid, in an inert organic liquid and in the presence of an 10 acid halogenating agent, with an ortho-amino-naphthol of the group consisting of 1-amino-2-naphthol and 1-amino-2-naphthol-4-sulfonic acid to give an intermediate condensation product, and further heating the said intermediate condensation product in an inert organic liquid to 15 effect conversion thereof into an oxazole compound.

No references cited.