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WHITENING AGENTS FOR CELLULOSIC FIBER

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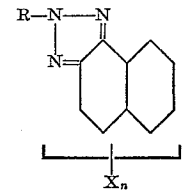
This invention relates to the production of novel organic compounds which are useful as whitening agents for fibrous material such as textiles or paper. It is an object of this invention to produce compounds of the above general nature, but which are characterized further by bleach fastness and by correct 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 fiber is yellowish, the most desirable shade in a fluorescent is blue. Many fluorescents of green or pink shade have been proposed and tried, but these can be used only in very minute concentration, inasmuch as larger concentrations of these tend to shade the fiber in undesirable green or pink shades. The blue-fluorescents, however, can be used in relatively large concentration (say up to 10% by weight of the fiber), and are very effective in producing bright, white textiles.

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. 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 to be commercially successful must be capable of being synthesized economically from readily available materials, and must 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 the fiber that is to be treated and must possess sufficient water-solubility to be applicable from an aqueous bath in the concentrations that would normally be used.

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



wherein R represents the 4'-radical of a compound of the group consisting of 2-phenyl-benzoxazole, 2-phenyl-methylbenzoxazole, 2-phenyl-methoxybenzoxazole, and the monosulfo derivatives of any of these, X stands for a water-solubilizing, acid radical such as sulfo, carboxy or a salt of such acid radical, such as the alkali-metal or ammonium salts thereof, while *n* designates the numeral 1 or 2.

These compounds may be synthesized by diazotizing the corresponding 2-(p-aminophenyl)-benzoxazole and coupling the diazo compound (in acid medium) to a 1-amino- or 2-amino-naphthalene having one or two sulfo groups or a carboxy group in the nucleus. The resulting ortho-amino azo compound is then converted into a triazole by oxidation in known manner, for instance by heating in an aqueous solution of cupric ammonium sulfate until the color of the intermediate azo dye has essentially disappeared, followed by recovery of the product in a desired physical or chemical form, for instance in the form of an alkali-metal or ammonium salt.

If it is found that the reaction mass after filtering contains residual color, the same may be destroyed by treating the filtrate with dilute hypochlorite solution or with reducing agents.

As suitable aminophenyl-benzoxazole for the aforegoing purpose may be mentioned 2-(4'-aminophenyl)-benzoxazole; 2-(4'-aminophenyl)-4-methyl-benzoxazole; 2-(4'-aminophenyl)-5-methyl-benzoxazole; 2-(4'-aminophenyl) - 6 - methyl - benzoxazole; 2 - (4' - aminophenyl) - 7 - methyl - benzoxazole; 2 - (4' - aminophenyl)-6-methoxy-benzoxazole; the monosulfo derivatives of any of these obtained by sulfonation of same with 20% oleum at 25° C. (position of SO_3H group unknown); or the alkali-metal or ammonium salts of such sulfo derivatives.

As coupling components for the intermediate aminoazo dyestuffs prepared above, may be used 1-amino-naphthalene-4-sulfonic acid, 2-amino-naphthalene-3-carboxylic acid, the various isomers of these; various 1-amino- and 2-amino-naphthalene-disulfonic acids; and the alkali-metal or ammonium salts of any of these.

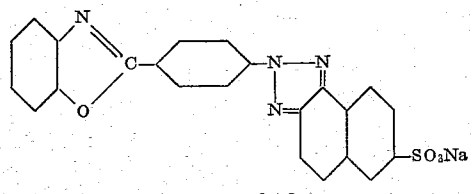
Without limiting this invention, the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

Example 1

21.0 parts (0.1 mole) of 2-(p-aminophenyl)-benzoxazole (Ber. 33, 2848; 1900) were diazotized, at 0°–5° C., with sodium nitrite and an excess of hydrochloric acid, in 1000 parts of water. A solution of 27 parts (0.11 mole) of Broenner's acid (2-aminonaphthalene-6-sulfonic acid) sodium salt in 400 parts of water was added. The acidity was reduced by the aid of sodium acetate to a weakly acid test on Congo Red paper, and the mixture was allowed slowly to assume room temperature. The mixture was then made alkaline to Brilliant Yellow paper, and the aminoazo dye was salted out and filtered off.

The wet dye cake thus prepared was dissolved in 2000 parts of water at 60° C. A solution of 50 parts of $CuSO_4.5H_2O$ in 100 parts of water and 300 parts of concentrated ammonia (28%) was added. The mixture was then heated to reflux for 16 hours and thereafter filtered. The cake was dissolved in 3000 parts of boiling water and filtered hot; the filtrate was mixed with

150 parts of a 5%, aqueous sodium hypochlorite solution and heated at 50° C. until completely decolorized (about ½ hour); the product was then salted out, filtered off and dried. It was a cream colored solid, soluble in water with bright bluish fluorescence. It is believed to have the formula



Example 2

Following the procedure of Example 1, 21.0 parts of 2-(p-aminophenyl)-benzoxazole were diazotized and coupled to the sodium salt of amino-R-acid (2-aminonaphthalene-3,6-disulfonic acid). The aminoazo dye thus obtained was then oxidized as in Example 1 and the crude oxidation product was purified by filtering the reaction mass at the boil, decolorizing the filtrate by warming at 40° C.–50° C. with 100 parts of 2N aqueous sodium carbonate solution and 10 parts of sodium hydrosulfite, and filtering again.

The product was isolated from the filtrate by salting out, filtering and drying. It was a cream colored solid, soluble in water with bright bluish fluorescence.

When the above procedure was repeated using the sodium salt of amino-J-acid (2-aminonaphthalene-5,7-disulfonic acid) in lieu of the amino-R-salt hereinabove named, a product of similar appearance and qualities was obtained.

Products of similar characteristics may also be obtained by using in the same procedure, in lieu of amino-R-salt, the sodium or potassium salt of any of the following:

Naphthionic acid—(1-NH_2:4-SO_3H)
Laurent's acid—(1-NH_2:5-SO_3H)
Amino-G-acid—(2-NH_2:6,8-diSO_3H)

Example 3

The starting material of this example, 2-(p-aminophenyl)-benzoxazole sulfonic acid, was obtained by sulfonation of 1 part of 2-(p-aminophenyl)-benzoxazole with 5 parts of 20% oleum at 25° C. for ½ hour, followed by drowning in ice water, filtering, washing with sodium chloride solution and drying.

29 parts (0.1 mole) of the 2-(p-aminophenyl)-benzoxazole sulfonic acid thus obtained were diazotized and coupled in separate experiments to the sodium salt of

(1) naphthionic acid,
(2) Broenner's acid,
(3) amino-J-acid,

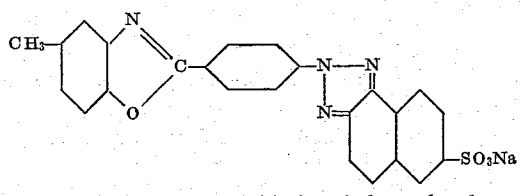
following the procedure indicated in Example 1. The obtained dyes were oxidized as in Example 1. The oxidation mixtures were filtered hot, the filtrates were decolorized with dilute, aqueous sodium carbonate and sodium hydrosulfite as in Example 2, and filtered again. The products were isolated from the filtrates by salting out, filtering and drying. They were cream colored solids, soluble in water with bright bluish fluorescence.

Similar compounds may also be prepared by coupling diazotized 2-(p-aminophenyl)-benzoxazole sulfonic acid to Laurent's acid, amino-R-acid, or amino-G-acid, and oxidizing the resulting aminoazo dyes as in this example.

Example 4

2-(p-aminophenyl)-5-methylbenzoxazole was prepared according to the procedure of E. Lellmann, Ber. 28, 1128 (1895), by reacting 4-hydroxy-3-nitrotoluene with p-nitrobenzoyl chloride to obtain 4-methyl-2-nitrophenyl-p-nitrobenzoate followed by reduction and ring-closing with stannous chloride and hydrochloric acid.

The above compound was diazotized, coupled to Broenner's acid, ring-closed to the triazole, purified and isolated as described in Example 1. The final product, of the structure



is a pearl gray powder, soluble in ethylene glycol monoethyl ether and exhibiting in solution or when spotted on paper or cotton a bright bluish-white fluorescence, when viewed in ultra-violet light.

In similar manner, but starting with 3-hydroxy-2-nitrotoluene, 2-(p-aminophenyl)-4-methyl - benzoxazole may be prepared and converted into the corresponding triazole with Broenner's acid.

By starting with 2-hydroxy-3-nitrotoluene, 2-(p-aminophenyl)-7-methyl-benzoxazole is obtained, and like the others it may be converted into a triazole.

Example 5

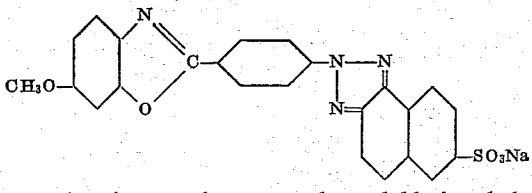
2-(p-aminophenyl)-6-methyl-benzoxazole is obtained from 5-methyl-2-nitrophenyl-p-nitrobenzoate as described by M. Schubert in Ann. 558, 31 (1947). When diazotized, coupled to Broenner's acid, ring-closed and isolated as in Example 1, one obtains the 6-methyl isomer of the product formulated in Example 4. The two compounds have similar fluorescent properties.

In lieu of Broenner's acid in Examples 4 and 5 above, any of the other hereinabove-mentioned sulfo-naphthylamines may be used.

The intermediate methyl compounds named in Examples 4 and 5 may also be sulfonated according to the procedure of Example 3 above. The resulting monosulfo-2-(p-aminophenyl)-methyl-benzoxazoles may then be diazotized, coupled with Broenner's acid, Laurent's acid, naphthionic acid, 2-naphthylamine-4-sulfonic acid or 2-naphthylamine-3-carboxylic acid, and the aminoazo compound thus obtained in each case may be oxidized to the corresponding triazole, according to the procedure of the aforegoing examples. Compounds of similar characteristics and fluorescent qualities are obtained.

Example 6

2-(p-aminophenyl)-6-methoxy-benzoxazole was prepared by the method described in Example 4 when 4-nitroresorcinol-1-methyl ether was used instead of 4-hydroxy-3-nitrotoluene. The methoxy-benzoxazole so obtained was substituted for 2-(p-aminophenyl)-benzoxazole in Example 1 to prepare a fluorescent agent of the structure



The product is a pearl gray powder, soluble in ethylene glycol monoethyl ether and exhibiting a bright bluish-white fluorescence when viewed under ultra violet light.

Example 7.—Practical application and testing

The following procedure was applied to several of the novel compounds hereinabove synthesized.

Cotton cloth was washed with a heavy duty detergent containing 80 p. p. m. (based on fabric) of the triazole sodium salt.

The heavy duty detergent referred to above was a commercial detergent (such as "Tide" or "Surf") com-

posed, by weight, of approximately 30% of the active ingredient (i. e., a long chain alkyl aryl sulfonate), 2% of carboxy methyl cellulose and 68% of sodium polyphosphate.

The treated cloth, which was considerably whiter than the untreated cloth, was then subjected to a bleach-fastness test as follows:

TEST A

The treated cloth was entered into an aqueous solution of sodium hypochlorite (in concentration equal to about 0.02% of available chlorine) and stirred therein at 110° F. for 15 minutes. The cloth was then removed, rinsed and dried. No noticeable change in the whiteness of the treated cloth was observed.

To further test the bleach-resistance of the novel compounds, the following additional and more rigorous test was carried out in each case.

TEST B

An aqueous solution containing by weight 0.4% of a heavy duty detergent (same as above) and 66 p. p. m. (based on the cloth to be treated) of the triazole sodium salt being tested was heated to 130° F., and sodium hypochlorite was added in quantity calculated to yield a concentration of 0.02% of available chlorine (based on bath weight). Two minutes later, cotton cloth was entered into the dye bath and the temperature of the mixture was maintained at 130° F. for twenty minutes. The cloth was then removed from the dye bath, rinsed, and dried. The cloth thus treated was measured by spectrophotometric methods and found to have 96%–100% of the fluorescence produced on a control sample of cloth treated under the same conditions in a similar bath but containing no bleach.

A third sample of cloth, treated under identical conditions in the presence of sodium hypochlorite, but using as fluorescent a present-day commercial product based on diaminostilbene, measured barely 10% of the fluorescence of a fourth piece of cloth (control) treated with the same fluorescent in the absence of bleach.

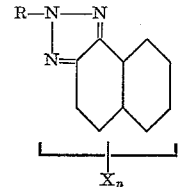
Tests for light-fastness, substantivity and wash fastness were also carried out, and showed my novel compounds to compare favorably in respect to these qualities with the best fluorescents which are now on the market.

The compounds given in the above examples have been isolated as the sodium salts of the 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 ultra-violet light is desirable, for instance to achieve fluorescent effects in costumes or stage settings, to achieve novel effects on photographic paper, as ultra-violet 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 represents the 4'-radical of a compound of the group consisting of 2-phenyl-benzoxazole, 2-phenyl-methyl-benzoxazole, 2-phenyl-methoxy-benzoxazole, and the monosulfo derivatives of any of these, X stands for a water-solubilizing, acid radical of the group consisting of sulfo, carboxy and their water-soluble salts, while *n* designates an integer not exceeding 2.

2. The process of producing a fluorescent agent of bluish fluorescence and good bleach-fastness, which comprises diazotizing a p-amino-phenyl-benzoxazole compound of the group consisting of 2-(p-aminophenyl)-benzoxazole, 2-(p-aminophenyl)-methyl-benzoxazole, 2-(p-aminophenyl)-methoxy-benzoxazole, and the monosulfo derivatives of any of these, coupling the diazonium compound to a sulfonated naphthalene having a primary amino group in one of the 1,2-positions and a hydrogen atom in the other of said positions, and oxidizing the resulting ortho-amino-azo compound to produce a triazole.

3. A process as in claim 2, the oxidation being effected by heating the compound in an aqueous solution of cupric-ammonium sulfate.

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