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FLUORESCENT WHITENING AGENTS

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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 cellulosic fibers or 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 ultra-violet 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 "tintorial strength") to give the desired effect at a minimum cost. It should also have affinity for cellulose or nylon fiber and should be capable of being dissolved or readily dispersed in water in the concentrations that would normally be used in the treatment of the respective fibers.

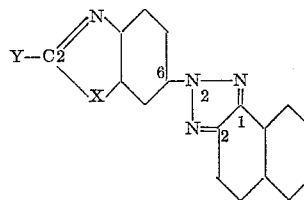
Now according to this invention new chemical compounds are synthesized which satisfy to an excellent degree all the foregoing qualifications. The novel compounds of this invention are aromatic triazoles which are obtained by oxidizing ortho amino azo dyes obtained by coupling various 6-amino-benzo-azoles to naphthylamines which are free to couple in position ortho to the amino group. They may be defined generally by the formula



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wherein R is the 6-C radical of the benzo-azole compound selected from the group consisting of benzoxazoles, benzothiazoles and benzimidazoles whose 2-position carries a lower alkyl or monocyclic aryl substituent, and the monosulfo derivatives of these; Q is a 1,2-naphthalene radical of the group consisting of naphthalene, and its monosulfo, disulfo, monocarboxy, dicarboxy, and sulfamyl derivatives. The term "sulfamyl" is used here in a generic sense, to include primary sulfamyl (SO_2NH_2), lower monoalkyl sulfamyl, and lower dialkyl sulfamyl; by lower alkyl radicals, I mean radicals having not over 4 C-atoms each. Where the triazole compound has sulfo or carboxy groups, these may be in the form of free acids, or in the form of common salts thereof, preferably water-soluble salts, such as the alkali-metal or ammonium salts.

As typical of the nomenclature of my novel series of compounds, may be named that subgroup which has no solubilizing substituents at all. It may be expressed by the general formula



wherein X designates oxygen, sulfur or an imino radical, while Y designates a neutral substituent such as lower alkyl, for instance methyl, ethyl or propyl, or monocyclic aryl, for instance phenyl, tolyl, or methoxy-phenyl. The compound wherein X is sulfur and Y is methyl, for instance, may be named 2-(2-methyl-6-benzothiazolyl)-2H-naphtho-(1,2)-triazole.

The compounds having sulfo and carboxy groups are generally water-soluble, and may be applied to textile fiber or paper from an aqueous bath. Those having only sulfamyl substituents or no substituents at all, are of interest as fluorescent for nylon fiber, and may be applied thereto from aqueous dispersions of the finely divided product or from dispersions made by pouring into water a solution of the fluorescent in an organic solvent such as the Cellosolves (lower monoalkyl ethers of diethylene glycol).

My novel compounds may be synthesized by diazotizing a 2-Y-6-amino-benzazole (wherein Y has the meaning above indicated), or a monosulfo derivative thereof, and coupling the diazo compound in acid medium to an amino naphthalene which may have carboxy, sulfo or sulfamyl radicals in the nucleus, but which is adapted for coupling in position ortho to the amino group. The last condition implies that the amino group is located in position 2 while the 1-position is free; or that a 1-naphthylamine is employed which will couple in the 2-position by virtue of having the 4-position blocked due to the presence of a carboxy, sulfo or sulfamyl group in position 4 or 5. Where the amino-benzothiazole selected is free from sulfo groups, two sulfo or two carboxy groups may be present in the naphthylamine component.

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 or in an aqueous alkaline solution of sodium hypochlorite until the color of the intermediate azo dye has essentially disappeared, and then recovering the product in a desired physical or chemical form, for

instance in the form of an alkali-metal or ammonium salt.

In the case of the water-soluble compounds of this invention, if it is found that the reaction product after filtering contains residual color, the same may be destroyed by treating the filtrate with dilute hypochlorite solution or with reducing agents. The solution may also be clarified with charcoal prior to recovery of the dissolved fluorescent agent. The water insoluble fluorescent agents of this invention may be purified by crystallization from organic solvents or by hypochlorite treatment of an aqueous slurry of the product.

As typical 6-amino-benzo-azole compounds suitable for the foregoing purpose may be mentioned 6-amino-2-methylbenzothiazole, 6-amino-2-phenylbenzothiazole, 6-amino-2-p-methoxyphenylbenzoxazole, 6-amino-2-phenylbenzimidazole, the monosulfo derivatives of any of these, obtained for instance by sulfonation of same with 20% oleum at room temperature, and the alkali-metal or ammonium salts of such sulfo derivatives.

As coupling components for the intermediate amino azo dyestuffs prepared above may be used 2-naphthylamine; 1-naphthylamine-4-sulfonic acid, 2-naphthylamine-6-sulfonic acid, and the various isomers of these; the various primary sulfamyl, monoalkyl sulfamyl and dialkyl sulfamyl derivatives of 1- or 2-naphthylamine; 2-amino-naphthalene-3-carboxylic acid; 1-amino- and 2-amino-naphthalene-4,5-dicarboxylic acid; the various 1-amino- and 2-amino-naphthalene-disulfonic acids; and the alkali-metal or ammonium salts of any of the foregoing.

The requisite sulfamyl derivatives of 1- or 2-naphthylamine, may be prepared by first acetylating the corresponding naphthylamine with acetic anhydride, to block the amino group; then sulfonating the compound with chlorosulfonic acid to convert it into a sulfonyl chloride. The latter is then treated with the appropriate amine (ammonia, methylamine, ethylamine, dimethylamine, etc.) to obtain the sulfonamide. Finally, hydrolysis with hot hydrochloric acid regenerates the amino group and gives the desired sulfonamide compound.

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

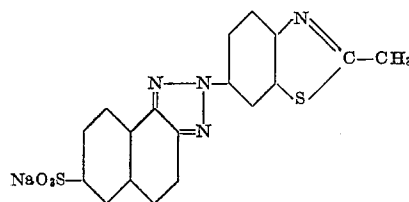
Example 1

16.4 parts (0.1 mol) of 6-amino-2-methylbenzothiazole (A. I. Kriprianov, Chem. Abst., 40, 2307) were diazotized, at 0° to 5° C., with sodium nitrite and an excess of hydrochloric acid, in 1000 parts of water. A solution of 27 parts (0.11 mol) of Broenner's acid (2-amino-naphthalene-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 by addition of 30% sodium hydroxide solution and the amino-azo dye was salted out with sodium chloride 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 parts of water and 300 parts of concentrated ammonia (28%) was added. The mixture was then heated to reflux for 12 hours and then filtered at 50° C.

The cake was slurried in boiling water, made strongly acid with concentrated hydrochloric acid and boiled for a few minutes. The precipitate was filtered off and slurried in water at 70°–80° C. To the suspension 30% aqueous sodium hydroxide was added until a clear solution was obtained and then the product was recovered by salting using sodium chloride, filtered and dried. It was a cream colored powder, soluble in water with bright blue fluorescence. The absorption maximum of this com-

pound in aqueous solution is located at 348 millimicrons. It is believed to have the formula



Similar compounds may also be prepared by coupling diazotized 6-amino-2-methylbenzothiazole to naphthionic acid (1-amino-naphthalene-4-sulfonic acid) or to Laurent's acid (1-amino-naphthalene-5-sulfonic acid), and oxidizing the amino azo dyes as above.

Compounds of similar characteristics are obtained, if the 16.4 parts of 6-amino-2-methylbenzothiazole in the above example are replaced by 22.6 parts of 6-amino-2-phenylbenzothiazole, the remainder of the procedure remaining the same.

Example 2

16.4 parts (0.1 mol) of 6-amino-2-methylbenzothiazole were diazotized, coupled to 39 parts of the disodium salt of amino-R acid (2-amino-3,6-disulfonic acid) and oxidized as in Example 1. The oxidation product was purified by filtering the reaction mass at the boil, decolorizing the filtrate with dilute aqueous sodium hydroxide and sodium hydrosulfite at 40°–50° C. and filtering again. The end product was isolated from the filtrate by salting out, filtering and drying. It was a cream colored powder, soluble in water with bright blue fluorescence. The absorption maximum of this compound in aqueous solution is located at 348 millimicrons.

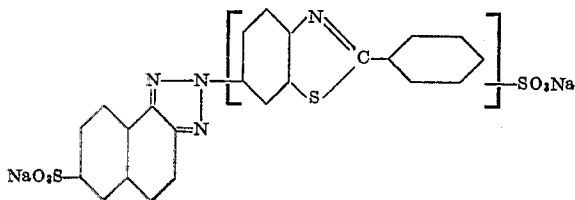
Similar compounds may be also prepared by coupling diazotized 6-amino-2-methylbenzothiazole to amino-J acid (2-amino-5,7-disulfonic acid) or to amino-G acid (2-amino-naphthalene-6,8 disulfonic acid) and oxidizing the amino azo dyes as above.

Compounds of similar characteristics are obtained, if the 16.4 parts of 6-amino-2-methylbenzothiazole in the above example are replaced by 22.6 parts of 6-amino-2-phenylbenzothiazole, the remainder of the procedure remaining the same.

Example 3

66 parts of 6-amino-2-phenylbenzothiazole were monosulfonated with 700 parts of 20% oleum at 30°–40° C. for 2 hours. The obtained 6-amino-2-phenylbenzothiazole-sulfonic acid was isolated from the reaction mixture by drowning in ice water, filtering, washing with sodium chloride solution and drying. A white powder, soluble in water with bright yellowish fluorescence was obtained.

32.4 parts (0.1 mol) of the above sulfonic acid were diazotized and coupled to Broenner's acid, and the resulting ortho-amino azo dye was oxidized as in Example 1. The oxidation mixture was filtered hot. The filtrate was decolorized with small amounts of aqueous sodium hydroxide and sodium hydrosulfite at 40°–50° C. and filtered at the boil. The end product was isolated from the filtrate by salting out with sodium chloride, filtering and drying. It was a light tan cake, soluble in water with bright blue fluorescence. The absorption maximum of this compound in aqueous solution is located at 360 millimicrons. This product is believed to have the formula



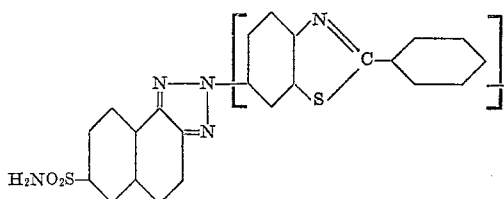
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Similar products may be prepared by coupling diazotized 6-amino-2-phenyl-benzothiazole-sulfonic acid to (a) naphthionic acid, (b) Laurent's acid or (c) any of 2-naphthylamine disulfonic acids named above, and oxidizing the resulting amino azo dyes as above.

Similar products are also obtained if the 6-amino-2-phenyl-benzothiazole in the above example is replaced in stoichiometric proportion by 6-amino-2-phenyl-benzothiazoles having inert substituents in the phenyl ring, for instance alkyl groups of 1 to 3 C-atoms, one or two methoxy groups, etc.

Example 4

32.4 parts of 6-amino-2-phenyl-benzothiazole-sulfonic acid, obtained as in Example 3, were diazotized and coupled to 24.4 parts (0.11 mol) of 2-amino-naphthalene-6-sulfonamide, following the procedure given in Example 1. The obtained azo dye was oxidized to the corresponding triazole as in Example 1. The oxidation mixture was made acid to Congo red paper with hydrochloric acid and filtered hot. The solid product was slurried in water, made alkaline to Clayton Yellow paper with 10% sodium hydroxide solution and treated with sodium hydrosulfite at 50° C. for 1 hour, during which time an excess of hydrosulfite was maintained (positive test on flavanthrone paper). The slurry was then made acid and filtered. The product was crystallized from dilute Cellosolve and dried. It was a cream powder, soluble in Cellosolve with blue fluorescence. The absorption maximum of this compound in Cellosolve solution is located at 360 millimicrons. The structure of the product is believed to be

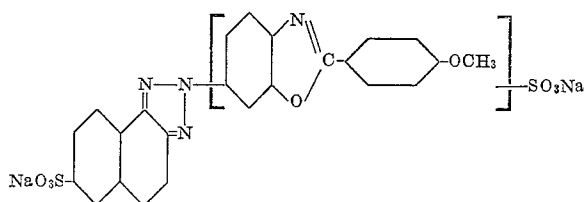


Similar compounds may be prepared by coupling diazotized 6-amino-2-phenyl-benzothiazole-sulfonic acid to the sulfonamides of naphthionic acid or of Laurent's acid.

Example 5

6-amino-2-(p-methoxyphenyl)-benzoxazole was prepared by condensing 2-amino-5-nitrophenol with p-anisoyl chloride and reducing the intermediate 2-(p-methoxyphenyl)-6-nitrobenzoxazole with stannous chloride and hydrochloric acid, following the method described by O. Kym, in *Berichte* 32, 1430, for preparing 5,7-dinitro-2-phenylbenzoxazole. The compound was then sulfonated with 100% sulfuric acid at room temperature.

3.4 parts (0.01 mol) of the resulting 6-amino-2-(p-methoxyphenyl)-benzoxazole sulfonic acid were diazotized and coupled to Broenner's acid, and the intermediate orthoamino azo dye was oxidized to the corresponding triazole as in Example 1. The oxidation mixture was filtered hot and the triazole was isolated from the filtrate by salting out with sodium chloride, filtering, washing the cake with 20% sodium chloride and drying. It was a white powder, soluble in water with blue fluorescence. The absorption maximum of this compound in water solution is located at 358 millimicrons. The product is believed to have the formula:



In like manner, the monosulfo compound of this ex-

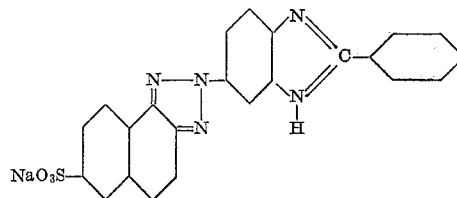
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ample or the unsulfonated 6-amino-2-(p-methoxyphenyl)-benzoxazole may be diazotized and coupled to any other of the coupling components mentioned hereinabove, to produce blue fluorescent agents.

Similar compounds are also obtained if the particular benzoxazole named in the above example is replaced by benzoxazoles prepared in similar manner from 2-amino-5-nitrophenol and various other benzoyl chlorides, for instance o-, m- or p-methyl benzoyl chloride; o-, m- or p-ethyl benzoyl chloride; n-propyl-benzoyl chloride; trimethyl-benzoyl chloride; 3,4-, 2,4- or 2,5-dimethoxybenzoyl chloride; etc.

Example 6

2.1 parts (0.01 mol) of 6-(or 5-)amino-2-phenylbenzimidazole, obtained following the method described by O. Kym in *Berichte* 32, 2178, were diazotized and coupled to Broenner's acid, and the resulting dye was oxidized to the corresponding triazole by the method described in Example 1. The reaction mass was filtered and the cake was slurried in water made acid to Congo red paper with hydrochloric acid. The slurry was heated to 80°-90° C. to dissolve all copper salts and filtered hot. The cake was washed with water until acid-free, slurried in water, made alkaline to Brilliant Yellow paper with sodium hydroxide, heated at 80° C. with an excess of sodium hypochlorite solution for 15 minutes, cooled, filtered, washed and dried. A white powder was obtained, soluble in Cellosolve with bluish fluorescence. The product is believed to possess the structure:



In similar manner, the imidazole diazo component of this example may be coupled to any of the coupling components named hereinabove, to produce blue fluorescent products. Also, this diazo component may be sulfonated with weak oleum at room temperature to form the monosulfo derivative, which, in turn, may be diazotized and coupled as above indicated.

Products of similar nature are also obtained if the 6-(5)-amino-2-phenyl-benzimidazole of this example is replaced by an equivalent quantity of a corresponding compound wherein the 2-phenyl group carries inert substituents such as lower alkyl (1 to 3 C-atoms), methoxy, etc.

The compounds of the foregoing examples are suitable for incorporation into soap or synthetic detergents, and endow a fluorescent or whitening effect to cotton or nylon 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 fluorescent whiteners 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 ultraviolet light is desirable, for instance to

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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 is the 6-C radical of a benzoazole compound selected from the group consisting of benzoxazoles, benzothiazoles and benzimidazoles having an inert organic radical in the 2-position and the monosulfo derivatives of such benzoazoles, said inert organic radical being a member of the group consisting of lower alkyl and monocyclic aryl, while Q represents the 1,2-radical of a naphthalene compound of the group consisting of naphthalene, its monosulfo, disulfo, monocarboxy, dicarboxy and monosulfamyl derivatives.

2. A compound of the formula



wherein R is the 6-C radical of sulfonated 2-phenyl-benzothiazole, while Q is the 1,2-radical of 6-sulfo-naphthalene.

3. A compound of the formula



wherein R is the 6-C radical of sulfonated 2-phenyl-benzothiazole, while Q is the 1,2-radical of 4-sulfo-naphthalene.

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4. A compound of the formula



5 wherein R is the 6-C radical of 2-phenylbenzimidazole, while Q is the 1,2-radical of 6-sulfo-naphthalene.

5. A compound of the formula



10 wherein R is the 6-C radical of sulfonated 2-p-methoxy phenyl-benzoxazole, while Q is the 1,2-radical of 6-sulfo-naphthalene.

6. The process of producing a fluorescence agent for textile fiber, which comprises diazotizing an azole compound of the group consisting of (a) the benzoxazoles, benzothiazoles and benzimidazoles having a primary amino group in position 6 and an inert organic radical in the 2-position, and (b) the monosulfo derivatives of the said azoles, said inert organic radical being a member of the group consisting of lower alkyl and monocyclic aryl, coupling the diazo compound thus formed to an amino-naphthalene which is adapted to couple ortho to the amino group and which is a member of the group consisting of the unsubstituted amino-naphthalenes and amino-naphthalenes bearing substituents of the group consisting of sulfo, carboxy and sulfamyl, and then oxidizing the coupled compound to the corresponding triazole.

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

No references cited.