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2,845,423

# N,N'-DISUBSTITUTED-3,7-DIAMINO-POLYSULFO-DIBENZOTHIOPHENE-DIOXIDES

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13 Claims. (Cl. 260—249.6)

This invention relates to a new group of chemical compounds falling within the broader class of blue-fluorescing, relatively colorless chemical compounds which are substantive to cellulosic materials.

The primary object of the invention is to provide a new group of chemical compounds of said class having a combination of properties which render said compounds especially useful as so-called "optical bleaches" or whitening and brightening agents particularly in the laundering of cellulosic materials, such as cotton, linen, regenerated cellulose, etc.

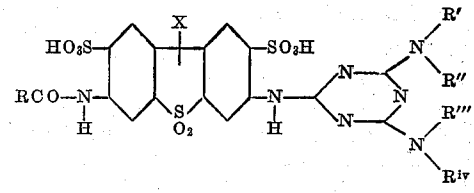
A number of chemical compounds are known which, although they are of diverse chemical structure, have the property of giving off a blue fluorescence when exposed to ultraviolet rays, such as daylight or light rich in ultraviolet. Some of them are sufficiently soluble in water and sufficeintly resistant to the alkaline action of soap to be capable of use as additives for soaps and other compositions used in laundering clothes and linens, whereby they impart a bluish fluorescence to the laundered goods which has the effect of whitening the appearance of white goods and brightening the appearance of colored goods. Certain of said compounds are substantive to cellulosic fibers, that is, they are taken up from their solutions and held by cellulosic fibers, similarly to direct coton dyestuffs.

Few of them, however, possess a combination of these and other properties in the desired balance to be useful commercially for the addition to soaps, laundering compositions, detergents, wetting agents, and the like. Thus, while some possess certain of the desired properties, they possess excessive substantivity to cellulosic fibers; so that excessive build-up of the compounds on the goods occurs upon repeated laundering, with resultant staining of cotton and linen goods laundered in a bath containing them. Others are unstable in aqueous solution against the destructive action of the chemical bleaching agents commonly employed, such as alkali metal hypochlorites, alkaline earth metal hypochlorites, alkali metal perborate, hydrogen peroxide, and the like.

According to the present invention, a new group of chemical compounds is provided having such a combination of the said desired properties as to make them especially suitable for use as "optical bleaches" and for other purposes. The compounds of said group are the unsymmetrically N,N'-disubstituted-3,7-diamino-polysulfo-dibenzothiophene dioxides having a sulfo group at least in each of the 2- and 8-positions and having, as the N-substituent in the 3-position, the radical of a chromophore-free 3,5-diaminotriazine, and as the N-substituent in the 7-position, the acyl radical of a chromophore-free aromatic carboxylic acid. (As employed herein, the term "sulfo" denotes generically the compounds in the form of their free sulfonic acids and in the form of their metal, ammonium and organic base salts.)



Said compounds, in the form of the free sulfonic acids, are represented by the formula:



wherein X represents H or —$SO_3H$; RCO represents the acyl radical of a chromophore-free aromatic carboxylic acid; and



and

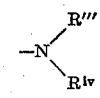


represent the same or different amino substituents in the triazine radical, R', R'', R''' and $R^{iv}$ being the same or different members of the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl, aryl, and heterocyclic radicals and their substituted derivatives, or being a part of a heterocyclic nucleus of which the amino nitrogen atom is also a part, all of which are chromophore-free.

They includes compounds in which the amino radicals represented by



and



in the above formula are chromophore-free residues of the following nitrogen bases:

Ammonia; primary and secondary alkylamines in which the alkyl groups range from methyl to those commonly called "higher alkyl groups," e. g. mono- and di-methylamines, ethylamine, propylamines, butylamines, amylamines, laurylamines, cetylamines, and kerylamines (in which keryl represents a higher alkyl hydrocarbon residue derived from a petroleum distillate, such as kerosene), as well as C-substituted derivatives of such alkylamines, e. g. mono-ethanolamine, diethanolamine, chlorethylamine, diethoxyethylamine, sarcosine, and methylsulfonethylamine; aralkylamines, e. g., benzylamine; cycloaliphatic amines, e. g. cyclohexylamine and N-ethylcyclohexylamine; primary and secondary aromatic amines wherein the amino nitrogen is attached directly to an aryl nucleus, and wherein the aryl nucleus may be substituted, e. g., aniline, N-methylaniline, N-benzylaniline, toluidine, anisidine, cresidine, mesidine, aminobenzoic acids, alpha- and beta-naphthylamines, dichloroaniline, and N-ethyl-alpha-naphthylamine; heterocyclic amines, e. g., aminopyridine and aminoquinoline; and heterocyclic organic nitrogen bases, e. g., morpholine, piperidine and pyrrolidine, and the acyl radical represented by RCO— in the above formula is the residue of the following aromatic carboxylic acids:

Chromophore-free mononuclear aromatic carboxylic acids, including those having simple substituents in the

nucleus, e. g., benzoic acid, p-methoxybenzoic acid, 2,4-dimethoxy-benzoic acid, toluic acids, aminobenzoic acids, 3-methyl-4-methoxy-benzoic acid, and p-chlorobenzoic acid; and chromophore-free polynuclear aromatic carboxylic acids, including those having simple substituents in the nucleus, e. g., 1-naphthoic acid and 2-napthoic acid.

I have discovered that the compounds represented by the above formula possess a combination of desirable properties which render them especially useful as members of the family of "optical bleaches." Thus, they are slightly colored substances which per se and in solutions or on fibers or substrates produce a blue fluorescence (between 4200 and 4925 Angstrom units) under the influence of ultraviolet radiation, e. g. between 2260 and 4045 Angstrom units. They are sufficiently substantive to cellulosic materials to impart to such materials the property of emanating a bluish fluorescence when excited by ultraviolet radiation; so that they are therefore valuable "optical bleaches," particularly useful in laundering compositions and processes, and adapted to enhance the "whiteness" as well as brilliancy of colors of household cellulosic materials, such as towels, tablecloths, napkins, sheets, pillow cases, shirts and the like. Yet they do not cause an undesirable accumulation of substantive deposits or decomposition products in or on such materials leading to staining of the materials when such cellulose fabrics are laundered repreatedly in solutions which contain a compound of the present invention at a concentration normally used in such washings.

A surprising property of all of the compounds of this invention is their unexpected stability towards the bleaching or oxidizing action of the bleaching agents commonly used in ordinary commercial and household laundering processes applied to household linens and cellulosic white and colored goods, such as alkali metal hypochlorite, alkaline earth metal hypochlorite, alkali metal perborate, hydrogen peroxide and the like, when used at the usual concentrations applied in such processes. I have found that the degree of fluorescence imparted to cellulosic material by treatment with a solution of a compound of the invention is not substantially altered by treatment with such bleaches.

In the form of their alkali metal, ammonium, alkylamine and alkylolamine salts, the compounds of the present invention are soluble to a limited extent in water to form solutions which are compatible with the usual detergents and wetting agents normally used in commercial and household laundering. They lend themselves readily to uniform incorporation into commercial laundering compositions in the form of cakes, powders and solutions, with cleaning agents such as soaps, ionic detergents (such as, alkylaryl sulfonates and alkyl sulfates) and non-ionic detergents (such as the polymerization products derived from ethylene and propylene oxides).

For general laundering purposes, concentrations up to 1,000 parts per million of compound, based on the weight of the fabric, are effective to impart distinctive brightening and whitening effects, but usually a concentration ranging from about 10 to about 100 parts per million is sufficient for most commercial and household laundry washings.

The new compounds of the present invention can be prepared in various ways. A method which I have found to be particularly useful comprises condensing a 3,7-diamino - polysulfo - dibenzothiophene - dioxide, having a sulfo group at least in each of the 2- and 8-positions, with one molecular proportion of a cyanuric halide (e. g., cyanuric chloride or bromide), preferably in the presence of an organic tertiary base (e. g., triethylamine, tripropylamine, tributylamine, or triamylamine) in sufficient amount to form the amine salt of the polysulfo-dibenzothiophene-dioxide compound, and in an organic solvent (e. g., mono-chlorobenzene, ortho-dichloro-benzene, toluene, xylene, or nitrobenzene) as reaction medium; condensing the resulting 3-(3',5'-dihalogen-)triazinylamino-7 - amino-polysulfo-dibenzothiophene-dioxide, preferably in the same reaction medium, with two molecular proportions of ammonia or an organic nitrogen base (e. g., one of those mentioned above), or a mixture of such bases, and preferably with the aid of an organic tertiary base; and reacting the resulting 3 - (3',5' - diamino-)triazinylamino - 7 - amino - polysulfo - dibenzothiophene-dioxide, preferably after an intermediate purification treatment, with one molecular proportion of an aromatic carboxylic acid halide (e. g., an acid bromide or chloride of one of the chromophore-free aromatic carboxylic acids referred to above), preferably in an organic solvent and with the assistance of an organic tertiary base (e. g., those mentioned above). They can also be prepared in other ways, such as by carrying out the condensations in the foregoing manner but in a different sequence; e. g. condensing a 3,7 - diamino - polysulfo-dibenzothiophene-dioxide of the aforesaid type with one molecular proportion of a suitable aromatic carboxylic acid halide, reacting the resulting 3 - amino - 7-aroylamino-polysulfo-dibenzothiophene-dioxide with one molecular proportion of a cyanuric chloride, and condensing the 3-(3',5'-dihalogen - )triazinylamino - 7 - aroylamino - polysulfo - dibenzothiophene-dioxide thus obtained with two molecular proportions of ammonia or a suitable organic nitrogen base.



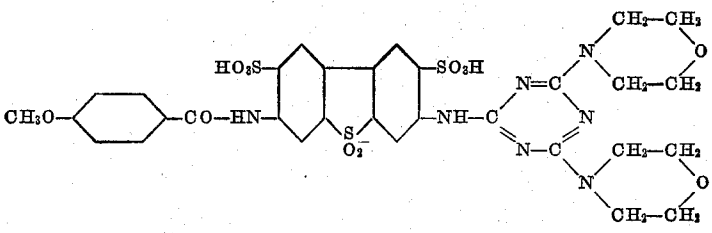
The invention will be illustrated by the following specific examples, but it is to be understood that the invention is not limited to the details thereof and that changes can be made without departing from its scope. The temperatures are in degrees centrigrade and the parts are by weight.

*Example 1*

A slurry produced by stirring 20.3 parts of 3,7-diamino-2,8-disulfo-dibenzothiophene-dioxide in the form of the free disulfonic acid, 10.1 parts of triethylamine and 12 parts of cyanuric chloride into 652 parts of solvent 74 (ortho-dichlorobenzene) was heated to 155°–165° and stirred at this temperature for about 12 hours, thus forming 3-(3',5'-dichloro-)triazinylamino-7-amino-2,8-disulfo-dibenzothiophene-dioxide. The reaction mass was cooled to 100°, and then admixed with 15 parts of morpholine and 10.1 parts of triethylamine. The resulting slurry was heated to 135°–140° and stirred at that temperature for about 8 hours, to form 3-(3',5'-dimorpholinyl-)triazinylamino - 7 - amino - 2,8 - disulfo - dibenzothiophene-dioxide in the form of the triethylamine salt. The reaction mixture was cooled to about room temperature and filtered, and the filter cake of the crude triethylamine salt of the disulfonic acid product was dried in vacuo at 70° to 80°. It was converted to the disodium salt and subjected to a purification treatment to remove water-soluble impurities, especially unreacted 3,7-diamino-2,8-disulfo-dibenzothiophene-dioxide, by adding the dry product to 500 parts of water; adding 6.3 parts of sodium carbonate until a solution alkaline to phenolphthalein was obtained; heating the resulting slurry to 80° and adding 50 parts of common salt to the resulting hot aqueous solution, to precipitate the disodium disulfonate; cooling the mass to 50°; filtering; and washing the filter-cake with 500 parts of 10% brine.

The filter-cake was dried, ground to powder form, and suspended in 522 parts of solvent 74. To the resulting slurry, 5 parts of triethylamine and 16 parts of para-anisoyl chloride were added, and the mixture was heated to, and stirred for about 8 hours at, 135°–145°. The resulting slurry was cooled to about room temperature, filtered, and the filter-cake of product was added to a solution of 12 parts of sodium carbonate (soda ash) in 300 parts of water. The resulting slurry was stirred for about two hours, then filtered, and the filter-cake was air dried.

The dry product was the disodium salt of 3-(3',5'-dimorpholinyl-)triazinylamino - 7 - para - anisoylamino - dibenzothiophene-dioxide-2,8-disulfonic acid, in the free acid form having the formula



It was a light tan powder, sparingly soluble in water to form a light tan solution. The powder and its solutions possessed a strong bluish fluorescence (4200 to 4925 Angstrom units) under the influence of ultra-violet radiation (e. g., 2260 to 4045 Angstrom units).

*Example 2*

*Part A.*—A 5-gram piece of white cotton cloth (6 x 12 inches) was washed for 20 minutes at 60° in 200 cc. of solution in distilled water containing

0.0003 gram of the product obtained in Example 1, and
1 gram of ordinary soap (Ivory).

The cloth was then rinsed and dried.

The cloth thus obtained appeared whiter in daylight than cloth washed in the same manner but in the absence of the product of Example 1.

*Part B.*—A 10-gram piece of white cotton cloth (12 inches square) was treated at 60° for 45 minutes in a bath composed of

0.01 gram of the compound obtained in Example 1, and
3 grams of ordinary soap (Ivory)

dissolved in 1000 cc. of distilled water. The cloth was then rinsed and dried.

The cloth thus treated with 17 times the amount of optical bleach compound normally required, as illustrated in part A, possessed excellent whiteness without noticeable change in the character of the whiteness. This shows that the compound of Example 1 produces no objectionable build-up shade when applied to cloth in large amounts which simulate the accumulation effect of repeated launderings in solutions containing normal concentrations of the whitening agent.

*Part C.*—A 4-inch square piece of the cloth obtained in part B by treatment with the compound of Example 1 was immersed for 1 hour at 30° in a bleach solution composed of

4 cc. sodium hypochlorite solution containing 4.8% available chlorine, and
100 cc. distilled water.

The cloth was then rinsed and dried. It showed essentially no alteration of shade or loss of whiteness; i. e., the compound of Example 1 possesses excellent fastness to the foregoing mild hypochlorite bleach.

*Part D.*—The compound of Example 1 was subjected to a severe hypochlorite bleach as follows:

A 5-gram piece of white cotton cloth (12 inches square) was treated for 20 minutes at 60° in a bath consisting of

0.03 g. of the compound obtained in Example 1,
200 cc. of 0.5% solution of ordinary soap (Ivory) in distilled water containing
0.8 cc. sodium hypochlorite solution containing 4.8% available chlorine.

The cloth was rinsed and dried.

The compound of Example 1 possessed excellent fastness to the severe hypochlorite bleach conditions, being in this respect superior to most commercially available optical bleach products.



*Example 3*

The process of Example 1 was repeated except for the substitution of 17.5 parts of 2,4-dimethoxy-benzoyl-chloride in place of the para-anisoylchloride.

The resulting product was a faintly colored powder having properties very similar to those of the product of Example 1.

*Example 4*

The process of Example 1 was repeated except for the substitution of 24.3 parts of 3,7-diamino-2,8,X-trisulfodibenzothiophene-dioxide in place of the disulfo compound employed as starting material, and corresponding increase in the amounts of salt (sodium chloride) and sodium carbonate employed.

The product was a weakly-tinged tan product with properties closely resembling those of the products of Examples 1 and 3.

*Example 5*

The process of Example 1 was repeated except for the substitution of 18 parts of para-aminobenzoic acid in place of the morpholine.

The resulting product was a very light tan-colored powder having substantivity and fluorescent characteristics similar to those of the products of the foregoing examples. It was, however, slightly more soluble in water than the products of said other examples, presumably because of the presence of the carboxyl groups.

*Example 6*

The process of Example 1 was repeated except that 12.6 parts of diethylamine were used in place of the morpholine.

The resulting product was a faintly colored powder possessing properties closely resembling those of the product of Example 1.

*Example 7*

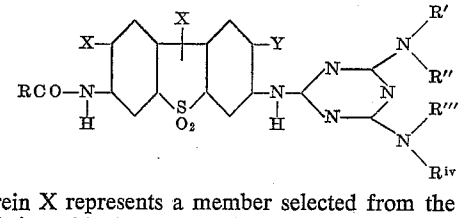
By replacing morpholine with a molecular equivalent proportion of n-butylamine in the process of Example 1, a product having closely similar properties was obtained.

*Example 8*

By employing a molecular equivalent amount of aniline in place of morpholine in the process of Example 1, a product possessing similar properties was obtained.

I claim:

1. A chromophore-free unsymmetrically N,N'-disubstituted-3,7-diaminopolysulfo - dibenzothiophene - dioxide having the formula



wherein X represents a member selected from the group consisting of hydrogen and the sulfo radical, Y represents the sulfo radical, RCO— represents the acyl radical of an aromatic carboxylic acid selected from the group

consisting of benzoic acid, naphthoic acid, and their methyl, methoxy, amino and chloro derivatives, and



and



each represents a member selected from the group consisting of $—NH_2$, radicals of primary and secondary alkylamines and cycloalkylamines, radicals of primary and secondary arylamines containing a maximum of two carbocyclic rings and in which the amino nitrogen is attached directly to the aryl nucleus, radicals of mononuclear aralkylamines, radicals of heterocyclic amines having a maximum of two heterocyclic rings, and radicals of mononuclear heterocyclic organic nitrogen bases.

2. An unsymmetrically N,N'-disubstituted-3,7-diamino-polysulfo-dibenzothiophene-dioxide as defined in claim 1, wherein the sulfo groups are in the form of their salts selected from the group consisting of the alkali metal, ammonium and organic base salts.

3. 7-N-substituted-amino-3-(3',5'-di-morpholinyl-) triazinylamino-polysulfo-dibenzothiophene-dioxide having a sulfo group at least in each of the 2- and 8-positions and having, as the N-substituent in the 7-position, the acyl radical of an aromatic carboxylic acid selected from the group consisting of benzoic acid, naphthoic acid, and their methyl, methoxy, amino and chloro derivatives.

4. 7-N-substituted-amino-3-(3',5'-di-morpholinyl-) triazinylamino-3,7-diamino-polysulfo-dibenzothiophene - dioxide as defined in claim 3, wherein the N-substituent in the 7-position is methoxy-substituted benzoyl.

5. 7-N-substituted-amino-3-(3',5'-di-morpholinyl-) triazinylamino-2,8-disulfo-dibenzothiophene-dioxide wherein the N-substituent in the 7-position is methoxy-substituted benzoyl.

6. 7-N-substituted-amino-3-(3',5'-di-morpholinyl-) triazinylamino-2,8-disulfo-dibenzothiophene-dioxide as defined in claim 5, wherein the sulfo groups are in the form of their sodium salts.

7. 7-N-substituted-amino-3-(3',5'-di-morpholinyl-) triazinylamino-2,8-disulfo-dibenzothiophene-dioxide, wherein the N-substituent in the 7-position is methoxy-substituted benzoyl having a methoxy group at least in para-position to the carbonyl group.

8. 7-N-substituted-amino-3-(3',5'-di-morpholinyl-) triazinylamino-2,8-disulfo-dibenzothiophene-dioxide as defined in claim 10, wherein the N-substituent in the 7-position is 4-methoxy-benzoyl.

9. 7-N-substituted-amino-3-(3',5'-di-morpholinyl-) triazinyl-amino-2,8-disulfo-dibenzothiophene-dioxide as defined in claim 10, wherein the N-substituent in the 7-position is 2,4-dimethoxy-benzoyl.

10. 7-N-substituted - amino - 3-(3',5'-di-carboxyphenyl-amino-)triazinylamino-2,8-disulfo-dibenzothiophene - dioxide wherein the N-substituent in the 7-position is methoxy-substituted benzoyl.

11. 7-N-substituted amino - 3-(3',5,-di-carboxylphenyl-



amino-)triazinylamino-2,8-disulfo-dibenzothiophene - dioxide as defined in claim 10, wherein the N-substituent in the 7-position is 4-methoxy-benzoyl and the sulfo groups are in the form of their sodium salts.

12. A method of preparing an unsymmetrically N,N'-di-substituted-3,7-diamino-polysulfo-dibenzothiophene - dioxide, which comprises heating a polysulfo derivative of 3,7-diamino-dibenzothiophene-dioxide, having a sulfo group at least in each of the 2- and 8-positions, with substantially one molecular proportion of cyanuric chloride in the presence of an organic tertiary base in sufficient amount to form the amine salt of the polysulfo-dibenzothiophene-dioxide compound and in an organic solvent as reaction medium until 3-(3',5'-dichloro-)triazinyl-amino-7-amino - polysulfo - dibenzothiophene - dioxide is formed; heating the resulting 3-(3',5'-dichloro-)triazinyl-amino-7-amino-polysulfo-dibenzothiophene-dioxide in the same reaction medium and in the presence of an organic tertiary base with substantially two molecular proportions of a member selected from the group consisting of ammonia, primary and secondary alkylamines and cycloalkylamines, primary and secondary arylamines containing a maximum of two carbocyclic rings and in which the amino nitrogen is attached directly to the aryl nucleus, mononuclear aralkylamines, heterocyclicamines having a maximum of two heterocyclic rings, and mononuclear heterocyclic organic nitrogen bases until a 3-(3',5'-diamino-)triazinylamino-7-amino - polysulfo - dibenzothiophene-dioxide is formed, and heating the resulting 3-(3',5'-diamino-)triazinylamino-7-amino-polysulfo - dibenzothiophene-dioxide with substantially one molecular proportion of the acid chloride of an aromatic carboxylic acid selected from the group consisting of benzoic acid, naphthoic acid, and their methyl, methoxy, amino and chloro derivatives in an organic solvent containing an organic tertiary base.

13. A method of preparing an unsymmetrically N,N'-disubstituted-3,7-diamino-2,8-disulfo - dibenzothiophene-dioxide, which comprises heating 3,7-diamino-2,8-disulfo-dibenzothiophene-dioxide with substantially one molecular proportion of cyanuric chloride in the presence of sufficient triethylamine to form the amine salt of the disulfo-dibenzothiophene-dioxide and in a chlorobenzene as reaction medium until 3-(3',5'-dichloro-)triazinylamino-7-amino-2,8-disulfo-dibenzothiophene-dioxide is formed; heating the resulting 3-(3',5'-dichloro-)triazinylamino-7-amino-2,8-disulfo-dibenzothiophene-dioxide in the same reaction medium with substantially two molecular proportions of morpholine in the presence of triethylamine until 3-(3',5'-dimorpholinyl-)triazinylamino-7-amino-2,8-disulfo-dibenzothiophene-dioxide is formed; and heating the resulting 3-(3',5'-dimorpholinyl-)triazinylamino-7-amino-2,8-disulfo-dibenzothiophene-dioxide with substantially one molecular proportion of the acid chloride of a methoxy-benzoic acid in a chlorobenzene reaction medium containing triethylamine.

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# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 2,845,423

Norman L. Anderson

July 29, 1958

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 65, for "X-" in the upper left-hand corner of the formula (the 8-position of the dibenzothiophene dioxide radical), read -- Y- --; column 7, lines 53 and 57, for the claim reference numeral "10", in each occurrence, read -- 7 --; line 63, for "-3-(3',5,-di-carboxylphenyl-" read -- -3-(3',5'-di-carboxyphenyl- --.

Signed and sealed this 4th day of November 1958.

(SEAL)

**Attest:**

KARL H. AXLINE

**Attesting Officer**

**ROBERT C. WATSON**
**Commissioner of Patents**