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3,410,847

4-(5,6-DI-SUBSTITUTED OXY BENZOTRIAZOLE-2-YL) STILBENESULFONIC ACID BRIGHTENERS AND METHODS FOR MAKING SAME

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No Drawing. Filed Feb. 9, 1965, Ser. No. 431,442
6 Claims. (Cl. 260-240)

This invention relates to new, useful and outstanding stilbene triazole compounds, and in particular, di-substituted oxy benzotriazolyl stilbenesulfonic acid compounds with their outstanding optical brighteners or whitening agents.

It is well known that textiles tend to develop a yellowish shade on aging which cannot be removed by ordinary methods of bleaching or washing. The heretofore used methods of "bluing" white materials with blue pigments or fugitive blue dyestuffs have become quite obsolete in modern laundry practice and have been largely superseded by methods employing fluorescent optical bleaching agents or brighteners as additives to the soap or detergent in the washing bath. These brightening agents are usually conveniently supplied commercially in the form of intimate admixtures with the soap or detergent in bars, flakes, powders, etc. The fluorescent optical bleaching agents perform their desired function by virtue of their characteristic absorption of ultra-violet radiations and subsequent conversion of this energy to light energy within the visible spectrum. This converted and emitted light energy tends to neutralize any yellowness of the material and thereby increase the apparent whiteness thereof.

Since the predominant textile material in conventional laundry practice is cotton, brightening agents for use in laundering operations in conjunction with the conventional detergents are generally characterized by the presence of ionic or water-solubilizing groups which are preferably sulfonic acid groups in order to obtain the necessary affinity for the cotton material. Such compounds may or may not also be effective with other synthetic textile fibers such as nylon and acetate rayon and the like, and while this is obviously desirable in many instances, such ionic brighteners which are useful with cotton may only be partially satisfactory with nylon and the like.

Compounds which have been suggested and employed as fluorescent brightening agents include the following:

(I) Acylated derivatives of 4,4'-diamino-stilbene-2,2'-disulfonic acid.

(II) Triazolyl derivatives of diamino stilbene disulfonic acid.

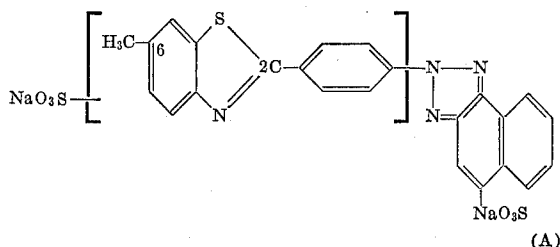
(III) Acylated derivatives of diamino dibenzothio-phenoxide, etc.

Compounds of Type I are disclosed in U.S. 2,581,059 and 2,643,198 and in British Patent 584,484.

Compounds of Type II are disclosed in U.S. Patent 2,618,636 and in application Ser. No. 381,856 published May 11, 1954 by the A.P.C.

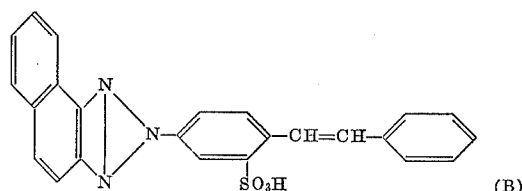
Compounds of Type III are exemplified in U.S. Patents 2,563,493 and 2,563,975.

In addition to the types mentioned above, other triazolyl compounds have been suggested. Thus U.S. Patent 2,713,054 discloses monotriazoles of the type:

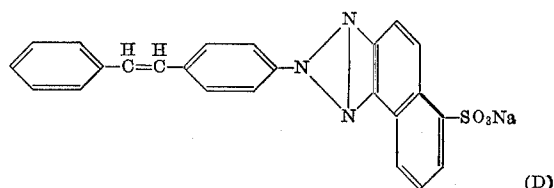
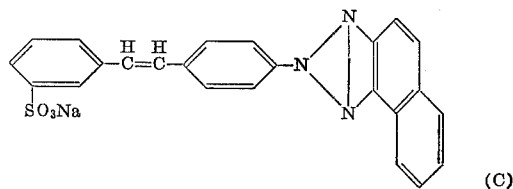


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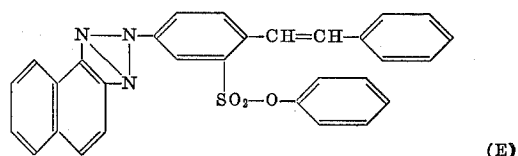
In addition to compounds of the above type, there have also been patented stilbenenaphthotriazoles containing ionic groups such as are shown in U.S. Patent 2,784,183 and a representative compound therein is the following:



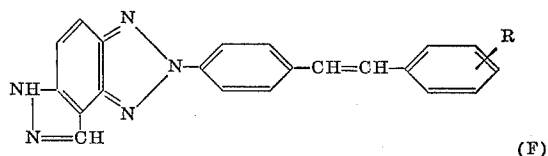
In U.S. Patent 2,993,892, there are disclosed ionic stilbenenaphthotriazoles of the following formulas:



There are numerous other disclosures relating to stilbenemonotriazoles as well as other stilbene compounds which are useful as brightening agents for fibers other than cotton, particularly, and which compounds do not necessarily contain ionic groupings. Examples of such patents are U.S. Patent 2,784,184, which describes compounds of the type:



and U.S. Patent 3,062,814, which exemplifies compounds of the type:



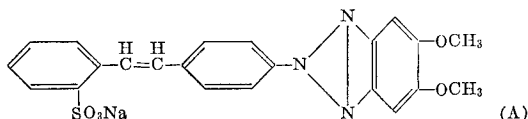
in which R is selected from the group consisting of hydrogen, chloro, bromo and lower alkyl.

As evidenced by the above described prior art, there is tremendous activity in the area of brightening agents suitable for use in laundering operations for brightening textile materials and particularly cotton textiles. Such activity is primarily based upon the need and desire as well as the constant striving for more efficient compounds which can do a better job of brightening at a lower cost. In addition, since normal laundering practice involves the use of chlorine bleaches, the need for brighteners which are stable in the presence of such bleaching agents becomes of paramount concern.

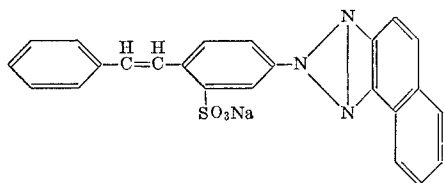
It has now been discovered that a class of benzotriazolyl stilbenesulfonic acid compounds containing two substituted oxy groups in a critical position in the molecule and at least one sulfonic acid group are not only

outstanding brighteners from both an esthetic point of view, but also from an economic point of view, and in addition, such compounds are extremely stable in the presence of chlorine bleaching agents.

Certain of these di-substituted oxy benzotriazole brighteners have unique brightness strength on cotton from non-ionic detergent baths in the presence of hypochlorite. For instance, only half as much of



is required to produce the same whitening effect on cotton from commercial "Ad" and "All," both non-ionic detergents, in the presence of sodium hypochlorite as of the most widely used commercial product:



It is thus in the presence of non-ionic detergents used in conjunction with hypochlorite bleach that the most outstanding advantages in performance of the new compounds occur. In fact there is no commercial brightener which has whitening effect in this application equal to the above described compound A at equal concentration. Further, there is no brightener described in all the prior art compounds which has whitening effect in this application equal to brightener A. Thus there is no non-sulfonated, mono-sulfonated, di-sulfonated, are tri-sulfonated brightener from all the mono-triazole, di-triazole, bis-benzoxazole, bis-benzimidazole, stilbene-amine-cyanuric amide, stilbene amine-benzoylamide, pyrazoline, coumarin, etc. classes which has anywhere near equal whitening power from non-ionic detergents with sodium hypochlorite on cotton.

It is therefore an object of the present invention to provide new and useful brightening agents, and particularly brightening agents of the stilbenetriazole type.

It is another object of the present invention to provide outstanding brighteners which are particularly adaptable for use in conventional laundering operations for brightening textile materials, and more particularly cotton textiles.

It is still another object of this invention to provide new brightening agents which are characterized as di-substituted oxy benzotriazolyl stilbenesulfonic acids which are particularly effective in conventional laundering operations in conjunction with detergent compositions, and which brightening agents are outstandingly stable in the presence of chlorine bleaching compounds.

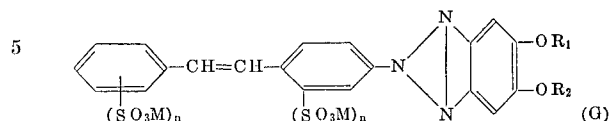
It is still another further object of this invention to provide new and outstanding detergent compositions containing the novel brightening agents herein disclosed.

It is still another further object of this invention to provide processes for organic materials, and particularly cotton textile materials employing the novel and outstanding brightening agents disclosed in this application.

It is still a further object of this invention to provide improved brightened organic material, and particularly cotton textile materials, by incorporation therewith the new and outstanding brightening agents of the present invention.

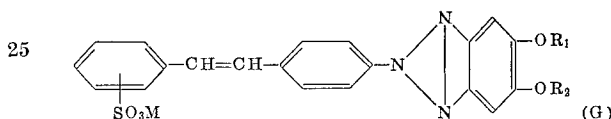
Other objects will appear hereinafter as the description proceeds.

The new brightening compounds of this invention have the following general formula:

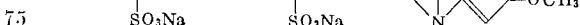
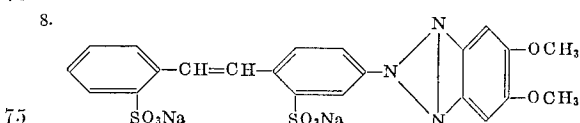
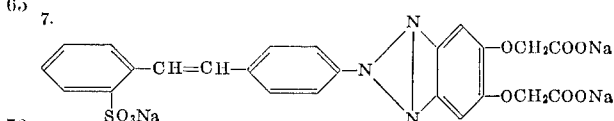
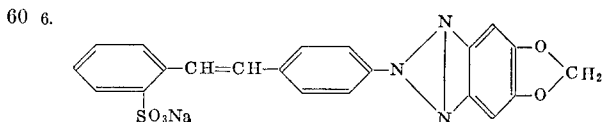
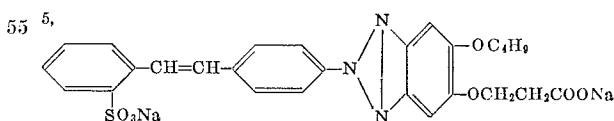
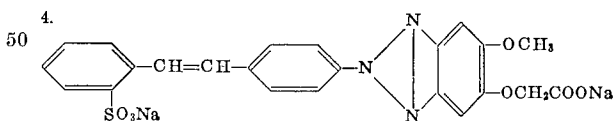
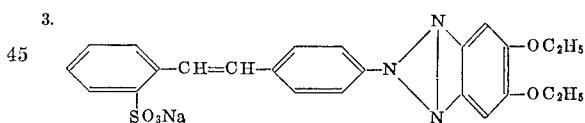
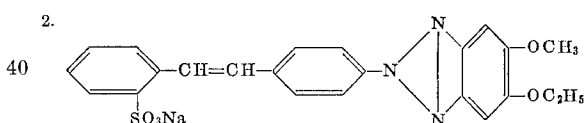
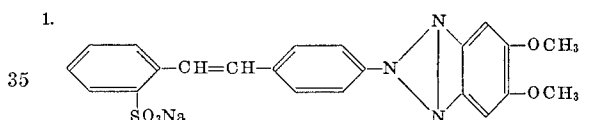


wherein R_1 and R_2 are independently lower alkyl, and preferably alkyl of 1 to 4 carbon atoms, carboxy lower alkyl and preferably carboxy methyl, or together R_1 and R_2 may be methylene; m and n have the values 0 or 1, and the sum of m and n is 1 or 2; M is hydrogen or a salt-forming cation, preferably an alkali metal (sodium, potassium or lithium and the like), ammonium, or substituent ammonium such as an amine and the like.

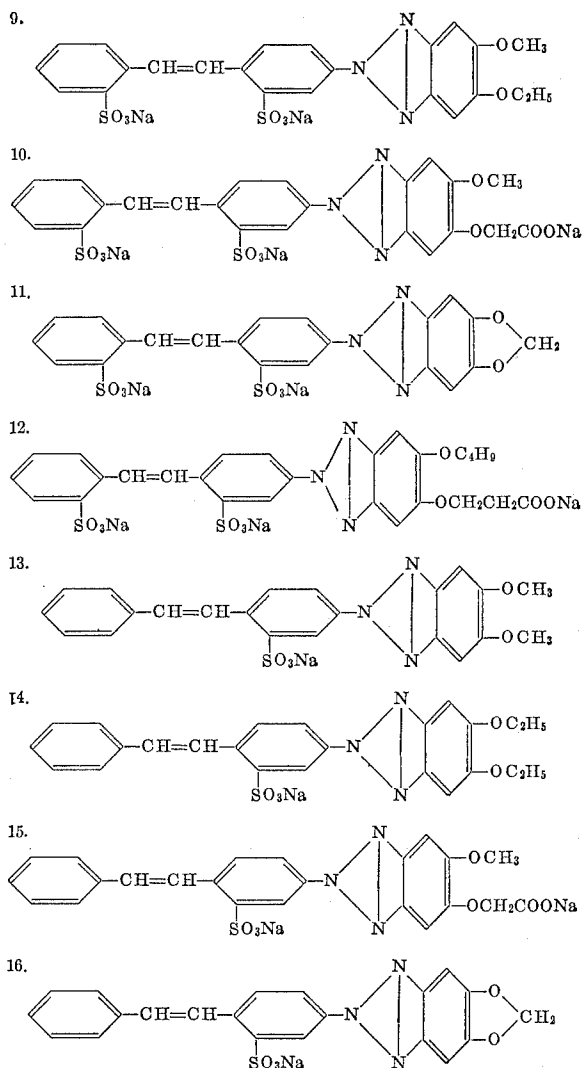
The preferred compounds are those containing one sulfo group, and this preferably in the benzene ring of the stilbene moiety remote from the triazole ring. Thus, the most preferred compounds are those having the following formula:



wherein R_1 , R_2 and M are as defined above. Some of the specific compounds are as follows:



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The novel compounds of this invention are characterized by excellent fiber substantivity, particularly for cellulosic and similar hydrophilic fibers, and esthetically desirable hue, an outstanding apparent whiteness, excellent resistance to bleaching agents such as chlorine, and extremely excellent light fastness characteristics. While the compounds are most preferred for use in detergent systems for application to the textile during laundering operations, the compounds may, nevertheless, be employed using techniques for incorporation into organic material. Thus, the compounds may be added to spinning solutions of cellulose acetate, they may be used to impregnate paper, they may be incorporated into paper by addition to the pulp in the beater stage or at any point prior to the drying of the paper, and they may, in general, be added to waxes, gums, resins and the like to effect a whitening thereof.

The compounds of this invention are prepared generally in the conventional manner known to the art which involves coupling a diazotized sulfo stilbene to the selected substituted dioxyaniline compound and thereafter oxidizing the resultant azoamino compound to the corresponding triazole. The procedure for the latter oxidation may vary depending upon the choice of the oxidizing agent. For example, when one uses ammoniacal (or other organic base, e.g., pyridine, etc.) copper sulfate as the oxidizing agent, the resultant by-products of such reagent may be removed by adjustment of the pH of the solution, i.e., the reduction products of the oxidizing agents may be solubilized by making the solution more acidic, so that the by-products are removed in the filtrate by a filtration

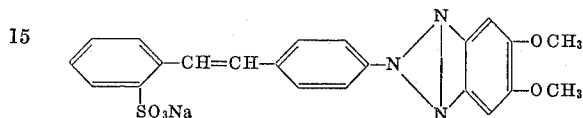
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step. Alternatively, the by-products may be removed in the filtrate by making the reaction medium alkaline with ammonia (pH 11) prior to filtration. While it is preferred to use metallic (ic-ous oxidizing agents such as copper sulfate, ferric chloride, ferric NH_4SO_4 , etc., one may also employ hydrogen peroxide, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CaCl_2 , Na perborate, oxygen, etc.

The following examples will serve to illustrate the present invention without being deemed limitative thereof. Parts are by weight unless otherwise indicated.

Example 1

Preparation of:



24 g. of 4'-amino-2-stilbenesulfonic acid (0.087 mole). 500 ml. water and 8.6 cc. NaOH (40% wt./vol.) are mixed at 40° C. to give a pH of 8.5. 17.4 cc. NaNO_2 (38% aqueous solution) are then added slowly. This is then poured slowly over a 1 hour period into a mixture at 5–10° C. of 240 cc. water, 1.4 cc. NaNO_2 (38% aqueous solution) and 27 ml. HCl in an ice bath. After stirring 2 hrs. at 5–10° C., excess nitrite is destroyed with 7 mls. sulfamic acid (10% aqueous solution). 14.7 g. of vacuum distilled 3,4-dimethoxyaniline is dissolved in 100 mls. acetic acid and added slowly at 5–10° C., stirred 1 hr., then made faintly Congo blue by addition of 48 g. sodium acetate. After stirring over night it is made Congo neutral by the addition of sodium acetate, then filtered, washed with 500 mls. 3% HCl, 500 mls. water and 200 cc. isopropanol to give 72 g. of product.

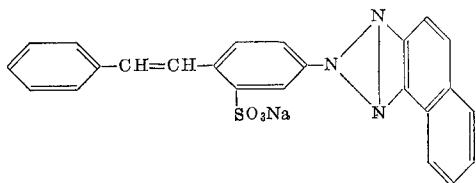
36 g. of this product, 200 ml. picoline, 100 ml. water and 20 ml. ammonium hydroxide (concentrated) are mixed and heated to solution at 95° C. To this is added 27.25 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 50 ml. water. The mixture is stirred 2½ hrs. at 95° C., cooled to 85° C. and treated with 75 ml. sodium sulfide (20% wt./vol.). The material is filtered at 95° C. and washed with a 3% picoline-in-water solution. The pH is adjusted to 9 by addition of aqueous sodium carbonate solution (20%), steam distilled, cooled to 75° C., then filtered, washed with 100 ml. warm water and air dried at 80° C. The final product has a $K_{\text{max}}=133$ at 358 m μ .

Example 2

To demonstrate the outstanding brightening action of the compound of Example 1, it is compared in a standard laundering operation with detergent with other brighteners, all at equivalent K value concentrations at the maximum absorption points of each of the compounds. A K value=80 is selected as the comparison point since each of the compounds tested has a K value at the maximum absorption in excess of this value and the purpose for comparing the compounds at equivalent K values is to obviate the possibility that the compounds may not be in their most absolutely pure state which would necessarily be a requirement for a meaningful comparison on a weight basis. The general procedure for testing the compounds is as follows. 50 mg. of brightener compound is dissolved in 10 ml. of dimethylformamide and then drowned into 1 liter of water. A proper aliquot is then taken to give the desired brightener concentration on a percentage basis at a K=80 concentration. To a laundrometer bath containing 1 g. of "All" (a nonionic ethylene oxide-phenolic condensate) in 500 ml. of water at 120° F., there is added the selected amount of brightener and 10 ml. of sodium hypochlorite solution containing 0.2% available chlorine. After standing 1 minute, a 5 g. swatch of cotton cloth is immersed in the bath and the laundrometer containing the slurry of detergent and cotton cloth is agitated for 20 minutes at 120° F., after which the cloth is removed, rinsed in clear water, and dried.

Following the above procedure and employing the compound of Example 1 at a brightener concentration of 0.0064% based on the weight of the 5 g. swatch of cotton, the resultant laundered, dried cloth has a brightness value of 76.

Following the identical procedure but using a concentration of 0.0096% based on the weight of the fiber of $K=80$ material of the compound having the following formula:



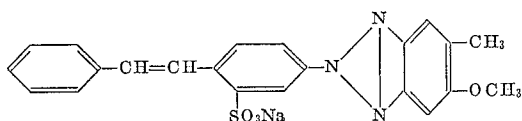
yields a product with a brightness value of 66. Thus, it is clearly seen that even though 50% more of the second brightener is used, a significantly lower brightness is obtained than with the brightener of Example 1.

Example 3

Example 2 is repeated except that in place of "All," the detergent employed is "Alfionol," a biodegradable nonionic compound based on the reaction of ethylene oxide and an aliphatic alcohol. Again, with both brighteners (that is, of Example 2), at equal K values of 80, the brightener of Example 1 gave a reading of 68 when used at a concentration of 0.0032% based on the weight of the fiber whereas the commercial brightener (i.e., the sulfostilbylnaphthotriazole shown in Example 2) gives a brightness value of 59 at a concentration of 0.0064% (based on the weight of the fiber). Again, it is clearly apparent that with only half as much of the brightener of Example 1 as compared with the commercial brightener, a distinctly higher brightness value is obtained.

Example 4

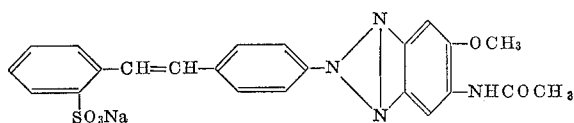
Example 3 is repeated except that the compound of Example 1 is used as a concentration of 0.004% on the weight of the fiber (again, at a $K=80$) and the resultant swatch has a brightness of 65. In place of the commercial brightener used in Example 3, there is used at the same concentration, i.e., 0.0064%, a compound having the formula:



and the resultant swatch has a brightness value of 65. This demonstrates that the compound of Example 1 is an effective in brightness characteristics at a concentration 50% less than is necessary using a somewhat similarly related compound which is disclosed in U.S. Patent 2,713,057, and specifically covered by claim 2 of this patent.

Example 5

Example 2 is again repeated employing the compound of Example 1 at the same concentration used in Example 2 and in place of the commercial brightener comparison of Example 2, there is used 0.0064% based on the weight of the fiber of the compound of the formula:

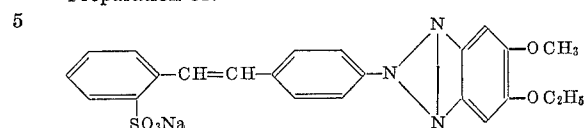


which compound is described in Example 4 of U.S. Patent 2,713,057. The "All" of Example 2 is replaced by "Tide" (anionic alkyl aryl sulfonate). The swatch laundered with the compound of Example 1 has a brightness of 87 whereas the swatch laundered with the com-

pound of Example 4 of U.S. Patent 2,713,057 has a value of 32.

Example 6

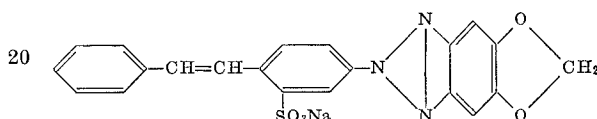
Preparation of:



This compound is prepared in the same manner as Example 1 with the exception that the 3,4-dimethoxyaniline is replaced by 16 g. of 3-methoxy-4-ethoxyaniline. When applied to cotton in the manner of Example 1 the results are commensurate.

Example 7

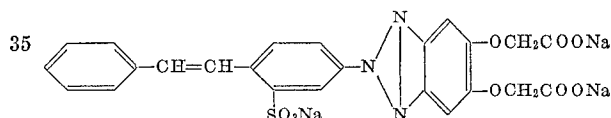
Preparation of:



This compound is prepared in the manner of Example 1 with the exceptions that the 4'-amino-2-stilbenesulfonic acid is replaced by 4-amino-2-stilbenesulfonic acid and the 3,4-dimethoxyaniline is replaced by 19 g. 3,4-methylenedioxyaniline. When applied in the manner of Example 1 commensurate results are obtained. This compound has a $K_{max}=138.8$ at 358 $m\mu$.

Example 8

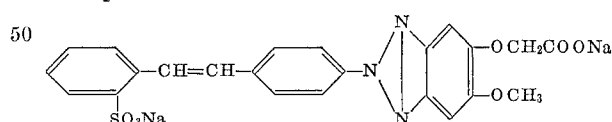
Preparation of:



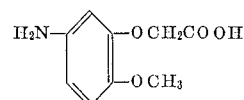
This compound is prepared in the manner of Example 1 with the exceptions that the 4'-amino-2-stilbenesulfonic acid is replaced by 4-amino-2-stilbenesulfonic acid and the 3,4-dimethoxyaniline is replaced by 21 g. 1,2-(4-aminophenylene)bisoxyacetic acid. When applied in the manner of Example 1, excellent results are obtained. This compound has a $K_{max}=76$ at 355 $m\mu$.

Example 9

Preparation of:



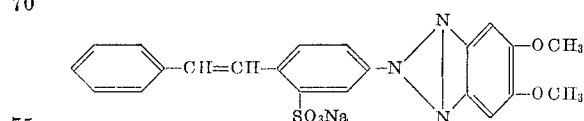
The intermediate of the formula:



is produced in known manner by treating an equimolar amount of 2-methoxy-5-nitrophenol with chloracetic acid and reducing. The brightener is then produced in the manner of Example 1 with the exception that the 3,4-dimethoxyaniline is replaced by 14.9 g. of 3-amino-6-methoxyphenoxyacetic acid. When applied in the manner of Example 1, commensurate results are obtained.

Example 10

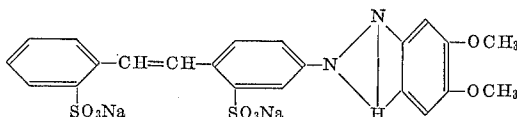
Preparation of:



This compound is prepared similarly as in Example 1 with the exception that the 4'-amino-2-stilbenesulfonic acid is replaced by 4-amino-2-stilbenesulfonic acid. When applied to cotton in the manner of Example 1 the results are excellent.

Example 11

Preparation of:



This compound is also prepared in the manner of Example 1 with the exception that the 4'-amino-2-stilbenesulfonic acid is replaced by 30.8 g. of 4-amino-2,2'-stilbenedisulfonic acid. When applied to cotton in the manner of Example 1, excellent results are obtained.

Example 12

Example 6 is repeated except that 4'-amino-2-stilbenesulfonic acid is replaced by 4-amino-2-stilbenesulfonic acid. Excellent results are obtained when applied to cotton following the procedure of Example 1.

Example 13

Example 11 is repeated except that the 3,4-dimethoxyaniline is replaced by 3-methoxy-4-ethoxyaniline. Excellent results are obtained when applied to cotton by the procedure of Example 1.

Example 14

The preceding example is further repeated except that in place of the aniline thereof, an equivalent weight of 3,4-methylene dioxyaniline is employed.

Example 15

The preceding example is further repeated except that the aniline compound used is an equivalent weight of 1,2-(4-aminophenylene)bisoxy acetic acid.

Example 16

The procedure of Example 9, is repeated except that in place of the stilbenesulfonic acid of that example, an equivalent amount of 4-amino-2,2'-stilbenedisulfonic acid is used.

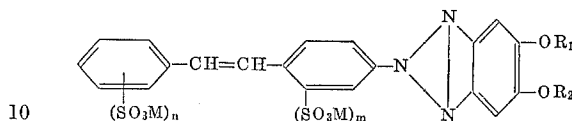
While several of the above examples demonstrate the use of the compounds of this invention for brightening of cotton material, it is clear that such compounds may be used generally for brightening cellulosic materials and cellulose derivative materials as well as other textile products also. The compounds may further be employed with any organic substrate to improve the brightness thereof. The amount of brightener to be used is not critical, and may be varied within wide limits. As little as 0.001% has been found to give effective results with the upper limit being governed solely by practical considerations of compatibility and price. In general, it has been found that no more than 5% by weight based on the weight of organic material is necessary under the most adverse conditions. When the compounds of this invention are used in conjunction with detergent products, it is advantageous to employ the brighteners in amounts ranging from about 0.1% to about 3% by weight thereof based on the weight of the detergent material.

Other variations in and modifications of the described

processes which will be obvious to those skilled in the art can be made in this invention without departing from the scope or spirit thereof.

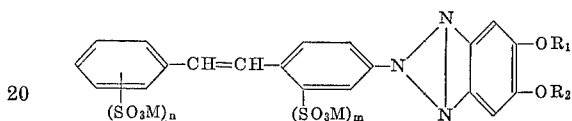
We claim:

1. A compound of the free acid form of the formula:



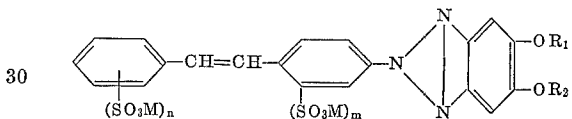
wherein R_1 and R_2 are carboxy lower alkyl; m and n have values from 0 to 1 and the sum of m and n is at least 1; M is a member selected from the group consisting of hydrogen and a salt-forming cation.

2. A compound in the free acid form of the formula:



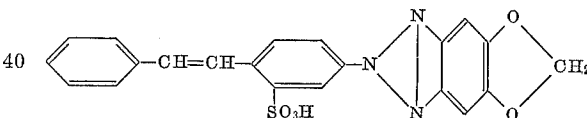
wherein R_1 is lower alkyl and R_2 is carboxy lower alkyl; m and n have values from 0 to 1 and the sum of m and n is at least 1; M is a member selected from the group consisting of hydrogen and a salt-forming cation.

3. A compound in the free acid form of the formula:

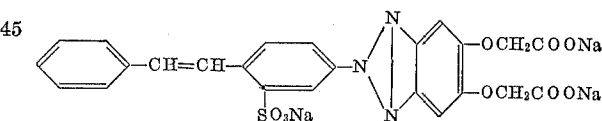


wherein R_1 and R_2 together are methylene; m and n have values from 0 to 1 and the sum of m and n is at least 1; M is a member selected from the group consisting of hydrogen and a salt-forming cation.

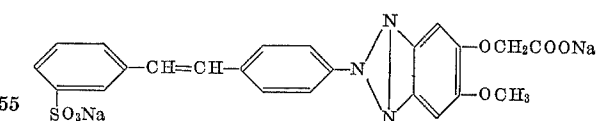
4. A compound of the formula:



5. A compound of the formula:



6. A compound of the formula:



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194,849	1/1958	Austria.
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65 JOHN D. RANDOLPH, *Primary Examiner.*