

[54] **SUBSTITUTED BIS-TRIAZINYLAMINO
STILBENE COMPOUNDS AND
COMPOSITIONS THEREOF**

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Related U.S. Application Data

[62] Division of Ser. No. 561,330, June 29, 1966, Pat. No.
3,546,218.

[52] U.S. Cl. **252/8.75**, 117/33.5 T, 252/524,
252/543, 260/240 B

[51] Int. Cl. **D06m 13/46**, C11d 3/42

[58] Field of Search.....252/8.75, 137, 152, 524, 543;
260/240 B; 117/33.5 T

[56]

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Attorney—Karl F. Jorda

[57]

ABSTRACT

Described herein are certain bis-triazinylamino stilbene type optical brighteners and their use in treating textiles and paper. The brighteners are particularly useful in conjunction with fabric softeners and in laundry detergents.

5 Claims, No Drawings

SUBSTITUTED BIS-TRIAZINYLAMINO STILBENE COMPOUNDS AND COMPOSITIONS THEREOF

This application is a division of application Ser. No. 561,330, filed June 29, 1966, now U.S. Pat. No. 3,546,218.

This invention relates to optical brightening agents and to compositions containing these new brightening agents.

The new compounds of this invention are optical brighteners of the bis-triazinylamino stilbene type. This class of compounds is finding rapidly increasing application in the textile, paper, detergent and other laundry product industries. The increased brightness which results from incorporating relatively minor amounts of such brighteners into paper, textiles, detergents and other laundry products greatly enhances the appearance and consequently, the marketable value of the finished products.

Optical brighteners improve the appearance of these products by neutralizing the familiar yellow tinge that is usually apparent in untreated products of the type mentioned. This yellow tinge is caused by the absorption of short wavelength light. Optical brighteners neutralize the yellow tinge resulting therefrom by absorbing invisible ultraviolet radiation and emitting the energy thereof in the form of visible blue to blue-violet light. The fluorescent properties of the optical brighteners of this invention are strikingly apparent under ultraviolet light in darkroom conditions.

One area in which the full benefit of previously available optical brighteners has not been obtainable is in the treatment of textile fabrics, either during mill manufacturing operations or in laundries, where fabric softeners have been applied to the fabrics.

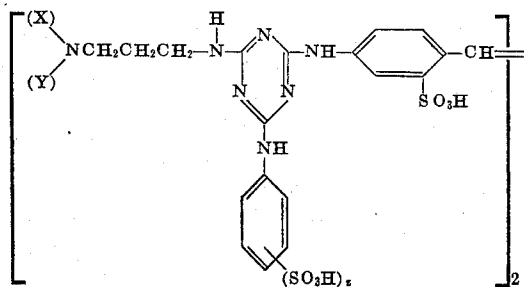
Whether the fabric softener is applied in the mill, after, or during the application of the brightener, or as a part of the finish cycle during laundering, i.e., after washing, the use of softeners has had a masking or quenching effect on the brighteners of the prior art.

This quenching effect is noted by the decrease in brightener fluorescence caused by a cationic softener. Thus, for example, a fabric washed in detergent containing prior art optical brighteners will achieve a certain fluorescence level. However, if the washed fabric is then treated with a cationic softener the fluorescence level will drop so much that practically the entire brightening affect is lost; even though no brightener is removed from the fabric during the application of the softener.

Thus the housewife may launder her family clothes with a relatively expensive detergent in order to achieve a brighter wash by virtue of the optical brightener contained in the detergent, and then in finishing the wash by the routine use of a cationic fabric softener, almost completely destroy the bright-white affect of the brightener for which she paid a premium price in purchasing her detergent.

The new optical brightening agents which I have discovered, besides being very useful for the usual applications of optical brighteners, surprisingly maintain their brightening affect on fabrics which are treated with cationic softeners either after, or concurrently, with the application of the brightener agent.

The new optical brightener compounds I have discovered have the following formula:



wherein
z has a value of 0-1, and

X and Y each independently are: $(CH_2)_a-(OH)_b-(H)_c-(NH_2)_d$

and a has a value of 1-3,

b has a value of 0-1,

c has a value of 0-1,

d has a value of 0-1.

or X and Y taken together may form a morpholino ring.

The alkaline salts of the compound of the above formula are also encompassed within the scope of the invention. Typical basic cations forming such salts are alkaline and alkaline earth metal cations, and cations derived from ammonia and mono-, di-, and tri-alkanolamines.

In the case of the preferred compound of this invention, X and Y both are CH_2CH_2OH , and z has a value of 0.

Thus the preferred compound of this invention is: 4,4'-bis-[4-anilino-6-[N-(3-aminopropyl)-diethanolamino]-1,3,5-triazin-2-Y1]-amino-stilbene-2,2'-disulfonic acid.

The brightener compounds of this invention may be applied to substrates comprised of cellulose, polyamides, and proteinaceous fibers, and other substrates, from dilute aqueous solutions.

The compounds of this invention are generally employed in their salt form, however, the acid form may be isolated if desired.

The compounds which I have discovered are particularly advantageous not only because of the high degree of brightness which they impart to fabrics, but because the fabrics substantially maintain their bright appearance even after treatment with cationic fabric softeners. As has been mentioned before, the brighteners currently on the market are masked or quenched when the fabrics containing them are subsequently or simultaneously treated with cationic softeners.

The application of the brighteners of this invention to fabrics can be effected by conventional methods well known to the art. The fabric can be padded with the brightener during the manufacture at the mill, or in the more familiar manner, the brightener may be incorporated into detergent compositions and thus be applied to the fabric during the laundry operation. Furthermore, the brighteners of this invention can be incorporated into cationic softener compositions and thus applied to the fabric at the same time the softener is applied. Generally, an aqueous solution of from about 0.05 to about 2 percent of brightener compound is employed.

Typical cationic softeners on the market are dialkyl dimethyl ammonium chloride solutions in which the alkyl groups generally are 12-18 carbon atoms in length. The alkyl groups in some formulations may be ethoxylated. 1-Methyl-1-alkylamido-ethyl-2-alkyl-imidazolinium methosulfate type softeners are representative of other cationic softeners also available.

The compounds of this invention can be combined with commercially available detergents. Typical detergent formulations comprise:

Compound	Amount by Weight
Linear Alkylbenzene Sulfonate	20%
Sodium Tripolyphosphate	50%
Sodium Metasilicate	5%
Sodium Sulfate	15%
Carboxymethyl-cellulose	0.8%
Moisture, etc.	9.2%

The compounds of this invention and their starting materials can be prepared readily by conventional procedures familiar to those skilled in the art.

Thus in one manner of preparation, 2 moles of cyanuric chloride are first reacted with 1 mole of diaminostilbenedisulfonic acid and the resulting intermediate in turn is reacted with 2 moles of aniline, or metanilic or sulfanilic acid, and then with 2 moles of the appropriate amine.

The preparation can also be accomplished by the reaction of the dichlorodianilino compound 4,4'-bis-[(6-anilino-4-chloro-1,3,5-triazin-2-Y1)-amino]-stilbene-2,2-disulfonic acid with the appropriate amine.

The following examples describing certain representative embodiments of this invention will serve to further illustrate the nature of the invention. It is to be understood that the examples are merely illustrative and intended to enable those skilled in the art to practice the invention in all of the embodiments flowing therefrom and do not in anyway limit the scope of the invention defined in the claims.

EXAMPLE 1

A slurry of 150 grams of 4,4'-bis-[(6-anilino-4-chloro-1,3,5-triazin-2-Yl)-amino]-stilbene-2,2'-disulfonic acid in 1,200 ml of water was prepared. To this slurry 71 grams of N-(3-aminopropyl)-diethanolamine are added with stirring and the mixture heated to 90° C. The pH decreased to 9.5 - 10 and thereafter was maintained at 10.5 - 11 by the addition of 16 grams of 50 percent sodium hydroxide. The reaction mixture was then cooled to room temperature. The mother liquor was decanted, and 1,200 ml of water and 300 grams sodium chloride added. The solids were ground in a wet slurry with 400 ml of 25 percent sodium chloride solution and acidified to pH 2 with 37 percent hydrochloric acid. The mixture was re-filtered, washed free of mineral acid and dried in vacuo at 60° C. Yield 120 grams of a light yellow solid. The resultant product is 4,4'-bis-[(4-anilino-6-[N-(3-aminopropyl)-diethanolamino]-1,3,5-triazin-2-Yl)-amino]-stilbene-2,2'-disulfonic acid.

EXAMPLE 2

After decanting mother liquors in Example 1 above, 60 grams of the semi-solid mass were dissolved in 240 ml of water and 150 ml of isopropyl alcohol at 50° C. At 45°-50° C the mixture was added dropwise to 3.5 liters of rapidly agitated concentrated isopropyl alcohol (20°-25° C). The mixture was filtered, washed with 1 liter conc. isopropyl alcohol and sucked dry. It was then dried in vacuo at 30° C initially, then at 60° C. Yield: 115 grams of a very light yellow powder.

EXAMPLE 3

276 grams of water and 300 grams of ice were placed in a flask and 70 grams of cyanuric chloride and 66 grams of sulfanilic acid added. The mixture was stirred for 1 hour at 0° C. After 3 hours a dropwise addition of 269 grams of 15 percent sodium carbonate was accomplished, bringing the pH to 7. At the end of the addition, 1,052 grams of 6.46 percent diamino-stilbenedisulfonic acid/ Na_2CO_3 solution were added all at once. The mixture was heated to 70° C and a pH 8 - 8.5 maintained. Thereafter the temperature was raised to 90 - 95° C, and 400 ml of hot water and 125 grams sodium chloride added; followed by seeding. Then the mixture was air cooled to 45° C and filtered.

All of the wet filter cake is mixed with 72.2 grams N-(3-aminopropyl) diethanolamine and 75.2 grams triethanolamine and a slurry is obtained in one-half hour at room temperature. The temperature is raised to 90° - 95° C and the mixture agitated at this temperature for 1 hour, then cooled to 55° C, and 96.4 grams of ethyl cellosolve added with 100 ml water. Thereafter the mixture is filtered through a filter aid. The resultant product is 4,4'-bis-[(4-sulfoanilino-6-[N-(3-aminopropyl)-diethanolamino]-1,3,5-triazin-2-Yl)-amino]-stilbene-2,2'-disulfonic acid triethanol amine salt solution.

EXAMPLE 4

The procedure of Example 1 is repeated but the N-(3-aminopropyl)-diethanolamine is replaced with N,N-dimethyl-1,3-propanediamine. The resultant product is 4,4'-bis-[(4-anilino-6-[N,N-dimethyl-1,3-propanediamino]-1,3,5-triazin-2-Yl)-amino]-stilbene-2,2'-disulfonic acid.

EXAMPLE 5

The procedure of Example 1 is repeated but the N-(3-aminopropyl)-diethanolamine is replaced with 4-(3-

aminopropyl)morpholine. The resultant product is 4,4'-bis-[(4-anilino-6-[4-(3-aminopropyl)morpholino]-1,3,5-triazin-2-Yl)-amino]-stilbene-2,2'-disulfonic acid.

EXAMPLE 6

The procedure of Example 1 is repeated but the N-(3-aminopropyl)-diethanolamine is replaced with (3,3'-diamino-N-methyldipropylamine). The resultant product is 4,4'-bis-[(4-anilino-6-[(3,3'-diamino-N-methyldipropylamino)-1,3,5-triazin-2-Yl)-amino]-stilbene-2,2'-disulfonic acid.

EXAMPLE 7

Softener formulations were made up using the brighteners of Example 1, 4, 5, and 6. Each formulation was comprised of:

5 ml triethanolamine

10 ml methyl cellosolve

31 ml water

4 gms distearyl-dimethyl ammonium chloride

160 mg of a brightener compound of this invention. The pH of each formulation was adjusted to 5 with acetic acid.

A. 20 Gram samples of unmercerized cotton fabric were washed in a Terg-O-Tometer washer with 600 ml of water for 10 minutes at 130° F using 1 gram of unbrightened anionic detergent. The fabric was then rinsed for 2 minutes in 600 ml of water.

B. Thereafter the fabrics were rinsed for 10 minutes in the Terg-O-Tometer at 100° F with 0.6 grams of the above softener formulation in 600 ml of water. The Lumetron and Hunter Values were then determined.

The following table illustrates the degree of brightness imparted to the fabric by the compounds of this invention in the presence of cationic softeners.

TABLE 1

Softener formulation with compound of example	Fluorescence (Lumetron value)	Hunter Values			
		L	a	b	L+3a-b
1 150	95.7	1.3	-0.4	100.8	
4 151	95.8	1.3	-0.3	100.6	
5 149	95.7	1.1	0.1	98.7	
6 140	95.8	1.3	-0.2	100.3	
Cotton washed in unbrightened detergent (See A) 20	96.5	-0.5	2.1	88.7	

EXAMPLE 8

Additional batches of softener formulations were made with the brightener compounds of Examples 1, 4, 5, and 6 in the same manner as Example 7; the pH was again adjusted to 5, this time with formic acid.

20 Gram samples of unmercerized, prewet, unwashed cotton were then rinsed in the Terg-O-Tometer for 10 minutes at 100° F with 0.6 grams of softener formulation in 600 ml of water.

Thereafter the Lumetron and Hunter values of each sample were determined and are shown in Table 2.

TABLE 2

Softener formulation with compound of example	Flourescence (Lumetron value)	Hunter Values			
		L	a	b	L+3a-b
1 160	95.6	1.8	-1.0	104.0	
4 160	95.8	1.7	-1.1	104.2	
5 134	95.7	1.1	0.0	99.0	
6 142	95.9	1.4	-0.6	101.9	

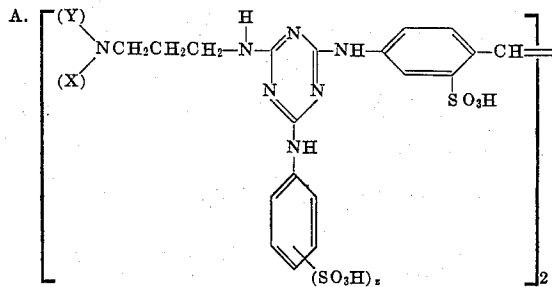
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The foregoing examples clearly demonstrate the high degree of brightness that is imparted to fabric treated with the brighteners of this invention. This high degree of brightness is very surprising when found on fabrics which have been treated with a cationic fabric softener.

While the invention has been explained by detailed description of certain specific embodiments, it is understood that various modifications and substitutions can be made in any of them within the scope of the appended claims which are intended also to include equivalents of such embodiments.

What is claimed is:

1. A composition of matter consisting essentially of an anionic-alkyl benzene sulfonate detergent and an effective amount of a brightener compound of the formula:



wherein z has a value of 0 or 1;

X and Y are each an hydroxyethyl group of taken together form a morpholino ring.

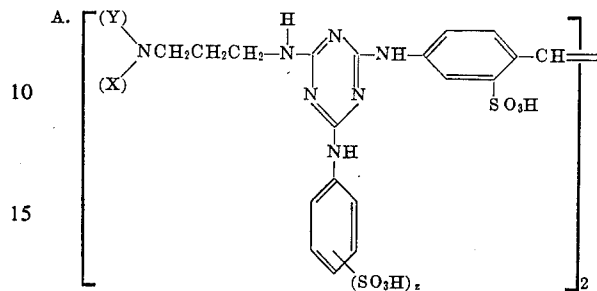
B. alkaline salts of A.

2. A composition of matter as claimed in claim 1 wherein the brightener compound is 4,4'-bis { [4-anilino-6-[N-(3-

6

aminopropyl)-diethanolamino]-1,3,5-triazin-2-Yl]-amino}-stilbene-2,2'-disulfonic acid or an alkaline salt thereof.

3. A composition of matter consisting essentially of a cationic fabric softener and an effective amount of a brightener compound of the formula:



20 wherein z has a value of 0 or 1;

X and Y are each an hydroxyethyl group or taken together form a morpholino ring.

B. alkaline salts of A.

4. A composition of matter as claimed in claim 3 wherein the brightener compound is 4,4'-bis { [4-anilino-6-[N-(3-aminopropyl)-diethanolamino]-1,3,5-triazin-2-Yl]-amino}-stilbene-2,2'-disulfonic acid or an alkaline salt thereof.

5. A composition of matter as claimed in claim 3 wherein the softener is a dialkyl dimethyl ammonium chloride said alkyl group containing 12 to 18 carbon atoms and the brightener compound is 4,4'-bis { [4-anilino-6-[N-(3-aminopropyl)-diethanolamino]-1,3,5-triazin-2-Yl]-amino}-stilbene-2,2'-disulfonic acid or an alkaline salt thereof.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,676,339
DATED : July 11, 1972
INVENTOR(S) : Christopher Johannes Tscharnner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet, Assignee, "Geigy Chemical Corporation" should read -- Ciba-Geigy Corporation --.

Column 3, line 14, "diethanolamino" should read -- diethanolamine --.

Signed and Sealed this

Twenty-first Day of February 1978

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks