United States Patent Office 3,272,805 Patented Sept. 13, 1966

3,272,805

BIS-TRIAZINYLAMINOSTILBENE COMPOUNDS

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No Drawing. Filed July 2, 1964, Ser. No. 380,033
Claims priority, application Switzerland, July 28, 1960, 8,637/60
6 Claims. (Cl. 260—240)

This application is a continuation-in-part of our co-pending application Serial No. 127,098, filed on July 27, 1961, now abandoned.

The present invention concerns new 4,4'-bis-triazinylaminostilbene compounds, processes for the production thereof, their use for the optical brightening of organic material, in particular of cellulose material, agents having a content of such compounds, as well as, as industrial product, the material brightened therewith.

It is well known that white textile material such as men's shirts, ladies' white dresses, underwear, bedlinen and the like are given a whiter appearance by adding to the washing agents used for their cleaning certain amounts of optical brighteners. Due to the fact that modern textile cellulosic materials, in particular cotton materials, are given increasing contents of textile finishes in the form of synthetic resins, for instance as anti-crease finish in dry state, and so-called non-resin finishes which yield so-called cross-linked cellulose as anti-crease finish in wet state, it is necessary to apply larger amounts of the aforesaid optical brighteners to such modern textile materials than had been required in the past in order to achieve at least the same or preferably even "whiter" whitening effect.

However, in applying such increased amounts of brightening agents, particularly those of the bistriazinylstilbene series, to the modern textile materials, the latter adopt an undesirable greenish shade, which becomes more and more pronounced, the more often the material has been washed. Such undesirable effect appears in particular with the modern synthetic so-called "non-soap" detergents as they are used, in particular in powder form in the operation of automatic washing machines, and also, especially, in the preferred washing of laundry at low range temperatures of about 25° to 40° C.

Moreover, the above-mentioned optical brighteners, especially those of the above-mentioned series which bear in their molecules hydroxyalkylamino substituents at the triazinyl radicals, impart to the "non-soap" detergents an undesirable yellowish to greenish aspect, while the public in this country demands the purest, whitest possible aspect of such "non-soap" detergents for use in washing machines.

It is also known that the appearance of textile cellulose materials can be improved by treating them with 4,4'-bis-triazinylaminostilbene-2,2'-disulfonic acids or the water-soluble salts thereof each triazine ring of which contains at least one and preferably two organically substituted

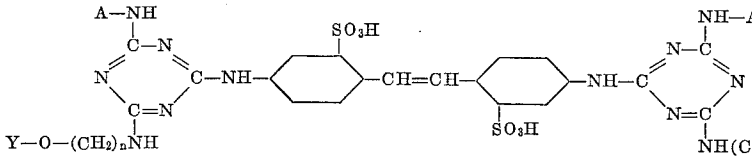
amino groups, i.e. that yellowed organic material, in particular cellulose material, can be given a more pleasant, whiter appearance.

When not used by industrial chemists but, for example, by a housewife, many of the previously known optical brightening agents having a basis of 4,4'-bis-triazinylaminostilbene compounds have great disadvantages. Often the drawing power is insufficient at the relatively low application temperatures preferred in such non-industrial uses. If, on the other hand, products having particular affinity to the fibers are used under the conditions described, spots due to bad levelling power occur on the treated goods. Also, the water-solubility of products having affinity to the fibers is often too slight at low temperatures which also causes spots to appear on the treated materials.

It has now been found that these disadvantages can be eliminated in household use if 4,4'-bis-triazinylaminostilbene compounds according to the invention are used. These compounds are obtained by reacting one mol of 4,4' - bis - (4'',6'' - dihalogen - 1'',3'',5'' - triazinyl - (2'')-amino)-stilbene-2,2'-disulfonic acid or the salts thereof, possibly in the presence of buffer salts, in steps and in any order desired with 2 mols of a primary aromatic amine of the general formula

$$H_2N—(CH_2)_n—O—Y \qquad (I)$$

to form a compound of the general formula



(II)

In Formulae I and II

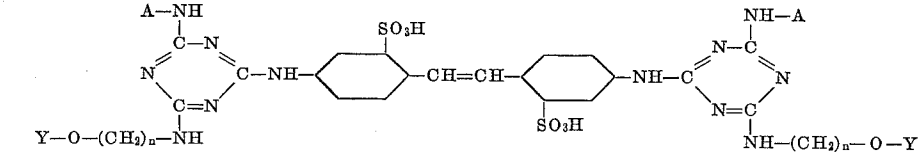
A represents a radical of the benzene series,

Y represents an alkyl radical having at most 2 carbon atoms, or an alkoxyalkyl radical in which the alkoxy group and the alkyl group each have at most 2 carbon atoms, and

n is a positive whole number of 2 to 3.

A is preferably an unsubstituted phenyl radical. However it can also contain substituents, for example the methyl group; the methoxy group; halogens such as, e.g., chlorine.

A particularly valuable class of 4,4'-bis-triazinylaminostilbene compounds according to the invention are those of the formula



wherein

A represents a member selected from the group consisting of phenyl, 3-methylphenyl, 4-methylphenyl, 3-methoxyphenyl, 3-chlorophenyl and 4-chlorophenyl,

Y represents a member selected from the group consisting of methyl, ethyl, methoxyethyl, ethoxyethyl, and

n is one of the integers 2 and 3.

The following are examples of aromatic amines used according to the invention:

aminobenzene, 2-, 3- or 4-methyl-1-aminobenzene, 2,4- or 2,5-dimethyl-1-aminobenzene, 2- or 3-methoxy-1-aminobenzene, 2-, 3- or 4-chloro-1-aminobenzene.

Examples of compounds of Formula I are:

2-methoxyethylamine, 2-ethoxyethylamine,
3-methoxypropylamine, 3-ethoxypropylamine,
2-(β-methoxyethoxy-ethylamine,
2-(β-ethoxyethoxy)-ethylamine, 3-(β-methoxyethoxy)-propylamine or 3-(β-ethoxyethoxy)-propylamine.

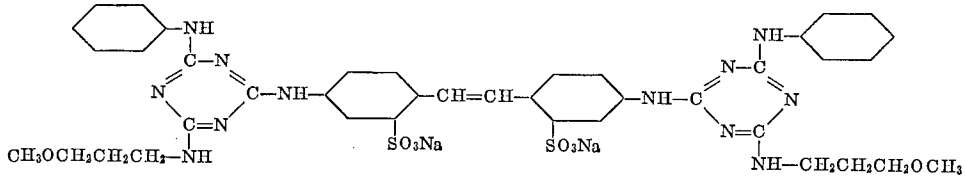
In the first step, the 4,4'-bis-(4'',6''-dihalogen-1'',3'',5''-triazinyl-(2'')-amino)-stilbene-2,2'-disulphonic acid is reacted preferably in the form of its water soluble salts in aqueous solution at 5–60° C. and, in the second step it is reacted at 70–100° C. by known methoxy with the amino compounds used according to the invention, possibly in the presence of alkali metal salts of low fatty acids or of carbonic acid such as, e.g., sodium acetate or sodium carbonate, as agents buffering the mineral acid.

The amines of Formula I used according to the invention are obtained, for example, by reacting esters, obtained from corresponding hydroxy compounds with strong acids such as halogen hydracid, with ammonia under pressure.

The new triazinylstilbene compounds according to the invention ares isolated from the reaction mixture preferably in the form of their alkali metal salts which, after drying, have good water solubility. In aqueous and in neutral or alkaline washing liquors they have good affinity to cellulose material and good levelling power. Compared with the previously known 4,4'-bis-(diaminotriazynylamino)-stilbene-2,2'-disulphonic acids or their water soluble salts, they are distinguished by the quality that, even at relatively low temperatures of about 35 to 60° C., they draw onto the fibre. They are therefore suitable for the household wash. Another advantage is that they improve the appearance of washing agents.

The following examples illustrate the invention. Where not otherwise stated, parts are given therein as parts by weight. The temperatures are in degrees centigrade. The relationship of parts by weight to parts by volume is as that of kilogrammes to litres.

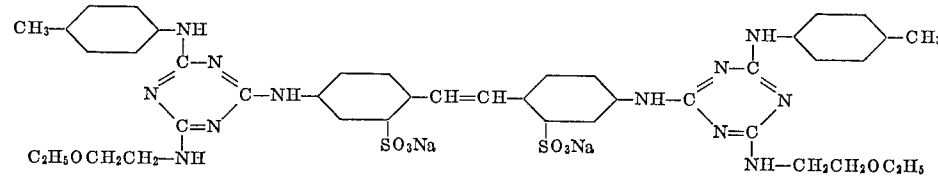
EXAMPLE 1



93 parts of cyanuric chloride are dissolved in 450 parts by volume of acetone. The solution is poured, while stirring, into 2250 parts of ice/water. A solution of 103.5 parts of the sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid and 27 parts of sodium carbonate in 1200 parts of water is poured, within 1 hour while stirring well at 0–5°, into the cyanuric chloride suspension so obtained. A solution of 46.5 parts of aminobenzene in 50 parts by volume of acetone is added dropwise at 5–15° to the yellowish suspension of the disodium salt of 4,4' - bis-[4'',6'' - dichloro - 1'',3'',5'' - triazinyl - (2'')- amino]-stilbene-2,2'-disulphonic acid formed and the acid liberated is neutralised by the simultaneous addition of an aqueous solution of 27 parts of sodium carbonate. The yellowish suspension is then stirred at room temperature (20–25°) until the aminobenzene has completely disappeared. 56 parts of 3-methoxypropylamine are then added and the alkaline mixture is stirred at 85–90° until a sample thereof no longer turns phenolphthaline paper red. The temperature is then raised to 90° and a solution of 20 parts of sodium hydroxide in 30 parts of water is added to the reaction mixture within 1 hour. After stirring for another hour at 90–95°, 175 parts of sodium chloride are added. The reaction product of the formula given above which is formed separates in liquid form as a heavy, yellowish mass and is decanted from the aqueous phase. On cooling, the product solidifies into a solid, yellowish mass which decomposes into a powder on drying. In aqueous solution in daylight, the new brightening agent has a blue to blue-violet fluorescence depending on the degree of dilution and, in spite of its very good water solubility, it has excellent affinity to cellulose fibres. If the product is incorporated into a usual marketed washing agent, then cellulose materials washed therewith are very beautifully optically brightened even when the washing is performed under mild conditions (40°).

If in this example, the 46.5 parts of aminobenzene are replaced by 53.5 parts of 3-methyl-1-aminobenzene or 61.5 parts of 3-methoxy-1-aminobenzene, then brightening agents with similar properties are obtained.

EXAMPLE 2

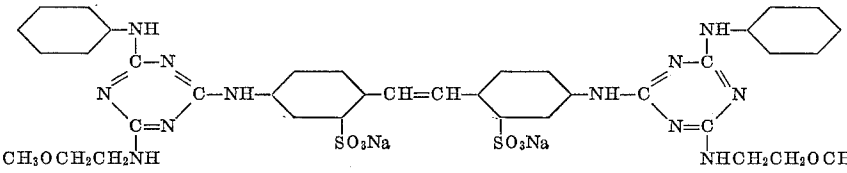


85.2 parts of the sodium salt of 4,4'-bis-[4''-chloro-6''-(p - methylphenylamino) - 1'',3'',5'' - triazinyl - (2'')-amino]-stilbene-2,2'-disulphonic acid (produced under the conditions given in Example 1) are distributed in 2500 parts of water while stirring and, after the addition of 22 parts of 2-ethoxyethylamine, are stirred for 20 minutes at 85–90°. The temperature is then raised to 90–95° and a solution of 8 parts of sodium hydroxide in 20 parts of water is poured in within 2 hours. The reaction mixture is stirred another hour at 90–100° and then 125 parts of sodium chloride are added. After cooling, the reaction product which separates is filtered off. It is washed with a 5% sodium chloride solution and the product is dried at 89–90° under vacuum. In this way the disodium salt of 4,4' - bis - [4'' - (β - ethoxyethylamino) - 6'' - (p-methylphenylamino) - 1'',3'',5'' - triazinyl - (2'') - amino]-stilbene-2,2'-disulphonic acid is obtained as a yellow powder which dissolves well in water. In daylight, the diluted aqueous solution of this product fluoresces blue to blue-violet. The product is excellently suitable as additive to washing agents.

Products very well suited for the purpose mentioned

are also obtained if, in this example, the 22 parts of 2-ethoxyethylamine are replaced by 18.5 parts of 2-methoxyethylamine, 22 parts of 3-methoxypropylamine or by 33 parts of 3-(β-methoxyethoxy)-propylamine. The latter amine is obtained by adding acrylonitrile to ethylene glycol monomethyl ether and then catalytically hydrogenating. B.P.$_{11}$ 76–78°.

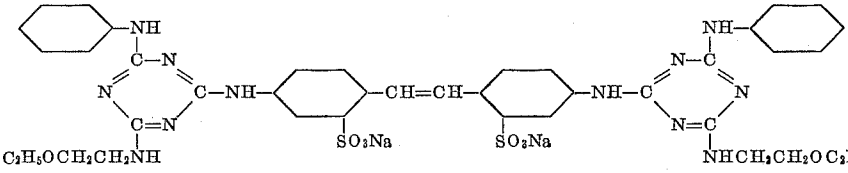
EXAMPLE 3



177 parts of the sodium salt of 4,4'-bis[4'',6''-dichloro-1'',3'',5'' - triazinyl-(2'')-amino]-stilbene-2,2'-disulphonic acid are distributed while stirring in 3000 parts of water and 38.5 parts of 2-methoxyethylamine are added within 30 minutes at 25°. After raising the temperature to 30–40°, an aqueous solution of 26.6 parts of sodium carbonate is poured in over a period of 1 to 2 hours in such a manner that the pH of the reaction mixture is always 7 to 8. 46.5 parts of aminobenzene are then added to the practically clear solution of the disodium salt of 4,4'-bis-[4''-chloro-6''-(β-methoxyethylamino)-1'', 3'',5'' - triazinyl - (2'') - amino]-stilbene-2,2'-disulphonic acid formed and the whole is refluxed for 5 hours while stirring. After the pH of the reaction mixture has been adjusted to 10–11 by the addition of sodium hydroxde, the product of the formula given above is separated out by the addition of 150 parts of sodium chloride, isolated and dried in vacuo at 70–90°. A yellowish powder which easily dissolves in water is obtained. It has properties similar to those of the compounds produced according to Example 1.

Very valuable products are also obtained if, in this example, the 46.5 parts of aminobenzene are replaced by 53.5 parts of 3-methyl-1-aminobenzene or by 61.5 parts of 3-methoxy-1-aminobenzene.

EXAMPLE 4



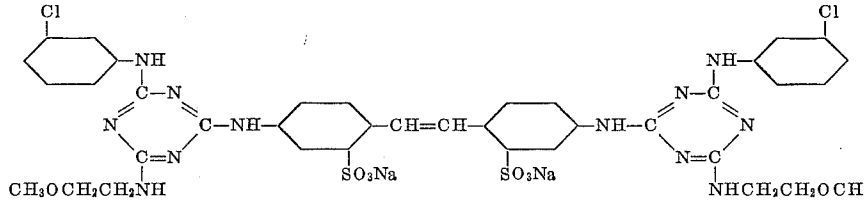
82.3 parts of the sodium salt of 4,4'-bis[4''-chloro-6''-phenylamino - 1'',3'',5''-triazinyl (2'')-amino]-stilbene-2,2'-disulphonic acid (produced under the conditions given in Example 1) are distributed ,while stirring in 3000 parts of water and reacted at 85–95° with 22 parts of 2-ethoxyethylamine in the presence of 8 parts of sodium hydroxide. The product is salted out with 150 parts of sodium chloride and has the formula given above. After drying, it is a pale yellowish powder which dissolves well in water and has properties similar to those of the compounds produced according to Examples 1 to 3. The product is also suitable as additive to washing agents.

If, in this example, the 22 parts of 2-ethoxyethylamine

are replaced by 33 parts of 2-(β-ethoxyethoxy)-ethylamine, then brightening agents which are also valuable for the purpose mentioned are obtained.

The 2-(β-ethoxyethoxy)-ethylamine is obtained from 2-(β-ethoxyethoxy)-ethyl chloride (produced from diethylene glycol monoethyl ether and $SOCl_2$) by heating in an autoclave with ammonia at 120°.

EXAMPLE 5



71 parts of the sodium salt of 4,4-bis-[4'',6''-dichloro-1'',3'',5'' - triazinyl-(2'')-amino]-stilbene-2,2'-disulphonic acid are distributed, while stirring, in 1500 parts of water and 25.5 parts of 3-chloro-1-aminobenzene are added at 20–30°. The pH of the mixture is kept at 6.5–7 by the gradual addition of aqueous sodium hydroxide solution and the whole is stirred until no more 3-chloro-1-aminobenzene can be traced for practical purposes by diazotising and coupling a sample.

18.5 parts of 2-methoxyethylamine are then added to the yellowish suspension of the disodium salt of 4,4'-bis-[4'' - chloro - 6''-(m-chlorophenylamino)-1'',3'',5''-triazinyl - (2'') - amino]-stilbene-2,2'-disulphonic acid obtained. The whole is stirred and heated to 90° and an aqueous solution of 8 parts of sodium hydroxide are added within 2 hours. After adding 75 parts of sodium chloride, the solution is cooled whereupon the reaction product, which was at first liquid, solidifies. It is filtered off under suction and dried in vacuo at 60–80°. The disodium salt of 4,4'-bis-[4''-(β-methoxyethylamino)-6''-(m - chlorophenylamino) - 1'',3'',5'' - triazinyl - (2'')-amino]-2,2'-disulphonic acid so obtained is a yellowish powder which dissolves easily in water; it is excellently suited for the optical brightening of white cotton fabrics in washing liquors.

Equally-active products are obtained if in this example, the 2-methoxyethylamine is replaced by 22 parts of 3-methoxypropylamine or if the 3-chloro-1-aminobenzene is replaced by the same amount of 4-chloro-1-aminobenzene. In the latter case, a somewhat more difficultly soluble product is obtained.

Other optical brightening agents which are suitable for combination with washing agents for the brightening of cellulose fibres are obtained if 1 mol of the sodium salt of 4,4'-bis-[4'',6''-dichloro-1'',3'',5''-triazinyl-(2'')-amino]-stilbene-2,2'-disulphonic acid is successively reacted in the manner described above with 2 mols of

each of the following arylamines and alkoxyalkylamines:

Table I

No.	Arylamine	Alkoxyalkylamine
1	Aminobenzene	$CH_3OCH_2CH_2OCH_2CH_2NH_2$*
2	do	$CH_3OCH_2CH_2OCH_2CH_2CH_2NH_2$
3	do	$C_2H_5OCH_2CH_2CH_2NH_2$
4	3-methyl-1-aminobenzene	$CH_3OCH_2CH_2OCH_2CH_2CH_2NH_2$
5	do	$C_2H_5OCH_2CH_2NH_2$
6	4-methyl-1-aminobenzene	$C_2H_5OCH_2CH_2CH_2NH_2$
7	3-methoxy-1-aminobenzene	$C_2H_5OCH_2CH_2NH_2$
8	do	$C_2H_5OCH_2CH_2OCH_2CH_2NH_2$
9	4-chloro-1-aminobenzene	$CH_3OCH_2CH_2CH_2NH_2$
10	do	$CH_3OCH_2CH_2OCH_2CH_2NH_2$

*This amine is produced from β-methoxyethoxyethyl chloride (produced from diethylene glycol monomethyl ether and $SOCl_2$) by heating in an autoclave with ammonia at 120°.

EXAMPLE 6

A heavy-duty non-soap detergent mixture consisting of 8 parts of lauryl sulfate, 11 parts of dodecylbenzene sulfonate, 11 parts of sodium tripolyphosphate, 17 parts of tetrasodium pyrophosphate and 37 parts of sodium sulfate is worked up into a paste with a solution of 0.1 part of the sodium salt of 4,4'-bis-[4''-(β-ethoxyethylamino) - 6'' - (p - methylphenylamino) - 1'',3'',5''-triazinyl-(2'')-amino]-stilbene-2,2'-disulfonic acid described in Example 2 in 170 parts of water. This paste is then dried at 60° and then milled. In daylight, the washing powder obtained has a considerably whiter appearance than the same washing composition produced without the addition of the optical brightening agent.

Beautiful white washing powders are also obtained if, instead of the brightening agent mentioned above, the same amount of the sodium salt of 4,4'-bis-[4''-(γ-methoxypropylamino) - 6'' - phenylamino - 1'',3'',5''-triazinyl-(2'')-amino]-stilbene-2,2' - disulfonic acid obtained according to Example 1 or of the 2-methoxyethylamine derivative produced according to Example 3 are incorporated into the above washing agent preparation.

EXAMPLE 7

1 part of household linen is washed for 20 minutes at 60° with 10 parts of a washing liquor which contains 8 g. per liter of the washing agent produced according to Example 6. The goods are then rinsed and dried. In spite of the relatively low washing temperature, a dazzling white wash is obtained.

EXAMPLE 8

A heavy duty detergent mixture consisting of

7.8 parts by weight of lauryl sulfate,
11.0 parts by weight of dodecyl benzene sulfonate,
11.0 parts by weight of sodium tripolyphosphate ($Na_5P_3O_{10}$),
16.6 parts by weight of tetrasodium pyrophosphate,
4.6 parts by weight of anhydrous sodium silicate,
1.4 parts by weight of carboxymethyl cellulose,
36.8 parts by weight of sodium sulfate,
8.0 parts by weight of sodium perborate ($NaBO_3$-$4H_2O$), and
0.3 part by weight of disodium 4,4'-bis-[4''-(β-methoxyethylamino)-6''-phenylamino-1'',3'',5''-triazinyl-(2'')-amino]-stilbene-2,2'-disulfonate

produced as described in Example 3, supra, is produced in the following manner.

The optical brightener is intimately mixed with normal aqueous sodium hydroxide solution (10 ml. per g. of brightener) and when the brightener is thoroughly dispersed, about 200 to 300 ml. of water (per gram of brightener) are added.

The other ingredients of the detergent mixture are mixed with each other separately and intimately using a sufficient amount of water to obtain a creamy paste, the latter is dried at 60° and granulated.

The detergent granules are then added to the slurry of brightener and the mixture is repeatedly and thoroughly stirred until a smooth, creamy mix is obtained. The resulting slurry is then spread into a uniform layer on a flat surface and dried in an oven at 85° for 16 hours. The resulting cake is allowed to cool to room temperature, left standing for at least 30 minutes and then crushed and placed in a desiccator. The dried chunks of detergent mixture are then forced through a 20 mesh screen and, if desired, the resulting powder is transferred to 60 mesh screen to remove the fine portion.

EXAMPLE 9

In a similar manner as described in Example 8 there is produced a synthetic, non-soap, heavy-duty detergent of the following composition (in percent by weight):

Dodecyl benzene sulfonate	15.2
Lauryl sulfate	3.8
Sodium tripolyphosphate	25.6
Tetrasodium pyrophosphate	7.6
Anhydrous sodium silicate	4.8
Magnesium silicate	1.9
Sodium carbonate	5.0
Carboxymethyl cellulose	1.4
Sodium ethylenediamine tetraacetate	0.3
Sodium sulfate	34.0
Disodium 4,4'-bis[-4''-(β-ethoxy ethylamino)-6'' phenylamino - 1'',3'',5'',-triazinyl-(2'') - amino]-stilbene-2,2'-disulfonate	0.4

EXAMPLE 10

A heat-liquifiable soap for use in washing machines is produced as follows:

To a hot mixture of

40 parts by weight of coconut oil fatty acid sodium soap
31 parts by weight of sodium tripolyphosphate
9 parts by weight of tetrasodium pyrophospate
6 parts by weight of sodium silicate
3 parts by weight of magnesium silicate
0.5 part by weight of sodium ethylenediamine tetraacetate
5 parts by weight of sodium carbonate
5.5 parts by weight of sodium sulfate and
70 parts of water

there is added 0.4 part by weight of disodium 4,4'-bis-[4''-(β-methoxyethylamino) - 6'' - (m - methylphenylamino)-1'',,3'',5''-triazinyl-(2'')-amino] - stilbene - 2,2'-disulfonate, mixed intimately and then dried in a spray tower.

A beautiful white, free-flowing washing powder is obtained which brightens anti-crease finished cotton increasingly with successive washings, and without greenish shade in spite of accumulation of the brightening agent on the fiber.

EXAMPLE 11

A non-ionogenic washing agent was prepared by intimately mixing with each other the following ingredients

	Parts by weight
Nonylphenol polyglycolether with 15 ethylenoxy groups	11
Water	11
Sodium tripolyphosphate	33
Tetrasodium pyrophosphate	11
Sodium silicate	10
Sodium sulfate	20
Sodium carbonate	2
Carboxymethyl cellulose	2
Disodium 4,4'-bis-[4''-(γ-methoxypropylamino)-6''-(phenylamino)-1'',3'',5'' - triazinyl-(2'')-amino] stilbene-2,2'-disulfonate	0.5

This washing agent is a powder of similar good properties as the agents described in the preceding example. Especially it is distinguished by a brilliant white appearance.

EXAMPLE 12

In order to produce a light duty, non-soap detergent, the following ingredients are mixed together

	Parts by weight
Sodium dodecyl-benzene sulfonate	20
Sodium laurylsulfate	8
Lauric acid mono-N-β-hydroxyethylamide	2
Sodium tripolyphosphate	8
Carboxymethyl cellulose	1.5
Sodium sulfate	60.5
4,4'-bis-[4''-(β-methoxy-ethylamino) - 6''-(p-methylphenylamino)-1'',3'',5'' - triazinyl-(2'')-amino] stilbene-2,2'-disulfonic acid	0.35
Water	80

whereby a homogenous slurry is obtained which is dried at 60° C. and pulverized.

The resulting powder has a brilliant white appearance and can be used for washing white cotton or rayon materials imparting to the same a pure white appearance which does not develop a greenish hue even after 20 washings.

EXAMPLE 13

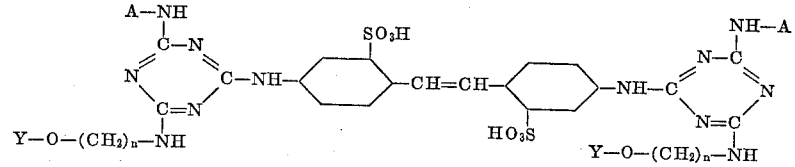
A light-duty non-soap detergent of similar good properties is obtained by repeating the preceding Example 12, but using instead of the brightening agent contained therein 0.4 part by weight of disodium 4,4'-bis-[4''-(β-ethoxy-ethylamino)-6''-(m - methoxyphenylamino) - 1'',3'',5''-triazinyl-(2'')-amino]-stilbene-2,2'-disulfonate.

EXAMPLE 14

A heavy duty non-soap detergent of good white appearance and improved solubility in water is obtained by repeating Example 9 but using, instead of the brightener contained therein, 0.5 part by weight of disodium salt of 4,4'-bis-[4''-(β-[2'''-methoxy-ethoxy]-ethylamino) 6''-phenylamino-1'',3'',5''-triazinyl - (2'') - amino]-stilbene-2,2'-disulfonate.

We claim:

1. A compound of the formula



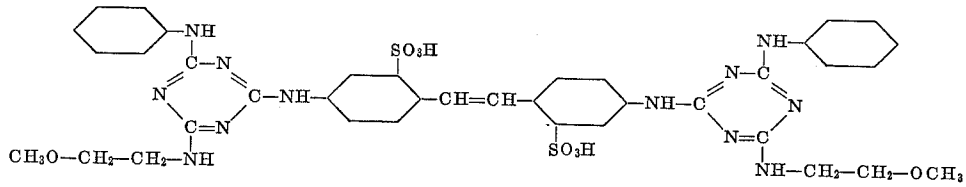
wherein

A represents a member selected from the group consisting of phenyl, 3-methylphenyl, 4-methylphenyl and 3-methoxyphenyl,

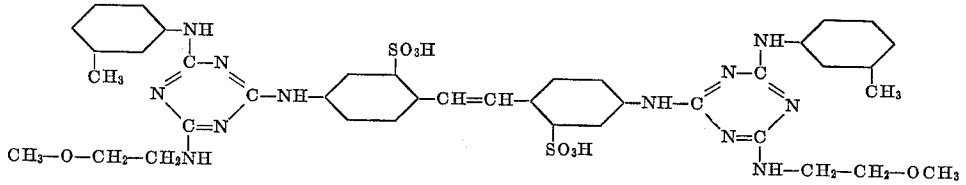
Y represents a member selected from the group consisting of methyl and ethyl, and

n is one of the integers 2 and 3.

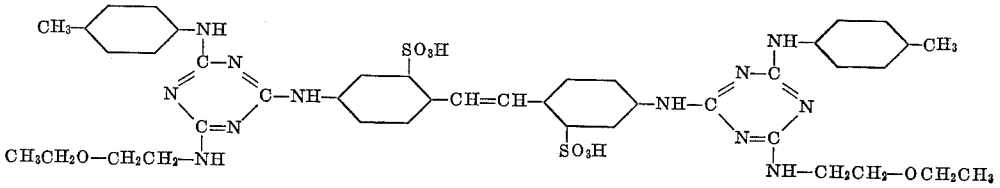
2. The 4,4'-bis-triazinylaminostilbene compound of the formula



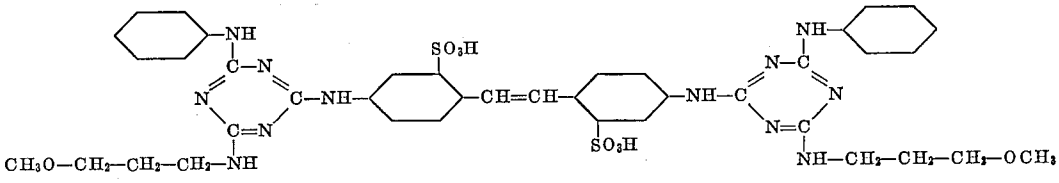
3. The 4,4'-bis-triazinylaminostilbene compound of the formula



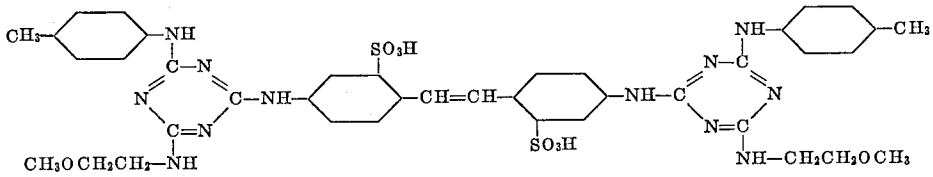
4. The 4,4'-bis-triazinylaminostilbene compound of the formula



5. The 4,4'-bis-triazinylaminostilbene compound of the formula



6. The 4,4'-bis-triazinylaminostilbene compound of the formula



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