

PATENT SPECIFICATION

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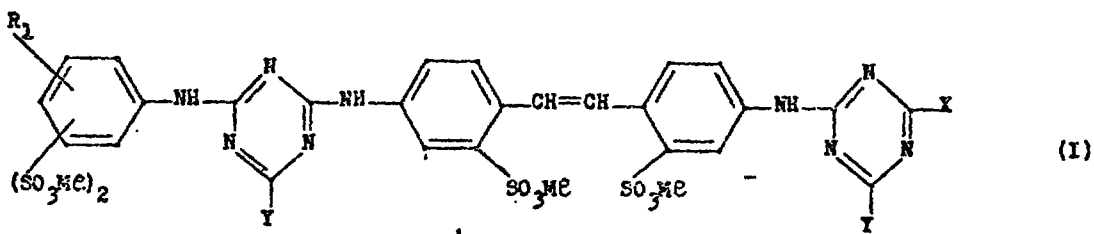


(54) BIS-(TRIAZINYLAMINO)-STILBENE DERIVATIVES

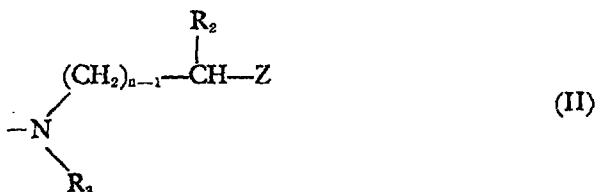
(71) We, SANDOZ LTD., of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to bis-(triazinylamino)-stilbene derivatives, a process for their production and their use as brightening agents.

The present invention provides a bis-(triazinylamino)-stilbene derivative of the formula



- wherein
 X represents an amino radical which may be substituted,
 Y represents a radical of the formula



Z represents

- COOR₄, —CON< $\begin{matrix} R_5 \\ R_6 \end{matrix}$, —CO—C_nH_{2m+1} or —CN,

R₁ represents hydrogen, halogen or a lower alkyl or alkoxy radical as herein defined,
 R₂ represents hydrogen or a lower alkyl radical as herein defined,

[Price 25p]

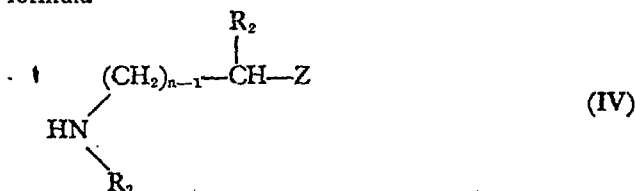
- 5 R_3 represents hydrogen, a lower alkyl, hydroxyalkyl, hydroxyalkoxyalkyl or alkoxy-alkyl radical as herein defined, an alkylaminoalkyl radical which may be substituted by one or more of hydroxyl and alkoxy radicals, a cycloalkyl radical which may be substituted by one or more lower alkyl radicals as herein defined, a phenyl radical which may be substituted by one or more of halogen atoms and lower alkyl and alkoxy radicals as herein defined, an aralkyl radical, an aryloxy-alkyl radical or a radical of the formula



- 10 with the proviso that when two radicals Z are present these may be different from one another,
- 10 R_4 represents a lower alkyl radical as herein defined which may be substituted by one or more of hydroxyl, alkoxy, phenyl or phenoxy,
- 15 each of
- 15 R_5 and R_6 , independently of one another, represents hydrogen or a lower alkyl or hydroxyalkyl radical as herein defined, or R_5 and R_6 together with the nitrogen atom form a heterocyclic radical,
- 20 Me represents hydrogen, an alkali metal, an alkaline earth metal, an ammonium group which may be substituted, or aluminium,
- 20 m represents a whole number from 1 to 5, and
- 20 n is 1 or 2.

As indicated above, when two radicals Z are present in the compound of formula (I), these need not have the same meaning within the above definition of Z, e.g. in Example 54 R_1 is 2-cyanopropyl which necessitates the Z portion of radical (III) being —CN, whereas the Z portion of the radical (II) is —CO—NH₂.

- 25 According to the present invention also, a bis-(triazinylamino)-stilbene derivative may be produced by reacting 2 mols of a cyanuric halide in any desired order with
- 30 a) 1 mol of 4,4'-diaminostilbene-2,2'-disulphonic acid or of a salt of this acid consistent with the definition of Me above,
- 30 b) 1 mol of an aminobenzenedisulphonic acid which may be substituted by R_1 as defined above or of a salt of this acid,
- 30 c) 1 mol of ammonia or of a primary or secondary amine, and
- 30 d) 2 mols of an amine of formula



- 35 or of a mixture of amines of formula (IV);
- 35 or reacting 1 mol of a cyanuric halide in any desired order with
- 35 a) 1 mol of 4-amino-4'-nitrostilbene-2,2'-disulphonic acid or of a salt of this acid consistent with the definition of Me above,
- 40 b) 1 mol of an aminobenzenedisulphonic acid which may be substituted by R_1 as defined above or of a salt of this acid,
- 40 c) 1 mol of an amine of formula (IV) or of a mixture thereof, reducing the resulting nitro group containing compound to give the corresponding amino group containing compound, reacting the latter with 1 mol of a cyanuric halide, and reacting the resulting dihalogenotriazinyl compound in either order with
- 45 d) 1 mol of ammonia or of a primary or secondary amine and
- 45 e) 1 mol of an amine of formula (IV) or of a mixture thereof.

50 Examples of suitable aminobenzenedisulphonic acids, which may be substituted, are 1-amino-2-methylbenzene-4,5- and -4,6-disulphonic acid, 1-amino-3-methylbenzene-2,4- and 4,6-disulphonic acid, 1-amino-4-methylbenzene-3,5-disulphonic acid, 1-amino-3-chlorobenzene-4,6-disulphonic acid, 1-amino-4-chlorobenzene-3,6-disulphonic acid, 1-aminobenzene-3,5-disulphonic acid and 1-amino-benzene-2,4- and -2,5-disulphonic acid, of which the two last named acids are preferred.

As referred to herein, the lower alkyl, hydroxyalkyl and alkoxy radicals contain 1 to 5 carbon atoms.

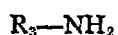
An especially suitable halogen atom is chlorine, though fluorine or bromine are also suitable.

The radical X represents preferably the amino radical or the radical of a primary or secondary aliphatic amine which has up to 8 carbon atoms and may bear one or more substituents, for instance hydroxyl, alkoxy or hydroxyalkoxy. Examples of such amines are methyl-, ethyl-, isopropyl-, n-propyl-, n-butyl-, n-hexyl-, 2-hydroxyethyl-, 2-hydroxypropyl-, N,N'-bis-(β -hydroxyethyl)-propylenediamine, 3-methoxypropyl-, 2-(β -hydroxyethoxy)-ethyl-, N-methyl-N-hydroxyethyl-, di-(hydroxyethyl)- and di-(2-hydroxypropyl-1)-amine, the radical of aromatic amines, preferably of the benzene series, which may be substituted with 1 or 2 lower alkyl or alkoxy radicals, halogen atoms, cyano, aminocarbonyl, alkoxy carbonyl, carboxyl or sulphonic acid radicals (for instance aminobenzene, 1-amino-3- and -4-chlorobenzene, 1-amino-2- and -4-methoxy- and -ethoxy-benzene, 1-amino-2-, -3- and -4-methylbenzene, 1-amino-2-, -3- and -4-cyanobenzene, 1-amino-2-, -3- and -4-amino-carbonylbenzene, -methoxycarbonylbenzene and -ethoxycarbonylbenzene, 1-amino-2-, -3- and -4-carboxybenzene, 1-aminobenzene-3- and -4-sulphonic acid, 1-aminobenzene-3,5-, -2,4- and -2,5-disulphonic acid), the radical of a heterocyclic, non-aromatic amine which contains nitrogen and may contain oxygen and is bound through the nitrogen atom to the triazine ring, for instance pyrrolidine, piperidine, hexamethylene-imine and morpholine. Alternatively, the radical X may be a radical of formula (II).

When R_3 represents a lower alkyl radical it may be, for example, methyl, ethyl, n-propyl, n-amyl, n-butyl, iso-amyl; when R_3 is a cycloalkyl radical which may bear lower alkyl radicals, suitable examples are cyclohexyl and 4-methylcyclohexyl; when R_3 is a hydroxyalkyl, alkoxyalkyl or hydroxyalkoxyalkyl radical, suitable examples are 2-hydroxyethyl, 2-hydroxypropyl, 3-methoxypropyl, 3-ethoxypropyl, 3-butoxypropyl and 2-(2'-hydroxyethoxy)-ethyl; when R_3 is an alkylaminoalkyl radical which may be substituted by hydroxyl or alkoxy, a suitable example is 2-(2'-hydroxyethylamino)-ethyl; when R_3 is an aralkyl or aryloxyalkyl radical, suitable examples are benzyl, phenylethyl or phenoxyethyl; when R_3 is a phenyl radical which may be substituted by one or more of lower alkyl and alkoxy radicals and halogen atoms, suitable examples are phenyl, 2-, 3- and 4-methylphenyl, 2- and 4-methoxy- or -ethoxyphenyl, 3- or 4-chlorophenyl, 4-bromo- or 4-fluorophenyl, 2,5-dichlorophenyl, 2,4- or 2,5-dimethylphenyl, 4-ethyl-, 4-tert.amyl- or 4-tert.butylphenyl.

Examples of the radical of the formula (III) are 2-cyanoethyl, 2-cyanopropyl, 2-oxopropyl, 2-oxobutyl, 3-oxobutyl, 2-aminocarbonyl-ethyl, 2-dimethylaminocarbonyl-ethyl, 2-diethylaminocarbonyl-ethyl, 2-morpholinocarbonyl-ethyl, 2-methoxycarbonyl-ethyl, 2-ethoxycarbonyl-ethyl, 2-n-butoxycarbonyl-ethyl, 2-(2-hydroxyethoxycarbonyl)-ethyl, 2-(2'-hydroxypropoxycarbonyl)-ethyl, 2-(2'-ethoxyethoxycarbonyl)-ethyl, 2-(2'-butoxyethoxycarbonyl)-ethyl, 2-benzoyloxycarbonyl-ethyl, 2-(2'-phenylethoxycarbonyl)-ethyl and 2-(2'-phenoxyethoxycarbonyl)-ethyl.

An amine of formula (IV) may be produced by reaction of an amine of the formula



(V)

with acrylonitrile, an unsubstituted or substituted alkyl ester or amide of acrylic acid, or with the corresponding derivative of methacrylic acid, or with a vinylalkyl ketone (for instance vinyl methyl ketone), at a temperature of 20° C to 100° C.

The reaction of the cyanuric halide, e.g. cyanuric bromide or chloride, with the amino compound can be carried out in aqueous medium with the cyanuric halide suspended in water only, or in aqueous-organic medium, the halide being dissolved in an organic solvent, e.g. acetone, benzene, toluene or chlorobenzene, and the aqueous solution of the amino compound then added to the solution. The addition of a dispersing agent can accelerate the rate of reaction and lead to a product of high purity.

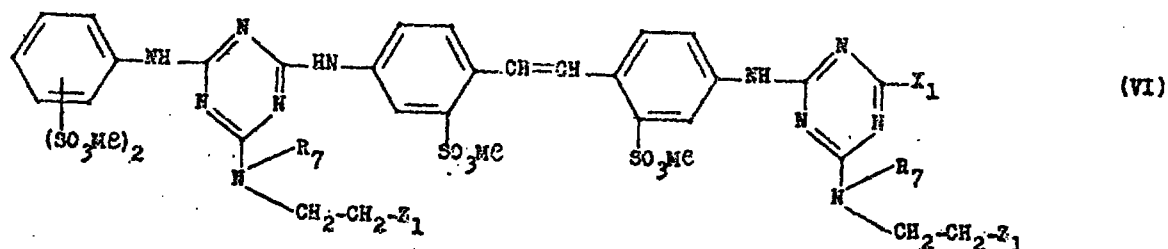
When the substituent X represents the radical of an aromatic aminosulphonic acid or another water soluble amine, a product of greater purity may sometimes be obtained if reaction is effected first with the amine or mixture of amines to replace the first halogen atom and subsequently condensation is effected of the second halogen atom with the 4,4'-diaminostilbene-2,2'-disulphonic acid. The first halogen atom of the cyanuric halide is preferably replaced at 0—15° C and at a pH value of 3 to 7. Condensation of the second halogen atom is best carried out at a temperature of 20° to 60° C at, e.g., a pH value of 4 to 8, while the third halogen atom is preferably reacted at 80—100° C and at a pH value of 4 to 10.

The hydrogen halide set free in the reaction is neutralized with an alkali, e.g. an alkali-metal hydroxide, carbonate or bicarbonate, or with a tertiary organic amine, e.g. tri-(2-hydroxyethyl)-amine.

The nitro compound can be reduced, for example, by treatment with an aqueous sodium sulphite or sodium hydrogen sulphide solution, preferably at a temperature of 60° C to 90° C, or by acidification of the solution with hydrochloric, sulphuric or acetic acid and treatment with zinc powder or iron turnings or powder at 50—100° C, preferably 80—100° C.

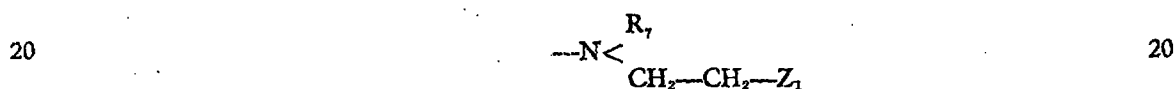
The compounds produced by the process of this invention may be isolated by precipitation with salt or acid or by evaporation of the reaction solution, from which they are obtained in powder form. Alternatively, after separation of the salts they can be worked up in form of liquid preparations by the addition of a dissolving assistant, e.g. a glycol, glycol ether, formamide, acetamide, urea, or a mono-di- or tri-(2-hydroxyethyl)- or -(2-hydroxypropyl)-amine.

Interesting compounds of the formula (I) have the formula

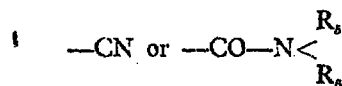


wherein

X₁ represents —NH₂, a phenylamino radical which may be substituted by one or more of methyl, methoxy, chlorine, cyano and —SO₃Me, or a radical of the formula



Z₁ represents



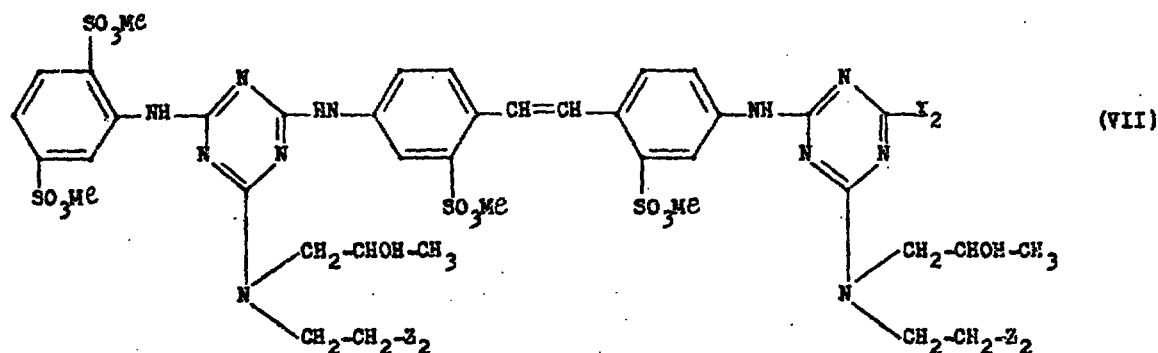
R₇ represents hydrogen, a lower alkyl, hydroxyalkyl or alkoxyalkyl radical as herein defined, an alkylaminoalkyl radical which may be substituted by one or more of hydroxyl and alkoxy radicals, or a radical —CH₂—CH₂—Z₁,

25

and

Me, R₅ and R₆ have the meaning given above.

Especially interesting compounds have the formula

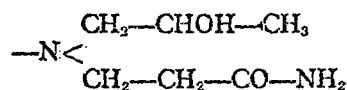


wherein

Z_2 represents $-\text{CN}$ or $-\text{CO}-\text{NH}_2$

and

X_2 represents $-\text{NH}_2$, phenylamino, 2,5-disulphophenylamino or



Me having the above meaning.

The compounds of this invention are optical brighteners suitable for brightening natural and regenerated cellulosic fibres, e.g. cotton, linen, hemp, ramie, jute, viscose rayon, viscose staple fibre and cuprammonium rayon, natural and synthetic polyamide and polyurethane fibres, e.g. wool, silk, hair, polyamide 6, polyamide 9, polyamide 11, polyamide 12, polyamide 66, polyamide 610, polyamide 6.66, the polyamide from decane-1,10-dicarboxylic acid and 4,4'-diaminodicyclohexylmethane, and the polyurethane fibres described in Textilveredlung 3, 11, pp. 663-673 (1968), and paper, especially by coating methods. Owing to their high solubility and relatively low substantivity they can be applied to paper by the dipping technique and to textile fabrics by the padding technique without appreciable reduction in the strength of the application medium. Their good stability to acids and aluminium ions is an important property for the brightening of paper in the stock before formation. In general, they are compatible with binders and fillers used for the manufacture of coated papers and produce good effects on these paper grades. Further, they are generally stable in the strongly acid liquors containing synthetic resins which are used for crease resistant finishes on cotton, and to the magnesium and zinc salts used as catalysts in finishes of this type.

The salts of the compounds of this invention can be extended with the commonly used hydrophilic compounds such as polyvinyl alcohol, polyethylene glycols, acylated polyethylene glycols, polyvinyl pyrrolidones or urea, which in many cases appreciably increases the brightening effect. The compounds of the present invention can be applied in combination with known brighteners to produce special effects.

In comparison to compounds described in U.K. Patent No. 1,008,457 the compounds of this invention show better substantivity and better wash fastness, which is reflected in higher effectiveness and greater stability to acids. Also the compounds of the present invention are very suitable for pad application.

The principal use of the compounds of the present invention is the optical brightening of (i) textiles of natural and regenerated cellulosic fibres by padding or by application from exhaust baths or synthetic resin finishing liquors, (ii) synthetic polyamide fibres by application from acid baths or in the spinning melt, and (iii) paper by application in the stock or by coating methods after sheet formation.

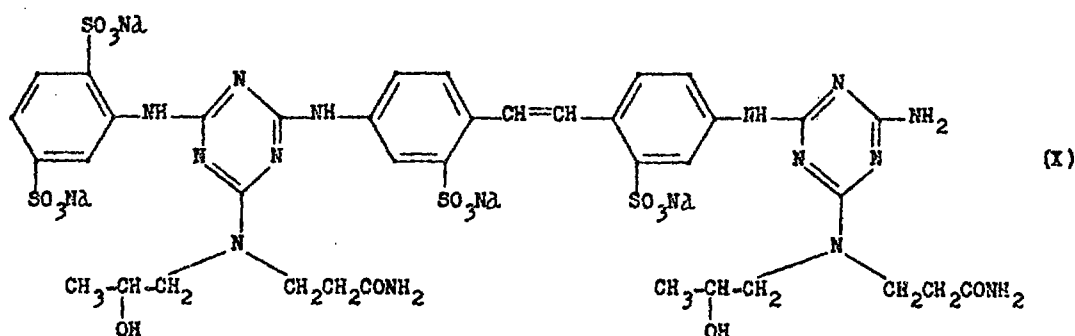
The following Examples illustrate the invention without limiting its scope; the parts and percentages are by weight, the temperatures are in degrees Centigrade and the parts by volume in relation to the parts by weight are as millilitres to grammes.

Example 1

A solution of 190 parts of cyanuric chloride in 800 parts by volume of acetone is run in 10 minutes with good stirring into 5000 parts of ice-water. In the course of 1 hour a solution of 253 parts of 1-aminobenzene-2,5-disulphonic acid and 106 parts of calcined sodium carbonate in 1500 parts of water is dropped into the suspension at $0-5^\circ$ with stirring. The pH is held at 3 to 4 by dropping in 15% sodium carbonate solution. During the addition the suspension goes slowly into solution. Stirring is continued at $0-5^\circ$ until the diazo reaction indicates that no further primary aromatic amino groups are present. A solution of 185 parts of 4,4'-diamino-stilbene-2,2'-disulphonic acid and 53 parts of calcined sodium carbonate in 1500 parts of water is added, the pH adjusted to 7 with 15% sodium carbonate solution and the solution held at 30° until the diazo reaction is negative. 205 Parts of β -(β' -hydroxypropylamino)-propionic acid amide are added to the clear solution, then its pH is increased to 9-10 with 15% sodium carbonate solution, and the temperature slowly increased to $95-100^\circ$ with distillation of the acetone. The solution is held at this temperature for about 90 minutes with reflux, the pH being maintained at 9-10 during this time by the addition of further sodium carbonate solution. Subsequently 3500 parts of sodium chloride are added to the clear solution, which is then allowed to cool. A pale yellow product settles out, which is filtered with suction and vacuum dried. It has the formula

Example 3

A solution of 190 parts of cyanuric chloride in 800 parts by volume of acetone is run in 10 minutes with thorough stirring into 2000 parts of ice-water. A solution of 185 parts of 4,4'-diaminostilbene-2,2'-disulphonic acid and 53 parts of calcined sodium carbonate in 1500 parts of water is dropped into the resulting suspension in 1 hour at 0—5°. When the diazo reaction indicates that no further primary aromatic amino groups are present a solution of 126 parts of 1-aminobenzene-2,5-disulphonic acid and 53 parts of calcined sodium carbonate in 750 parts of water is added in 30 minutes at 20—30°. At the same time 15% sodium carbonate solution is added to keep the pH at 7. As soon as no further diazotizable amine is indicated, 250 parts of a 25% ammonia solution are added. The mixture is then stirred for 2 hours at 40° and the excess ammonia removed by means of a water-jet vacuum pump. 205 Parts of β -(β '-hydroxypropylamino)-propionic acid amide are added, followed by sufficient 15% sodium carbonate solution to increase the pH to 9—10, and the mixture is then held for 3 hours at 95—100°. The product thus obtained is dried in an atomizer drier. It has the formula



In place of the ammonia solution, 46 parts of a 35% aqueous solution of mono-methylamine, 33 parts of a 70% aqueous solution of monoethylamine, 35 parts of diethylamine, 31 parts of 2-hydroxyethylamine or 53 parts of di-(2-hydroxyethyl)-amine can be used, on which products with similar properties are obtained.

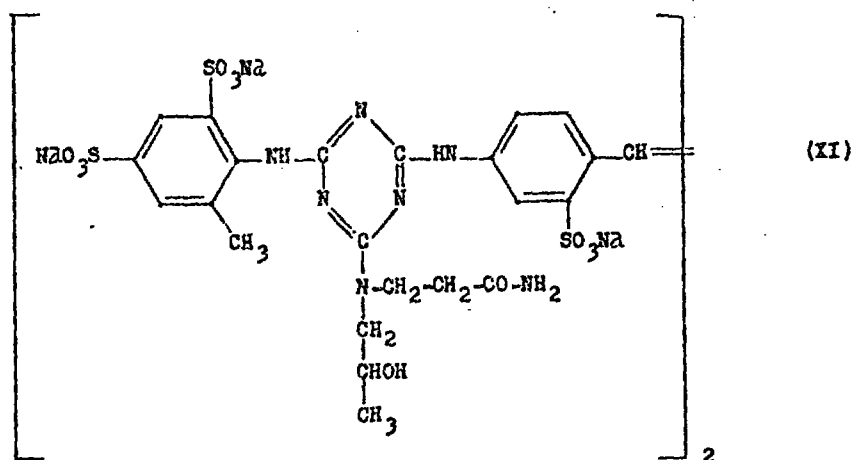
The ammonia solution can be replaced by a further 73 parts of β -(β '-hydroxypropylamino)-propionic acid amide with equally good results.

In place of the β -(β '-hydroxypropylamino)-propionic acid amide, the secondary amines bearing negative substituents named in Example 1 can be employed to give products of comparable quality.

Example 4

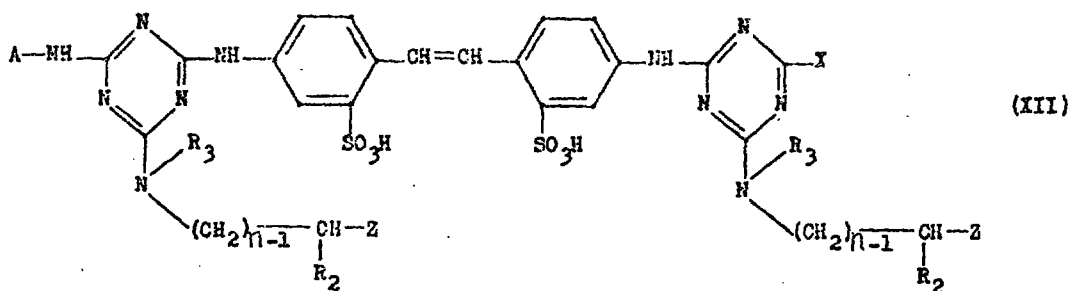
A solution of 190 parts of cyanuric chloride in 800 parts by volume of acetone is run in 10 minutes into 5000 parts of ice-water with thorough stirring. In 1 hour a solution of 267 parts of 1-amino-2-methylbenzene-4,6-disulphonic acid and 106 parts of calcined sodium carbonate in 1500 parts of water is dropped into the suspension at 10—15° with stirring. The pH is maintained at 3—4 by adding 15% sodium carbonate solution dropwise at the same time. The suspension goes slowly into solution during the addition. Stirring is continued at 10—15° until the diazo reaction shows that no further primary aromatic amino groups are present. Then a solution of 185 parts of 4,4'-diaminostilbene-2,2'-disulphonic acid and 53 parts of calcined sodium carbonate in 1500 parts of water is added, the pH adjusted to 7 with 15% sodium carbonate solution, and the solution maintained at 30° until the diazo reaction is negative. 205 Parts of β -(β '-hydroxypropylamino)-propionic acid amide are added to the clear solution, the pH is increased to 9—10 with 15% sodium carbonate solution, and the solution raised slowly to 95—100° with distillation of the acetone. The solution is boiled for about 90 minutes with reflux, the pH being held at 9—10 by adding further sodium carbonate solution. Finally, 3500 parts of sodium chloride are added to the clear solution and it is allowed to cool. The pale yellow product settles out and is filtered with suction and vacuum dried. It has the formula

(IX)



In place of β -(β' -hydroxypropylamino)-propionic acid amide, one of the β -amino-propionic acid amides or β -aminopropionitriles named at the end of Example 1 can be used, which give optical brighteners of equally good quality.

In the following table further optical brighteners of formula



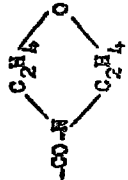
conforming to this invention are specified by the meanings of the symbols A, R₂, R₃, X, Z and n.

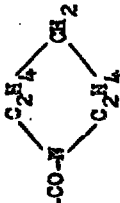
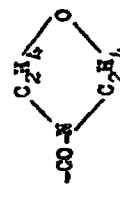
TABLE

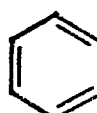
Example No.	A	R ₂	R ₃	Z	X	n
5	2,4-Disulphophenyl	CH ₃	—C ₂ H ₄ —OH	—CO—NH ₂	2,4-Disulphophenyl-amino	2
6	do	H	do	—CN	do	2
7	do	H	do	—CO—NH ₂	3-Sulphophenylamino	2
8	do	H	H	do	Di-(2-hydroxyethyl)-amino	2
9	3,5-Disulphophenyl	H	—CH ₃	do	3,5-Disulphophenylamino	2
10	3-chloro-4,6-disulphophenyl	H	—CH ₂ —CHOH—CH ₃	do	3 Chloro-4,6-disulphophenylamino	2
11	2,5-Disulphophenyl	H	—C ₂ H ₅	do	4 Sulphophenylamino	2
12	do		—C ₂ H ₄ —OH	do	do	1
13	do	H	—C ₂ H ₄ —OH	—CN	do	1

Example No.	A	R ₁	R ₃	Z	X	n
14	2,4-Disulphophenyl	CH ₃	-CH ₂ -CHOH-CH ₃	-CN	2,4-Disulphophenylamino	2
15	2,5-Disulphophenyl	CH ₃	do	-CN	2,5-Disulphophenylamino	2
16	do	CH ₃	do	-CONH ₂	do	2
17	do	H	-C ₂ H ₅	do	do	1
18	do	H	-CH ₃	do	4-Sulphophenylamino	1
19	do	H	-CH ₃	do	Phenylamino	1
20	do	H	H	-COOCH ₃	3-Sulphophenylamino	1
21	do	H	H	-COO-C ₄ H _{9n}	do	1
22	do	H	H	-CO-NH-CH ₃	2,5-Disulphophenylamino	1
23	do	H	H	-CO-NH-C ₄ H _{9n}	do	1
24	do	H	H	-CO-N(CH ₃) ₂	do	1
25	do	H	H	-CO-N(C ₂ H ₅) ₂	do	1
26	do	H	-nC ₄ H ₉	do	do	2
27	do	H	-C ₂ H ₄ -OH	-CONH-C ₂ H ₄ OH	do	2
28	do	H	do	do	do	1

Example No.	A	R ₁	R ₃	Z	X	n
29	3,5-Disulphophenyl	H	—C ₂ H ₄ —OH	—CN	3,5-Disulphophenylamino	1
30	do	H	CH ₃	—CO—NH ₂	do	1
31	2,4-Disulphophenyl	H	do	do	2,4-Disulphophenylamino	1
32	do	H	—nC ₄ H ₉	do	do	1
33	2,5-Disulphophenyl	H	3-Methoxypropyl	do	2,5-Disulphophenylamino	1
34	do	H	do	do	do	2
35	do	H	—CH ₂ —CHOH—CH ₃	do	4-Methylphenylamino	2
36	do	H	do	do	do	1
37	do	H	do	do	3-Chlorophenylamino	1
38	do	H	do	do	do	2
39	do	H	do	do	4-Methoxyphenylamino	2
40	do	H	do	do	do	1
41	do	CH ₃	C ₂ H ₅	do	2,5-Disulphophenylamino	2
42	do	H	—C ₂ H ₄ OH	do	N-β-Hydroxyethyl-N-β-aminocarbonyl-ethyl-amino	2

Example No.	A	R ₂	R ₃	Z	X	n
43	2,5-Disulphophenyl	H	CH ₃	—CO—NH ₂	N-Methyl-N-β-amino-carbonyl-ethyl-amino	2
44	2,4-Disulphophenyl	H	2-Methoxyethyl	do	4-Sulphophenylamino	2
45	2,5-Disulphophenyl	H	do	do	do	
46	do	H	2-Ethoxyethyl	do	2,5-Disulphophenylamino	2
47	do	H	2-n-Butoxy-ethyl	do	do	2
48	do	H	2-Cyanoethyl	—CN	do	2
49	do	H	2-Aminocarbonyl-ethyl	—CO—NH ₂	do	
50	do	H	2-Morpholinocarbonyl-ethyl		do	2
51	do	H	2-Dimethylamino-carbonyl-ethyl	—CO—N(CH ₃) ₂	do	2
52	do	H	Methylamino-carbonyl-ethyl	—CO—NH—CH ₃	do	2
53	do	H	—C ₂ H ₄ —OH	—CO—N(C ₂ H ₄ OH) ₂	Phenylamino.	2
54	do	H	2-Cyanopropyl	—CO—NH ₂	3-Sulphophenylamino	2
55	do	H	2-Methoxycarbonyl-ethyl	—CO—O—CH ₃	do	2
56	do	H	2-n-Butoxycarbonyl-ethyl	—COO C ₄ H ₉	2,5-Disulphophenylamino	2

Example No.	A	R ₂	R ₃	Z	n	
57	2,5-Disulphophenyl	H	n-Amyl	-CO-NH ₂	2,5-Disulphophenylamino	2
58	do	H	Cyclohexyl	do	do	2
59	do	H	Benzyl	do	do	2
60	do	H	-C ₂ H ₄ OH	-CO-CH ₃	do	2
61	do	H	do	-CO-NH ₂	-NH-CH ₃	2
62	do	H	-CH ₂ -CHOH-CH ₃	-CO-NH-C ₄ H _{9n}	-NH ₂ -C ₂ H ₄ OH	2
63	do	H	do	-CO-N(C ₄ H _{9n}) ₂	2,5-Disulphophenylamino	2
64	do	H	-C ₂ H ₄ -OH	do	do	1
65	do	H	-C ₂ H ₄ OH	-CO-NH ₂	Di-(2-hydroxypropyl)-amino	2
66	do	H	Phenyl	-CO-NH ₂	2,5-Disulphophenylamino	2
67	do	H	CH ₃		do	2
68	do	H	do		do	1
69	do	H	-CH ₂ -CHOH-CH ₃	do	do	2
70	do	H	3-dimethylamino-propyl	-CO-NH ₂	do	2

Example No.	A	R ₂	R ₃	Z	X	n
71	2,5-Disulphophenyl	H	-CH ₃	-CO-NH ₂	-NH ₂	1
72	do	H	4-Methylphenyl	do	do	2
73	do	H	-CH ₂ -CHOH-CH ₃	-CO-N(CH ₂ -CHOH-CH ₃) ₂	-NH-CH ₂ -CHOH-CH ₃	2
74	do	H	do	-CO-NH ₂	-N(C ₄ H ₉) ₂	2
75	do	H	do	do	-NH-(CH ₂) ₃ -O-CH ₃	2
76	do	H	do	do	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---N---} \\ \\ \text{C}_2\text{H}_4\text{---OH} \end{array}$	2
77	do	H	do	do	4-Carboxyphenylamino	2
78	do	H	do	do	4-Cyanophenylamino	2
79	do	H	do	do	4-Methoxycarbonylphenyl-amino	2
80	do	H	do	do	4-Aminocarbonylphenylamino	2
81	do	H	2-(2'-Hydroxyethyl)-amino)-ethyl	do	2,5-Disulphophenylamino	2
82	do	H	2-(2'-Hydroxyethoxy)-ethyl	do	4-Sulphophenylamino	2
83	2,5-Disulphophenyl	H	2-Benzoyloxycarbonyl-ethyl	$\text{---CO---O---CH}_2\text{---}$ 	2,5-Disulphophenylamino	2
84	do	H	-CH ₂ CHOH-CH ₃	-CONH ₂	-NH-C ₆ H _{13n}	2

Application Example A

A cotton fabric is conveyed through a bath of 240 parts of dimethylolethylene urea, 28 parts of 48.5% sulphuric acid, 2 parts of the brightener of Example 1 and 730 parts of water, expressed between a pair of rollers to retain 100% of its weight of liquor, and dried at 90° to 8% residual moisture content. The fabric is rolled up and stored for 17 hours at room temperature. Afterwards it is rinsed with cold water, neutralized with a 2 g/l solution of anhydrous sodium carbonate, rinsed again with cold water, expressed and dried at 100°. The treated fabric shows a brilliant white effect of neutral shade.

Application Example B

A cotton fabric is conveyed through a solution of 8 parts of the brightener of Example 2 in 1000 parts of water, expressed to an increase of 100% on the dry weight, and dried at 60—70°. A good white effect is obtained. If 8 parts of a polyethylene glycol with a molecular weight of 5000—6000 is added to the solution, the brightening effect is greatly intensified.

Application Example C

A sized paper made from sulphite pulp is coated with a paste of the composition:

66 parts china clay
33 parts water
10 parts of 50% dispersion of a butadiene-styrene copolymer
5 parts of a 10% casein solution
0.3 part of a 10% solution of the brightener of Example 1.

The degree of whiteness shown by the coated paper is appreciably greater than the whiteness of a coating without optical brightener. The whiteness can be enhanced further by including in the coating composition 1% of a 10% solution of a polyethylene glycol of molecular weight 5000—6000.

Application Example D

A solution of 0.3 part of one of the brighteners of Example 3 in 300 parts of water is added to a suspension of 100 parts of bleached sulphite pulp beaten to 40 degrees Schopper-Riegler in 4000 parts of water containing 10 parts of aluminium sulphate. The suspension is carefully stirred for 30 minutes, sized with a solution of 20 parts of 10% rosin size and 3 parts of aluminium sulphate in 10 parts of water, then diluted with water to 20,000 parts, and converted into sheet. The sheet thus produced is well brightened. This result shows that the brighteners of this invention can be applied in paper stocks at low pH values, which is very important in paper manufacture where backwaters with a high content of aluminium sulphate have to be used.

Application Example E

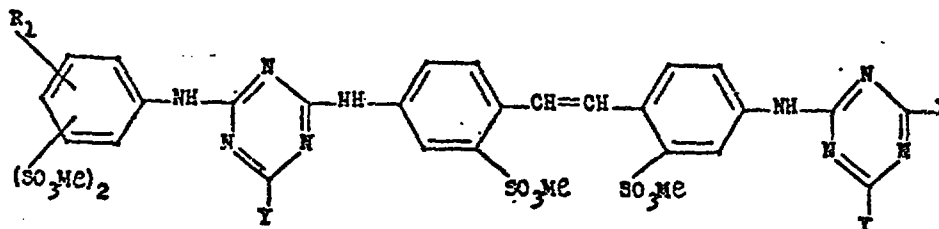
A coating mixture consisting of 66 parts of china clay, 33 parts of water, 10 parts of a 50% dispersion of a butadiene-styrene copolymer, 1 part of a 10% solution of a polyethylene glycol of molecular weight 5000—6000 and 0.3 part of a 10% solution of a brightener of Example 1 or 2 is mechanically applied to sized paper made from stock consisting of 50% bleached sulphite pulp and 50% mechanical wood-pulp. An attractive brightened paper is obtained.

A further addition of 5 parts of a 10% solution of a reduced starch can be included in the above coating mixture, which gives a slight improvement in the brightening effect.

Application Examples A to C were repeated with the brightener of Example 4, similar results being obtained.

WHAT WE CLAIM IS:—

1. A bis-(triazinylamino)-stilbene derivative of the formula



(I)

Application Example A

A cotton fabric is conveyed through a bath of 240 parts of dimethylethylene urea, 28 parts of 48.5% sulphuric acid, 2 parts of the brightener of Example 1 and 730 parts of water, expressed between a pair of rollers to retain 100% of its weight of liquor, and dried at 90° to 8% residual moisture content. The fabric is rolled up and stored for 17 hours at room temperature. Afterwards it is rinsed with cold water, neutralized with a 2 g/l solution of anhydrous sodium carbonate, rinsed again with cold water, expressed and dried at 100°. The treated fabric shows a brilliant white effect of neutral shade.

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A cotton fabric is conveyed through a solution of 8 parts of the brightener of Example 2 in 1000 parts of water, expressed to an increase of 100% on the dry weight, and dried at 60—70°. A good white effect is obtained. If 8 parts of a polyethylene glycol with a molecular weight of 5000—6000 is added to the solution, the brightening effect is greatly intensified.

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The degree of whiteness shown by the coated paper is appreciably greater than the whiteness of a coating without optical brightener. The whiteness can be enhanced further by including in the coating composition 1% of a 10% solution of a polyethylene glycol of molecular weight 5000—6000.

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Application Example E

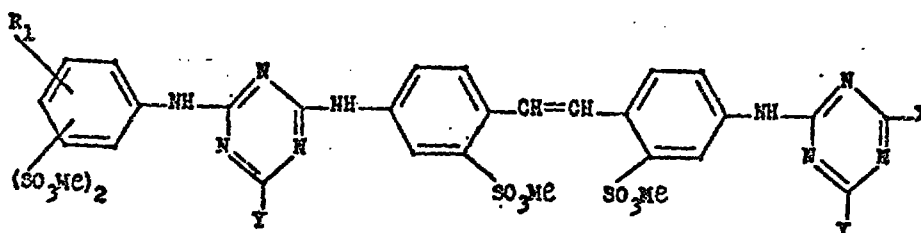
A coating mixture consisting of 66 parts of china clay, 33 parts of water, 10 parts of a 50% dispersion of a butadiene-styrene copolymer, 1 part of a 10% solution of a polyethylene glycol of molecular weight 5000—6000 and 0.3 part of a 10% solution of a brightener of Example 1 or 2 is mechanically applied to sized paper made from stock consisting of 50% bleached sulphite pulp and 50% mechanical wood-pulp. An attractive brightened paper is obtained.

A further addition of 5 parts of a 10% solution of a reduced starch can be included in the above coating mixture, which gives a slight improvement in the brightening effect.

Application Examples A to C were repeated with the brightener of Example 4, similar results being obtained.

WHAT WE CLAIM IS:—

1. A bis-(triazinylamino)-stilbene derivative of the formula



(I)

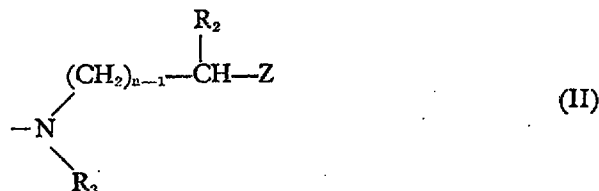




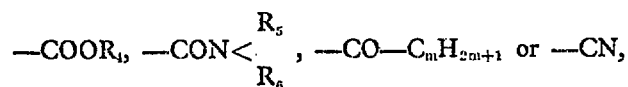
wherein

X represents an amino radical which may be substituted,

Y represents a radical of the formula



5 Z represents



R₁ represents hydrogen, halogen or a lower alkyl or alkoxy radical as herein defined,

R₂ represents hydrogen or a lower alkyl radical as herein defined,

10 R₃ represents hydrogen, a lower alkyl, hydroxyalkyl, hydroxyalkoxyalkyl or alkoxyalkyl radical as herein defined, an alkylaminoalkyl radical which may be substituted by one or more of hydroxyl and alkoxy radicals, a cycloalkyl radical which may be substituted by one or more lower alkyl radicals as herein defined, a phenyl radical which may be substituted by one or more of halogen atoms and lower alkyl and alkoxy radicals as herein defined, an aralkyl radical, an aryloxyalkyl radical or
15 a radical of the formula



with the proviso that when two radicals Z are present these may be different from one another,

20 R₄ represents a lower alkyl radical as herein defined which may be substituted by one or more of hydroxyl, alkoxy, phenyl or phenoxy,

each of

R₅ and R₆, independently of one another, represents hydrogen or a lower alkyl or hydroxyalkyl radical as herein defined, or R₅ and R₆ together with the nitrogen atom form a heterocyclic radical,

25 Me represents hydrogen, an alkali metal, an alkaline earth metal, an ammonium group which may be substituted, or aluminium,

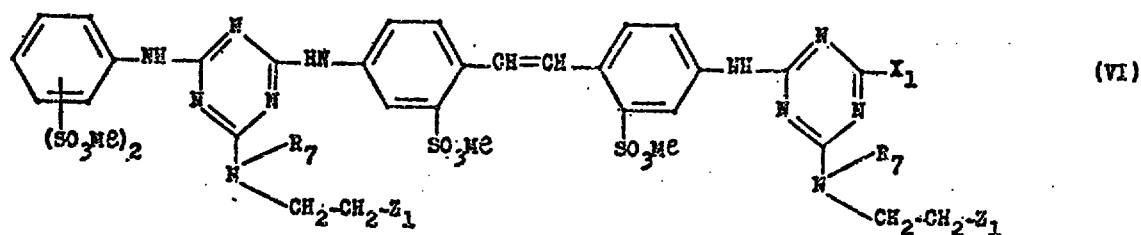
m represents a whole number from 1 to 5, and

n is 1 or 2.

2. A bis-(triazinylamino)-stilbene derivative according to Claim 1, wherein Z is



3. A bis-(triazinylamino)-stilbene derivative of the formula





* C L M S *

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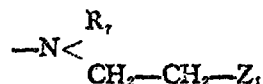
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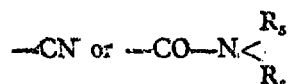
wherein

X_1 is $-NH_2$, a phenylamino radical which may be substituted by one or more of methyl, methoxy, chlorine, cyano and $-SO_3Me$, or a radical of the formula



5 Z_1 represents

5



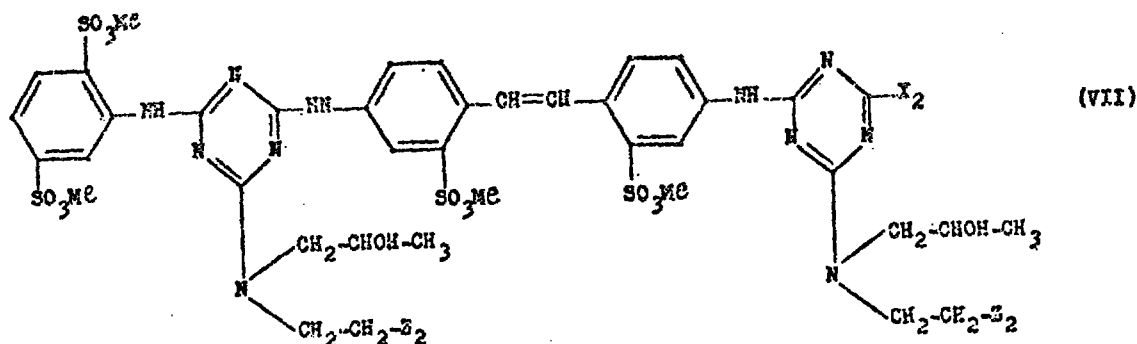
5

R_7 represents hydrogen, a lower alkyl, hydroxyalkyl or alkoxyalkyl radical as herein defined, an alkylaminoalkyl radical which may be substituted by one or more of hydroxyl and alkoxy radicals, or a radical $-CH_2-CH_2-Z_1$, and

10 Me , R_5 and R_6 have the significance stated in Claim 1.

10

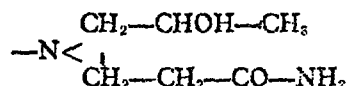
4. A bis-(triazinylamino)-stilbene derivative of the formula



wherein

Z_2 represents $-CN$ or $-CO-NH_2$,

15 X_2 represents $-NH_2$, phenylamino, 2,5-disulphophenylamino or



Me having the meaning stated in Claim 1.

5. Each of the bis-(triazinylamino)-stilbene derivative end products referred to in Examples 1 to 3.

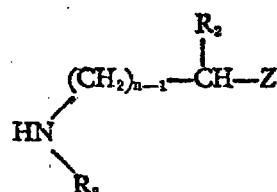
6. A process for the production of a bis-(triazinylamino)-stilbene derivative,

a) 1 mol of 4,4'-diaminostilbene-2,2'-disulphonic acid or of a salt of this acid consistent with the definition of Me in Claim 1,

b) 1 mol of an aminobenzenedisulphonic acid which may be substituted by R_1 as defined in Claim 1 or of a salt of this acid,

c) 1 mol of ammonia or of a primary or secondary amine and

d) 2 mols of an amine of formula



(IV)

where R_2 , R_3 , Z and n have the significance given in Claim 1, or of a mixture of amines of formula (IV).



7. A process for the production of a bis-(triazinylamino)-stilbene derivative, which comprises reacting 1 mol of a cyanuric halide in any desired order with
- 5 a) 1 mol of 4-amino-4'-nitrostilbene-2,2'-disulphonic acid or of a salt of this acid consistent with the definition of Me in Claim 1,
- b) 1 mol of an aminobenzenedisulphonic acid which may be substituted by R₁ as defined in Claim 1 or of a salt of this acid,
- 10 c) 1 mol of an amine of formula (IV) stated in Claim 6 or of a mixture thereof, reducing the nitro group containing compound to give the corresponding amino group containing compound, reacting the latter with 1 mol of a cyanuric halide, and reacting the resulting dihalogenotriazinyl compound in either order with
- d) 1 mol of ammonia or of a primary or secondary amine, and
- e) 1 mol of an amine of formula (IV) or of a mixture thereof.
8. A process according to Claim 6 or 7, wherein the first halogen atom of the cyanuric halide is replaced at 0—15° C and at a pH value of 3 to 7.
- 15 9. A process according to Claim 6, 7 or 8, wherein the condensation of the second halogen atom is carried out at a temperature of 20° to 60° C.
10. A process according to Claim 9, in which said condensation is effected at a pH value of 4 to 8.
- 20 11. A process according to any one of Claims 6 to 10, wherein the third halogen atom is reacted at 80—100° C and at a pH value of 4 to 10.
12. A process according to any one of Claims 6 to 11, wherein the nitro group containing compound is reduced by treatment with an aqueous sodium sulphite or sodium hydrogen sulphite solution.
- 25 13. A process according to Claim 12, wherein the reduction is effected at a temperature of 60° C to 90° C.
14. A process according to any one of Claims 6 to 11, wherein the nitro group containing compound is reduced by acidification with hydrochloric, sulphuric or acetic acid and treatment with zinc powder or iron turnings or powder at a temperature of 50 to 100° C.
- 30 15. A process according to Claim 14, wherein said temperature is 80 to 100° C.
16. A process for the production of a bis-(triazinylamino)-stilbene derivative substantially as herein described with reference to any one of Examples 1 to 3.
- 35 17. A bis-(triazinylamino)-stilbene derivative whenever produced by a process claimed in any one of Claims 6 to 16.
18. A brightening process which comprises brightening natural or regenerated cellulosic fibres, natural or synthetic polyamide or polyurethane fibres or paper with a bis-(triazinylamino)-stilbene derivative claimed in any one of Claims 1 to 5 and 17.
- 40 19. A brightening process substantially as described herein with reference to any one of Application Examples A to E.
20. Natural or regenerated cellulosic fibres, natural or synthetic polyamide or polyurethane fibres or paper brightened with a bis-(triazinylamino)-stilbene derivative claimed in any one of Claims 1 to 5 and 17.
- 45 21. The bis-(triazinylamino)-stilbene derivative end product referred to in Example 4.
22. A process for the production of a bis-(triazinylamino)-stilbene derivative substantially as herein described with reference to Example 4.
- 50 23. A bis-(triazinylamino)-stilbene derivative whenever produced by a process claimed in Claim 22.
24. A brightening process which comprises brightening natural or regenerated cellulosic fibres, natural or synthetic polyamide or polyurethane fibres or paper with a bis-(triazinylamino)-stilbene derivative claimed in Claim 21 or 23.
- 55 25. Natural or regenerated cellulosic fibres, natural or synthetic polyamide or polyurethane fibres or paper brightened with a bis-(triazinylamino)-stilbene derivative claimed in Claim 21 or 23.
26. Each of the bis-(triazinylamino)-stilbene derivative end products referred to in Examples 5 to 84.
- 60 27. A brightening process which comprises brightening natural or regenerated cellulosic fibres, natural or synthetic polyamide or polyurethane fibres or paper with a bis-(triazinylamino)-stilbene derivative claimed in Claim 26.
28. Natural or regenerated cellulosic fibres, natural or synthetic polyamide or polyurethane fibres or paper brightened with a bis-(triazinylamino)-stilbene derivative claimed in Claim 26.

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