

PATENT SPECIFICATION

(11) 1 476 526

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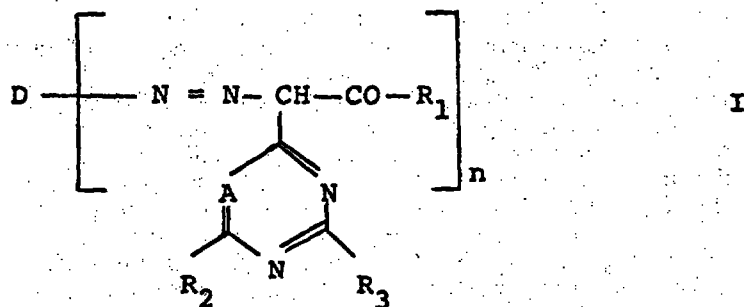
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(54) AZO AND DISAZO COMPOUNDS

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, 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 azo compounds, their production and use. Accordingly, the present invention provides compounds of formula I,



in which

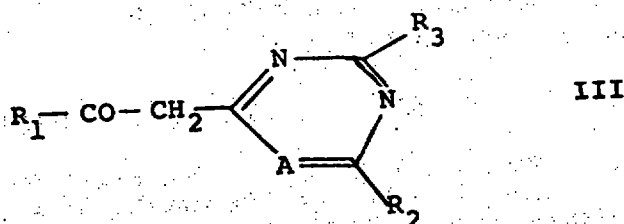
- R_1 signifies a group of formula $-\text{NH}_2$, $-\text{NH}-\text{R}_4$ or $-\text{O}-\text{R}_4$, in which R_4 signifies a (C_{1-8}) alkyl radical, (C_{5-8}) cycloalkyl radical, unsubstituted phenyl, naphthyl or heterocyclic radical of aromatic character, or a phenyl, naphthyl or heterocyclic radical of aromatic character substituted by up to 3 substituents selected from up to 2 substituents selected from chlorine, bromine, (C_{1-8}) alkyl and (C_{1-8}) alkoxy and up to one of each of trifluoromethyl, sulphoguanidine, nitro, cyano, $-\text{CO}-\text{NH}-\text{R}_5$ and $-\text{SO}_2-\text{NH}-\text{R}_5$ groups, in which R_5 signifies a (C_{1-8}) alkyl, (C_{5-8}) cycloalkyl, an unsubstituted phenyl or naphthyl radical or a phenyl or naphthyl radical substituted by up to three substituents selected from up to 2 substituents selected from halogen, (C_{1-8}) alkyl and (C_{1-8}) alkoxy radicals, and up to one of each of trifluoromethyl, nitro, cyano, phenylaminocarbonyl or -sulphonyl, each of
- R_2 and R_3 , which may be the same or different, signifies a hydrogen atom, a hydroxyl, (C_{1-8}) alkoxy, amino, (C_{5-8}) cycloalkylamino, (C_{1-8}) alkylamino, (C_{1-8}) dialkylamino, phenyl- or naphthylamino or N-phenyl-N- (C_{1-8}) alkylamino group,
- A signifies a nitrogen atom or a group of formula $>\text{C}-\text{R}_6$ in which R_6 signifies a hydrogen or halogen atom or a (C_{1-8}) alkyl radical, either
- n signifies 1 and D signifies the radical of a diazo component, or
- n signifies 2 and D signifies the radical of a tetrazo component,
- and the molecule is free from sulphonic acid groups.

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The present invention also provides a process for the production of compounds of formula I as defined above, comprising coupling the diazotized or tetrazotized amine of formula II,



in which D and n are as defined above with a compound of formula III,



in which R₁, R₂, R₃ and A are as defined above, preferably in a 1:1 (where n is 1) or 1:2 (where n is 2) molar ratio.

The coupling reaction is carried out according to known methods. Suitably the compound of formula III is dissolved in an organic solvent, for example, dimethyl formamide, or is suspended in water, and is reacted therein.

In the compounds of formula I, where R₁ signifies a radical of formula —NH—R₄ or —O—R₄ and where R₄ signifies an unsubstituted or substituted heterocyclic radical of aromatic character, the heterocyclic radical is suitably a five or six membered ring containing one or two hetero atoms, which may be the same or different, selected from nitrogen and sulphur; in addition the heterocyclic ring may be fused with a carbocyclic ring, for example a benzene ring. Examples of suitable heterocyclic radicals for R₄ include phthalimidyl, phthalazinyl, quinazolonyl, quinoxaliny, quinoxaline-2,3-dion-yl radical, benzimidazolonyl, 2-, 3-, or 4-pyridyl, 2- or 3-thienyl or 2-thiazolyl. Among these, the benzimidazolonyl radical is preferred.

The diazo or tetrazo component radicals as D in the compounds of formula I may be any of the radicals which would be used in the chemistry of azo pigments, for example, radicals of the phenyl, naphthyl, quinolyl, benzimidazolonyl, quinoxalyl or anthraquinonyl series in which the aromatic nuclei are unsubstituted or substituted by a total of up to 3 substituents selected from up to 3 substituents selected from fluorine, chlorine and bromine atoms, (C₁₋₈)alkyl and (C₁₋₈)alkoxy groups, up to 2 substituents selected from cyano, nitro, (C₁₋₈)alkoxycarbonyl and (C₁₋₈)alkylsulphonyl groups and up to one of each of trifluoromethyl, aminocarbonyl, aminosulphonyl (C₁₋₈)alkylaminocarbonyl, (C₁₋₈)alkylaminosulphonyl, di - (C₁₋₈)alkylaminocarbonyl, di - (C₁₋₈)alkylaminosulphonyl, phenylaminocarbonyl, sulphoguanidine, benzoylamino, phenylazo and phenoxycarbonyl groups, in which the phenyl nuclei are unsubstituted or substituted by a chlorine or bromine atom or by an (C₁₋₈)alkyl, trifluoromethyl, cyano, nitro, aminocarbonyl or (C₁₋₈)alkoxycarbonyl or (C₁₋₈)alkylaminocarbonyl group.

When n is 3, a preferred tetrazocomponent radical of 4,4'-diphenylene substituted by 1 to 4 substituents selected from the group consisting of chlorine and bromine atoms, nitro, cyano, methyl and (C₁₋₈)alkoxy groups.

In the compounds of formula I as defined above, the preferred cycloalkyl radical is cyclohexyl. Preferred alkyl and alkoxy radicals are those containing 1, 2, 3 or 4 carbon atoms.

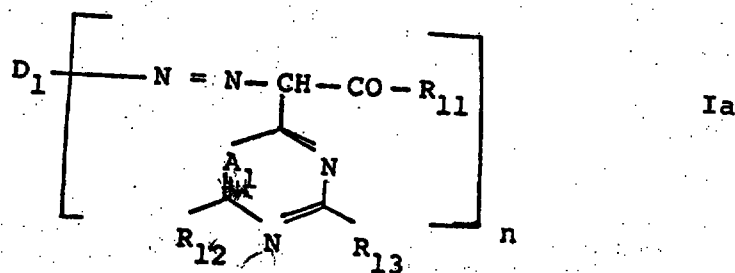
When n is 1, preferably D is a phenyl radical having a total of up to three substituents selected from up to three chlorine and bromine atoms, up to two (C₁₋₈)alkoxycarbonyl, nitro, cyano or (C₁₋₈)alkylsulphonyl groups and one aminocarbonyl, aminosulphonyl, (C₁₋₈)alkylaminocarbonyl, (C₁₋₈)alkylaminosulphonyl, di - (C₁₋₈)alkylaminocarbonyl, di - (C₁₋₈)alkylaminosulphonyl or phenylaminocarbonyl radical; an α- or β-(preferably α-)anthraquinonyl or benzimidazolonyl-5 radical.

When n is 2, preferably D is derived from a benzidine substituted one or twice by chlorine, bromine, nitro, cyano, methyl, methoxy or ethoxy.

Preferably R₁ is a phenylamino radical which is unsubstituted or substituted by a total of up to 3 substituents selected from up to two substituents selected from chlorine and bromine atoms (C₁₋₄)alkyl and (C₁₋₄)alkoxy groups and/or up to one of each of trifluoromethyl, sulphoguanidine, nitro and cyano groups; a naphthyl-amino radical, an ethoxy radical or a methoxy radical, particularly the former two, and more particularly unsubstituted or substituted phenylamino.

By halogen as used herein is meant chlorine, bromine or fluorine.

A preferred group of compounds of formula I, are those of formula Ia,



in which

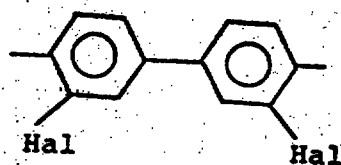
R₁₁ signifies an unsubstituted phenylamino, naphthylamino, methoxy or ethoxy radical or a phenylamino radical substituted by up to three substituents selected from the group consisting of chlorine, bromine, methyl and methoxy, (a maximum of 2 of each), each of

R₁₂ and R₁₃, which may be the same or different, signifies an amino dimethyl-amino, diethylamino or, preferably, a hydroxy group,

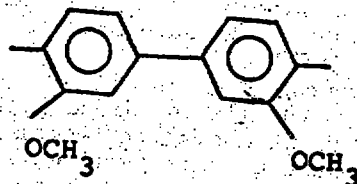
A₁ signifies a group of formula $\geq\text{CH}$ or $\geq\text{C}-\text{Cl}$ or, preferably, a nitrogen atom, and either

n is 1 and R₁ signifies a phenyl radical substituted by up to two substituents selected from chlorine, bromine, methoxycarbonyl and ethoxycarbonyl; a benzimidazolonyl-5 or an α -anthraquinonyl radical, or

n is 2 and D₁ signifies a radical of formula



or



in which Hal signifies chlorine or bromine.

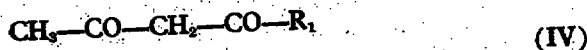
Of the compounds of formula Ia those where

R₁₁ signifies an unsubstituted phenylamino radical or a phenylamino radical substituted by up to 3 substituents selected from one chlorine atom and/or one or two methyl or methoxy groups, each of

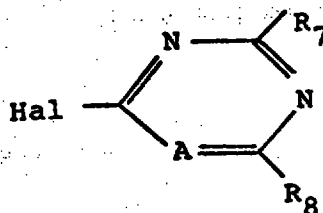
R₁₂ and R₁₃, signifies a hydroxy group,

A₁ signifies a nitrogen atom,

n is 1 and D₁ is an iso- or terephthalic acid dimethyl ester radical are preferred. The compounds of formula III may be produced by condensing a compound of formula IV,



in which R₁ is as defined above, with a compound of formula V,



in which each of R₇ and R₈, which may be the same or different, signifies a fluorine, chlorine or bromine atom, or has one of the significances given for R₂ and R₃ above,

Hal signifies chlorine or bromine, and

A is as defined above,

in a 1:1 molar ratio, and if necessary, subsequently splitting off the CH₃—CO—group and/or exchanging any halogen atoms as R₇ and R₈ for an amino, alkoxy or hydroxy group.

The reaction of the compounds of formula IV with the compounds of formula V is preferably carried out in a weakly alkaline to strongly alkaline medium, for example, at a pH up to 12. The reaction temperature is suitably between 0° and 100° C. Suitable solvents are water, dioxane or acetone or mixtures of these solvents. An alkaline metal carbonate or hydroxide may be used to bind the free hydrogen halide.

The splitting-off of the CH₃—CO—group is advantageously effected in a weakly alkaline or acid medium, for example at a pH value of from 1 to 8, in a polar solvent, such as water, acetone, dioxane, alcohol, e.g. ethanol, isopropanol, benzyl alcohol; glycols, e.g. ethylene glycol, propylene glycol, diethylene glycol; or an amide, e.g. dimethyl formamide, dimethylacetamide; dimethyl sulphoxide and hexamethyl phosphorous triamide. The reaction temperature is between room temperature and boiling temperature of the reaction mixture, preferably between 60° and 150° C. Thus, if the condensation reaction is carried out in a weakly alkaline medium, the CH₃—CO— can be split-off simultaneously with the condensation reaction.

Water or alkaline metal hydroxides (sodium, potassium or lithium hydroxide), alkaline earth metal oxides or hydroxides (magnesium oxide, calcium oxide or calcium hydroxide) are suitable for the replacement of halogens as R₇ and/or R₈ by hydroxyl groups; alkaline metal alcoholates (sodium or potassium alcoholate) are suitable for replacement by alkoxy groups.

Halogens may be replaced by amino groups by reaction with the corresponding amines optionally in the presence of alkali metal carbonates, bicarbonates or hydroxides. The above-mentioned groups can be introduced simultaneously with the hydrolytic splitting-off of the group CH₃CO—.

The compounds of formula I, as defined above, are useful as pigments. They are suitable for dyeing synthetic substrates, including plastics or synthetic resins, in the mass, with or without the use of a solvent. They may be used in paints having an oil or aqueous base, in varnishes, in spin-dyeing of viscose or cellulose acetate, for pigmenting polyethylene, polystyrene, polyvinyl chloride, rubber or artificial leather. Furthermore, they are useful in printing inks, for the stock dyeing of paper, for coating textiles and for pigment printing.

The dyeings obtained have notable fastness to heat, light and weather, they are resistant to chemicals such as SO₂ and alkalis. They have notable fastness to migration, effluorescence, overvarnishing, flocculation, crystallization and solvents. They have a good depth of colour and good dispersibility and covering capacity.

The pigment properties may be further improved by subsequent treatment of

the crude pigment in organic solvents at increased temperatures, e.g. 110° to 200° C. Suitable organic solvents (in which the pigments themselves are not dissolved) are chlorobenzenes (mixture), nitrobenzene, dimethylformamide, glacial acetic acid, ethylene glycol or quinoline.

Compounds of formula I, in which R₂ and R₃ signify hydroxy, are preferred pigments.

The compounds of formula I, where R₂ and R₃ have a significance other than hydroxy, are also useful as disperse dyes. They are useful for dyeing organic substrates of high molecular weight and hydrophobic character, for example substrates consisting of or comprising linear or aromatic polyesters, cellulose acetates or synthetic polyamides.

The dyeing methods employed are conventional methods, for example the methods described in French Patent No. 1,443,371.

The dyeings obtained have notable fastness to light, sublimation, washing, solvents, rubbing, gas fumes, reduction and chlorine.

The following Examples serve to illustrate the invention further.

In the Examples all parts and percentages are by weight and all temperatures in degrees Centigrade.

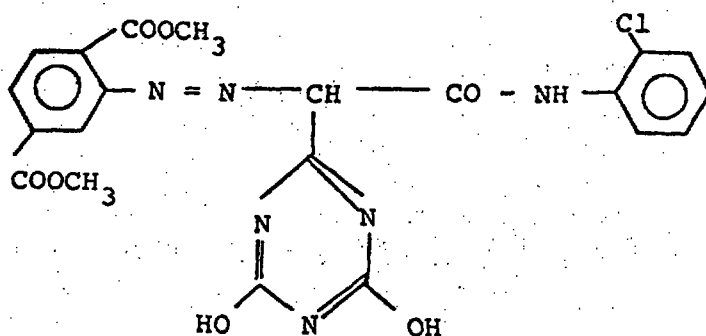
Example 1.

41.8 parts of aminoterephthalic acid dimethyl ester are dissolved in 100 parts of glacial acetic acid at 100° and are entered into a mixture of 400 parts of water and 65 parts of 35% hydrochloric acid. It is cooled to 0°, 14 parts of sodium nitrite are added with stirring, stirring is continued for about 5 minutes, 60 parts of urea are added to the solution and it is filtered.

56.1 parts of 2-chloro-(4',6'-dihydroxy-1',3',5'-triazinyl)-acetylaminobenzene are dissolved in 300 parts of dimethyl formamide, a solution of 300 parts of anhydrous sodium acetate in 300 parts of water is added to the mixture, it is cooled to 0°, the diazonium salt solution is added with stirring over the course of about 10 minutes, it is stirred for 1 hour at 0° to 5° and for a further 12 hours at room temperature. Finally, the precipitate is filtered off, washed to neutral with water and dried.

In order to improve the fastness and applicatory properties, especially the rheological behaviour and the dispersibility, the pigment is subjected to treatment for 1 hour in dimethyl formamide at about 150°.

The pure pigment so obtained of formula



has a melting point of over 300° and dyes polyvinyl chloride in yellow shades with excellent fastness.

The elementary analysis is as follows:—

	C	H	Cl	N	O
theory:	50.4	3.4	7.1	16.8	22.4
found:	50.5	3.4	7.0	16.8	22.3

The above dye may also be produced as follows:—

52.57 Parts of aminoterephthalamic acid dimethyl ester are entered with stirring into a mixture of 25 parts of water and 25 parts of glacial acetic acid. It is stirred further for 1 hour, 62.5 parts of water and 73.1 parts of 35% hydrochloric acid are

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added and the mixture is stirred for 5 hours. The mixture is cooled in an ice bath and 75 parts of ice are added. A solution of 15.5 parts of sodium nitrite in 50 parts of water are subsequently introduced beneath the surface, at a temperature of 0°—5°, over the course of 30 minutes. After stirring for 1 further hour, 4 parts of 1N-amidosulphonic acid are added, the pH is adjusted to 3.4 with 30% sodium hydroxide solution and the mixture is stirred at 0—5° for approximately 10 minutes. Impurities which may be present are filtered off.

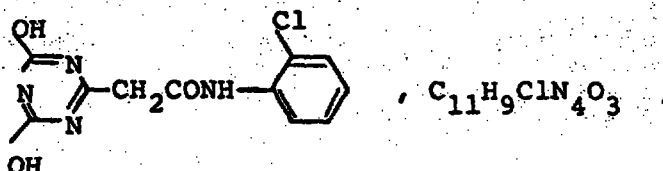
70.15 Parts of 2 - chloro - (4',6' - dihydroxy - 1',3',5' - triazinyl) - acetylaminobenzene are dissolved in a mixture of 62.5 parts of water and 62.5 parts of 30% sodium hydroxide solution. Glacial acetic acid is added to the solution until the pH is 6.9. The resulting suspension which is heated to 40° is combined with stirring over the course of 2 hours with the diazonium salt solution and the mixture is stirred at 40° for 1 hour. Subsequently, it is heated to 80° and stirred for 1 further hour. The pigment is filtered off, washed with approximately 7000 parts of hot water and dried at 70° in a vacuum.

In order to improve the dyeing properties the pigment is subjected to treatment for 1 hour in boiling ethanol.

2 - chloro - (4',6' - dihydroxy - 1',3',5' - triazinyl) - acetylaminobenzene may be produced as follows:

A solution of 396 parts of cyanuric chloride in 1000 parts of dioxane is entered slowly with stirring into 1000 parts of ice-water mixture. To the resultant mixture is added a mixture of 247 parts of 2 - chloroacetoacetyl - aminobenzene, 920 parts of water and 80 parts of sodium hydroxide, this being added very slowly (over the course of about 40 minutes) at a temperature of 0° to 5°. The mixture is stirred for a further 30 minutes at the above temperature and is filtered. The precipitate is washed with ice-cold water, it is then entered into 5000 parts of ethanol and heated at reflux, with stirring, for 20 hours. After cooling to 20°, the precipitate is filtered, washed several times with hot water and vacuum dried at 100°.

The product thus obtained corresponds to the formula



which is demonstrated by the elementary analysis

	C	H	Cl	N	O
theory:	47.1	3.2	12.6	20.0	17.1
found:	47.0	3.4	12.8	20.2	17.3

In the following Table 1 further pigments are given which may be produced in analogy with the procedures set forth above. They are of the general formula

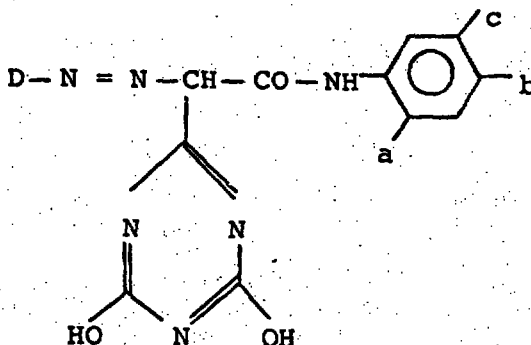
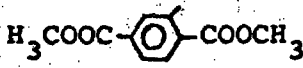
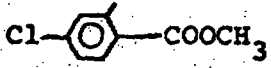
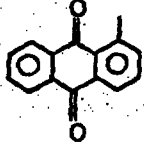


Table 1

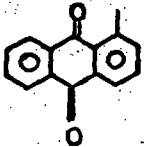
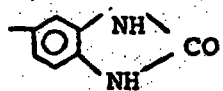
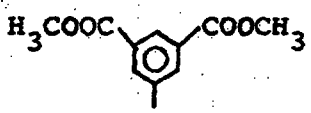
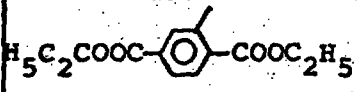
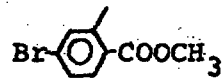
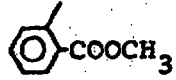
Example No.	D	a	b	c	Shade in P V C
2		-OCH ₃	Cl	-OCH ₃	yellow
3	do.	do.	H	do.	do.
4	do.	H	Cl	H	do.
5	do.	-OCH ₃	H	H	do.
6	do.	H	H	H	do.
7	do.	-CH ₃	H	H	do.
8		H	H	H	do.
9	do.	H	Cl	H	do.
10	do.	Cl	H	H	do.
11	do.	-OCH ₃	Cl	-OCH ₃	do.
12	do.	do.	H	H	do.
13	do.	do.	H	-OCH ₃	do.
14	do.	-CH ₃	H	H	do.
15		-Cl	H	H	do.
16	do.	-OCH ₃	Cl	-OCH ₃	orange

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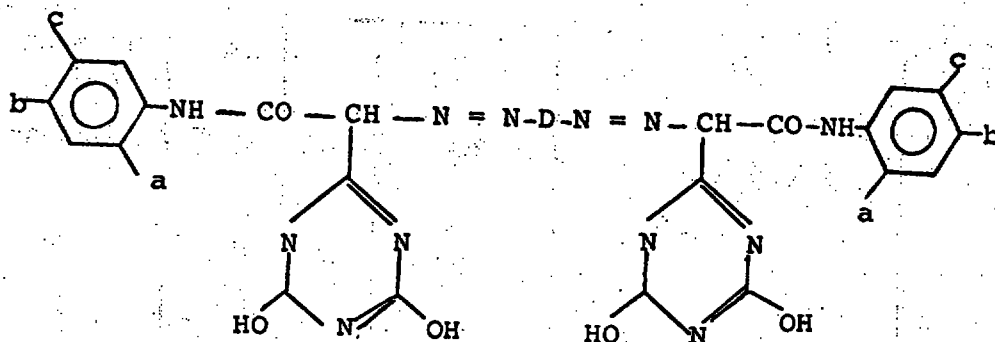
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Example No.	D	a	b	c	Shade in P V C
17		H	Cl	H	yellow
18		Cl	H	H	do.
19	do.	-OCH ₃	Cl	-OCH ₃	orange
20	do.	do.	H	do.	do.
21		H	H	H	yellow
22	do.	H	Cl	H	do.
23	do.	Cl	H	H	do.
24	do.	-OCH ₃	Cl	-OCH ₃	orange
25	do.	do.	H	H	yellow
26	do.	do.	H	-OCH ₃	orange
27	do.	-CH ₃	H	H	yellow
28		do.	H	H	do.
29		H	H	H	do.
30		H	-CH ₃	H	do.

(17)

In Table 2 dyes are given which may be produced in analogy with the procedure as set out above, they are of the general formula



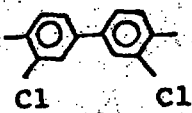
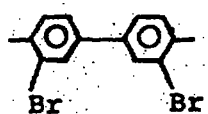
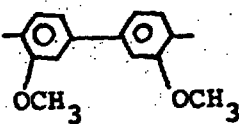
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Table 2

Example No.	D	a	b	c	Shade in P V C
31		Cl	H	H	orange
32	do.	-OCH ₃	H	H	do.
33	do.	do.	Cl	-OCH ₃	do.
34	do.	do.	H	do.	do.
35	do.	-CH ₃	H	H	do.
36	do.	H	H	H	do.
37	do.	H	Cl	H	do.
38		-OCH ₃	Cl	-OCH ₃	do.
39		Cl	H	H	red
40	do.	-OCH ₃	H	H	orange
41	do.	do.	Cl	-OCH ₃	red
42	do.	do.	H	do.	do.
43	do.	-CH ₃	H	H	orange
44	do.	H	H	H	do.
45	do.	H	Cl	H	red
46	do.	H	Br	H	do.

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Further dyes are shown in Table 3. They may be produced in analogy with the procedures as set forth in Example 1 and correspond to the general formula

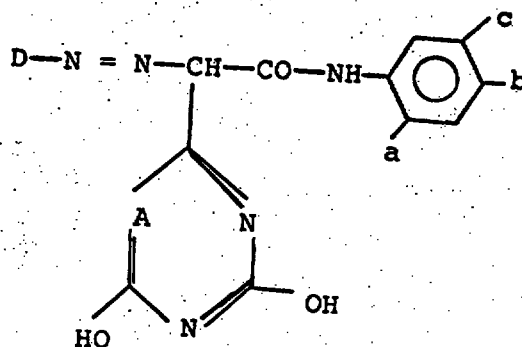


Table 3

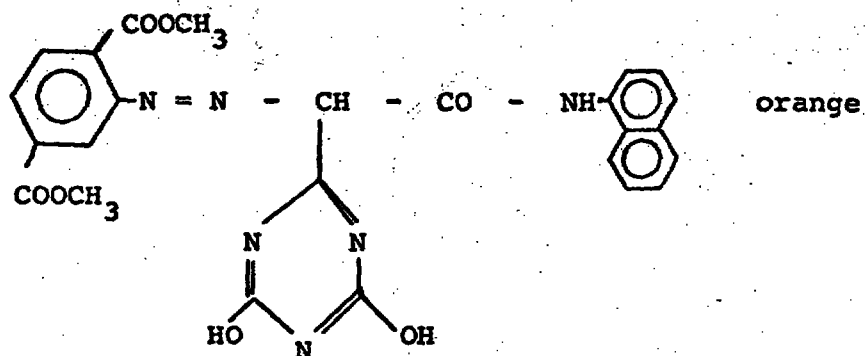
Example No.	D	A	a	b	c	Shade in P V C
47	$\text{H}_3\text{COOC}-\text{C}_6\text{H}_4-\text{COOCH}_3$	$\text{C}=\text{Cl}$	H	H	H	yellow
48	do.	do.	$-\text{CH}_3$	H	H	do.
49	do.	do.	$-\text{OCH}_3$	H	H	do.
50	do.	do.	Cl	H	H	do.
51	do.	$\text{C}=\text{H}$	Cl	H	H	do.
52	$\text{Cl}-\text{C}_6\text{H}_4-\text{COOCH}_3$	do.	Cl	H	H	do.

The dyes of the following formulae are produced in a manner analogous to that of the first operating process of Example 1:

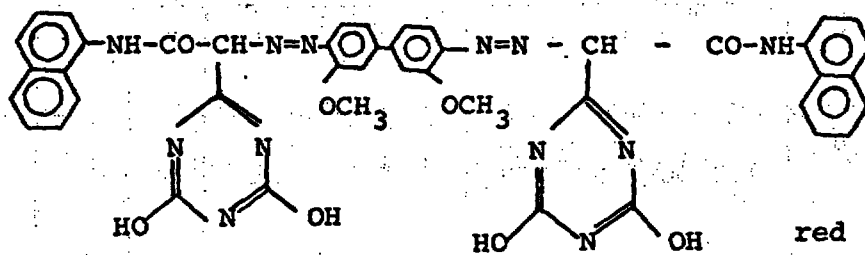
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Example 53

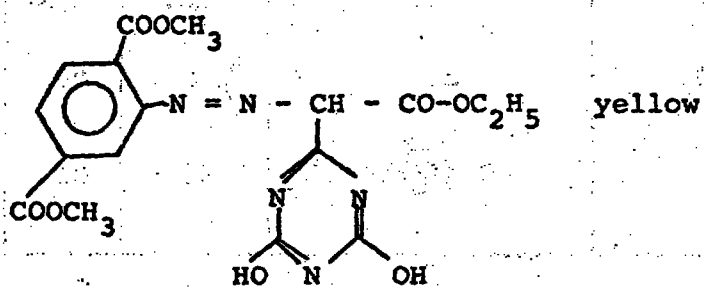
Shade in
P V C



Example 54



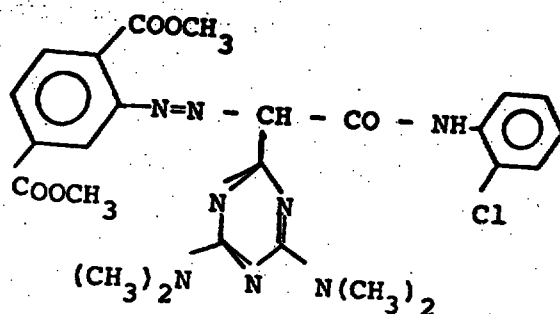
Example 55



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Example 56

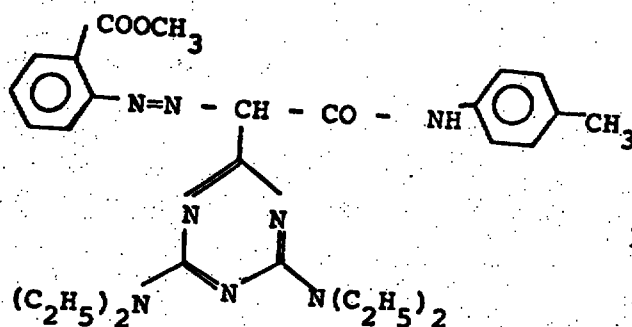
Disperse dye,
sample dyeing in
a fabric of poly-
ester fibre



yellow

Example 57

oil-soluble dye



yellow

APPLICATION EXAMPLE A.

To a basic mixture consisting of

- 63 parts of polyvinyl chloride emulsion,
- 32 parts of dioctyl phthalate,
- 3 parts of commercial epoxy softener,
- 1.5 parts of stabilizer (barium-cadmium-stearate mixture, also commercial) and
- 0.5 parts of a chelator (commercial)

are added 0.5 parts of the pigment of Example 1 and 5 parts of titanium dioxide pigment, and they are mixed together intimately.

The mixture is rolled for 8 minutes in a roll mixer heated to 160° C and having friction rollers (one roller at 20, the other at 25 revolutions per minute) so as to obtain better pigment distribution, the sheet obtained, of 0.3 mm thickness and having a yellow shade, is removed.

The dyeing is very fast to light and migration, and is heat-resistant.

APPLICATION EXAMPLE B.

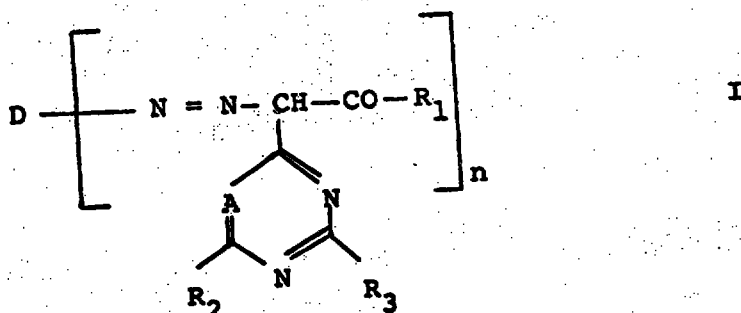
A mixture of 7 parts of the dye produced in accordance with Example 56, 4 parts of sodium dinaphthyl methane disulphonate, 4 parts of sodium cetyl sulphate and 5 parts of anhydrous sodium sulphate is ground in a ball mill over the course of 48 hours to give a fine powder.

1 Part of the obtained dyeing preparation is pasted with a small amount of water and the resulting suspension is added through a sieve to a bath of 4000 parts of water containing 3 parts of sodium lauryl sulphate. The liquor ratio is 1:40. 100 Parts of a purified fabric of polyester fibre are entered into the dyebath at 40°-50° which is then set with an emulsion of 20 parts of a chlorinated benzene in water. The

bath is slowly heated to 100° and the fabric dyed at 95—100° for 1 to 2 hours. The fabric dyed in a yellow shade is washed, soaped, washed again and dried. The level dyeing has notable fastness to light, cross dyeing, washing, water, sea water, perspiration, sublimation, gas fumes, thermofixation, pleating and permanent press finishing.

WHAT WE CLAIM IS:—

1. A compound of formula I,



in which

R_1 signifies a group of formula $-\text{NH}_2$, $-\text{NH}-\text{R}_4$ or $-\text{O}-\text{R}_4$, in which R_4 signifies a (C_{1-8}) alkyl radical, (C_{5-8}) cycloalkyl radical, unsubstituted phenyl, naphthyl or heterocyclic radical of aromatic character or a phenyl, naphthyl or heterocyclic radical of aromatic character substituted by up to 3 substituents selected from up to 2 substituents selected from chlorine, bromine, (C_{1-8}) alkyl and (C_{1-8}) alkoxy and up to one of each of trifluoromethyl, sulphonyl, sulphonyl, nitro, cyano $-\text{CO}-\text{NH}-\text{R}_5$ and $-\text{SO}_2-\text{NH}-\text{R}_5$ groups, in which R_5 signifies a (C_{1-8}) alkyl, (C_{5-8}) cycloalkyl, an unsubstituted phenyl or naphthyl radical, or a phenyl or naphthyl radical substituted by up to three substituents selected from up to two substituents selected from halogen, (C_{1-8}) alkyl and (C_{1-8}) alkoxy, and up to one of each of trifluoromethyl, nitro, cyano, phenylaminocarbonyl or sulphonyl, each of

R_2 and R_3 , which may be the same or different, signifies a hydrogen atom, a hydroxyl, (C_{1-8}) alkoxy, amino, (C_{5-8}) cycloalkylamino, (C_{1-8}) alkylamino, (C_{1-8}) dialkylamino, phenyl- or naphthylamino or N-phenyl-N (C_{1-8}) alkylamino group

A signifies a nitrogen atom or a group of formula $>\text{C}-\text{R}_6$, in which R_6 signifies a hydrogen atom or halogen atom or a (C_{1-8}) alkyl radical, either

n signifies 1 and D signifies the radical of a diazo component, or

n signifies 2 and D signifies the radical of a tetrazo component, and the molecule is free from sulphonic acid groups.

2. A compound according to Claim 1, in which any alkyl radical contains 1 to 4 carbon atoms and any cycloalkyl radical is a cyclohexyl radical.

3. A compound according to Claim 1 or Claim 2, in which either n is 1 and D is a phenyl radical substituted by a total of up to three substituents selected from up to three chlorine and/or bromine atoms, up to two substituents selected from (C_{1-8}) alkoxycarbonyl, nitro, cyano or (C_{1-8}) alkylsulphonyl and up to one of each of aminocarbonyl, aminosulphonyl, (C_{1-8}) alkylaminocarbonyl, (C_{1-8}) alkylaminosulphonyl, di- (C_{1-8}) alkylaminocarbonyl, di- (C_{1-8}) alkylaminosulphonyl or phenylaminocarbonyl radicals; an α - or β -anthraquinonyl or benzimidazolonyl-5 radical or n is 2 and D is 4,4'-diphenylene substituted once or twice by chlorine, bromine, nitro, cyano, methyl, methoxy or ethoxy.

4. A compound according to any one of the preceding claims, in which R_1 is an unsubstituted phenylamino radical; a phenylamino radical substituted by a total of up to three substituents selected from up to two substituents selected from chlorine and bromine atoms, (C_{1-8}) alkyl and (C_{1-8}) alkoxy groups, and/or up to one of each of trifluoromethyl, sulphonyl, sulphonyl, nitro and cyano groups; or a naphthylamino radical.



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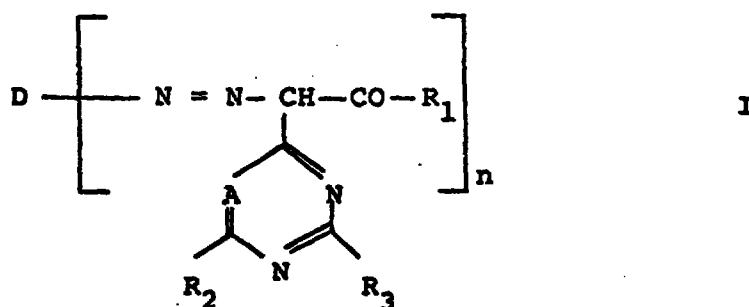
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bath is slowly heated to 100° and the fabric dyed at 95—100° for 1 to 2 hours. The fabric dyed in a yellow shade is washed, soaped, washed again and dried. The level dyeing has notable fastness to light, cross dyeing, washing, water, sea water, perspiration, sublimation, gas fumes, thermofixation, pleating and permanent press finishing.

WHAT WE CLAIM IS:—

1. A compound of formula I,



in which

R_1 signifies a group of formula $-\text{NH}_2$, $-\text{NH}-\text{R}_4$ or $-\text{O}-\text{R}_4$, in which R_4 signifies a (C_{1-8}) alkyl radical, (C_{5-8}) cycloalkyl radical, unsubstituted phenyl, naphthyl or heterocyclic radical of aromatic character or a phenyl, naphthyl or heterocyclic radical of aromatic character substituted by up to 3 substituents selected from up to 2 substituents selected from chlorine, bromine, (C_{1-3}) alkyl and (C_{1-3}) alkoxy and up to one of each of trifluoromethyl, sulphoguanidine, nitro, cyano $-\text{CO}-\text{NH}-\text{R}_5$ and $-\text{SO}_2-\text{NH}-\text{R}_5$ groups, in which R_5 signifies a (C_{1-8}) alkyl, (C_{5-8}) cycloalkyl, an unsubstituted phenyl or naphthyl radical, or a phenyl or naphthyl radical substituted by up to three substituents selected from up to two substituents selected from halogen, (C_{1-3}) alkyl and (C_{1-3}) alkoxy, and up to one of each of trifluoromethyl, nitro, cyano, phenylaminocarbonyl or -sulphonyl, each of

R_2 and R_3 , which may be the same or different, signifies a hydrogen atom, a hydroxyl, (C_{1-8}) alkoxy, amino, (C_{5-8}) cycloalkylamino, (C_{1-8}) alkylamino, (C_{1-8}) dialkylamino, phenyl- or naphthylamino or N-phenyl-N (C_{1-8}) alkylamino group

A signifies a nitrogen atom or a group of formula $\geq \text{C}-\text{R}_6$ in which R_6 signifies a hydrogen or halogen atom or a (C_{1-8}) alkyl radical, either n signifies 1 and D signifies the radical of a diazo component, or n signifies 2 and D signifies the radical of a tetrazo component, and the molecule is free from sulphonic acid groups.

2. A compound according to Claim 1, in which any alkyl radical contains 1 to 4 carbon atoms and any cycloalkyl radical is a cyclohexyl radical.

3. A compound according to Claim 1 or Claim 2, in which either

n is 1 and D is a phenyl radical substituted by a total of up to three substituents selected from up to three chlorine and/or bromine atoms, up to two substituents selected from (C_{1-4}) alkoxycarbonyl, nitro, cyano or (C_{1-4}) alkylsulphonyl and up to one of each of aminocarbonyl, aminosulphonyl, (C_{1-4}) alkylaminocarbonyl, (C_{1-4}) alkylaminosulphonyl, di- (C_{1-4}) alkylaminocarbonyl, di- (C_{1-4}) alkylaminosulphonyl or phenylaminocarbonyl radicals; an α - or β -anthraquinonyl or benzimidazolonyl-5 radical or

n is 2 and D is 4,4'-diphenylene substituted once or twice by chlorine, bromine, nitro, cyano, methyl, methoxy or ethoxy.

4. A compound according to any one of the preceding claims, in which

R_1 is an unsubstituted phenylamino radical; a phenylamino radical substituted by a total of up to three substituents selected from up to two substituents selected from chlorine and bromine atoms, (C_{1-4}) alkyl and (C_{1-4}) alkoxy groups, and/or up to one of each of trifluoromethyl, sulphoguanidine, nitro and cyano groups; or a naphthylamino radical.



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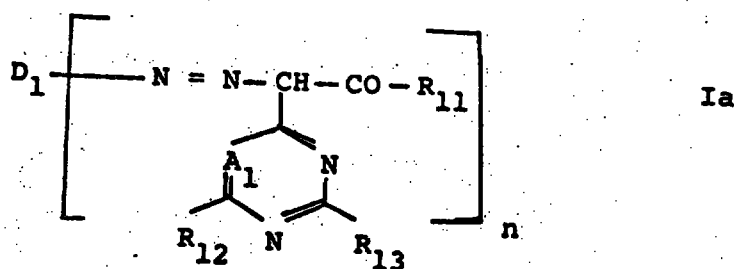
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(23)

5. A compound according to any one of the preceding claims, in which each of R_2 and R_3 signifies a hydroxy group.

6. A compound according to any one of Claims 1 to 4, in which each of R_2 and R_3 has a significance other than a hydroxy group.

7. A compound according to any one of Claims 1 to 3, of formula Ia,

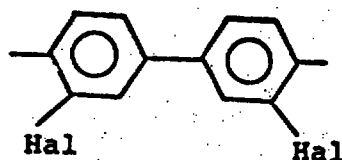


in which

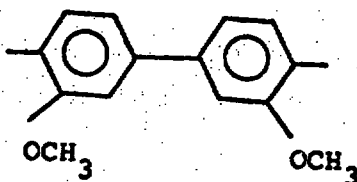
R_{11} signifies an unsubstituted phenylamino, naphthylamino, methoxy or ethoxy radical or a phenylamino radical substituted by up to three substituents selected from the group consisting of chlorine and bromine atoms, methyl and methoxy groups (a maximum of 2 of each), each of

R_{12} and R_{13} , which may be the same or different, signifies an amino, dimethylamino, diethylamino or a hydroxy group,

A_1 signifies a group of formula $\geq \text{CH}$ or $\geq \text{C}-\text{Cl}$ or a nitrogen atom, and either n is 1 and D_1 signifies a phenyl radical substituted by up to two substituents selected from chlorine and bromine atoms, methoxycarbonyl and ethoxycarbonyl groups; a benzimidazolonyl-5 or an α -anthraquinonyl radical, or n is 2 and D_1 signifies a radical of formula



or



in which Hal signifies chlorine or bromine.

8. A compound according to Claim 7, in which

R_{11} signifies an unsubstituted phenylamino radical or a phenylamino radical substituted by up to three substituents selected from one chlorine atom and/or one or two methyl or methoxy groups, each of

R_{12} and R_{13} signifies a hydroxy group,

A_1 signifies a nitrogen atom, and

n is 1.

9. A compound according to Claim 7, in which

R_{11} signifies an unsubstituted phenylamino radical or a phenylamino radical substituted by up to three substituents selected from one chlorine atom and/or one or two methyl or methoxy groups, each of

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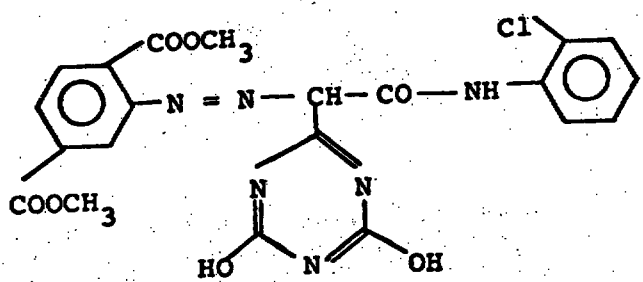
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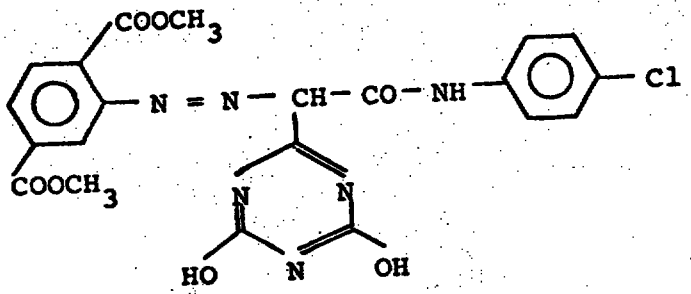
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R_{12} and R_{13} , signifies a hydroxy group,
 A_1 signifies a nitrogen atom,
 n is 1 and D_1 is an iso- or terephthalic acid dimethyl ester radical.
10. A compound according to Claim 7, in which each of R_{12} and R_{13} signifies a hydroxy group.

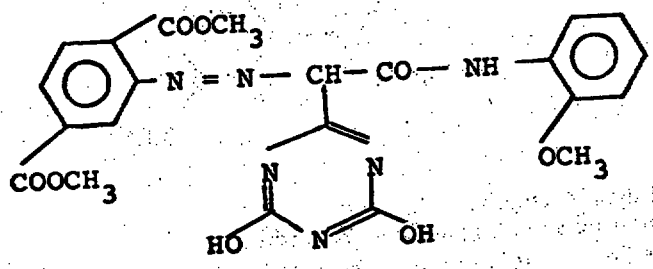
11. A compound of formula



12. A compound of formula



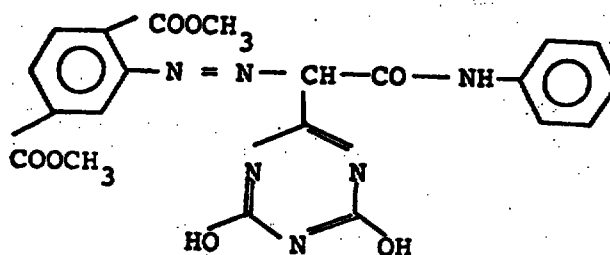
13. A compound of the formula



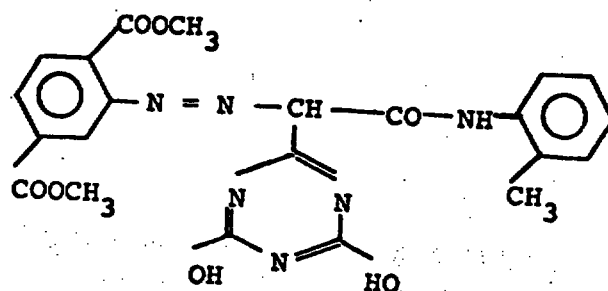


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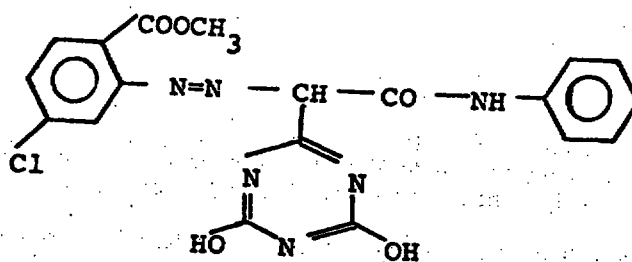
14. A compound of the formula



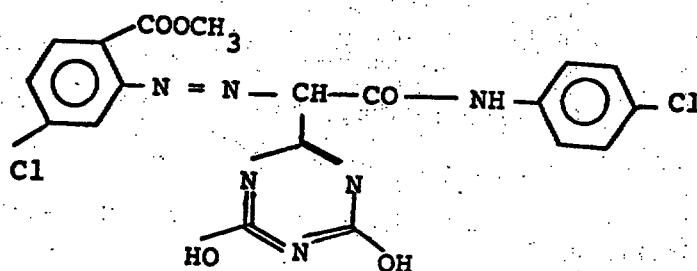
15. A compound of the formula



16. A compound of the formula



17. A compound of formula

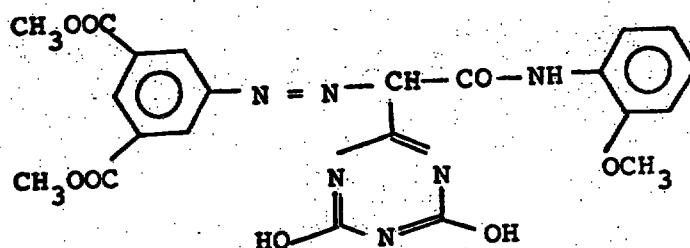




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18. A compound of formula



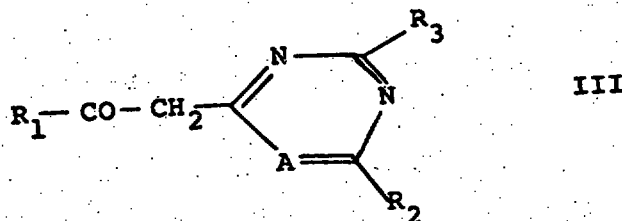
19. A compound according to any one of Examples 2, 3, 10 to 24, 26, 27, 31 to 37, 39 to 45, 53 and 54.

20. A compound according to any one of Examples 28 to 30, 38, 46 to 52 and 55 to 57.

21. A process for the production of a compound of formula I, as defined in Claim 1, comprising coupling a diazotized or tetrazotized amine of formula II,



in which D and n are as defined in Claim 1, with a compound of formula III,



in which R₁, R₂, R₃ and A are as defined in Claim 1.

22. A process for the production of a compound of formula I, as defined in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 57.

23. A compound of formula I, whenever produced by a process according to Claim 21 or Claim 22.

24. A process for pigmenting synthetic plastics materials or resins comprising incorporating therein a compound according to any one of Claims 1 to 20 or 23 as pigmenting agent.

25. A process for pigmenting synthetic plastics materials or resins substantially as described hereinbefore with reference to Example A.

26. A process for dyeing or printing organic substrates of high molecular weight and hydrophobic character comprising using a compound according to Claim 6 as dyeing or printing agent.

27. A process for dyeing or printing substantially as hereinbefore described with reference to Example B.

28. Pigmented substrates whenever obtained by a process according to Claim 24 or Claim 25.

29. Dyed or printed organic substrates whenever obtained by a process according to Claim 26 or Claim 27.



* C L M S *

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