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PATENT SPECIFICATION

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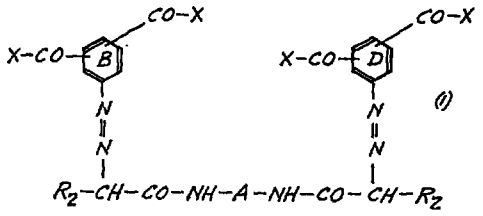
(72) Inventors DR. WILLY FORTER and DR. JÜRGEN GOLDMANN

(54) AZO COMPOUNDS OF LOW SOLUBILITY, THEIR PRODUCTION AND USE AS PIGMENTS

(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: —

This invention relates to disazo compounds of formula



(I)

in which the symbols X are identical and stand for a group of formula R_1—O—, —NH_2 or R_1—NH— where R_1 is a hydrocarbon radical which may be substituted and/or may contain one or more hetero atoms, the symbols R_2 stand for identical or different carboxylic acid acyl radicals, A stands for a divalent hydrocarbon radical which may be substituted and/or may contain one or more hetero atoms, and the rings B and D may each bear one or more further substituents, and where the molecule is free from carboxylic acid and sulphonic acid groups.

The hydrocarbon radicals R_1 which may be substituted and/or may contain hetero atoms include alkyl and cycloalkyl radicals, notably those which contain 1 to 6 carbon atoms and may be substituted by, e.g. one or more halogen atoms, hydroxyl, alkoxy, phenyl, phenoxy, cyano, acyl, acyloxy or acylamino groups; and phenyl, thiazolyl, thienyl or pyridyl radicals which may bear one or more of the aforenamed substituents and, additionally, one or more nitro or alkyl groups. These substituents may in turn be further substituted.

The carboxylic acid acyl radicals R_2 are understood to cover, among others, alkylcarbonyl radicals which have 1, 2, 3 or 4 carbon atoms in the alkyl radical and may bear one or more substituents (e.g. halogen atoms, hydroxyl, alkoxy, phenyl or phenoxy groups), and benzoyl radicals in which the phenyl radical, besides the aforementioned substituents, may bear one or more nitro or alkyl groups.

Examples of divalent hydrocarbon radicals A bearing, if desired, one or more substituents and/or containing one or more hetero atoms are alkylene and cycloalkylene radicals which have preferably up to 8 carbon atoms and like the aforenamed alkyl radicals may be substituted; phenylene radicals, in particular 1,4-phenylene radicals; 2,6- and 1,5-naphthylene radicals; 4,4'-diphenylene radicals and radicals of the formulae

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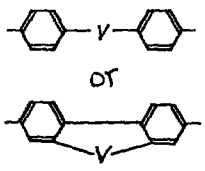
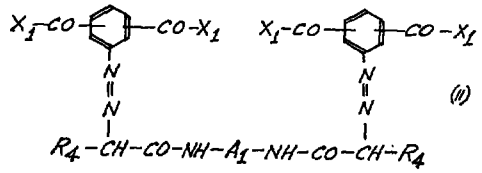


where V represents a group of formula —CH_2—, —NH—, —O—, —S—, —CO— or —SO_2—.

In addition to the two carboxylic acid ester or amide groups —CO—X, each of the rings B and D in formula (I) may bear one or more substituents such as halogen atoms, methyl, halogenomethyl ,alkoxy, cyano or nitro groups.

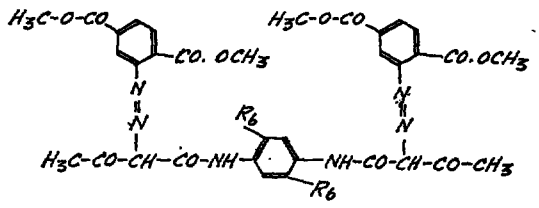
The term "acyl" refers to groups of the formula R—Y— or R' —Z—, where R stands for a hydrocarbon radical which may bear one or more substituents (e.g. halogen atoms, hydroxyl, alkoxy, phenyl or phenoxy groups) and/or may contain one or more hetero atoms, preferably for an alkyl or phenyl radical, Y for a radical of formula —O—CO— or —SO_2—, R' for a hydrogen atom or for one of the meanings of R, Z for a radical —CO—, —NR''CO— or —NR''SO_2—, and R'' for a hydrogen atom or for one of the meanings of R.

By "halogen" is understood fluorine, chlorine or bromine. Preferred compounds of formula (I) conform to the formula



(II)

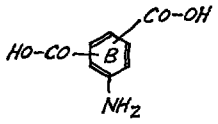
in which the symbols X_1 are identical and stand for groups of formula R_3—O—, —NH_2 or R_3—NH— where R_3 is alkyl with 1 to 3 carbon atoms, unsubstituted phenyl or phenyl substituted by one or more substituents selected from chlorine, bromine, methyl, methoxy and ethoxy; the symbols R_4 stand for acetyl or benzoyl; A_1 stands for unsubstituted phenylene or phenylene substituted by one or more substituents selected from fluorine, chlorine, bromine, methyl, methoxy, ethoxy, trifluoromethyl and cyano, unsubstituted diphenylene or diphenylene substituted by one or more substituents selected from chlorine, bromine, methyl and methoxy, or naphthyl, and in which the groups —CO—X_1 are bound in meta- or para-position to each other on the pertinent benzene nuclei. Especially preferred compounds are those in which the X symbols are identical and stand for groups of formula R_3—O— where R_3 has the aforestated meaning, preferably those in which R_4 stands for acetyl. Compounds of the formula



(III)

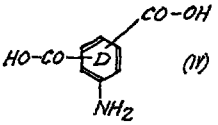
in which the symbols R_6 each stand for hydrogen, chlorine, bromine, methyl, methoxy or ethoxy.

The compounds of formula (I) may be produced by the diazotization of 1 mole of an amine of the formula



(IV)

and 1 mole of an amine of the formula



(V)

followed by coupling of the resulting diazonium compound or compounds with 1 mole of a compound of formula

$$R_2—CH_2—CO—NH—A—NH—CO—CH_2—R_2 \qquad (V)$$

wherein R_2 and A have the aforestated meanings, drying the resulting tetracarboxylic acid, converting it with a halogenating agent into the tetracarboxylic acid halide and condensing the halide with 4 moles of a compound of formula

$$X — H \qquad (VI)$$

wherein X has the aforestated meaning.

A corresponding method of production for the compounds of formula (II) is analogous and comprises diazotization of 2 moles of amino-isophthalic acid or amino-terephthalic acid, coupling with 1 mole of a compound of the formula

$$R_4—CH_2—CO—NH—A_1—NH—CO—CH_2—R_4 \qquad (VII),$$

where R_4 and A_1 have the aforestated meanings, drying the resulting compound, converting the resulting tetracarboxylic acid into the tetracarboxylic acid halide and condensing the halide with 4 moles of a compound of the formula

$$X_1 — H \qquad (VIII),$$

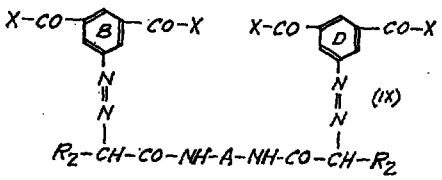
where X_1 has the aforestated meanings.

Special preference is given to 1,4-bis-(acetoacetylamino)-benzene as coupling component.

The coupling reaction is generally carried out in weakly acid medium within the temperature range of −5°C to +20°C, more especially at 0°C to +5°C.

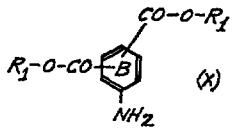
The disazo-tetracarboxylic acid compounds formed in these processes must be thoroughly dried before the subsequent steps of the process in each case, in view of the sensitivity of the halogenating agents and acid halides.

Phosphorus chlorides and bromides or thionyl chloride are the preferred halogenating agents. Halogenation is preferably carried out in an inert solvent such as benzene, toluene, a xylene mixture, nitrobenzene or chlorinated benzenes, at temperatures up to the region of the boiling point of the mixture present. Similarly, condensation of the tetracarboxylic halides with the compounds of formulae (VI) or (VIII) is best carried out in one of the aforenamed solvents at the boiling temperature of the solvent. It is generally of advantage to add an anhydrous acid-binding agent, e.g. an alkali metal carbonate, bicarbonate or acetate, pyridine or dimethyl formamide. A number of the compounds of formula (I), namely those in which X in each case represents an $R_1—O—$ group and those of the formula



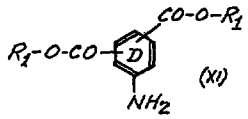
(IX)

in which X in each case represents a group of formula R_1—O—, —NH_2 or R_1—NH— and where R_1, R_2 and A are as defined above, can be prepared by the diazotization of 1 mole of an amine of the formula



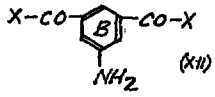
(X)

and of 1 mole of an amine of the formula



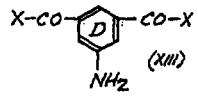
(XI)

or by the diazotization of 1 mole of an amine of the formula



(XII)

and 1 mole of an amine of the formula



(XIII)

followed by coupling of the resulting diazonium compound or compounds with 1 mole of a compound of formula (V).

With compounds of formulae (X) to (XIII) the coupling reaction is again carried out as given above.

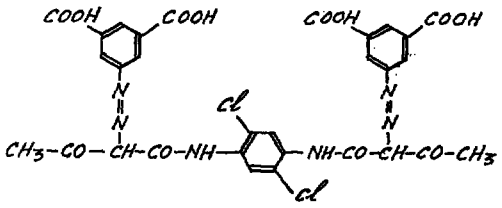
The final disazo compounds, especially when they are submitted to the normal preparatory treatments for pigments, are suitable for the mass pigmentation of synthetic polymers and synthetic resins such as polyethylene, polystyrene, polyvinyl chloride, poromerics (synthetic leather) and rubber latices, in the presence or absence of solvents. Further suitable uses include the dyeing of viscose rayon and cellulose acetate fibres in the spinning solution, the pigmentation of oil and water based paints including lacquers and enamels, the pigmentation of printing inks, paper dyeing in the stock, and the coloration and printing of textiles.

The yellow coloration imparted by the pigments in these various materials is resistant to migration and fast to light. The fastness to washing, cross dyeing, blind vats, rubbing, overspraying, solvents and bleaching with chlorine, hypochlorite or peroxide is good to very good. The pigments show notably good transparency and heat stability.

In the following Examples the parts and percentages are by weight and the temperatures in degrees centigrade.

Example 1.

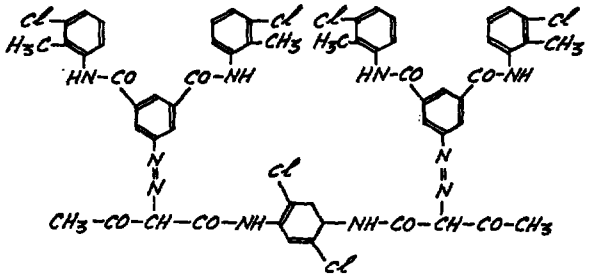
The dye of the formula



is produced by the diazotization of 5-amino-isophthalic acid and coupling the resulting diazonium compound with 1,4-bis-(acetoacetylamino)-2,5-dichlorobenzene.

14.6 Parts of it are added to 300 parts of chlorobenzene and 3 parts of dimethyl formamide with stirring and the temperature is increased to 95—100°. At this temperature 10 parts of thionyl chloride are allowed to flow it, after which stirring is continued for about 2 hours at 130°. The reaction mixture takes on the form of a thick yellow crystalline slurry. The end-point of the reaction is indicated when no further hydrogen chloride escapes. The temperature is reduced to 80°, the product filtered and washed with chlorobenzene, then, after further cooling, it is washed with benzene and finally with petroleum ether. The acid chloride thus obtained is vacuum dried at 70°.

A solution of 8.03 parts of this product in 100 parts of chlorobenzene is raised to 100°, at which temperature a solution of 5.64 parts of 2-methyl-3-chloroaniline and 3.2 parts of pyridine in 20 parts of chlorobenzene is added. The temperature is increased to 130° and the reaction solution stirred well for 10 hours at this temperature. The pigment formed is filtered, washed with hot chlorobenzene until the filtrate runs clear, washed again with methanol to free it from the adhering chlorobenzene, and dried at 70° with vacuum. A loose powder is obtained which has the formula



In polyvinyl chloride it produces bright greenish yellow pigmentation with very good light fastness and migration resistance.

In place of 5.64 parts of 2-methyl-3-chloroaniline, 4.32 parts of benzyl alcohol can be used, which results in a yellow pigment with comparable fastness properties.

The procedure of Example 1 can be employed to produce the pigments specified in Table 1 below, starting from the diazo components, coupling components and amines named in columns I, II and III respectively. The shade of these pigments in polyvinyl chloride is given in the final column.

TABLE

Example No.	I	II	III	IV
2	5-Amino-isophthalic acid	1,4-Bis-(acetoacetylamino)-benzene	2-Methoxyaniline	yellow
3	do.	do.	2-Methyl-5-chloroaniline	do.
4	do.	do.	2-Methyl-3-chloroaniline	do.
5	do.	1,4-Bis-(acetoacetylamino)-2-chlorobenzene	do.	do.
6	do.	do.	2-Methyl-5-chloroaniline	do.
7	do.	1,4-Bis-(acetoacetylamino)-2,5-dichlorobenzene	Aniline	do.
8	do.	do.	2-Methyl-5-chloroaniline	do.
9	do.	1,4-Bis-(acetoacetylamino)-2,5-dimethylbenzene	2-Methyl-5-chloroaniline	do.
10	do.	do.	ortho-Toluidine	do.
11	do.	1,4-Bis-(acetoacetylamino)-2-methyl-5-chlorobenzene	2-Methyl-5-chloroaniline	do.
12	do.	do.	2-Methyl-3-chloroaniline	do.
13	do.	1,4-Bis-(acetoacetylamino)-2,5-dimethoxybenzene	Aniline	do.

TABLE (Cont.)

Example No.	I	II	III	IV
14	5-Amino-isophthalic acid	1,4-Bis-(acetoacetylamino)-2,5-dimethoxybenzene	ortho-Toluidine	yellow
15	do.	4,4'-Bis-(acetoacetylamino)-diphenyl	2-Methyl-3-chloroaniline	do.
16	do.	do.	ortho-Toluidine	do.
17	do.	4,4'-Bis-(acetoacetylamino)-3,3'-dichlorodiphenyl	2-Methyl-3-chloroaniline	do.
18	do.	do.	2-Methyl-5-chloroaniline	do.
19	do.	4,4'-Bis-(acetoacetylamino)-3,3'-dimethyldiphenyl	do.	do.
20	do.	do.	2-Methyl-3-chloroaniline	do.
21	2-Aminoterephthalic acid	1,4-Bis-(acetoacetylamino)-benzene	do.	do.
22	do.	do.	2-Methyl-5-chloroaniline	do.
23	do.	1,4-Bis-(acetoacetylamino)-2,5-dichlorobenzene	do.	do.
24	do.	do.	2-Methyl-3-chloroaniline	do.
25	do.	4,4'-Bis-(acetoacetylamino)-diphenyl	do.	do.
26	do.	4,4'-Bis-(acetoacetylamino)-3,3'-dichlorodiphenyl	do.	do.

TABLE (Cont.)

Example No.	I	II	III	IV
27	2-Aminotere-phthalic acid	1,4-Bis-(acetoacetyl-amino)-3,3'-dimethyl-diphenyl	2-Methyl-3-chloro-aniline	yellow
28	do.	1,4-Bis-(acetoacetyl-amino)-2-chlorobenzene	do.	do.
29	do.	1,4-Bis-(acetoacetyl-amino)-2-methylbenzene	do.	do.
30	do.	1,4-Bis-(acetoacetyl-amino)-2-methoxy-benzene	do.	do.
31	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dimethyl-benzene	do.	do.
32	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dimethoxy-benzene	do.	orange
33	do.	1,4-Bis-(acetoacetyl-amino)-benzene	Ammonia	yellow
34	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dichloro-benzene	do.	do.
35	do.	1,4-Bis-(acetoacetyl-amino)-2-chlorobenzene	do.	do.
36	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dimethyl-benzene	do.	do.
37	do.	1,4-Bis-(benzoylacetyl-amino)-benzene	do.	do.

Example 38.

10.74 Parts of 5-amino-iso-phthalic acid diamide are dissolved in 300 parts of glacial acetic acid with heating. After cooling to 20°, 20 parts of concentrated hydrochloric acid and 200 parts of water are added. The suspension of the amine salt is diazotized in the normal way with 60 parts of 1/normal sodium nitrite solution. A clear yellow diazo solution is formed which is buffered to pH 4 with 50% sodium acetate solution. A solution of 10 parts of 1,4-bis-(acetoacetylamino)-2,5-dimethyl-benzene in 100 parts of water, 10 parts of 30% sodium hydroxide solution and 10 parts of ethanol are dropped in at about +5° with good stirring.

On completion of coupling, stirring is continued for a further hour at 80°. The precipitate is filtered, washed with hot water to free it from salt, and vacuum dried at 70°.

The product is a reddish yellow pigment, which, as a colorant in plasticized polyvinyl chloride, is migration resistant, heat stable and very fast to light.

If the crude pigment is treated with a solvent such as dimethyl formamide with heating, the pigmentations are more brilliant and of more intense colour.

Example 39.

Following the procedure of Example 38, 10.74 parts of 5-amino-iso-phthalic acid diamide are diazotized and the diazo solution is buffered to pH 4. A solution of 10.9 parts of 1,4-bis-(acetoacetylamino)-2,5-dichlorobenzene in 100 parts of water is added dropwise with vigorous stirring, together with 10 parts of 30% sodium hydroxide solution and 10 parts of ethanol. Continuing as in Example 38, a greenish yellow pigment is obtained which has excellent pigmentary properties.

Example 40.

6.62 Parts of 5-amino-iso-phthalic acid-di-(phenylamide) are dissolved in a mixture of 150 parts of glacial acetic acid and 150 parts of propionic acid with heating. After the solution has cooled to 20° it is set with 20 parts of concentrated hydrochloric acid and diazotized at 5° with 20 parts of 1/normal sodium nitrite solution.

The diazo solution is buffered to pH 4 with 50% sodium acetate solution, then, at about +5°, a solution of 3.3 parts of 1,4-bis-(acetoacetylamino)-2,5-dimethylbenzene in 100 parts of water, together with 10 parts of ethanol and 10 parts of 30% sodium hydroxide solution, are dropped in with vigorous stirring.

Stirring is continued after completion of coupling for 1 hour at 80°, after which the precipitate is filtered, washed with hot water to free it from salt and dried at 70° with vacuum.

A reddish yellow pigment is obtained which produces migration and heat resistant shades of very good light fastness in plasticized polyvinyl chloride.

In the following Table 2 diazo (column I) and coupling (column II) components are named, with which further pigments can be produced by reaction procedures analogous to those of Examples 38 to 40.

TABLE 2

Example No.	I	II	IV
41	5-Amino-iso-phthalic acid diamide	1,4-Bis-(acetoacetyl-amino)-benzene	yellow
42	do.	1,4-Bis-(acetoacetyl-amino)-2-chlorobenzene	do.
43	do.	1,4-Bis-(acetoacetyl-amino)-2-chloro-5-methylbenzene	do.
44	do.	1,4-Bis-(acetoacetyl-amino)-2-methylbenzene	do.
45	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dimethoxy-benzene	orange
46	do.	1,4-Bis-(acetoacetyl-amino)-2-methoxybenzene	yellow
47	do.	4,4'-Bis-(acetoacetyl-amino)-diphenyl	do.
48	do.	4,4'-Bis-(acetoacetyl-amino)-3,3'-dichloro-diphenyl	do.
49	do.	4,4'-Bis-(acetoacetyl-amino)-3,3'-dimethoxy-diphenyl	do.
50	do.	4,4'-Bis-(acetoacetyl-amino)-3,3'-dimethyl-diphenyl	do.
51	5-Amino-iso-phthalic acid di-(phenylamide)	1,4-Bis-(acetoacetyl-amino)-benzene	do.
52	do.	1,4-Bis-(acetoacetyl-amino)-2-chlorobenzene	do.

Example 53.

8.4 Parts of 5-amino-iso-phthalic acid dimethylester are dissolved in 300 parts of water and 20 parts of concentrated hydrochloric acid with heating. The solution is allowed to cool to 20°, clarified by filtration and diazotized at 5° with 40 parts of 1/normal sodium nitrite solution. The diazo solution is adjusted to pH 4 with 50% sodium acetate solution, after which a solution of 7.6 parts of 1,4-bis-(acetoacetyl-amino)-,2,5-dichlorobenzene in 100 parts of water, cooled to about +5°, is slowly dropped in, along with 20 parts of ethanol and 10 parts of 30% sodium hydroxide solution.

After the coupling reaction is complete, stirring is continued for 1 hour at 80°, then the precipitate is filtered, washed free from salt and vacuum dried at 70°.

A loose yellow powder pigment is obtained which has very good migration and heat resistance, light fastness and, in paints and lacquers, very good overspraying fastness.

Example 54.

A solution of 8.4 parts of 2-aminoterephthalic acid dimethylester in 200 parts of water and 10 parts of concentrated hydrochloric acid is stirred for 2 hours at room temperature. It is then unloaded onto 200 parts of ice and diazotized with 40 parts of 1/normal sodium nitrite solution. The clear diazo solution is adjusted to pH 4 with 50% sodium acetate solution and to it is slowly added a solution of 7.15 parts of 1,4-bis-(acetoacetylamino)-2-chloro-5-methylbenzene in 100 parts of water, cooled to about +5°, together with 20 parts of ethanol and 10 parts of 30% sodium hydroxide solution.

Subsequent to coupling, the mixture is stirred for 1 hour at 80°, then the product is isolated by filtration, freed from salt by washing with hot water, and dried at 70° under vacuum. It is a loose yellow pigment with notably good migration and heat resistance, light and overspraying fastness.

The procedures of Examples 53 or 54 can be employed with the diazo and coupling components named in columns I and II of Table 3 below, the pigments thus formed having the shades noted in column IV of the table.

TABLE 3

Example No.	I	II	IV
55	2-Amino-isophthalic acid dimethylester	1,4-Bis-(acetoacetylamino)-benzene	yellow
56	do.	1,4-Bis-(acetoacetylamino-2,5-dimethylbenzene	do.
57	do.	1,4-Bis-(acetoacetylamino)-2,5-dimethoxybenzene	orange
58	do.	1,4-Bis-(acetoacetylamino)-2-methyl-5-chlorobenzene	yellow
59	do.	1,4-Bis-(acetoacetylamino)-2-methylbenzene	do.
60	do.	1,4-Bis-(acetoacetylamino)-2-chlorobenzene	do.
61	do.	1,4-Bis-(acetoacetylamino)-2-methoxybenzene	do.
62	do.	1,4-Bis-(acetoacetylamino)-2-methoxy-5-chlorobenzene	do.
63	do.	1,4-Bis-(acetoacetylamino)-2,3,5,6-tetrachlorobenzene	do.
64	do.	1,4-Bis-(acetoacetylamino)-2,5-dimethyl-3,6-dichlorobenzene	do.

TABLE 3 (Cont.)

Example No.	I	II	IV
65	do.	4,4'-Bis-(acetoacetyl-amino)-diphenyl	do.
66	do.	4,4'-Bis-(acetoacetyl-amino)-3,3'-dichloro-diphenyl	do.
67	2-Amino-iso-phthalic acid ester	4,4'-Bis-(acetoacetyl-amino)-3,3'-dimethyldi-phenyl	yellow
68	do.	4,4'-Bis-(acetoacetyl-amino)-3,3'-dimethoxy-diphenyl	do.
69	do.	4,4'-Bis-(acetoacetyl-amino)2,2'-dichloro-5,5'-dimethyldiphenyl	do.
70	do.	1,5-Bis-(acetoacetyl-amino)-naphthalene	do.
71	do.	1,4-Bis-(acetoacetyl-amino)-2-trifluoro-methylbenzene	do.
72	2-Aminotere-phthalic acid dimethylester	1,4-Bis-(acetoacetyl-amino)-benzene	do.
73	do.	1,4-Bis-acetoacetyl-amino)-2-chlorobenzene	do.
74	do.	1,4-Bis-acetoacetyl-amino)-2,5-dichloro-benzene	do.
75	do.	1,4-Bis-(acetoacetyl-amino)-2-methylbenzene	do.
76	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dimethoxy-benzene	orange
77	do.	1,4-Bis-(acetoacetyl-amino)-2-methoxybenzene	yellow
78	do.	4'4-Bis-(acetoacetyl-amino)-diphenyl	do.
79	do.	4,4'-Bis-(acetoacetyl-amino)-3,3'-dichloro-diphenyl	do.

TABLE 3 (Cont.)

Example No.	I	II	IV
80	2-Aminotere-phthalic acid di-methylester	4,4'-Bis-(acetoacetyl-amino)-3,3'-dimethoxy-diphenyl	yellow
81	do.	4,4'-Bis-(acetoacetyl-amino)-3,3'-dimethyl-diphenyl	do.
82	2-Aminotere-phthalic acid dimethylester	1,4-Bis-(acetoacetyl-amino)-2,5-dimethyl-benzene	yellow
83	do.	1,4-Bis-(acetoacetyl-amino)-2-methyl-5-methoxybenzene	do.
84	do.	1,4-Bis-(acetoacetyl-amino)-2-methoxy-5-chlorobenzene	do.
85	2-Aminotere-phthalic-dimethyl-ester	1,4-Bis-(acetoacetyl-amino)-2-bromobenzene	yellow
86	do.	1,4-Bis-(acetoacetyl-amino)-2-trifluoromethyl-benzene	do.
87	do.	1,4-Bis-(acetoacetyl-amino)-2,5-diethoxy-benzene	orange
88	do.	1,4-Bis-(acetoacetyl-amino)-2,3,5,6-tetra-chlorobenzene	yellow
89	do.	1,4-Bis-(acetoacetyl-amino)-2,3,5,6-tetra-methylbenzene	do.
90	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dimethyl-3,6-dichlorobenzene	do.
91	do.	2,7-Bis-(acetoacetyl-amino)-naphthalene	do.
92	do.	1,4-Bis-(acetoacetyl-amino)-2,6-dichloro-benzene	do.
93	do.	1,4-Bis-(acetoacetyl-amino)-2,6-dimethyl-benzene	do.
94	do.	1,4-Bis-(acetoacetyl-amino)-naphthalene	do.
95	do.	1,5-Bis-(acetoacetyl-amino)-naphthalene	do.

TABLE 3 (Cont.)

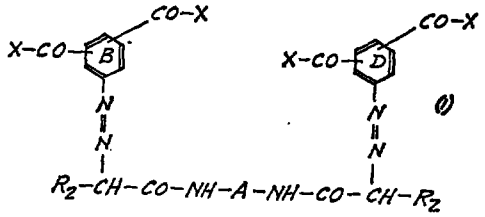
Example No.	I	II	IV
96	2-Aminotere-phthalic acid dimethylester	2,6-Bis-(acetoacetyl-amino)-naphthalene	yellow
97	4-Amino-iso phthalic acid dimethylester	1,4-Bis-(acetoacetyl-amino)-benzene	do.
98	do.	1,4-Bis-(acetoacetyl-amino)-2,5-dichloro-benzene	do.
99	5-Aminotere-phthalic acid diethylester	1,4-Bis-(acetoacetyl-amino)-benzene	do.
100	5-Aminotere-phthalic acid di-n-propylester	1,4-Bis-(acetoacetyl-amino)-2,5-dichloro-benzene	do.
101	5-Amino-iso-phthalic acid di-(methylamide)	1,4-Bis-(acetoacetyl-amino)-benzene	do.
102	5-Amino-iso-phthalic acid di-(ethylamide)	1,4-Bis-(acetoacetyl-amino)-benzene	do.
103	5-Amino-iso-phthalic acid di-(n-propylamide)	do.	do.
104	5-Amino-iso-phthalic acid di-(cyclohexylamide)	do.	do
105	5-Amino-iso-phthalic acid di-cyclohexylester	do	do
106	5-Amino-iso-phthalic acid di-(2'-methoxy-phenylamide)	1,4-Bis-(acetoacetyl-amino)-benzene	do.
107	5-Amino-iso-phthalic acid di-(2'-ethoxy-phenylamide)	do.	do.
108	5-Amino-iso-phthalic acid di-(2'-methyl-3'-bromophenylamide)	do.	do.

TABLE 3 (Cont.)

Example No.	I	II	IV
109	2-Aminotere-phthalic acid dimethylester	1,4-Bis-(acetoacetyl-amino)-2,5-difluoro-benzene	yellow
110	do.	1,4-Bis-(benzoylacetyl-amino)-benzene	do.

WHAT WE CLAIM IS:—

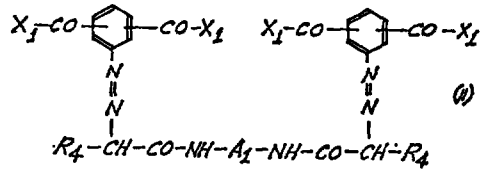
1. Azo compounds of formula



(I)

in which the symbols X are identical and stand for a group of formula R_1—O—, —NH_2 or R_1—NH— where R_1 is a hydrocarbon radical which may be substituted and/or may contain one or more hetero atoms, the symbols R_2 stand for identical or different carboxylic acid acyl radicals, A stands for a divalent hydrocarbon radical which may be substituted and/or may contain one or more hetero atoms, and the rings B and D may each bear one or more further substituents, and where the molecule is free from carboxylic acid and sulphonic acid groups.

2. Azo compounds according to Claim 1 and of the formula



(II)

in which the symbols X_1 are identical and stand for groups of formula R_3—O—, —NH_2 or R_3—NH— where R_3 is alkyl with 1 to 3 carbon atoms, cyclohexyl, unsubstituted phenyl or phenyl substituted by one or more substituents selected from chlorine, bromine, methyl, methoxy and ethoxy; R_4 stands for acetyl or benzoyl; A_1 stands for unsubstituted phenylene or phenylene substituted by one or more substituents selected from fluorine, chlorine, bromine, methyl, methoxy, ethoxy, trifluoromethyl and cyano, unsubstituted diphenylene or diphenylene substituted by one or more substituents selected from chlorine, bromine, methyl and methoxy; or naphthyl; and where the groups —CO—X_1 are bound in meta- or para-position to each other on the pertinent benzene nuclei.

3. Azo compounds according to claim 2 in which the symbols X_1 are identical and stand for groups of formula R_3—O— where R_3 has the meaning given to it in claim 2.

4. Azo compounds according to claim 3, in which R_4 stands for acetyl.

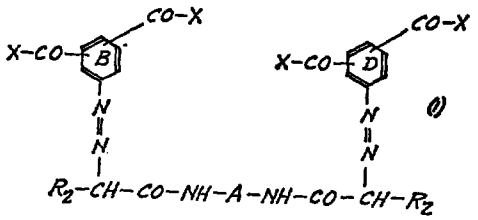
5. Azo compounds according to claim 4 of the formula

TABLE 3 (Cont.)

Example No.	I	II	IV
109	2-Aminotere-phthalic acid dimethylester	1,4-Bis-(acetoacetyl-amino)-2,5-difluoro-benzene	yellow
110	do.	1,4-Bis-(benzoylacetyl-amino)-benzene	do.

WHAT WE CLAIM IS:—

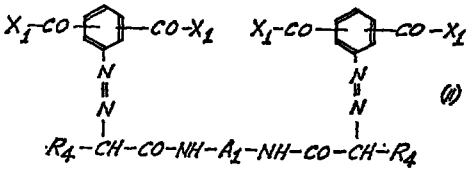
1. Azo compounds of formula



(I)

in which the symbols X are identical and stand for a group of formula R_1—O—, —NH_2 or R_1—NH— where R_1 is a hydrocarbon radical which may be substituted and/or may contain one or more hetero atoms, the symbols R_2 stand for identical or different carboxylic acid acyl radicals, A stands for a divalent hydrocarbon radical which may be substituted and/or may contain one or more hetero atoms, and the rings B and D may each bear one or more further substituents, and where the molecule is free from carboxylic acid and sulphonic acid groups.

2. Azo compounds according to Claim 1 and of the formula



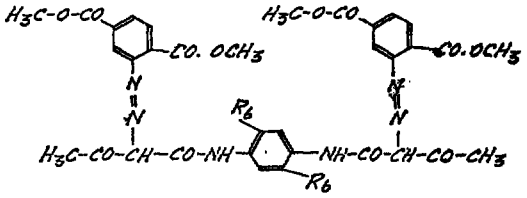
(II)

in which the symbols X_1 are identical and stand for groups of formula R_3—O—, —NH_2 or R_3—NH— where R_3 is alkyl with 1 to 3 carbon atoms, cyclohexyl, unsubstituted phenyl or phenyl substituted by one or more substituents selected from chlorine, bromine, methyl, methoxy and ethoxy; R_4 stands for acetyl or benzoyl; A_1 stands for unsubstituted phenylene or phenylene substituted by one or more substituents selected from fluorine, chlorine, bromine, methyl, methoxy, ethoxy, trifluoromethyl and cyano, unsubstituted diphenylene or diphenylene substituted by one or more substituents selected from chlorine, bromine, methyl and methoxy; or naphthyl; and where the groups —CO—X_1 are bound in meta- or para-position to each other on the pertinent benzene nuclei.

3. Azo compounds according to claim 2 in which the symbols X_1 are identical and stand for groups of formula R_3—O— where R_3 has the meaning given to it in claim 2.

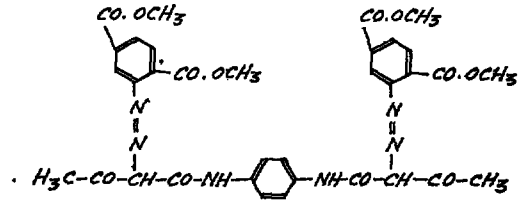
4. Azo compounds according to claim 3, in which R_4 stands for acetyl.

5. Azo compounds according to claim 4 of the formula

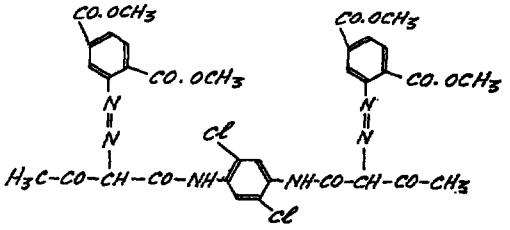


in which the symbols R_6 each stand for hydrogen, chlorine, bromine, methyl, methoxy or ethoxy.

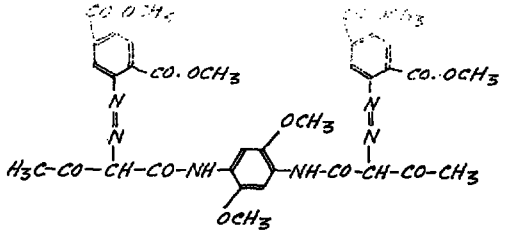
6. The azo compound of the formula



7. The azo compound of the formula

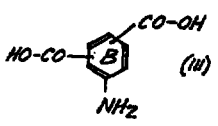


8. The azo compound of the formula

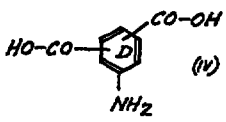


9. The particular azo compounds of formula (I) according to claim 1 herein described and exemplified.

10. A process for the production of an azo compound of formula (I) according to claim 1, which comprises the diazotization of 1 mole of an amine of the formula



and 1 mole of an amine of the formula



followed by coupling of the resulting diazonium compound or compounds with 1 mole of a compound of the formula

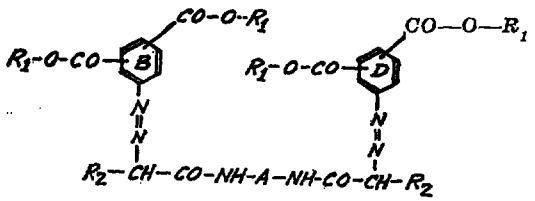
$$R_2—CH_2—CO—NH—A—NH—CO—CH_2—R_2 \qquad (V)$$

where R_2 and A have the meanings given to them in claim 1, drying the resulting tetracarboxylic acid, converting it with a halogenating agent into the tetracarboxylic acid halide, and condensing the halide with 4 moles of a compound of the formula

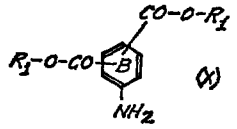
$$X — H \qquad (VI)$$

where X has the meaning given to it in claim 1.

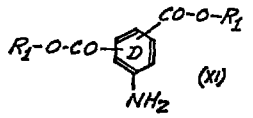
11. A process for the production of an azo compound according to claim 1 of formula



where R_1, R_2 and A have the meanings given to them in claim 1, which comprises the diazotization of 1 mole of an amine of the formula



wherein R_1 has the meaning given to it in claim 1 and 1 mole of an amine of the formula

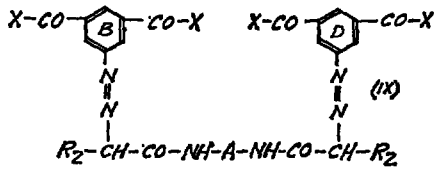


where R_1 has the meaning given to it in claim 1, and coupling the resulting diazonium compound or compounds with 1 mole of a compound of the formula

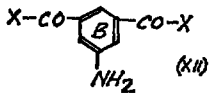
$$R_2—CH_2—CO—NH—A—NH—CO—CH_2—R_2 \qquad (V),$$

where R_2 and A have the meanings given to them in claim 1.

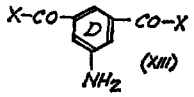
12. A process for the production of an azo compound according to claim 1 of the formula



where X, R_2 and A have the meanings given to them in claim 1 which comprises the diazotization of 1 mole of an amine of the formula



where X has the meaning given to it in claim 1, and 1 mole of an amine of the formula



(XIII)

where X has the meaning given to it in claim 1, and coupling the resulting diazonium compound or compounds with 1 mole of a compound of the formula

$$R_2—CH_2—CO—NH—A—NH—CO—CH_2—R_2 \qquad (V),$$

where R_2 and A have the meanings given to them in claim 1.

13. A process for the production of an azo compound of the formula (I) according to claim 1 conducted substantially as herein described and exemplified.

14. Azo compounds of the formula (I) according to claim 1 whenever prepared by a process according to any one of claims 10 to 13.

15. A process for the pigmentation of a plastics material in which a compound of the formula (I) according to claim 1 is used.

16. Plastics materials pigmented with an azo compound of the formula (I) according to claim 1.

MEWBURN ELLIS & CO.,
Agents for the Applicants,
70/72 Chancery Lane,
London, WC2A 1AD.

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