

PATENT SPECIFICATION

(11) 1 436 448

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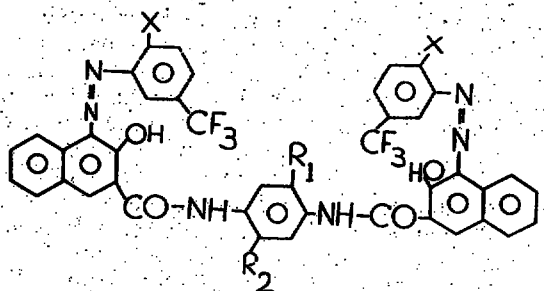
(72) Inventors BORIS TCHERKINSKY and HANS WASEM



(54) DISAZO PIGMENTS

(71) We, SANDOZ LTD., of Lichtstrasse 35, 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:—

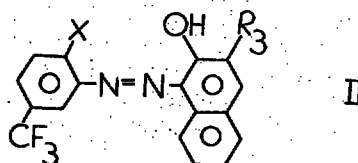
The invention relates to azo compounds free from sulphonic acid groups.
 The invention provides compounds of formula I,



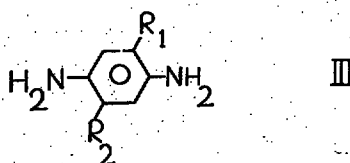
in which the X's, R₁ and R₂, independently, signify a fluorine, chlorine or bromine atom.

In the compounds of formula I, the X's preferably signify chlorine or bromine. The X's are preferably the same. R₁ and R₂, independently, preferably signify chlorine or bromine. R₁ and R₂ are preferably the same.

The invention also provides a process for the production of a compound of formula I, stated above, characterised by
 a) condensing a compound of formula II,

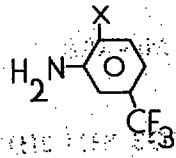


in which X is as defined above, and
 R₃ signifies a carboxyl group or a functional derivative thereof, with a diamine of formula III,

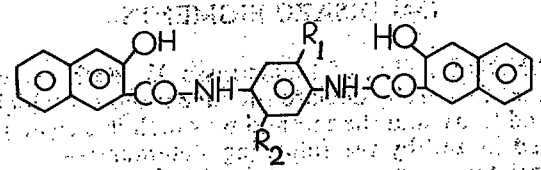


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in which R_1 and R_2 are as defined above,
in an inert organic solvent, or
b) coupling a diazotised amine of formula IV,



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



10 in which R_1 and R_2 are as defined above.
Processes a) and b) are carried out in conventional manner.
In process a), where R_1 signifies a functional derivative of a carboxyl group, as
15 examples of such derivatives may be given the low molecular weight esters, e.g. the
 C_{1-4} alkyl esters, and the acid halides, particularly the acid bromide or chloride
and preferably carried out in an anhydrous organic solvent, preferably in an
aromatic solvent. Where, as is preferred, R_1 signifies an acid halide radical, the
20 condensation of the compound of formula II with the compound of formula III is
advantageously carried out in the presence of an acid binding agent such as
anhydrous alkali-metal acetates, bicarbonates or carbonates or organic bases such
as pyridine. Where R_2 signifies the free acid, the reaction is preferably carried out
in the presence of a condensation agent such as phosphorus trichloride.
In process a), the mol ratio of the compound of formula II to the compound of
25 formula III is preferably 2:1.
The production of compounds of formula II, in which R_1 signifies an acid
chloride or bromide, may be carried out by reacting the corresponding free acid
with phosphorus chlorides or bromides or thionyl chloride, in conventional
manner, preferably in an aromatic solvent such as toluene, nitrobenzene or a
30 chlorobenzene, optionally in the presence of dimethylformamide or
dimethylacetamide and at temperatures up to the boiling point of the reaction
mixture.
Process b) is preferably carried out in a pH4-6 buffered solution of the
diazonium compound by slow addition of the diamide of formula V dissolved in
alkaline medium. The preferred mol ratio of compound IV to compound V is 2:1.
The resulting compound of formula I may be isolated and purified in
conventional manner, isolation from the reaction medium being easily carried out
35 due to the poor solubility of the compounds in aqueous medium and organic
solvents.
The compounds of formula II, employed in process a) may be obtained by
coupling the diazotized amine of formula IV, stated above, with 2-hydroxy-3-
carboxy-naphthalene, where desired the free acid in the resulting compound being
converted into a functional derivative thereof in conventional manner.
40 The compounds of formula V, employed in process b) may be obtained by
condensing 2-hydroxy-3-carboxy-naphthalene, or a functional derivative thereof
as described above, with a diamine of formula III, above, in analogous manner to
process a), described above.
The compounds of formula I are indicated for use as pigments. The
45 compounds are particularly suitable for the pigmentation of synthetic polymeric
materials in the mass, in the presence or absence of solvents, particularly after
having been conditioned in the normal methods for pigments, the incorporation of
the compounds in the materials being carried out in conventional manner. By
synthetic polymeric material is to be understood synthetic polymers and resins
50 such as polyethylene, polystyrene, polyvinyl chloride, synthetic rubber and
synthetic leathers. The compounds are also suitable for use in emulsion paints and

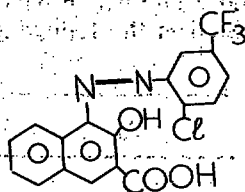
other surface coating media of an oil, water or solvent base, in printing inks and in viscose and cellulose acetate spinning solutions for the production of spun dyed filaments. The compounds can also be used for dyeing paper in the stock prior to sheet formation and for printing and coating textiles.

The dyeings obtained have notable migration and light fastness properties, together with notable fastness to overspraying and solvents and notable transparency and heat stability characteristics. The last named property permits the use of the pigments in the pigmentation of polyvinyl chloride and polypropylene in the mass followed by extruding or otherwise shaping the polymer at elevated temperatures.

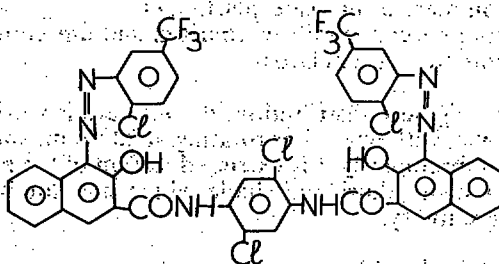
The following Examples, in which all parts and percentages are by weight and temperatures in degrees Centigrade, illustrate the invention.

Example 1.

41.5 Parts of dry monoazocarboxylic acid of formula

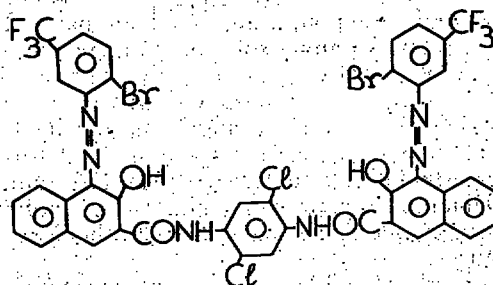


obtained by coupling diazotized 4-chloro-3-amino-benzo-trifluoride with 2-hydroxynaphthalene-3-carboxylic acid, are heated in 480 parts of ortho-dichlorobenzene and 18 parts of thionyl chloride for 4 hours at 105—110° with stirring. Subsequently, the solution is cooled to 70—80° and the excess thionyl chloride, together with some ortho-dichlorobenzene distilled off under vacuum. To the remaining solution, 8.9 parts of 2,5-dichloroparaphenylenediamine are added and the solution is heated for 15 hours at 140—145° with stirring. The pigment precipitates as insoluble, fine-crystalline particles. The pigment is filtered off while still warm, washed with hot ortho-dichlorobenzene, then with methanol and finally with water and then vacuum dried at 80°. The pigment obtained agrees with the formula



Example 2.

3.6 Parts of sodium nitrite are introduced into 50 parts of sulphuric acid with stirring, the temperature is raised to 60—70°. When the sodium nitrite is dissolved, 12 parts of 3-amino-4-bromobenzotrifluoride are added dropwise at 20—25° and the mixture stirred for a further 2 hours. It is then discharged onto ice and water and filtered. 13 Parts of N,N'-bis-(2'-hydroxy-3'-naphthoyl)-2,5-dichloro-1,4-diaminobenzene are dissolved in 250 parts of methanol and 20 parts of 30% sodium hydroxide solution at 20—25°. Subsequently, over a period of 30 minutes, the diazo solution is run in. With simultaneous addition of 30% sodium hydroxide solution the pigment suspension is kept alkaline. On completion of the coupling reaction the pigment suspension is acidified, heated to 80—90°, filtered off and then vacuum dried at 70°. The pigment obtained agrees with the formula



To improve the properties, the red pigment may be heated, for example for 30 minutes at 140° in a solvent such as mono-, di- or trichlorobenzene, nitrobenzene or dimethylformamide. On synthetic polymers it gives dyeings of red shade with notable fastness properties.

Further pigments of formula I, which are obtainable in accordance with the procedures of Examples 1 and 2 and which have similar properties to those the pigment of Example 1, are listed in the following Table.

Example No.	R ₁	R ₂	X	Shade in PVC
3	Br	Br	Br	red
4	Cl	Cl	F	do
5	Br	Br	Cl	do

Application Example

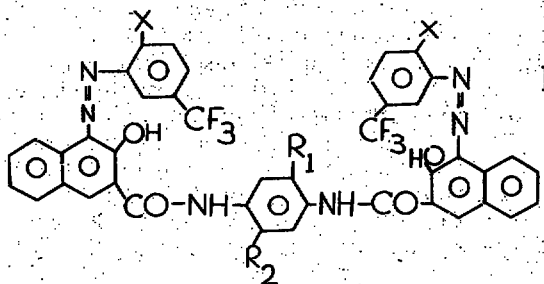
0.5 Parts of the pigment produced according to Example 1, and 5 parts of titanium dioxide white pigment are intimately mixed with 100 parts of moulding material consisting of:

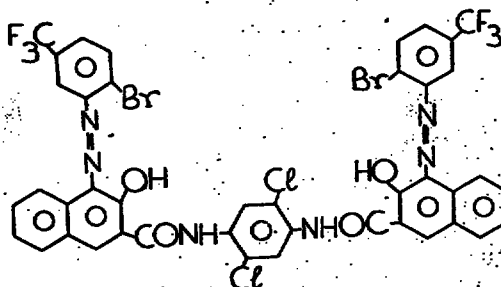
- 83 parts of a polyvinyl chloride emulsion
- 32 parts of a dioctyl phthalate plasticizer
- 3 parts of a commercial epoxide plasticizer
- 1.5 parts of a commercial stabilizer (barium-cadmium complex)
- 0.5 parts of a commercial chelator.

For improved pigment distribution, the mixture is worked for 8 minutes on a roller mill set at 160°, with one roller rotating at 20 r.p.m. and the other at 25 r.p.m. to exert friction. Subsequently it is extruded as film of 0.3 mm thickness. The film is pigmented in a slight bluish red shade which has notable light and migration fastness and heat stability.

WHAT WE CLAIM IS :—

1. A compound of formula I,





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Application Example

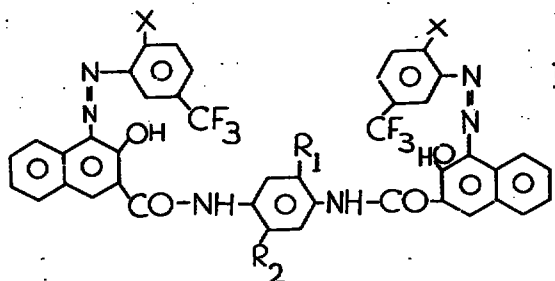
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WHAT WE CLAIM IS :—

1. A compound of formula I,





* C L M S *

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in which the X's, R₁ and R₂, independently, signify a fluorine, chlorine or bromine atom.

2. A compound of Claim 1, wherein R₁ and R₂, independently, signify chlorine or bromine.

3. A compound of Claim 1 or Claim 2, wherein R₁ and R₂ have the same significance.

4. A compound of any of Claims 1 to 3, wherein the X's, independently, signify chlorine or bromine.

5. A compound of any of Claims 1 to 4, wherein the X's have the same significance.

6. A compound of Claim 1, wherein the X's both signify chlorine and R₁ and R₂ both signify chlorine.

7. A compound of Claim 1, wherein the X's both signify bromine and R₁ and R₂ both signify chlorine.

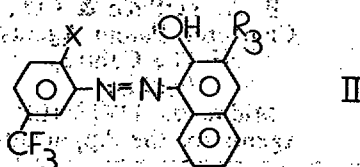
8. A compound of Claim 1, wherein the X's both signify bromine and R₁ and R₂ both signify bromine.

9. A compound of claim 1, wherein the X's both signify fluorine and R₁ and R₂ both signify chlorine.

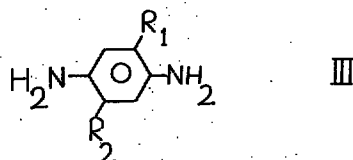
10. A compound of claim 1, wherein the X's both signify chlorine and R₁ and R₂ both signify bromine.

11. A process for the production of a compound of formula I, stated in Claim 1, characterised by

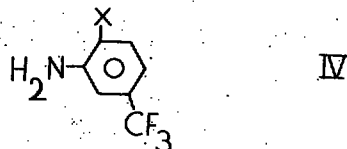
a) condensing a compound of formula II,



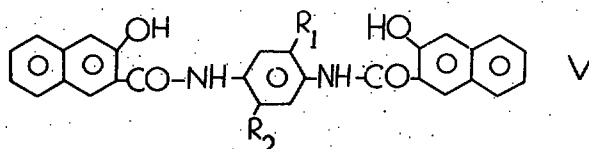
in which X is as defined in claim 1, and R₃ signifies a carboxyl group or a functional derivative thereof, with a diamine of formula III,



in which R₁ and R₂ are as defined in claim 1, in an inert organic solvent, or b) coupling a diazotised amine of formula IV,



in which X is as defined in claim 1, with a compound of formula V,





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in which R_1 and R_2 are as defined in claim 1.

12. A process according to Claim 11, substantially as hereinbefore described with reference to any one of the foregoing Examples 1 to 5.

13. A compound of formula I, stated in Claim 1, whenever produced by a process of Claim 11 or 12.

14. A process for the pigmentation of synthetic polymeric material in the mass, comprising incorporating therein a compound according to any one of Claims 1 to 10 or 13.

15. A process for the production of spun dyed filaments of viscose or cellulose acetate comprising in the spinning solution a compound of any one of claims 1 to 10 or 13.

16. A process for dyeing paper comprising incorporating in the stock a compound of any one of claims 1 to 10 or 13.

17. A surface coating medium comprising a compound of any one of claims 1 to 10 or 13.

18. A printing ink comprising a compound of any one of claims 1 to 10 or 13.

19. A process according to Claim 14, wherein said synthetic polymeric material is selected from polyvinylchloride and polypropylene.

20. A process according to Claim 14 or 19, substantially as hereinbefore described with reference to the foregoing Application Example.

21. Synthetic polymeric material whenever pigmented by a process of any Claim 14, 19 or 20.

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