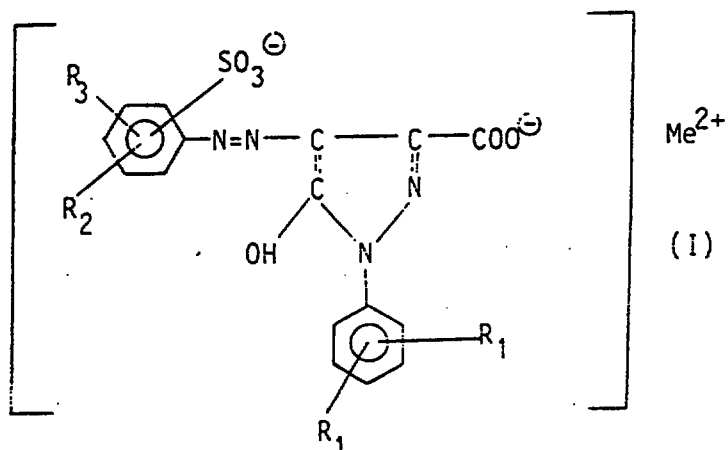


NEW MONOAZO PIGMENTS

The invention relates to new azo pigments, preferably in a polymeric substrate or in a lacquer composition.

According to the invention, there is provided a compound of
5 formula I



in which each R₁ independently is hydrogen, halogen, C₁-₄alkyl,
C₁-₄alkoxy or nitro;
R₂ is hydrogen or halogen;
R₃ is halogen; and
10 Me is a divalent metal.

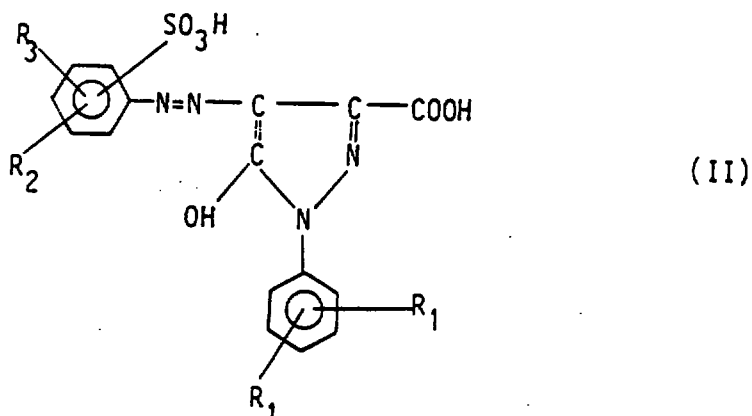
Preferably in a compound according to the invention the SO₃⁻ group is in an ortho or para position to the azo group, most preferably in para-position.

Preferably R_2 is hydrogen, chlorine or bromine, more preferably hydrogen or chlorine. Preferably R_3 is chlorine or bromine, more preferably chlorine.

Preferably R_1 is R_1' where R_1' is hydrogen, chloro, bromo, methyl, ethyl, methoxy, ethoxy or nitro; more preferably R_1 is R_1'' where R_1'' is hydrogen, chloro, methyl, methoxy or nitro. Most preferably both groups R_1 are hydrogen.

Preferably Me is Me' where Me' is selected from cobalt, calcium, strontium, barium, magnesium or manganese, most preferred being manganese and cobalt.

Compounds of formula I can be prepared by reacting a compound of formula II



with a salt of a divalent metal, preferably a Ca-, Sr-, Ba-, Co-, Mg- or Mn-salt (e.g. chloride or sulphate).

Compounds of formula II are known or can be made from known compounds by known methods. The salts of a divalent metal are known or can be made from known compounds by known methods.

The reaction of a compound of formula II with a salt of a divalent metal is preferably carried out in water (as a suspension or solution) preferably at a temperature of 20-100°C, more preferably at a temperature of 50 to 90°C.

The compounds according to the invention are suitable for pigmenting polymeric material such as polyethylene, polystyrene, polyvinylchloride, natural rubber and synthetic leather. The compounds according to the invention are also suitable for use in
5 lacquers of various types for example oil or water based paints. The compounds according to the invention are also suitable for pigmenting in the mass (either in solvent containing or solvent free systems) for example spin dyeing of cellulose acetate. The compounds according to the invention are also suitable for printing inks, for pigmenting
10 paper and for applying to coatings of textiles.

The resulting pigmentations have excellent fastness properties to heat, light, weathering, chemicals, migration, bleeding, overlacquering and solvents. Further, the compounds according to the invention maintain their depth of colour and have good application
15 properties, for example resistance to flocculation, resistance to crystallisation and dispersibility.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight and all temperatures are in °C unless indicated to the contrary. Any part by volume used
20 corresponds to the equivalent volume of 1 part by weight of water.

Example 1

24.2 Parts of 4-amino-2,5-dichlorobenzene sulphonic acid are stirred at 20 to 22° into 30 parts of water and 30 parts by volume of conc. HCl and stirred for 1 hour. The mixture is cooled to 0 to 5°
25 and then 7.1 parts of sodium nitrite dissolved in 21 parts of water are added over 15 minutes maintaining the temperature at 0 to 5°. The mixture is then stirred for 1 hour at about 5° and then excess sodium nitrite is destroyed by the addition of 0.2 parts of aminosulphonic acid.

30 20.4 Parts of 1-phenylpyrazolone-3-carboxylic acid is dissolved in 100 parts of water and 4.0 parts of sodium hydroxide at 50°. A mixture of 10 parts by volume glacial acetic acid, 40 parts of sodium

acetate, 150 parts of water and 150 parts of ice is very slowly added to the form of a fine suspension, the 1-phenyl pyrazolone-3-carboxylic acid precipitating out and the resulting suspension whilst cooling at 0 to 5° is slowly reacted with the diazonium salt suspension.

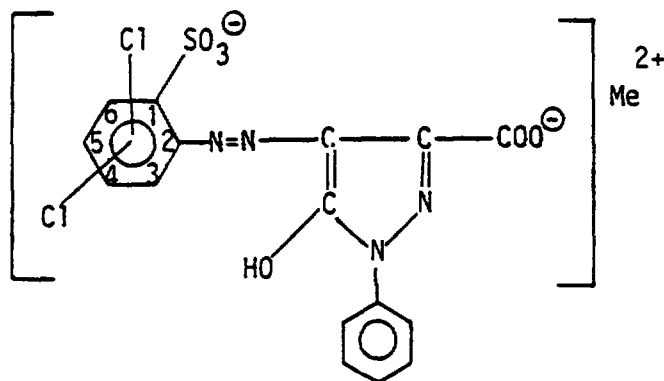
The resultant orange-coloured suspension is then stirred for a further 4 hours at 0 to 5° and is then stirred at room temperature for a further 2 hours.

A solution of 15.8 parts manganese sulphate in 100 parts water is added very slowly, whilst stirring to the resultant azo suspension. The mixture is then heated to about 80°, stirred for 2 hours at 80 to 85°, filtered hot and the resultant pigment is washed with hot water until the filtrate is chloride free. The resulting presscake is dried and milled. The resultant dye when incorporated into PVC has good fastness properties (e.g. to light).

Instead of using manganese sulphate solution, an equivalent amount of magnesium, calcium, strontium or barium chloride can be used as complexing agent. The resultant pigments have similar properties to that of the manganese complex.

Examples 2 to 11

Compounds of the formula



in which the position of the two chloro atoms and Me are defined in Table 1 below, can be prepared from the appropriate diazo component (for Examples 2 to 6 2-amino-3,5-dichlorobenzene sulphonic acid and for Examples 7 to 11, 2-amino-4,5-dichlorobenzene sulphonic acid) and 1-phenylpyrazolone-3-carboxylic acid followed by complexing with the appropriate metal complexing solution, according to the method of Example 1

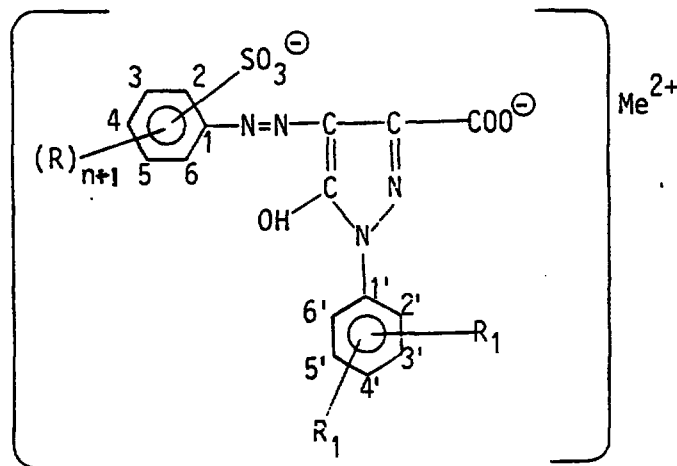
TABLE 1

<u>Ex. No.</u>	<u>position of two Cl atoms</u>	<u>Me</u>
2	3,5	Barium
3	3,5	Calcium
4	3,5	Strontium
5	3,5	Magnesium
6	3,5	Manganese
7	4,5	Manganese
8	4,5	Barium
9	4,5	Strontium
10	4,5	Calcium
11	4,5	Manganese

The pigments of Examples 1 to 11 colour PVC a yellow nuance.

Examples 12 to 21

10 Compounds of the formula



in which Me, R, n and R₁ are defined in Table 2 below, as are their positions where appropriate, can be made by a method similar to that for Examples 2 to 11 from appropriate diazo components (for Examples 12 to 14, 4-amino-2,5-dichlorobenzene sulphonic acid and for Examples 15 to 21, 3-amino-4-chlorobenzene sulphonic acid) and coupling components (for Examples 12 and 15 to 18, 1-phenyl-3-carboxy-5-pyrazolone, for Examples 13 and 19 1-(2',5'-dimethylphenyl)-3-carboxy-5-pyrazolone and for Examples 14, 20 and 21, 1-(2',5'-dichlorophenyl)-3-carboxy-5-pyrazolone) followed by complexing with a metal atom.

Table 2

Ex. No.	pos. of SO ₃ ⁻	R	n	position of R or both groups R	R ₁	position of R ₁	Me
12	4	Cl	1	2,5	H	-	cobalt
13	4	Cl	1	2,5	CH ₃	2',5'	manganese
14	4	Cl	1	2,5	Cl	2',5'	manganese
15	5	Cl	0	2	H	-	manganese
16	5	Cl	0	2	H	-	strontium
17	5	Cl	0	2	H	-	barium
18	5	Cl	0	2	H	-	cobalt
19	5	Cl	0	2	CH ₃	2',5'	manganese
20	5	Cl	0	2	Cl	2',5'	manganese
21	5	Cl	0	2	Cl	2',5'	cobalt

Pigments of Examples 12 to 21 colour PVC a yellow nuance.

Application Example A

0.05 Parts of the manganese complex of Example 1 are homogenised in a mixing roller mill at 150-160° for about 8 minutes, with 2 parts of dibutyl-tin-bis-thioglycollic acid hexyl ester and 50 parts of a mixture consisting of 65 % polyvinylchloride and 35 % diethylhexylphthalate.

The polymer is rolled into a sheet and then is glossed in a double roller calender. The resultant transparent sheet has good light fastness properties.

Application Example B

5 Four parts of the manganese complex of Example 1 are added to 96 parts of a mixture of:

- 50 parts of a 60 % solution of coco aldehyde-melamine resin of 32 % of fat content in xylene,
- 30 parts of a 50 % melamine resin solution in butanol,
- 10 10 parts of ethylene glycol monoethylether and
- 10 parts of xylene,

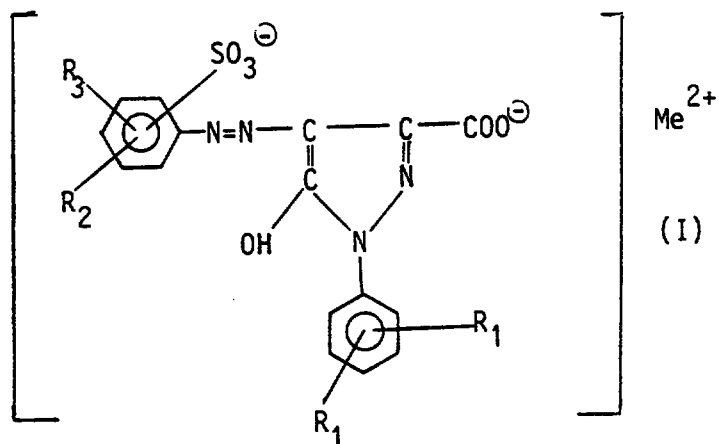
and the mixture ground for 24 hours in a ball mill. The dispersion obtained is sprayed on an aluminium sheet, the spray coating allowed to dry in the air for 30 minutes and then stoved for 30 minutes at 15 120°. A yellow film with good light and weathering fastness is obtained.

In the Application Examples A and B, instead of the manganese complex of Example 1 an appropriate amount of any other complex of Example 1 or of Examples 2 to 11 may be used.



CLAIMS: -

1. A compound of formula I



in which each R_1 independently is hydrogen, halogen, C_{1-4} alkyl,
 C_{1-4} alkoxy or nitro;
 5 R_2 is hydrogen or halogen;
 R_3 is halogen; and
 Me is a divalent metal.

2. A compound according to Claim 1 in which Me is selected from
 cobalt, calcium, strontium, barium, manganese, manganese.

10 3. A compound according to Claim 2, in which Me is Me' where
 Me' is selected from cobalt and manganese.

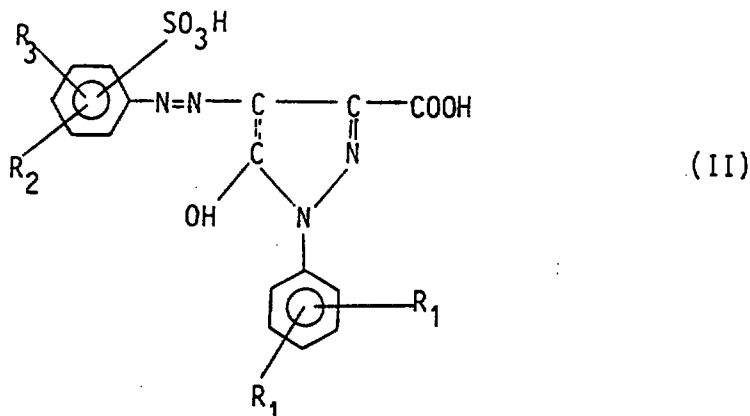
4. A compound according to any one of the preceding claims in
 which R_1 is R_1' where R_1' is hydrogen, chloro, bromo, methyl, ethyl,
 methoxy, ethoxy or nitro.

15 5. A compound according to any one of the preceding claims in
 which R_2 is hydrogen or chlorine.

6. A compound according to any one of the preceding claims in
 which R_3 is chlorine.



7. A process for preparing a compound of formula I comprising complexing a compound of formula II



with a salt of a divalent metal.

8. A process according to Claim 7 in which the reaction is
5 carried out in water at a temperature of 50 to 90°C.

9. A process according to Claim 7 or Claim 8 in which the salt of a divalent metal is a Ca-, Sr-, Ba-, Co-, Mg- or Mn- chloride or sulphate.

10. A substrate to which a compound of formula I, defined in
10 Claim 1 has been applied.

11. A method of pigmenting a substrate comprising applying to the substrate a compound of formula I, defined in Claim 1.

12. A compound of formula I defined in Claim 1 substantially as herein described with reference to any one of Examples 1 to 21.

15 13. A method of pigmenting substantially as herein described with reference to Application Example A.

14. A process for preparing a compound of formula I substantially as herein described with reference to any one of Examples 1 to 21.

20 15. A substrate to which any one of the pigments of Examples 1 to 21 has been applied.