

MONOAZO PIGMENTS

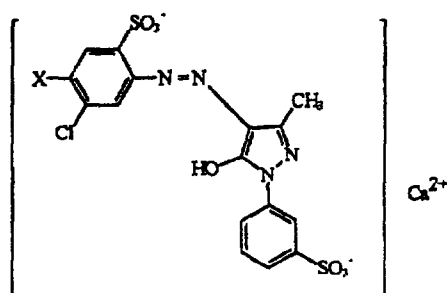
This invention relates to monoazo pigments and more particularly to greenish-yellow pigments of the azo pyrazolone series.

The use of pigments for the colouring of plastics materials is well known. For the production of yellow colorations, it has been traditional to employ inorganic pigments such as cadmiums and lead chromes but these are now being phased out because of environmental pressures.

Organic pigments that have been proposed as replacements for these inorganic materials include compounds of the formula :

10

15

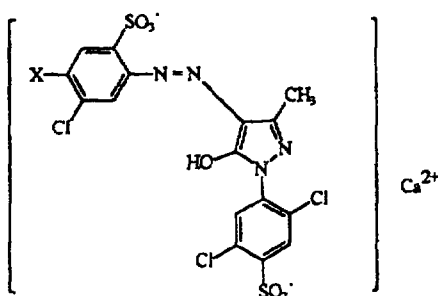


20 wherein X is Cl (DE-OS 2616981) or CH₃ (US 5047517).

Other yellow pigments, described in DE-OS 3318073, include compounds of the formula :

25

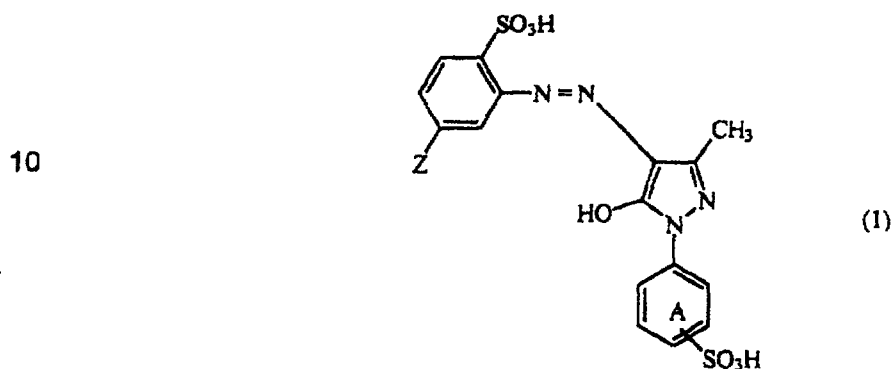
30



wherein X is again Cl or CH₃

The above mentioned organic pigments are generally suitable for the production of reddish-yellow colorations but it has now been found that greenish-yellow shades having superior light stability, together with excellent heat stability and bleed fastness can be obtained from the compounds hereinafter defined.

5 Accordingly, the invention provides an azo pyrazolone compound of the formula :



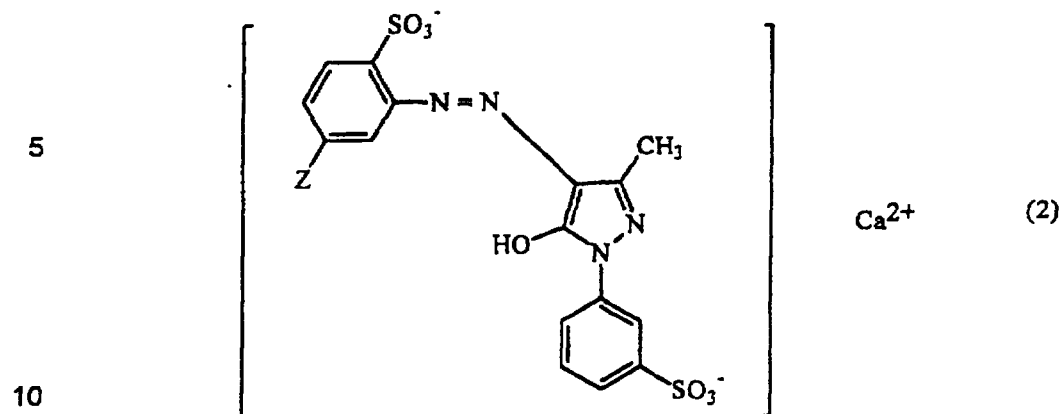
wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R and R¹ are hydrocarbyl and the sulphonic acid group of ring A is in the 3- or 4-position relative to the pyrazolyl group, said compound being in the form of a salt.

20

The salt of the azo pyrazolone compound of Formula 1 may be a metal salt, for example an alkali metal, alkaline earth metal or heavy metal salt, or a salt of a nitrogenous base, for example a primary, secondary or tertiary amine or quaternary ammonium salt, particularly useful pigments being the salts of barium, strontium, manganese, magnesium, sodium and, especially, calcium.

25

Preferred compounds of the invention have the formula :

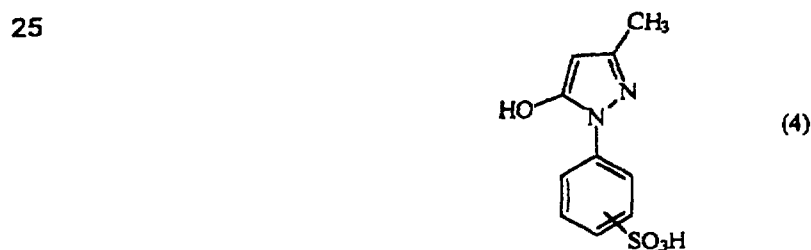


wherein Z is as defined above, R preferably being an alkyl, for example C₁₋₆-alkyl, group and R¹ preferably being an aryl, for example phenyl or tolyl, group.

15 The azo pyrazolone compounds of the invention may be prepared by diazotising a substituted sulphonated aniline of the formula :



wherein Z is as defined above and coupling the resulting diazo compound with a sulphonated 3-methyl-1-phenylpyrazol-5-one of the formula :



wherein the sulphonic acid group is in the 3- or 4-position relative to the pyrazolyl group, and converting the resulting monoazo compound to the desired salt form.



The diazotisation and coupling reactions may be performed in a conventional manner appropriate to the classes of compound being used.

The preferred substituted sulphonated aniline for use in preparing the compounds of the invention is 2-amino-4-chlorobenzene sulphonic acid whilst the
5 preferred coupling component is 3-methyl-1-(3'-sulphophenyl)pyrazol-5-one.

It is often convenient to prepare the compound of Formula 1 in the form of a sodium salt and then to convert the sodium salt to, for example, an alkaline earth or heavy metal lake by adding the required amount of a water-soluble alkaline earth or heavy metal salt, usually in the form of an aqueous solution.

10 Surface active agents and/or organic solvents may optionally be present during the synthesis of the compound of Formula 1 and/or during precipitation of the pigment.

The compounds of the invention, which may be subjected to conventional milling operations and/or thermal treatments in order to provide products of the desired
15 particle size and/or crystal structure, are useful yellow pigments which may be used in conventional manner. In particular, they may be used alone or in conjunction with other pigments for the coloration of plastics materials, for example polyvinyl chloride, polyolefins, polystyrene and ABS where they exhibit excellent properties. The compounds of the invention are also valuable for the pigmentation of surface coatings.

20 The invention is illustrated but not limited by the following Examples.

Example 1

2-Amino-4-chlorobenzene sulphonic acid (4.15g), deionised water (50ml) and hydrochloric acid (5.1ml) were stirred together in a vessel surrounded by an ice-
25 bath, followed by sufficient 48% sodium hydroxide solution to form a solution alkaline to Brilliant Yellow paper. The solution was then cooled to 0-5°C and a further amount (5.1ml) of hydrochloric acid was added. A solution of sodium nitrite (1.56g) in de-ionised water (5ml) was added all at once and the mixture was stirred at 0-5°C for 30 mins. Excess nitrite was then removed by adding a few ml of 10% sulphamic acid solution.

30 3-Methyl-1-(3'-sulphophenyl)pyrazol-5-one (5.4g) was added to de-ionised water (50ml) and the pH was adjusted to 6.5 by the addition of 48% sodium hydroxide solution. The solution was then stirred at 0-5°C and the diazo suspension obtained as described above was added over 10 mins whilst maintaining the pH at 6.5 by the



addition of 48% sodium hydroxide solution. The coupling mixture was then stirred overnight at room temperature.

The reaction mixture was then heated to 90°C and a solution of calcium chloride (32g CaCl_2 in 40ml water) was added all at once and the mixture stirred for a
5 further 3 hours at 90°C. The mixture was then filtered hot and the product was washed chloride-free with de-ionised water (1000ml) and dried giving 9.1g of a greenish-yellow solid.

Example 2

10 2-Amino-4-(toluene-4-sulphonylamino)-benzene sulphonic acid (6.85g), deionised water (50ml) and hydrochloric acid (5.1ml) were stirred together in a vessel surrounded by an ice bath, followed by sufficient 48% sodium hydroxide solution to form a solution alkaline to Brilliant Yellow paper. The solution was then cooled to 0-5°C and a further amount (5.1ml) of hydrochloric acid was added. A solution of sodium nitrite
15 (1.56g) in deionised water (5ml) was added all at once and the mixture was stirred at 0-5°C for 30 mins. Excess nitrite was then removed by adding a few ml of 10% sulphamic acid solution.

3-Methyl-1-(3'-sulphophenyl)pyrazol-5-one (6.58g) was added to deionised water (50ml) and the pH was adjusted to 6.5 by the addition of 48% sodium hydroxide
20 solution. The solution was then stirred at 0-5°C and the diazo suspension obtained as described above was added over 10 minutes whilst maintaining the pH at 6.5 by the addition of 48% sodium hydroxide solution. The coupling mixture was then stirred overnight at room temperature.

The reaction mixture was then heated to 90°C and a solution of calcium
25 chloride (30g CaCl_2 in 40ml water) was added all at once and the mixture stirred for a further 3 hours at 90°C. The mixture was then filtered hot and the product was washed chloride-free with deionised water (1000ml) and dried giving 12g of an orange-yellow solid.

30 Example 3

2-Amino-4-benzoylamino benzene sulphonic acid (5.85g), deionised water (50ml) and hydrochloric acid (5.1ml) were stirred together in a vessel surrounded by an ice bath, followed by sufficient 48% sodium hydroxide solution to form a solution alkaline to Brilliant Yellow paper. The solution was then cooled to 0-5°C and a further amount

(5.1ml) of hydrochloric acid was added. A solution of sodium nitrite (1.56g) in deionised water (5ml) was added all at once and the mixture was stirred at 0-5°C for 30 mins. Excess nitrite was then removed by adding a few ml of 10% sulphamic acid solution.

3-Methyl-1-(3'-sulphophenyl)pyrazol-5-one (6.58g) was added to deionised water (50ml) and the pH was adjusted to 6.5 by the addition of 48% sodium hydroxide solution. The solution was then stirred at 0-5°C and the diazo suspension obtained as described above was added over 10 minutes whilst maintaining the pH at 6.5 by the addition of 48% sodium hydroxide solution. The coupling mixture was then stirred overnight at room temperature.

10 The reaction mixture was then heated to 90°C and a solution of calcium chloride (30g CaCl_2 in 40ml water) was added all at once and the mixture stirred for a further 3 hours at 90°C. The mixture was then filtered hot and the product was washed chloride-free with deionised water (1000ml) and dried giving 2.7g of a greenish-yellow solid.

15

Example 4

2-Amino-4-nitrobenzene sulphonic acid (5.18g), deionised water (50ml) and hydrochloric acid were stirred together in a vessel surrounded by an ice bath. A solution of sodium nitrite (1.56g) in deionised water (5ml) was added all at once and the mixture was stirred at 0-5°C for 30 mins. Excess nitrite was then removed by adding a few ml of 10% sulphamic acid solution.

3-Methyl-1-(3'-sulphophenyl)pyrazol-5-one (6.58g) was added to deionised water (50ml) and the pH was adjusted to 6.5 by the addition of 48% sodium hydroxide solution. The solution was then stirred at 0-5°C and the diazo suspension obtained as described above was added over 10 minutes whilst maintaining the pH at 6.5 by the addition of 48% sodium hydroxide. The coupling mixture was then stirred overnight at room temperature.

The reaction mixture was then heated to 90°C and a solution of calcium chloride (30g CaCl_2 in 40ml water) was added all at once and the mixture stirred for a further 3 hours at 90°C. The mixture was then filtered hot and the product was washed chloride-free with deionised water (1000ml) and dried giving 6.0g of an orange-yellow solid.

Example 5

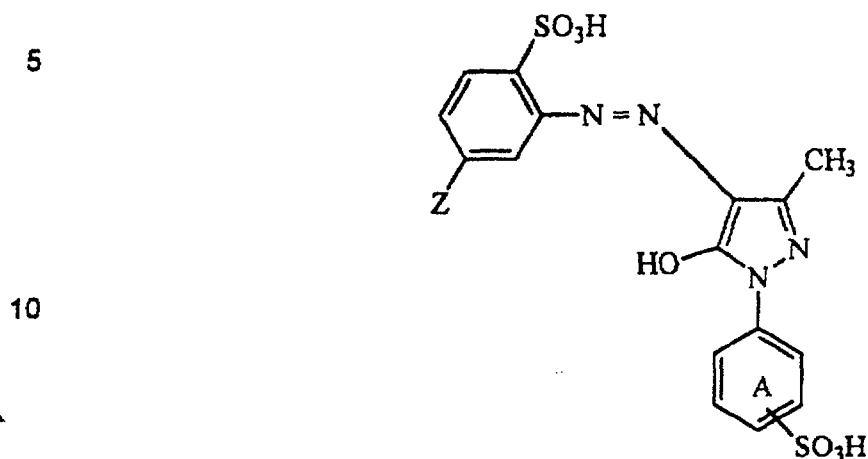
2-Amino-4-chlorobenzene sulphonic acid (4.14g), deionised water (50ml) and hydrochloric acid (5.1ml) were stirred together in a vessel surrounded by an ice bath, followed by sufficient 48% sodium hydroxide solution to form a solution alkaline to
5 Brilliant Yellow paper. The solution was then cooled to 0-5°C and a further amount (5.1ml) of hydrochloric acid was added. A solution of sodium nitrite (1.56g) in deionised water (5ml) was added all at once and the mixture was stirred at 0-5°C for 30 mins. Excess nitrite was then removed by adding a few ml of 10% sulphamic acid solution.

3-Methyl-1-(4'-sulphophenyl)pyrazol-5-one (5.6g) was added to deionised
10 water (50ml) and the pH was adjusted to 6.5 by the addition of 48% sodium hydroxide solution. The solution was then stirred at 0-5°C and the diazo suspension obtained as described above was added over 10 mins whilst maintaining the pH at 6.5 by the addition of 48% sodium hydroxide solution. The coupling mixture was then stirred overnight at room temperature.

15 The reaction mixture was then heated to 90°C and a solution of calcium chloride (32g CaCl₂ in 40ml water) was added all at once and the mixture stirred for a further 3 hours at 90°C. The mixture was then filtered hot and the product was washed chloride-free with deionised water (1000ml) and dried giving 4.2g of a yellow solid.

**CLAIMS**

1. An azo pyrazolone compound of the formula :

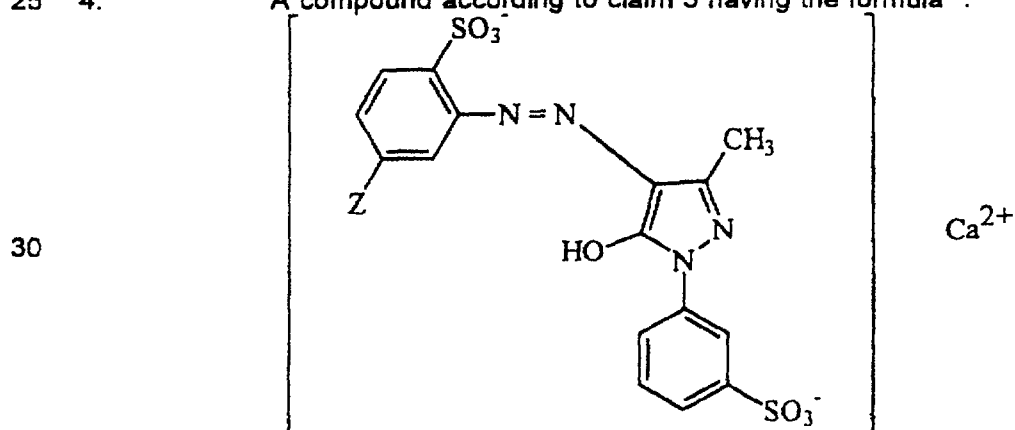


- 15 wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R and R¹ are hydrocarbyl groups and the sulphonic acid group in ring A is in the 3- or 4-position relative to the pyrazolyl group, said compound being in the form of a salt.

- 20 2. A compound according to claim 1 wherein the salt is a metal salt or a salt of a nitrogenous base.

3. A compound according to claim 2 wherein the salt is a calcium salt.

- 25 4. A compound according to claim 3 having the formula :

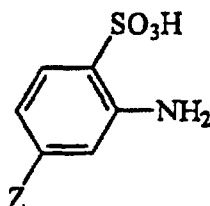




wherein Z is as defined in claim 1.

5. A method for the preparation of an azo pyrazolone compound as defined in claim 1 which comprises diazotising a substituted sulphonated aniline of the formula :

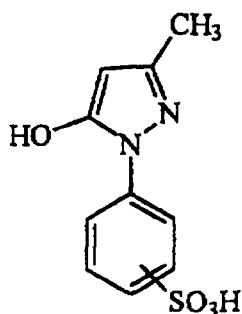
5



10

wherein Z is as defined in claim 1 and coupling the resulting diazo compound with a sulphonated 3-methyl-1-phenylpyrazol-5-one of the formula :

15



20

wherein the sulphonic acid group is in the 3- or 4-position relative to the pyrazolyl group, and converting the resulting monoazo compound to the desired salt form.

6. A method according to claim 5 wherein the substituted sulphonated aniline comprises 2-amino-4-chlorobenzene sulphonic acid.

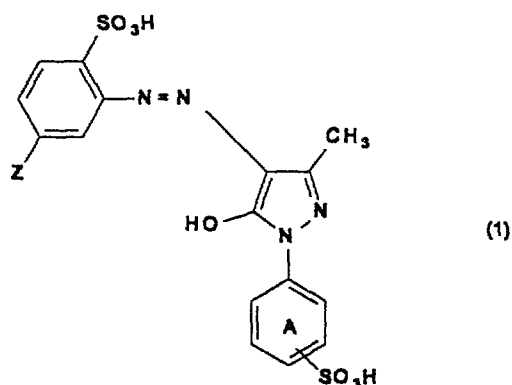
7. A method according to claim 5 or claim 6 wherein the sulphonated 3-methyl-1-phenylpyrazol-5-one comprises 3-methyl-1-(3'-sulphophenyl)pyrazol-5-one.

8. The use of an azo pyrazolone compound as defined in claim 1 as a pigment.



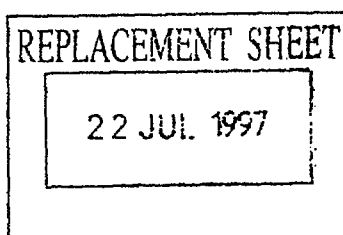
The above mentioned organic pigments are generally suitable for the production of reddish-yellow colorations but it has now been found that greenish-yellow shades having superior light stability, together with excellent heat stability and bleed fastness can be obtained from the compounds hereinafter defined.

Accordingly, the invention provides an azo pyrazolone compound of the formula :

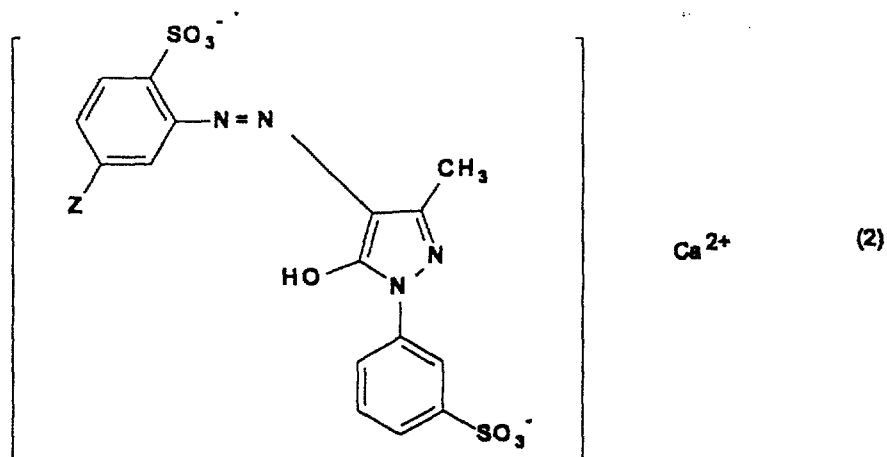


wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R is hydrocarbyl, R¹ is aryl and the sulphonic acid group of ring A is in the 3-position relative to the pyrazolyl group, said compound being in the form of a salt.

The salt of the azo pyrazolone compound of Formula 1 may be a metal salt, for example an alkali metal, alkaline earth metal or heavy metal salt, or a salt of a nitrogenous base, for example a primary, secondary or tertiary amine or quaternary ammonium salt, particularly useful pigments being the salts of barium, strontium, manganese, magnesium, sodium and, especially, calcium.



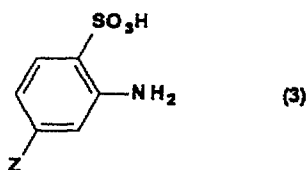
Preferred compounds of the invention have the formula :



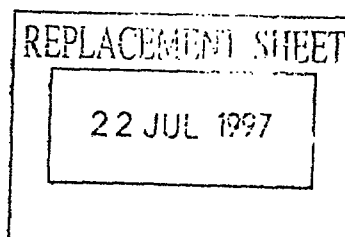
wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R and R¹ are hydrocarbyl.

R is preferably alkyl, for example C₁₋₆-alkyl and R¹ is preferably aryl, for example phenyl or tolyl.

The azo pyrazolone compounds of the invention may be prepared by diazotising a substituted sulphonated aniline of the formula :



wherein Z is as defined above and coupling the resulting diazo compound with 3-methyl-1-(3'-sulphophenyl)pyrazol-5-one, and converting the resulting monoazo compound to the desired salt form.



The diazotisation and coupling reactions may be performed in a conventional manner appropriate to the classes of compound being used.

The preferred substituted sulphonated aniline for use in preparing the compounds of the invention is 2-amino-4-chlorobenzene sulphonic acid.

It is often convenient to prepare the compound of Formula 1 in the form of a sodium salt and then to convert the sodium salt to, for example, an alkaline earth or heavy metal lake by adding the required amount of a water-soluble alkaline earth or heavy metal salt, usually in the form of an aqueous solution.

Surface active agents and/or organic solvents may optionally be present during the synthesis of the compound of Formula 1 and/or during precipitation of the pigment.

The compounds of the invention, which may be subjected to conventional milling operations and/or thermal treatments in order to provide products of the desired particle size and/or crystal structure, are useful yellow pigments which may be used in conventional manner. In particular, they may be used alone or in conjunction with other pigments for the coloration of plastics materials, for example polyvinyl chloride, polyolefins, polystyrene and ABS where they exhibit excellent properties. The compounds of the invention are also valuable for the pigmentation of surface coatings.

The invention is illustrated but not limited by the following Examples.

Example 1

2-Amino-4-chlorobenzene sulphonic acid (4.15g), deionised water (50ml) and hydrochloric acid (5.1ml) were stirred together in a vessel surrounded by an ice-bath, followed by sufficient 48% sodium hydroxide solution to form a solution alkaline to Brilliant Yellow paper. The solution was then cooled to 0-5°C and a further amount (5.1ml) of hydrochloric acid was added. A solution of sodium nitrite (1.56g) in de-ionised water (5ml) was added all at once and the mixture was stirred at 0-5°C for 30 mins. Excess nitrite was then removed by adding a few ml of 10% sulphamic acid solution.

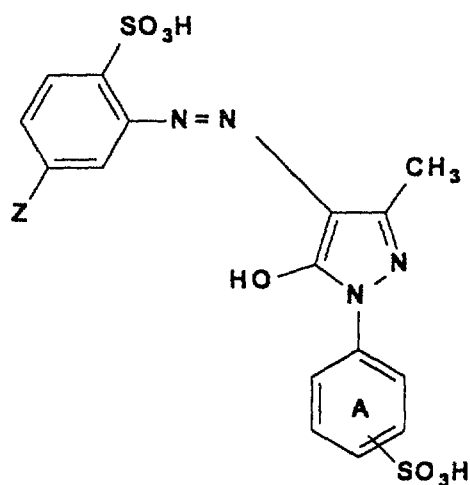
3-Methyl-1-(3'-sulphophenyl)pyrazol-5-one (5.4g) was added to de-ionised water (50ml) and the pH was adjusted to 6.5 by the addition of 48% sodium hydroxide solution. The solution was then stirred at 0-5°C and the diazo suspension obtained as described above was added over 10 mins whilst maintaining the pH at 6.5 by the

REPLACEMENT SHEET

22 JUL 1997

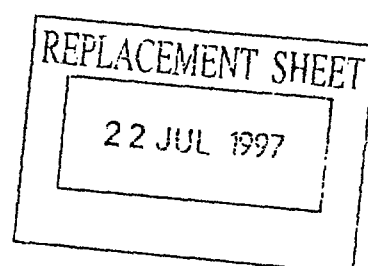
CLAIMS

1. An azo pyrazolone compound of the formula :



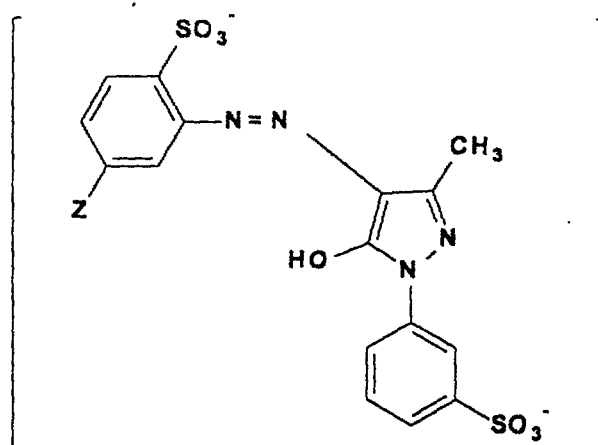
wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R is a hydrocarbyl group, R¹ is aryl and the sulphonic acid group in ring A is in the 3- position relative to the pyrazolyl group, said compound being in the form of a salt.

2. A compound according to claim 1 wherein R¹ is phenyl or tolyl.
3. A compound according to either claim 1 or claim 2 wherein the salt is a metal salt or a salt of a nitrogenous base.
4. A compound according to claim 3 wherein the salt is a calcium salt.

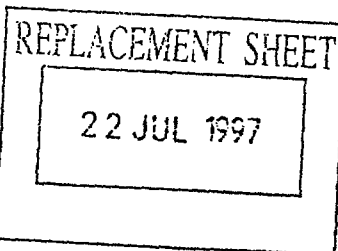




5. A compound having the formula :



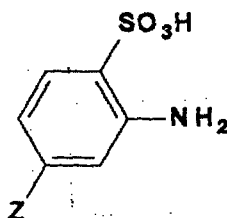
Ca²⁺



wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R and R¹ are hydrocarbonyl groups.

6. A compound according to claim 5 wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R is alkyl and R¹ is aryl.

7. A method for the preparation of an azo pyrazolone compound as defined in claim 1 which comprises diazotising a substituted sulphonated aniline of the formula :



wherein Z is as defined in claim 1 and coupling the resulting diazo compound with 3-methyl-1-(3'-sulphophenyl)pyrazol-5-one, and converting the resulting monoazo compound to the desired salt form.

8. A method according to claim 7 wherein the substituted sulphonated aniline comprises 2-amino-4-chlorobenzene sulphonic acid.

9. The use of an azo pyrazolone compound as defined in claim 1 as a pigment.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



PTMP's copy

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09B 63/00, 69/04, 29/36	A1	(11) International Publication Number: WO 96/22333 (43) International Publication Date: 25 July 1996 (25.07.96)
(21) International Application Number: PCT/GB95/02832 (22) International Filing Date: 5 December 1995 (05.12.95) (30) Priority Data: 9501088.0 20 January 1995 (20.01.95) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): CHORLTON, Alan, Patrick [GB/GB]; 22 Cote Green Road, Marple Bridge, Stockport, Cheshire SK6 5EW (GB). MASON, James [GB/GB]; 5 Pikehouse Cottages, Lightowlers Lane, Littleborough, Rochdale, Lancashire OL15 0LW (GB). (74) Agents: STEPHENSON, Kenneth; Intellectual Property Group, Zeneca Specialties, P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB) et al.		(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
(54) Title: MONOAZO PIGMENTS (57) Abstract An azo pyrazolone compound of formula (I), wherein Z represents a substituent selected from Cl, Br, F, NO₂, SO₂R, CO₂R, NHSO₂R¹ and NHCOR¹ in which R and R¹ are hydrocarbyl groups and the sulphonic acid group in ring A is in the 3- or 4-position relative to the pyrazolyl group, said compound being in the form of a salt, and its use as a pigment. (I)		