PATENT SPECIFICATION

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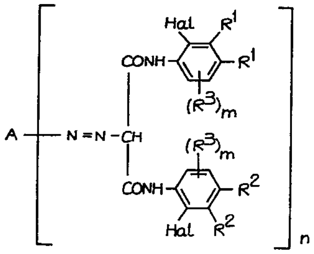
(54) AZOANTHRAQUINONE PIGMENTS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised and existing under the laws of Germany, of Leverkusen, Federal Republic of Germany, 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 azoanthraquinone pigments of the formula



(I)

processes for their preparation and their use.

In the formula (I),

Hal represents halogen, such as fluorine, chlorine or bromine,
one of the substituents R^1 represents halogen, such as fluorine, chlorine and bromine, and the other represents hydrogen,
one of the substituents R^2 represents halogen, such as fluorine, chlorine and bromine, and the other represents hydrogen,
R^3 represents a substituent,
m represents 0, 1 or 2,
n represents 1 or 2 and
A denotes an anthraquinone radical or more highly fused anthraquinone radical, or a derivative thereof (as hereinafter defined), which is optionally further substituted.

Suitable substituents R^3 are, for example, halogen, such as fluorine, chlorine and bromine, C_1—C_4-alkyl, C_1—C_4-alkoxy, nitro-trifluoromethyl, cyano or optionally substituted carbamoyl or sulphamoyl.

Possible substituents of the carbamoyl and sulphamoyl groups R^3 are C_1—C_4-alkyl or phenyl or benzyl optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, fluorine, chlorine, bromine or nitro.

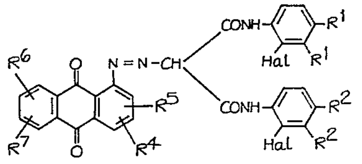
Possible more highly fused anthraquinone radicals A are phthaloylacridone and phthaloylbenzimidazole. The "derivatives" in respect of radical A means an anthrapyrimidine, isothiazolanthrone, pyrazolanthrone or anthrapyridone or 4,4′-diamino-1,1′-dianthrimide.

The anthraquinone radicals and more highly fused anthraquinone radicals can contain the following substituents: fluorine, chlorine, bromine, nitro, C_1—C_{12}-alkyl, trifluoromethyl, cyclopentyl, cyclohexyl, benzyl, C_1—C_4-alkoxy, C_1—C_{12}-alkylamino, cyclohexylamino, benzylamino, C_1—C_4-alkylmercapto, phenylmercapto which is optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, chlorine or nitro, C_1—C_4-alkylcarbonyl, C_1—C_4-alkoxycarbonyl, phenylamino which is optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, chlorine or nitro, aminocarbonyl which is optionally monosubstituted or disubstituted by C_1—C_4-alkyl, benzyl or phenyl, it being possible for phenyl and benzyl to be substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, fluorine, chlorine, bromine or nitro, carboxyl, hydroxyl, C_1—C_4-alkylcarbonylamino, benzoylamino or naphthoylamino optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, chlorine or nitro, C_1—C_4-alkylsulphonylamino or phenylsulphonylamino which is optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, chlorine or nitro.

Suitable aminoanthraquinones or more highly fused aminoanthraquinone compounds and derivatives thereof are, for example, 1-aminoanthraquinone, 2-aminoanthraquinone, 1-amino-2-chloroanthraquinone, 1-

amino - 4 - chloroanthraquinone, 1 - amino - 5 - chloroanthraquinone, 1 - amino - 6 - chloroanthraquinone, 1 - amino - 6(7) - chloroanthraquinone (mixture), 1 - amino - 5,8 - dichloroanthraquinone, 1 - amino - 2 - bromoanthraquinone, 1 - amino - 2,4 - dibromoanthraquinone, 1 - amino - 6,7 - dichloroanthraquinone, 1 - amino - 6 - fluoroanthraquinone, 1 - amino - 7 - fluoroanthraquinone, 1 - amino - 6,7 - difluoroanthraquinone, 2 - amino - 1 - chloroanthraquinone, 2 - amino - 3 - chloroanthraquinone, 2 - amino - 3 - bromoanthraquinone, 1 - amino - 4 - nitroanthraquinone, 1 - amino - 5 - nitroanthraquinone, 1 - amino - 2 - methylanthraquinone, 1 - amino - 2 - methyl - 4 - chloroanthraquinone, 1 - amino - 2 - methyl - 4 - bromoanthraquinone, 1 - aminoanthraquinone - 2 - carboxylic acid, 1 - aminoanthraquinone - 2 - carboxylic acid amide, 1 - aminoanthraquinone - 2 - carboxylic acid methyl ester, 1 - amino - 4 - nitroanthraquinone - 2 - carboxylic acid, 1 - amino - 2 - acetylanthraquinone, 1 - amino - 4 - acetylaminoanthraquinone, 1 - amino - 5 - acetylaminoanthraquinone, 1 - amino - 5 - benzoylaminoanthraquinone, 1 - amino - 4 - benzoylaminoanthraquinone, 1 - amino - 8 - benzoylaminoanthraquinone, 1 - amino - 4 - hydroxyanthraquinone, 1 - amino - 5 - hydroxyanthraquinone, 1 - amino - 4 - methoxyanthraquinone, 1 - amino - 2 - methoxy - 4 - hydroxyanthraquinone, 1 - amino - 4 - methylaminoanthraquinone, 1 - amino - 4 - benzylaminoanthraquinone, 1 - amino - 4 - cyclohexylaminoanthraquinone, 1 - amino - 4 - anilinoanthraquinone, 1 - amino - 2 - bromo - 4 - methylmercaptoanthraquinone, 1 - amino - 4 - (4 - methylphenylsulphonylamino) - 2 - phenylthioanthraquinone, 1 - amino - 6 - methylmercaptoanthraquinone, 2 - phenyl - 6 - amino - 4,5 - phthaloylbenzimidazole, 6 - chloro - 2 - amino - 3,4 - phthaloylacridone, 7 - chloro - 2 - amino - 3,4 - phthaloylacridone, 5 - chloro - 8 - amino - 3,4 - phthaloylacridone, 3 - aminobenzanthrone, 5 - aminopyrazolanthrone, 4 - aminoanthrapyrimidine, 6 - aminoanthrapyrimidine, 6 - amino - 3 - methylanthrapyridone, 7 - amino - 3 - methylanthrapyridone, 1,5 - diaminoanthraquinone, 1,4 - diaminoanthraquinone, 1,8 - diaminoanthraquinone, 1,6 - /1,7 - diaminoanthraquinone (mixture), 2,6 - diaminoanthraquinone, 1,5 - diamino - 4 - chloroanthraquinone, 1,4 - diamino - 5 - nitroanthraquinone, 1,5 - diamino - 2,4,6,8 - tetrabromoanthraquinone, 1,5 - diamino - 4,8 - dihydroxyanthraquinone, 1,8 - diamino - 4,5 - dihydroxyanthraquinone and 1 - amino - 2 - bromo - 4 - (4 - methylphenylsulphonylamino)-anthraquinone.

Preferred dyestuffs correspond to the formula



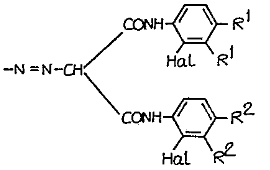
(II)

wherein

Hal, R^1 and R^2 have the abovementioned meaning, R^4 and R^6 independently denote hydrogen, fluorine, chlorine, bromine, nitro, C_1—C_4-alkyl, C_1—C_4-alkoxy, C_1—C_4-alkylamino, benzylamino, cyclohexylamino, C_1—C_4 - alkylmercapto phenylmercapto which is optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, chlorine or nitro, C_1—C_4 - alkylcarbonyl, C_1—C_4 - alkoxycarbonyl, phenylamino which is optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, chlorine or nitro, carboxamide which is optionally monosubstituted or disubstituted by C_1—C_4-alkyl, benzyl or phenyl, it being possible for phenyl to be substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, fluorine, chlorine, bromine or nitro, carboxyl, hydroxyl, C_1—C_4 - alkylcarbonylamino, C_1—C_4 - alkylsulphonylamino, benzoylamino which is optionally substituted by C_1—C_4 - alkyl, C_1—C_4 - alkoxy, chlorine, bromine or nitro or phenylsulphonylamino which is optionally substituted by C_1—C_4-alkyl, C_1—C_4-alkoxy, chlorine or nitro,

R^5 denotes hydrogen, fluorine, chlorine, bromine or carboxyl and

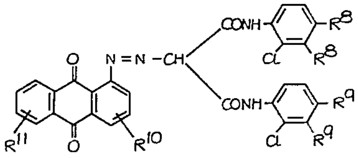
R^7 denotes hydrogen, fluorine, chlorine, bromine, carboxyl or a radical of the formula



wherein

Hal, R^1 and R^2 have the abovementioned meaning.

Dyestuffs of the formula



(III)

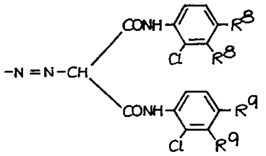
wherein

one R^8 denotes chlorine and the other denotes hydrogen,

one R^9 denotes chlorine and the other denotes hydrogen,

R^{10} denotes hydrogen, fluorine, chlorine, bromine, C_1—C_4 - alkylcarbonylamino, benzoylamino which is optionally substituted by 1 or 2 nitro group or 1—5 chlorine or bromine atoms, C_1—C_4-alkylsulphonylamino, or phenylsulphonylamino which is optionally monosubstituted by methyl, methoxy, or chlorine, carboxyl or C_1—C_4-alkoxycarbonyl and

R^{11} denotes hydrogen, fluorine, chlorine, bromine, carboxyl, C_1—C_4-alkoxycarbonyl, aminocarbonyl which is optionally monosubstituted or disubstituted by C_1—$_4$-alkyl or phenyl, C_1—C_4 - alkylcarbonylamino, benzoylamino which is optionally substituted by 1 or 2 nitro groups or 1—5 chlorine or bromine atoms, C_1—C_4-alkylsulphonylamino, phenylsulphonylamino which is optionally monosubstituted by methyl, methoxy or chlorine or the radical of the formula



wherein

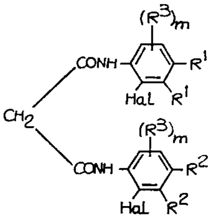
R^8 and R^9 have the abovementioned meaning, are very particularly preferred.

The azo pigments (I) are prepared by coupling diazotised aminoanthraquinones of the formula

$$A—(NH_2)_n \qquad (IV)$$

wherein

A and n have the abovementioned meaning, to malonic acid dianilides of the formula



(V)

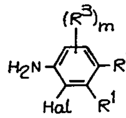
wherein

Hal, R^1, R^2, R^3 and m have the abovementioned meaning.

In general, the coupling reaction is carried out by diazotising the diazo component (IV) with organic nitrites, such as methyl nitrite, ethyl nitrite, iso-amyl nitrite or, advantageously, with nitrites of glycols and glycol derivatives, such as methoxyethyl nitrite or ethoxyethyl nitrite, or alkali metal nitrites, such as sodium nitrite, in an organic solvent, such as dimethylformamide, dimethylacetamide, dimethylsulphoxide, tetramethylenesulphone, tetraphenylurea, N - methylpyrrolidone, nitrobenzene, o-dichlorobenzene, 1,2,4 - trichlorobenzene, ethylene glycol dimethyl ether, ethylene glycol diethyl ether or acetic acid, in the presence of an acid, such as sulphuric acid, phosphoric acid, benzenesulphonic acid, ethanesulphonic acid, p-toluenesulphonic acid, naphthalene - 2,6-disulphonic acid, formic acid, acetic acid, dichloroacetic acid, 2,4 - dichlorobenzoic acid, oxalic acid, succinic acid, maleic acid, tartaric acid or terephthalic acid. A suspension of the coupling component, appropriately in the same solvent, is then stirred in. After the coupling reaction has ended, the crude product is purified by raising the temperature in the coupling solution to 90 to 200°C and is isolated by filtering off.

The process can also be varied to the effect that the diazo component and coupling component are initially introduced in the organic solvent and the alkyl nitrite or alkali metal nitrite is added so that diazotisation and coupling take place simultaneously. In this process variant also, a temperature treatment appropriately follows for the purification of the pigment thus prepared.

The coupling components of the formula (V) are obtained by reacting functional derivatives of malonic acid with halogenoanilines of the formula



(VI)

wherein

Hal, R^1, R^3 and m have the abovementioned meaning.

Malonic acid derivatives and halogenoaniline are reacted in molar ratios of 1:2, in general the halogenoaniline being employed in a 0.1 to 10 fold excess. The reaction is reacted at 120 to 220°C undiluted or in an inert organic solvent, such as 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, xylene or nitrobenzene.

Malonic acid derivatives which can be used are, in particular, the malonic acid halides, above all malonic acid dichloride, the malonic acid dialkyl esters, above all the dimethyl and diethyl esters, the malonic acid iminoalkyl esters, in particular the dimethyl and diethyl esters, and malodinitrile.

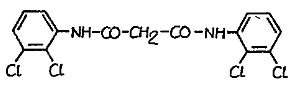
The pigments of the formula I are obtained in a form suitable for pigments or can be converted into the suitable form by after-treatment processes which are in themselves known, for example by dissolving or swelling in strong inorganic acids, such as sulphuric acid, and discharging onto ice. Fine division can also be achieved by grinding with or without grinding auxiliaries, such as inorganic salts or sand, optionally in the presence of solvents, such as toluene, xylene, dichlorobenzene or N-methylpyrrolidone. The tinctorial strength and transparency of the pigment can be influenced by varying the after-treatment.

Because of their fastness to light and migration, the pigments of the formula I are suitable for the most diverse pigment applications. The pigments according to the invention can be used for the preparation of very fast pigmented systems, such as mixtures with other substances, formulations, paints, printing pastes, coloured paper and coloured macromolecular substances. Mixtures with other substances can be understood, for example, as those with inorganic white pigments, such as titanium dioxide (rutile) or with cement. Formulations are, for example, flush pastes with organic liquids or pastes and fine pastes with water, dispersing agents and, if appropriate, preservatives. The designation paint represents, for example, lacquers which dry physically or by oxidation, stoving lacquers, reactive lacquers, two-component lacquers, emulsion paints for weatherproof coatings and distempers. Printing pastes are to be understood as those for paper, textile and tinplate printing. The macromolecular substances can be of natural origin, such as rubber, or they can be obtained by chemical modification, such as acetylcellulose, cellulose butyrate or viscose, or produced synthetically, such as polymers, polyaddition products and polycondensates. Plastic compositions, such as polyvinyl chloride, polyvinyl acetate, polyvinyl propionate, polyolefines, for example polyethylene or polypropylene, polyesters, for example polyethylene terephthalate, polyamides, high molecular weight-polyamides, polymers and copolymers of acrylic esters, methacrylic esters, acrylonitrile, acrylamide, butadiene and styrene, as well as polyurethanes and polycarbonates may be mentioned. The substances pigmented with the claimed products can be present in any desired form.

Furthermore, the pigments I according to the invention have excellent fastness to water, oil, acid, lime, alkali, solvents, over-lacquering, over-spraying and sublimation, resistance to heat and resistance to vulcanisation, are very economical in use and can be readily distributed in plastic compositions.

Example 1.

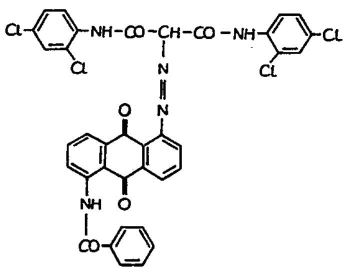
20 g of malonic acid diethyl ester and 50 g of 2,3-dichloroaniline are stirred in 100 ml of o-dichlorobenzene at 170°C. After 6 hours, the mixture is cooled, whilst stirring, and the precipitate is filtered off, washed with o-dichlorobenzene and methanol and dried. 30 g (75% of theory) of the compound of the formula



are obtained as a crystalline, colourless substance of melting point: 218—220°C.

Example 2.

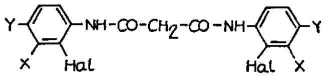
a) 4 g of isoamyl nitrite are added to 7 g of 1 - amino - 5 - benzoylaminoanthraquinone (87% pure), 8 g of 2,4,2',4'-tetrachloromalonic acid dianilide and 5 g of dichloroacetic acid in 150 ml of nitrobenzene at 70°C. The mixture is stirred for 3 hours at 70°C and for 1 hour at 140°C. After cooling to 100°C, the precipitate is filtered ox, washed with nitrobenzene and methanol and dried. 11 g (83% of theory) of the pigment of the formula



are obtained as a reddish-tinged, yellow, crystalline substance.

b) 8 g of industrial formic acid (85% strength) are added dropwise to a mixture of 100 ml of nitrobenzene, 7 g of 1-amino-5 - benzoylaminoanthraquinone (87% pure), 8 g of 2,4,2',4'-tetrachloromalonic acid dianilide and 3 g of sodium nitrite at 50°C, the mixture is kept at 50°C for 3 hours and then stirred for 1 hour at 130°C. After filtering off at 100°C and washing with nitrobenzene, methanol and hot water, the precipitate is dried. 11 g (83% of theory) of the pigment mentioned in Example 2a are obtained.

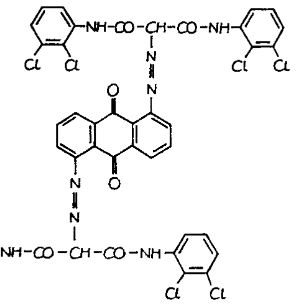
Further pigments having the colour shades indicated in the table which follows are obtained by the process indicated in Example 2(a) when the aminoanthraquinones indicated in column 2 are used instead of 1-amino-5-benzoylaminoanthraquinone and the coupling components of the formula (VII) with the radicals Hal, X and Y, indicated in columns 3 to 5 are used instead of 2,4,2',4'-tetrachloromalondianilide.



Example	Aminoanthraquinone	Hal	X	Y	Colour shade
3	1-aminoanthraquinone	Cl	Cl	H	yellow
4	1-aminoanthraquinone	Cl	H	Cl	yellow
5	1-aminoanthraquinone	Br	H	Br	yellow
6	1-amino-5-benzoyl-amino-anthraquinone	Cl	Cl	H	reddish-tinged yellow
7	2-aminoanthraquinone	Cl	Cl	H	yellow
8	1-amino-4-benzoyl-amino-anthraquinone	Cl	H	Cl	red
9	1-amino-4-chloro-anthraquinone	Cl	Cl	H	yellow
10	1-amino-2-methyl-anthraquinone	Cl	Cl	H	yellow
11	1-aminoanthraquinone-2-carboxylic acid	Cl	H	Cl	yellow

Example 12.

6 g of 1,5-diaminoanthraquinone are stirred in 80 ml of glacial acetic acid and 15 ml of concentrated hydrochloric acid for 2 hours, 12.5 ml of 4 N sodium nitrite are added at 5°C and, after stirring for 3 hours, the mixture is diluted with 25 ml of water and filtered. The filtrate is added dropwise to a mixture of 200 ml of dimethylformamide, 3 g of concentrated sulphuric acid and 19.6 g of 2,3,2′,3′-tetrachloromalonic acid dianilide. The mixture is stirred for 3 hours at 50°C and for 1 hour at 100°C and the precipitate is filtered off. 24 g (91% of theory) of the reddish-tinged yellow pigment of the formula



are obtained.

Example 13.

A further reddish-tinged yellow pigment is obtained by using the same amount of 2,4,2′,4′-tetrachloromalonic acid dianilide instead of 2,3,2′,3′-tetrachloromalonic acid dianilide.

Example 14.

a) 8 g of the finely divided pigment obtained according to Example 2 are ground with a stoving lacquer consisting of 25 g of coconut oil alkyd resin (40% of coconut oil), 10 g of melamine resin, 50 g of toluene and 7 g of glycol monomethyl ether, on an automatic "Hoover" (Trade Mark) Muller grinding machine. The mixture is applied to the substrate to be lacquered, the lacquer is hardened by stoving at 130°C and reddish-tinged yellow lacquerings of very good fastness to over-lacquering and excellent fastness to light and weathering are obtained.

Pigmented stoving lacquers with the same fastness properties are obtained when 15—25 g of the alkyd resin indicated or of an alkyd resin based on cottonseed oil, dehydrated castor oil, castor oil or synthetic fatty acids are used and 10—15 g of the melamine resin mentioned or of a condensation product of formaldehyde and urea or benzoguanamine are employed instead of the amount of melamine resin indicated.

b) If 1 to 10 g of a mixture of titanium dioxide (rutile type) and the pigment indicated in Example 14(a) in the ratio 0.5—50:1

is ground into the lacquer indicated in Example 14(a) instead of the amount of pigment indicated, the same further processing gives lacquerings having the same fastness properties and, with an increase in content of titanium dioxide, a reddish-tinged yellow colour shade shifted towards white.

Example 15.

6 g of the finely divided pigment according to Example 6 are ground into 100 g of a nitrocellulose lacquer which consists of 44 g of collodion cotton (low viscosity, 35% strength, butanol-moist), 5 g of dibutyl phthalate, 40 g of ethyl acetate, 20 g of toluene, 4 g of n-butanol and 10 g of glycol monomethyl ether. After brushing out and drying, reddish-tinged yellow lacquerings of outstanding fastness to light and over-lacquering are obtained. The same results are obtained when nitrocellulose lacquers are used which have a nitrocellulose content of 10—15 g and a plasticiser content of 5—10 g and contain 70—80 g of a solvent mixture, preferably using aliphatic esters, such as ethyl acetate and butyl acetate, and aromatic compounds, such as toluene and xylene, and relatively small proportions of aliphatic ethers, such as glycol ethers, and alcohols, such as butanol. Plasticisers can be understood, for example, as: phthalic acid esters, such as dioctyl phthalate and butyl phthalate, esters of phosphoric acid and castor oil, alone or in combination with oil-modified alkyd resins.

Lacquerings with similar fastness properties are obtained by using other spirit lacquers, "Zapon" (Trade Mark) lacquers and nitrocellulose lacquers which dry physically, oil lacquers, synthetic resin lacquers and nitro combination lacquers which are air-drying and epoxide resin lacquers which are oven-drying and which are air-drying, optionally in combination with urea resins, melamine resins, alkyd resins or phenolic resins.

Example 16.

5 g of a finely divided pigment according to Example 4 are ground in 100 g of an unsaturated polyester resin, which dries without paraffin, in a porcelain ball mill. 10 g of styrene, 59% of a melamine/formaldehyde resin and 1 g of a paste consisting of 40 g of cyclohexanone peroxide and 60% of dibutyl phthalate are stirred thoroughly with the ground material and finally 4 g of a dryer solution (10% strength cobalt naphthenate in white spirit) and 1 g of a silicone oil solution (1% strength in xylene) are admixed. The mixture is applied to primed wood and a very glossy, water-resistant yellow lacquering which is fast to weathering and has excellent fastness to light is obtained.

If amine-curing epoxide resin lacquers containing dipropylenediamine as the amino component are used instead of the reactive lacquer based on unsaturated polyester resins, yellow lacquerings of outstanding fastness to weathering and blooming are obtained.

Example 17.

100 g of a 65% strength solution of an aliphatic polyester, containing about 8% of free hydroxyl groups, in glycol monoethyl ether-acetate are ground with 5 g of the pigment obtained according to Example 2 and the mixture is then mixed thoroughly with 44 g of a 67% strength solution of the reaction product of 1 mol of trimethylolpropane and 3 mols of toluylene diisocyanate. Without impairing the pot life, after the mixture has been applied and the components have reacted, very glossy reddish-tinged yellow polyurethane lacquerings of outstanding fastness to blooming, light and weathering result.

A pigmentation of similar fastness properties is obtained by using other two-component lacquers based on aromatic or aliphatic isocyanates and polyethers or polyesters containing hydroxyl groups, and with polyisocyanate lacquers which give polyurea lacquerings which dry in the presence of moisture.

Example 18.

5 g of a fine paste obtained by kneading 50 g of the pigment obtained according to Example 6 with 15 g of an aryl polyglycol ether emulsifier and 35 g of water are mixed with 10 g of barite, as a filler, 10 g of titanium dioxide (rutile type), as a white pigment and 40 g of an aqueous emulsion paint containing about 50% of polyvinyl acetate. The paint is brushed out and after drying, reddish-tinged yellow paint films of very good fastness to lime and cement and outstanding fastness to weathering and light are obtained.

The fine paste obtained by kneading is likewise suitable for pigmenting clear polyvinyl acetate emulsion paints, for emulsion paints which contain copolymers of styrene and maleic acid as the binder and emulsion paints based on polyvinyl propionate, polymethacrylate or butadiene/styrene.

Example 19.

10 g of the pigment paste mentioned in Example 18 are mixed with a mixture of 5 g of chalk and 5 g of 50% strength size solution. A reddish-tinged yellow wallpaper paint is obtained, with which coatings of outstanding fastness to light are achieved. Other non-ionic emulsifiers, such as the reaction products of nonylphenyol and ethylene oxide, or ionic wetting agents, such as the sodium salts of alkylarylsulphonic acids, for example of dinaphthylmethanedisulphonic acid, sodium salts of substituted sulpho-fatty acid esters and sodium salts of paraffinsulphonic acids in combination with alkyl polyglycol ethers can also be used for the preparation of the pigment paste.

Example 20.

A mixture of 65 g of polyvinyl chloride, 35 g of diisooctyl phthalate, 2 g of dibutyltin mercaptide, 0.5 g of titanium dioxide and 0.5 g of the pigment from Example 6 is coloured on mixing rolls at 165°C. An intensely reddish-tinged yellow mass is obtained which can be used for the preparation of sheets or shaped articles. The dyeing is distinguished by outstanding fastness to light and very good fastness to plasticiser.

Example 21.

0.2 g of the pigment according to Example 2 is mixed with 100 g of polyethylene, polypropylene or polystyrene granules. The mixture can either be injection-moulded directly in an injection moulding machine at 220 to 280°C or processed to coloured rods in an extruder or to coloured hides on a mixing roll. The rods or hides are optionally granulated and injection moulded in an injection moulding machine.

The reddish-tinged yellow moulded articles have very good fastness to light and migration. Synthetic polyamides of caprolactam or adipic acid and hexamethylenediamine or the condensates of terephthalic acid and ethylglycol can be coloured in a similar manner at 280 to 300°C, optionally under a nitrogen atmosphere.

Example 22.

1 g of the pigment according to Example 6, 10 g of titanium dioxide (rutile type) and 100 g of a copolymer, present in powdered form, based on acrylonitrile/butadiene/styrene are mixed and coloured on a roll mill at 140—180°C. A reddish-tinged yellow hide is obtained which is granulated and injection moulded in an injection moulding machine at 200 to 250°C. Reddish-tinged yellow moulded articles of very good fastness to light and migration and excellent heat stability are obtained.

Plastics based on cellulose acetate, cellulose butyrate and mixtures thereof are coloured, with similar fastness properties, in a similar manner, but at temperatures from 180—220°C and without the addition of titanium dioxide.

Example 23.

0.2 g of the pigment according to Example 2 is mixed, in the finely divided form, with 100 g of a plastic based on polycarbonate in an extruder or in a kneading screw at 250—280°C and the mixture is processed to granules. Reddish-tinged yellow, transparent granules of outstanding fastness to light and outstanding heat stability are obtained.

Example 24.

90 g of a slightly branched polypropylene glycol having a molecular weight of 2,500 and a hydroxyl number of 56, 0.25 g of endoethylenepiperazine, 0.3 g of tin-II octoate, 1.0 g of a polyether-siloxane, 3.5 g of water and 12.0 g of the material obtained by grinding 10 g of the pigment according to Example 6 in 50 g of the polypropylene glycol indicated are mixed thoroughly with one another and then intimately mixed with 45 g of toluylene diisocyanate (80% of the 2,4 and 20% of the 2,6-isomer) and the mixture is poured into a mould. The mixture becomes turbid after 6 seconds and foam formation takes place. After 70 seconds, an intensively reddish-tinged yellow soft polyurethane foam has formed, the pigmentation of which has outstanding fastness to light.

Example 25.

90 g of a slightly branched polyester of adipic acid, diethylene glycol and trimethylolpropane having a molecular weight of 2,000 and a hydroxyl number of 60 are mixed with the following components: 1.2 g of dimethylbenzylamine, 2.5 g of sodium castor oilsulphate, 2.0 g of an oxyethylated, benzylated hydroxydiphenyl, 1.75 g of water and 12 g of a paste prepared by grinding 10 g of the pigment according to Example 2 in 50 g of the polyester indicated above. After mixing, 40 g of toluylene diisocyanate (65% of the 2,4-isomer and 35% of the 2,6-isomer) are stirred in, whilst stirring, and the mixture is poured into a mould and foamed. After 60 seconds, a reddish-tinged yellow, soft polyurethane foam has formed, the coloration of which is distinguished by very good fastnesses to light.

Example 26.

Reddish-tinged yellow offset prints of high brilliance and good depth of colour and very good fastness to light and lacquering are obtained with a printing paste prepared by grinding 35 g of the pigment according to Example 6 and 65 g of linseed oil and adding 1 g of sicoative (Co naphthenate, 50% strength in white spirit). If this printing paste is used in letterpress printing, collotype printing, lithographic printing or die stamping it leads to reddish-tinged yellow prints of similar fastness properties. If the pigment is used for colouring tinplate printing or low viscosity gravure printing pastes or printing inks, reddish-tinged yellow prints of similar fastness properties are obtained.

Example 27.

A printing paste is prepared from 10 g of the fine pigment paste indicated in Example 18, 100 g of 3% strength tragacanth, 100 g of an aqueous 50% strength egg albumin solution and 25 g of a non-ionic wetting agent. A textile fibre fabric is printed and steamed at 100°C and a reddish-tinged yellow print which is distinguished by excellent fastness properties, in particular fastnesses to light, is obtained. Instead of tragacanth and egg albumin, further binders which can be used for the fixing on the fibre, for example those based on synthetic resins, British gum or cellulose glycollate, can be used in the printing mixture.

Example 28.

A mixture of 100 g of light crêpe, 2.6 g of sulphur, 1 g of stearic acid, 1 g of mercaptobenzthiazole, 0.2 g of hexamethylenetetramine, 5 g of zinc oxide, 60 g of chalk and 2 g of titanium dioxide (anatase type) is coloured with 2 g of the pigment obtained according to Example 2 at 50°C on mixing rolls and is then vulcanised for 12 minutes at 140°C. A reddish-tinged yellow vulcanisate of very good fastness to light is obtained.

Example 29.

100 g of a 20% strength aqueous paste of the pigment according to Example 6, prepared, for example, by dissolving the dyestuff in 96% strength sulphuric acid, discharging the solution onto ice, filtering and washing the residue with water until neutral, are added to 22.5 l of an aqueous, approximately 9% strength viscose solution in a stirring apparatus. The coloured mass is stirred for 15 minutes and then de-aerated and subjected to a spinning and desulphurisation process.

Reddish-tinged yellow filaments or sheets of very good fastness to light are obtained.

Example 30.

10 kg of a paper pulp containing 4 g of cellulose per 100 g, are treated in a hollander for about 2 hours. During this time, at intervals of a quarter of an hour each, 4 g of resin size, then 30 g of an about 15% strength pigment dispersion, obtained by grinding 4.8 g of the pigment obtained according to Example 2 with 4.8 g of dinaphthylmethanedisulphonic acid and 22 g of water in a ball mill, and then 5 g of aluminium sulphate are added.

After finishing on the paper machine, a reddish-tinged yellow paper of outstanding fastness to light is obtained.

Example 31.

The paper, pigmented reddish-tinged yellow, prepared according to Example 30 is impregnated with a 55% strength solution of a urea/formaldehyde resin in n-butanol and stoved at 140°C. A reddish-tinged yellow laminated paper of very good fastness to migration and outstanding fastness to light is obtained.

A laminated paper with the same fastness properties is obtained by laminating a paper which has been printed, by the gravure printing process, with a printing paste which contains the reddish-tinged yellow fine pigment paste indicated in Example 18 and water-soluble or saponifiable binders.

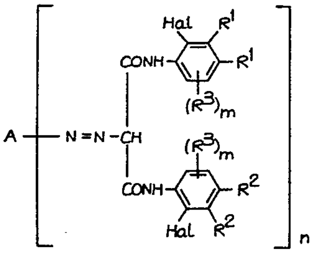
Example 32.

20 g of the colour pigment according to Example 6 are pre-dispersed in 50 g of dimethylformamide with a dissolver and subjected to grinding in 50 g of a 10% strength polyacrylonitrile solution in dimethylformamide in a bead mill, with the addition of a dispersion auxiliary. After separating off coarse particles which remain by processes which are known, the pigment mass is added in portions to a spinning solution of polyacrylonitrile, homogenised and spun to filaments by a dry spinning or wet spinning process which is customary and known in the art.

Reddish-tinged yellow dyeings obtained in this manner have a very good brilliance and very good fastness to rubbing, migration, heat, light and weathering.

WHAT WE CLAIM IS:—

1. An azoanthraquinone pigment of the general formula



(I)

in which

Hal denotes a halogen atom

one of the substituents R^1 denotes a halogen atom and the other denotes a hydrogen atom,

one of the substituents R^2 denotes a halogen atom and the other denotes a hydrogen atom,

R^3 denotes a substituent,

m is 0, 1 or 2

n is 1 or 2 and

A denotes an anthraquinone radical or more highly fused anthraquinone radical, or a derivative thereof (as hereinbefore defined) which is optionally further substituted.

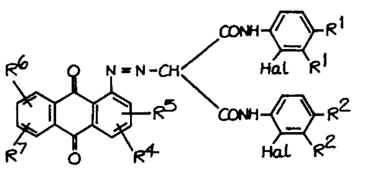
2. An azoanthraquinone pigment according to Claim 1, in which R^3 denotes a halogen atom, a C_1 to C_4 alkyl, C_1 to C_4 alkoxy, nitro, trifluoromethyl or cyano group or a carbamoyl or sulphonamoyl group which is optionally substituted.

3. An azoanthraquinone pigment according to Claim 1 or 2, in which the halogen atoms present are fluorine, chlorine or bromine atoms.

4. An azoanthraquinone pigment according to any of the foregoing claims, in which A denotes any of those anthraquinone, or more

highly fused anthraquinone radicals hereinbefore specifically identified.

5. An azoanthraquinone pigment according to claim 1, of the general formula

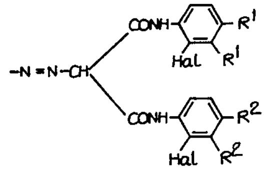


(II)

in which Hal, R^1 and R^2 have the same meanings as in claim 1, R^4 and R^6 independently denote a hydrogen, fluorine, chlorine or bromine atom, or a nitro, C_1 to C_4 alkyl, C_1 to C_4 alkoxy, C_1 to C_4 alkylamino, benzylamino, cyclohexylamino, or C_1 to C_4 alkylmercapto group, a phenylmercapto group which is optionally substituted by C_1 to C_4 alkyl, C_1 to C_4 alkoxy, chlorine or nitro, a C_1 to C_4 alkylcarbonyl or C_1 to C_4 alkoxycarbonyl group, a phenylamino group which is optionally substituted by C_1 to C_4 alkyl, C_1 to C_4 alkoxy, chlorine or nitro, a carboxamide group which is optionally monosubstituted or disubstituted by C_1 to C_4 alkyl, benzyl or phenyl, it being possible for phenyl to be substituted by C_1 to C_4 alkyl, C_1 to C_4 alkoxy, fluorine, chlorine, bromine or nitro, a carboxyl, hydroxyl, C_1 to C_4 alkylcarbonylamino or C_1 to C_4 alkylsulphonylamino group, a benzoylamino group which is optionally substituted by C_1 to C_4 alkyl, C_1 to C_4 alkoxy, chlorine, bromine or nitro or a phenylsulphonylamino group which is optionally substituted by C_1 to C_4 alkyl, C_1 to C_4 alkoxy, chlorine or nitro,

R^5 denotes a hydrogen, fluorine, chlorine or bromine atom or a carboxyl group and

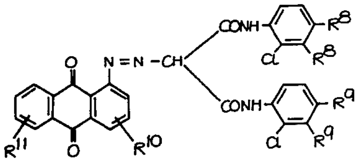
R^7 denotes a hydrogen, fluorine, chlorine or bromine atom, a carboxyl group or a radical of the general formula



in which Hal, R^1 and R^2 have the above-mentioned meanings.

6. An azoanthraquinone pigment according to claim 5, in which R^4 and R^6 independently have any of the meanings specified in claim 5, other than the optionally substituted benzoylamino group.

7. An azoanthraquinone pigment according to claim 1, of the general formula

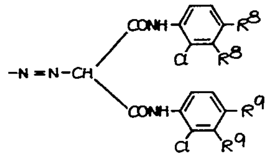


(III)

in which one radical R^8 denotes a chlorine atom and the other denotes a hydrogen atom, one radical R^9 denotes a chlorine atom and the other denotes a hydrogen atom,

R^{10} denotes a hydrogen, fluorine, chlorine or bromine atom, a C_1 to C_4 alkylcarbonylamino group, a benzoylamino group which is optionally substituted by 1 or 2 nitro groups or 1 to 5 chlorine or bromine atoms, a C_1 to C_4 alkylsulphonylamino group, a phenylsulphonylamino group which is optionally monosubstituted by methyl, methoxy or chlorine, or a carboxyl or C_1 to C_4 alkoxycarbonyl group and

R^{11} denotes a hydrogen, fluorine, chlorine or bromine atom, a carboxyl or C_1 to C_4 alkoxycarbonyl group, an aminocarbonyl group which is optionally monosubstituted or disubstituted by C_1 to C_4 alkyl or phenyl, a C_1 to C_4 alkylcarbonylamino, a benzoylamino group which is optionally substituted by 1 or 2 nitro groups or 1 to 5 chlorine or bromine atoms, a C_1 to C_4 alkylsulphonylamino group, a phenylsulphonylamino group which is optionally monosubstituted by methyl, methoxy or chlorine or a radical of the general formula



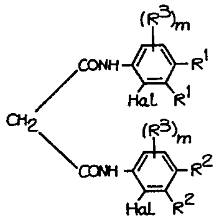
in which R^8 and R^9 have the above-mentioned meanings.

8. An azoanthraquinone pigment according to claim 1, as hereinbefore specifically identified.

9. A process for the production of an azoanthraquinone pigment as claimed in claim 1, in which an aminoanthraquinone of the general formula

$$A\text{—}(NH_2)_n \qquad \text{(IV)}$$

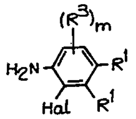
in which A and *n* have the same meanings as in claim 1, is diazotised and coupled with a malonic acid dianilide of the general formula



(V)

in which R_1, R_2, R_3, Hal and *m* have the same meanings as in claim 1.

10. A process according to claim 9, in which the malonic acid dianilide of formula (V) is formed by reacting a functional derivative of malonic acid with a halogeno-aniline of the general formula



(VI)

in which Hal, R^1, R^3 and *m* have the same meanings as in claim 1.

11. A process for the production of an azoanthraquinone pigment as claimed in claim 1, when carried out substantially as described in any one of Examples 2 to 13.

12. An azoanthraquinone pigment when produced by the process of any of claims 9 to 11.

13. A process for the preparation of a pigment formulation, a paint, a printing paste, a coloured paper or a coloured macromolecular substance, comprising incorporating therein an azoanthraquinone pigment as claimed in any of claims 1 to 4, 6 to 8 and 12.

14. A process according to claim 13, when carried out substantially as described in any one of Examples 14 to 31.

15. A process according to claim 13, in which an azoanthraquinone pigment as claimed in claim 5 is used.

16. A process according to claim 13, when carried out substantially as described in Example 32.

17. A pigment formulation, a paint, a printing paste, a coloured paper or a coloured macromolecular substance when prepared by the process of claim 13 or 14.

18. A pigment formulation, a paint, a printing paste, a coloured paper or a coloured macromolecular substance, when prepared by the process of claim 15 or 16.

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