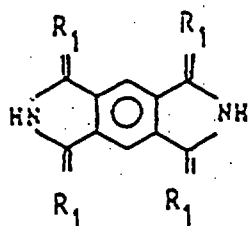


HETEROCYCLIC PIGMENTS

The invention relates primarily to pigments suitable for pigmenting plastics in the mass.

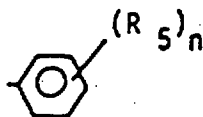
According to the invention, there is provided the use of a pigment, for pigmenting in the mass, the pigment being of formula I



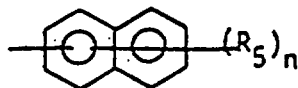
(I)

in which each R_1 independently is selected from =NH or =N- R_2 , where R_2 is an aromatic or heteroaromatic group, provided not more than two groups R_1 are selected from =NH.

Preferably when R_2 is an aromatic group, it is a group of formula α or β



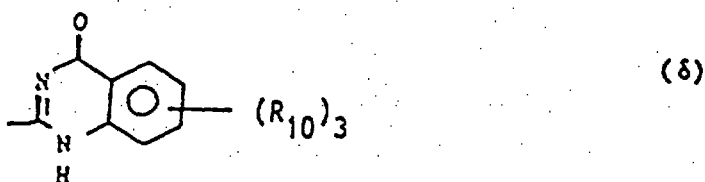
(α)



(β)

where n is 0, 1, 2 or 3 and

each R_5 independently is selected from halogen, $(C_{1-4}$ alkyl)aminocarbonyl, $(C_{1-4}$ alkyl)carbonylamino, carboxyl, $(C_{1-4}$ alkoxy)carbonyl, phenylaminocarbonyl, benzoylamino or phenyloxycarbonyl or R_5 is a group of formula δ



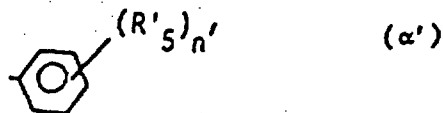
where each R_{10} independently is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, cyan or nitro; provided not more than one group R_5 attached to any one phenyl group is a group of formula δ .

Preferably each R_{10} is hydrogen.

Preferably when R_2 is a heteroaromatic group, R_2 is R_2' where R_2' is a thienyl, thiazolyl, pyrazolyl, imidazolyl, benzthiazolyl, or benzimidazolyl group.

Preferably R_1 is R_1' where each R_1' independently is selected from $=NH$ and $=N-R_2$ where R_2 is a group of formula α , provided that not more than two groups R_1' in the compound of formula I are selected from $=NH$.

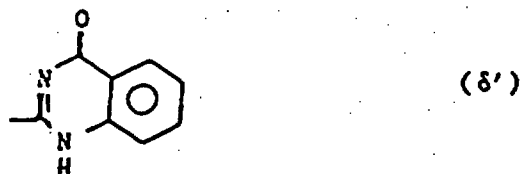
More preferably R_1 is R_1'' where each group R_1'' independently is $=N-R_2''$ where R_2'' is a group of formula α'



where n' is 2 or 3; and

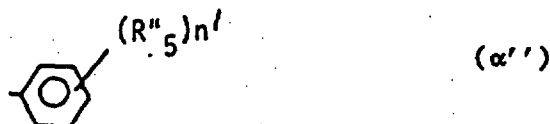
each R_5' independently is chloro, bromo, $(C_{1-4}$

alkyl)aminocarbonyl, (C₁₋₄ alkyl)carbonylamino, carboxyl, (C₁₋₄ alkoxy)carbonyl, phenylaminocarbonyl, benzoylamino, phenoxycarbonyl or a group of formula δ'



provided that not more than one group R₅' attached to any one phenyl group is a group of the formula δ' .

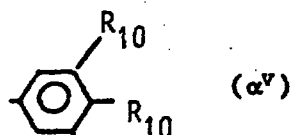
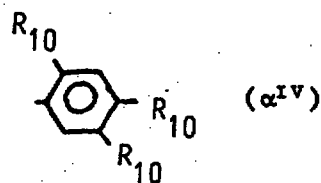
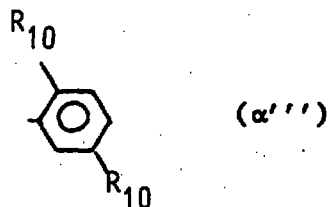
Most preferably R₁ is R₁^{'''} where each group R₁^{'''} independently is =N-R₂^{''} where R₂^{''} is a group of the formula α''



where n' is 2 or 3; and

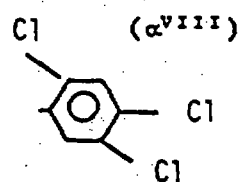
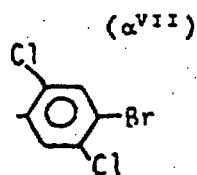
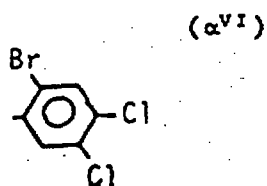
each R₅^{''} independently is benzoylamino, chloro or bromo.

Especially preferred R₁^{'''} is R₁^{IV} where each R₁^{IV} independently is =N-R₂^{'''} where R₂^{'''} is a group of formula α''' , α^{IV} and α^V

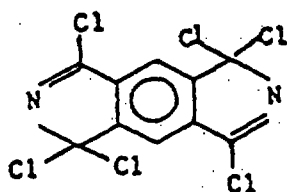


where each R₁₀ independently is selected from Br and Cl.

Preferred groups of R₂^{'''} are of formula α^{VI} - α^{VIII}



Compounds of formula I can be prepared by reacting one mole of the compound of formula II



(II)

with a) four moles of a compound of formula III



or b) three moles of a compound of formula III and one mole of ammonia; or

c) two moles of a compound of formula III and two moles of ammonia.

The compounds of formula II and III are known or may be made from known compounds by known methods.

The reaction of the compound of formula II with a compound of formula III can take place at an elevated temperature, preferably from 80-120°C according to known methods.

Compounds of formula I are useful for colouring oil based or water based paints or lacquers, and pigmenting of polyethylene, polyvinylchloride, rubber and artificial leather.

The compounds of formula I can also be used for pigments printing.

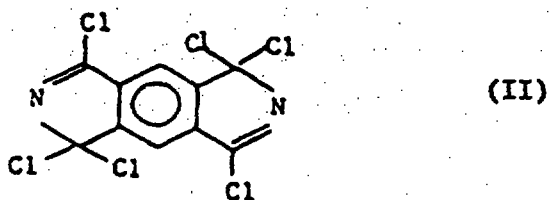
Compounds of formula I where R_1 is $=N-R_2$ where R_2 is a group of formula α , $n'=2$ or 3 of formula α and where R_5 is R_5'' are especially useful pigments.

The pigment colourings have good heat fastness, good light fastness, good weather fastness, good fastness to chemicals, good migration fastness, good fastness to blooming, good fastness to overcoating, good fastness to solvents. The colouring strength is good and the compounds have good application properties, for instance good flocculation ability, good crystallinity and good dispersability.

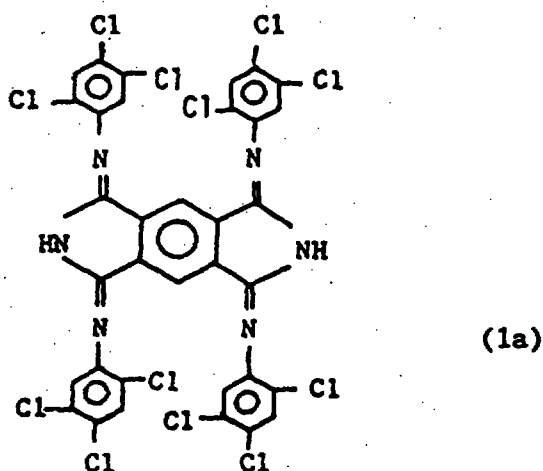
The invention will now be illustrated by the following Examples in which all temperatures are in °C.

Example 1.

18.15 g of the compound of formula II



are dispersed in 100 mls of ortho dichlorobenzene whilst stirring at 120°C. The dispersion is cooled to 100°C and mixed with 49.0 g of 2,4,5 trichloroaniline in 150 moles of ortho dichlorobenzene. The resulting mixture is heated to 110°C and stirred at this temperature for 12 hours. The resulting pigment is of formula 1a



The pigment of formula 1a is filtered hot and then washed with ortho dichlorobenzene, methanol and finally water.

a) The pigment can be used as such without any further treatment for dyeing or pigmenting of plastics and lacquers. By incorporating the pigment into a clear lacquer containing pigment and TiO_2 in a ratio of 1:10, a reddish yellow colouring of the lacquer is produced

with good fastness properties. Such a dyeing has a colorimetric value of H^* (Hue)= 60.27 , C^* (Chroma)= 52.12 , and L^* (Lightness)= 77.69 .

b) The pigment may, instead of being used directly, be recrystallised in dimethylformamide and a β modification is formed having an X ray pattern significantly different to the α -form. The β modification can also be used to dye or pigment directly in plastics and lacquers. When the pigment is added to a clear commercially available alkyl-melamine-formaldehyde a yellowish colouring is imparted to the lacquer with good fastness properties. The Colorimetric Values in a clear lacquer containing pigment and TiO_2 in a 1:10 ratio is H^* = 70.82 , C^* = 63.66 and L^* = 82.06.

The X-ray data for the α -modification is:

5,6(w); 4,18(w); 3,99(w); 3,81(w); 3,57(w); 3,53(w);
3,45(w); 3,34(w); 3,22(w); 2,94(w).

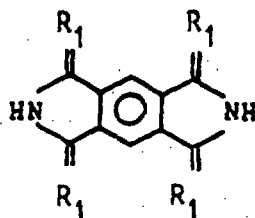
The X-ray data for the β -modification is:

10,6(w); 6,5(w); 6,2(w); 5,8(w); 4,4(w); 3,5(w); 3,35(w);
3,11(w).

in which w is weak; m is medium; wd is weak/diffuse and md is medium/diffuse.

Examples 2 to 10.

Compounds of the formula I



where R_1 is defined in the Table below can be prepared from appropriate reactant according to the method of Example 1.

Ex.	R ₁	Nuance of Dyeing	Colorimetric		
			H*	C*	L*
2	2,5-dichloro-4-benzoylamino-phenylimino	orange	43,73	50,90	67,45
3	2,5-dichlorophenylimino	yellow	76,60	50,59	86,19
4	3,4-dibromophenylimino	brownish-yellow	74,34	42,97	70,10
5	2,5-dibromophenylimino	yellow	80,40	56,22	85,60
6	2,5-dichloro-4-bromophenylimino	reddish-yellow	59,31	52,39	76,60
7	2-bromo-4,5-dichlorophenylimino	reddish-yellow	63,94	58,22	79,05
8	2,4-dibromophenylimino	yellow	70,83	58,11	81,46
9	2,4-dichlorophenylimino	yellow	-	-	-
10	2,5-dichloro-4-acetylamino-phenylimino	brown yellow	-	-	-

Application Example

4 g of the β modification of Example 1 and 40 g of titanium dioxide pigment are milled in a ball mill for 24 hours with 96 g of a mixture of

- 50 g of a 60% solution of coco-aldehyde-melamine resin (with 32% fatty content) in xylene;
- 30 g of a 50% melamine resin solution in butan-1-ol;
- 10 g of xylene; and
- 6 g of ethylene glycolmonoethyl ether.

The resulting dispersion is sprayed on an aluminium piece, air dried for 30 minutes and stored for 30 minutes at 120°C. A brilliant yellow film results with good light and weathering fastnesses.

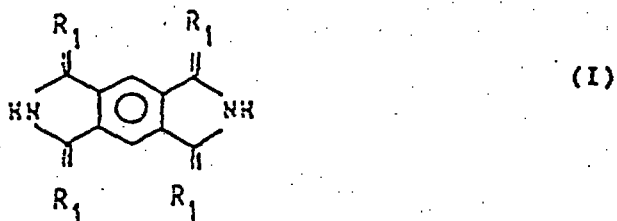
The Application Example can be repeated using, instead of 4 g of β modification of Example, 4 g of any one of the products of Examples 2 to 10 or of the α modification of Example 1.



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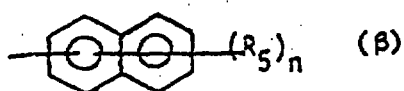
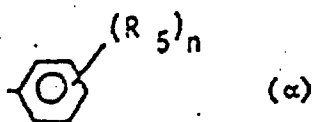
CLAIMS

1. The use of a pigment, for pigmenting of plastics in the mass, the pigment being of formula I

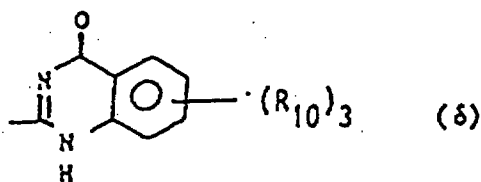


in which each R_1 independently is selected from $=NH$ and $=N-R_2$ where R_2 is an aromatic or heteroaromatic group, provided not more than two groups R_1 are selected from $=NH$.

2. The use of a pigment according to Claim 1 in which R_2 is a group of formula α or β



where n is 0, 1, 2 or 3 and each R_5 independently is selected from halogen, $(C_{1-4}alkyl)aminocarbonyl$, $(C_{1-4}alkyl)carbonylamino$, carboxyl, $(C_{1-4}alkoxy)carbonyl$, phenylaminocarbonyl, benzoylamino and phenoxy carbonyl or R_5 is a group of formula δ



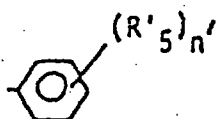


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where each R_{10} independently is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, cyano or nitro; provided not more than one group R_5 attached to any one phenyl group is a group of formula δ ; or

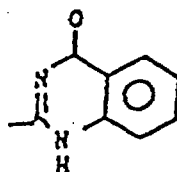
R_2 is a thienyl, thiazolyl, pyrazolyl, imidazolyl, benzthiazolyl or benzimidazolyl group.

3. The use of a pigment according to Claim 1 or Claim 2 in which R_1 is R_1' where each R_1' independently is selected from $=NH$ and $=N-R_2'$ where R_2' is a group of formula α defined in Claim 2, provided not more than two groups R_1' in the compound of formula I are selected from $=NH$.
4. The use of a pigment according to Claim 3 in which R_1 is R_1'' where each group R_1'' independently is $=N-R_2''$ where R_2'' is a group of formula α'



(α')

where n' is 2 or 3 and each R_5' independently is selected from chloro, bromo, $(C_{1-4}$ alkyl)aminocarbonyl, $(C_{1-4}$ alkyl)carbonylamino, carboxyl, $(C_{1-4}$ alkoxy)carbonyl, phenylaminocarbonyl, benzoylamino, phenoxy carbonyl and a group of formula δ'



(δ')

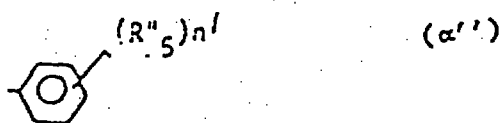
provided that not more than one group R_5' attached to any one phenyl group is a group of formula δ' .

5. The use of a pigment according to Claim 4 in which R_1 is R_1''' where each group R_1''' independently is $=N-R_2'''$ where R_2''' is a



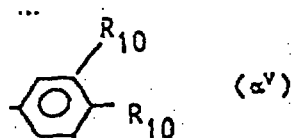
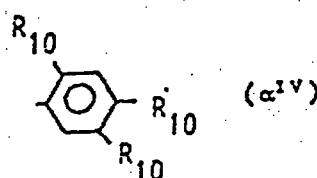
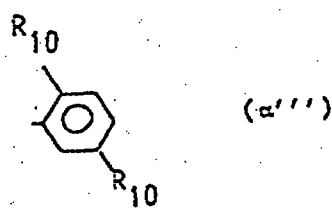
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group of formula α''



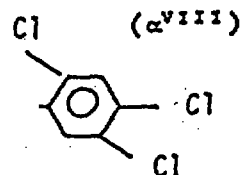
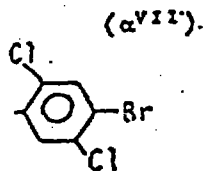
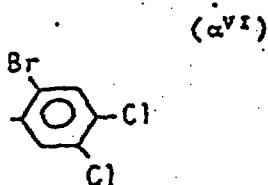
where n' is 2 or 3; and each R_5'' independently is benzoylamino, chloro or bromo.

6. The use of a pigment according to Claim 5 in which R_1 is R_1^{IV} where each R_1^{IV} independently is $=N-R_2^{III}$ where R_2^{III} is a group of formula α''' , α^{IV} or α^V



where each R_{10} independently is chloro or bromo.

7. The use of pigment according to Claim 6 in which R_1 is $=N-R_2^{IV}$ where R_2^{IV} is a group of the formula α^{VI} , α^{VII} or α^{VIII}

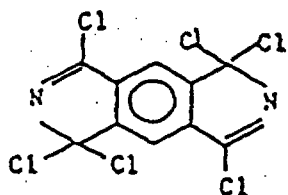


8. A process for preparing a pigment of formula I defined in Claim 1



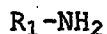
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comprising reacting one mole of the compound of formula II



(II)

with a) four moles of a compound of formula III



(III)

or b) three moles of a compound of formula III and one mole of ammonia; or

c) two moles of a compound of formula III and two moles of ammonia.

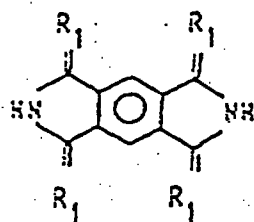
9. A polymeric substrate to which a pigment of formula I defined in any one of Claims 1 to 7 has been applied.
10. A compound of formula I substantially as herein described with reference to any one of Examples 1 to 10.
11. A substrate according to Claim 9, substantially as herein described with reference to the Application Example.
12. The α -modification of the compound of formula Ia defined in Example 1 having X-ray data
5.6(w); 4.18(w); 3.99(w); 3.81(w); 3.57(w); 3.53(w); 3.45(w);
3.34(w); 3.22(w); 2.94(w).
13. The β -modification of the compound of formula Ia defined in Example 1 having X-ray data.



10.6(w); 6.5(w); 6.2(w); 5.8(w); 4.4(w); 3.5(w); 3.35(w); 3.11(w).

14. A coloured polymeric material comprising polymer and a pigment according to any one of the claims 1-7 or compound of claim 12 or 13.

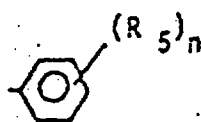
15. A method of mass pigmenting a plastic material comprising applying in the mass a pigment of formula I,



(I)

in which each R_1 independently is selected from $=NH$ and $=N-R_2$ where R_2 is an aromatic or heteroaromatic group, provided not more than two groups R_1 are selected from $=NH$.

16. A method according to claim 15 in which R_2 is a group of formula α or β

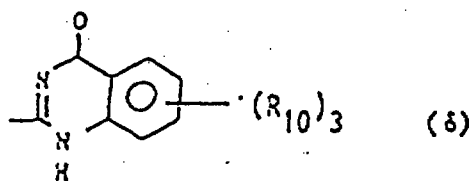


(α)



(β)

where n is 0, 1, 2 or 3 and each R_5 independently is selected from halogen, $(C_{1-4}alkyl)aminocarbonyl$, $(C_{1-4}alkyl)carbonylamino$, carboxyl, $(C_{1-4}alkoxy)carbonyl$, phenylaminocarbonyl, benzoylamino and phenoxy carbonyl or R_5 is a group of formula δ



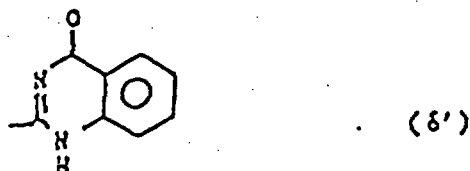
where each R_{10} independently is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, cyano or nitro; provided not more than one group R_5 attached to any one phenyl group is a group of formula δ ; or

R_2 is a thienyl, thiazolyl, pyrazolyl, imidazolyl, benzthiazolyl or benzimidazolyl group.

17. A method according to claim 15 or 16 in which R_1 is R_1' where each R_1' independently is selected from $=NH$ and $=N-R_2'$ where R_2' is a group of formula α defined in Claim 2, provided not more than two groups R_1' in the compound of formula I are selected from $=NH$.
18. A method according to claim 17 in which R_1 is R_1'' where each group R_1'' independently is $=N-R_2''$ where R_2'' is a group of formula α'



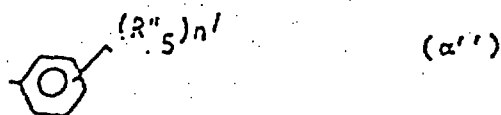
where n' is 2 or 3 and each R_5' independently is selected from chloro, bromo, $(C_{1-4}$ alkyl)aminocarbonyl, $(C_{1-4}$ alkyl)carbonylamino, carboxyl, $(C_{1-4}$ alkoxy)carbonyl, phenylaminocarbonyl, benzoylamino, phenoxycarbonyl and a group of formula δ'



provided that not more than one group R_5' attached to any one phenyl group is a group of formula δ' .

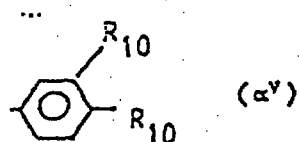
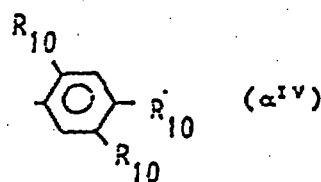
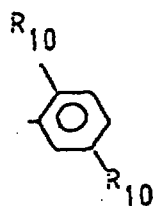


19. A method according to claim 18 in which R_1 is R_1'' where each group R_1'' independently is $=N-R_2''$ where R_2'' is a group of formula α''



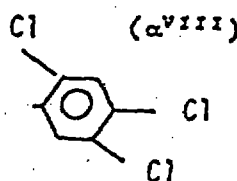
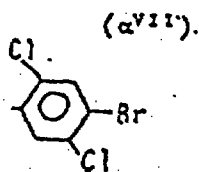
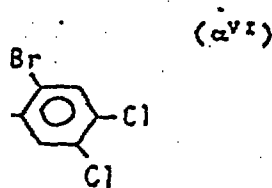
where n' is 2 or 3; and each R_5'' independently is benzoylamino, chloro or bromo.

20. A method according to claim 19 in which R_1 is R_1^{IV} where each R_1^{IV} independently is $=N-R_2^{IV}$ where R_2^{IV} is a group of formula α''' , α^{IV} or α^V



where each R_{10} independently is chloro or bromo.

21. A method according to claim 20 in which R_1 is $=N-R_2^{IV}$ where R_2^{IV} is a group of the formula α^{VI} , α^{VII} or α^{VIII}





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22. A method according to any one of claims 15 to 21 substantially as herein described with reference to any one of Examples 1 to 10.

23. A method according to any one of claims 15 to 21 substantially as herein described with reference to the Application Example.

24. A method according to any one of claims 15 to 21 in which the pigment is the α -modification of the compound of formula Ia defined in Example 1 having X-ray data

5.6(w); 4.18(w); 3.99(w); 3.81(w); 3.57(w); 3.53(w); 3.45(w);
3.34(w); 3.22(w); 2.94(w).

25. A method according to any one of claims 15 to 21 in which the the pigment is the β -modification of the compounds of formula Ia defined in Example 1 having X-ray data.

10.6(w); 6.5(w); 6.2(w); 5.8(w); 4.4(w); 3.5(w); 3.35(w); 3.11(w).
