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NEW PIGMENTS

The invention relates to new organic compounds which are practically insoluble salts of acid dyestuffs with basic compounds which have at least one sterically hindered amine group. These compounds are excellent as pigments particularly for the dyeing of solvent free and solvent containing plastics material.

According to the invention there is provided a salt of formula I

$$F_n \cdot A$$

(I)

in which F is the residue of a metal free anionic dyestuff having 1 to 4 acids groups,

n is 1 or 2; and

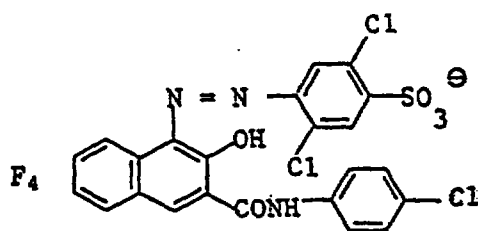
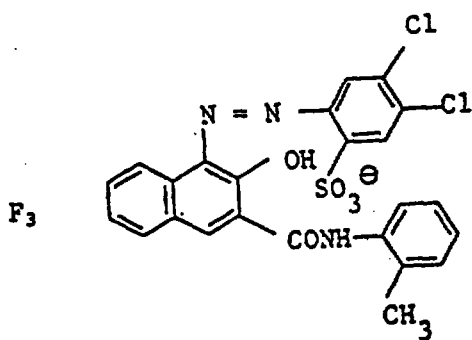
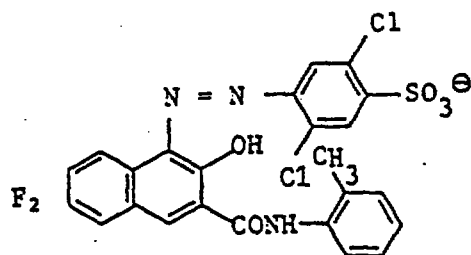
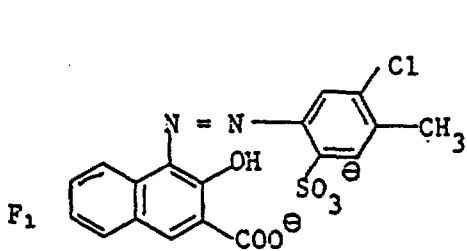
A is group containing 1 to 4 sterically hindered amine groups and at least n ammonium or immonium groups.

The pigments according to the invention are excellent for coloring PVC, all types of polyolefin (HDPE or LDPE high density polyethylene or low density polyethylene or polypropylene) polyisobutylene, poly-4-methylpentene and copolymers of these. Further the compounds according to the invention can be used for coloring of polystyrene (and copolymers thereof) ABS, Polyvinylacetate, Polyvinylalcohol, Polyacetate, POM, Polyacrylate, Polyacrylnitril, Polyacrylamide, Polywinylidenechloride, Polyester, Polyether, Polythioethers and Thioplasts, Polycarbonates, Polyurethanes, Cellulose derivatives, Maleic acid, Melamine, Phenol, Aniline, Furane, Carbamide, Epoxide and Silicone resins. The compounds of formula I can also be used in lacquers and printing inks for graphic fabrics.

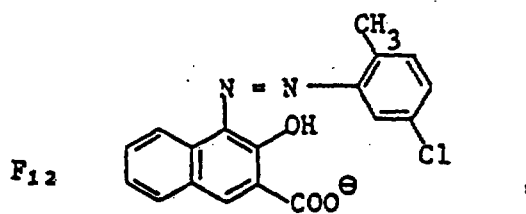
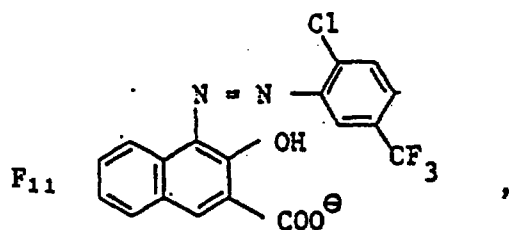
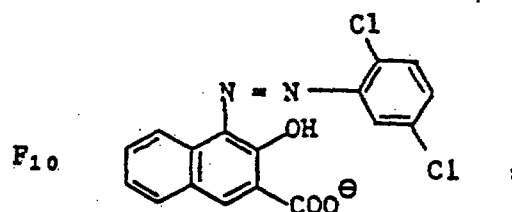
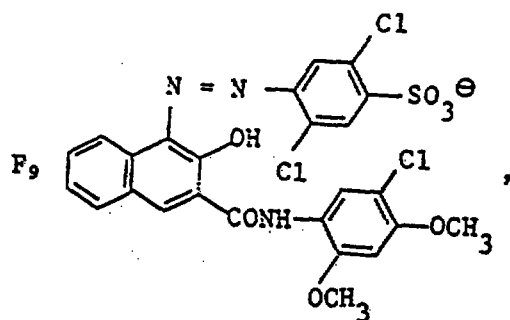
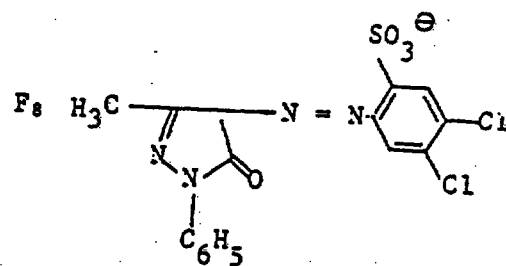
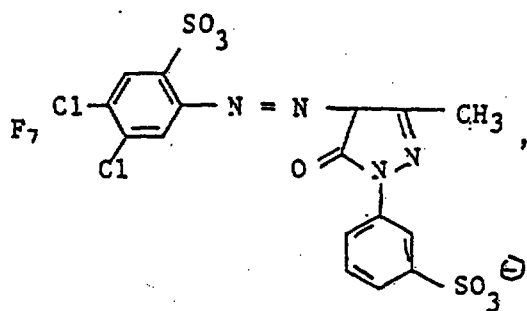
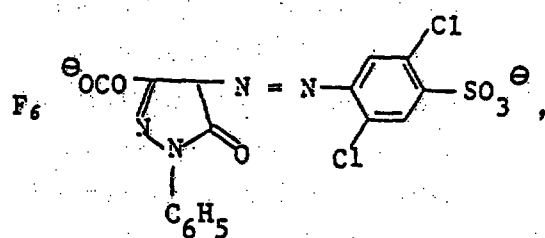
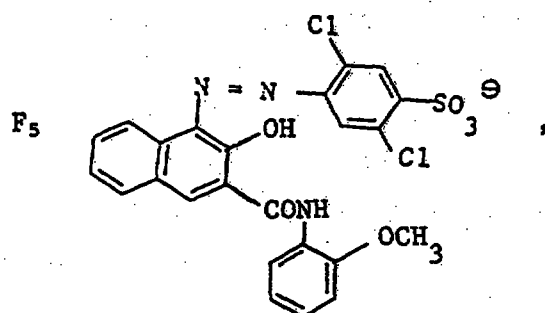
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Preferably F is F' where F' is a group derived from an acid group containing non-metallised dyestuff, of the azo series, of the phthalocyanine series, of the anthraquinone series, of the perylene series, of the indigo series, of the thioindigo series, of the perinone series, of the quinacridone series, of the dioxazine series, of the isoindoline series, of the isoindolinone series, of the diketopyrrole series or of the pyrrole series, especially of the azo, the phthalocyanine, the indigo, the anthraquinone, the dioxazine and the isoindoline series.

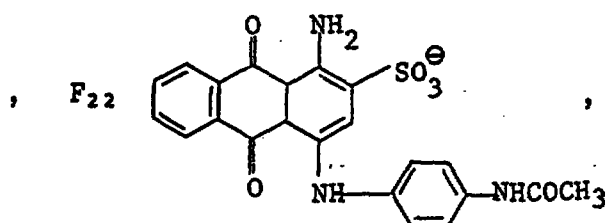
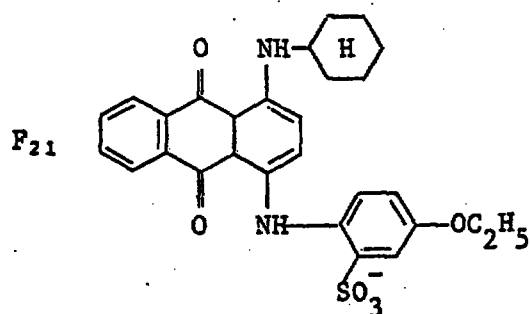
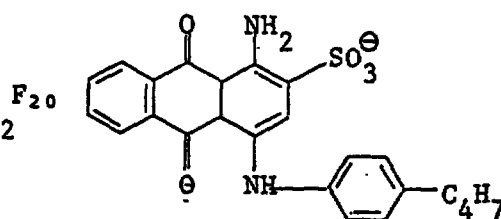
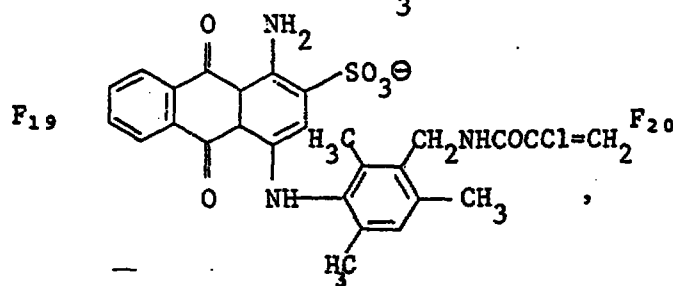
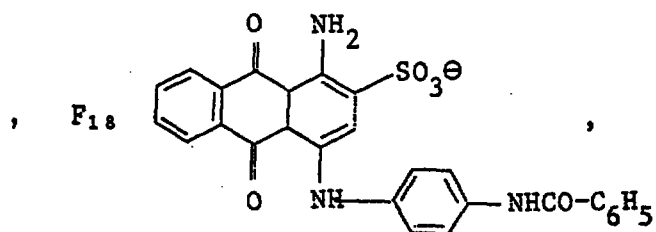
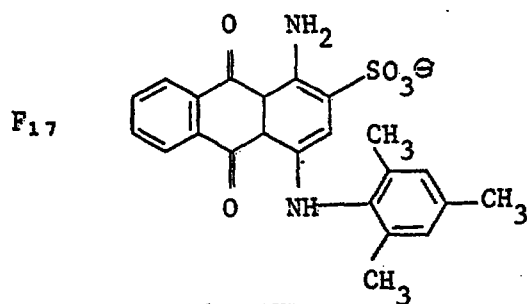
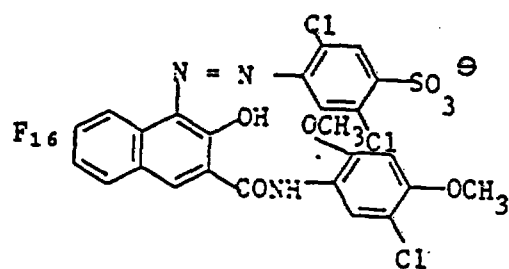
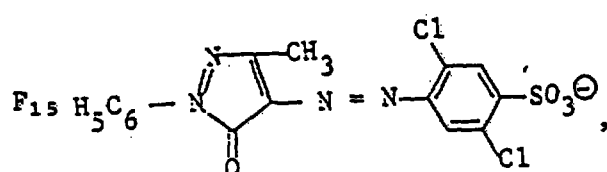
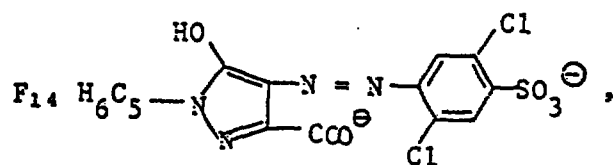
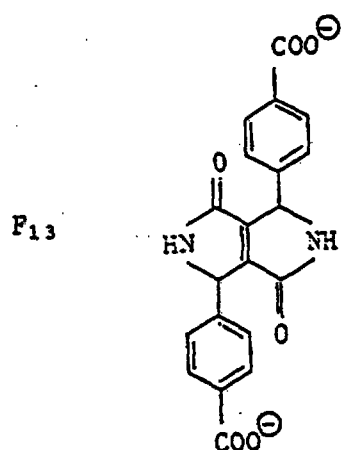
More preferably F is F", where F" is a compound of formula F1 to 43



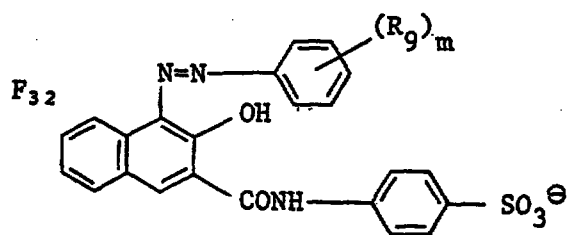
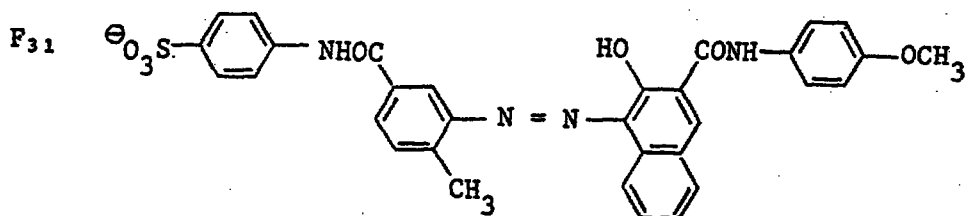
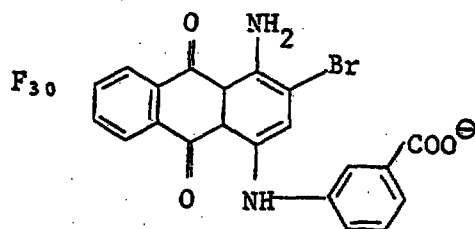
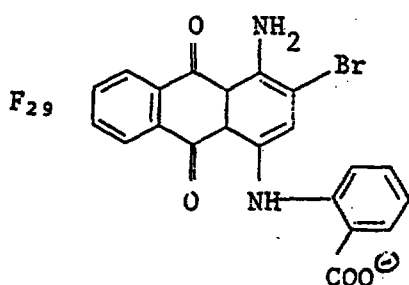
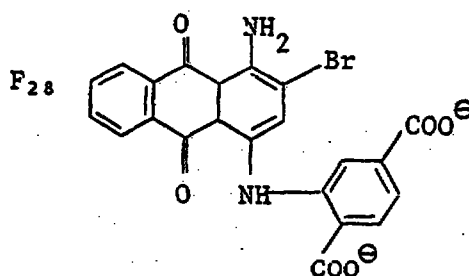
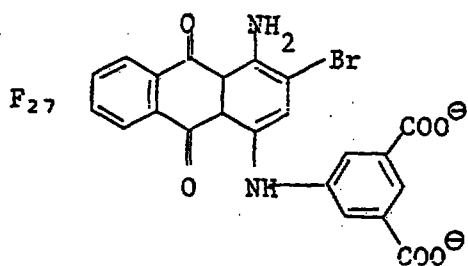
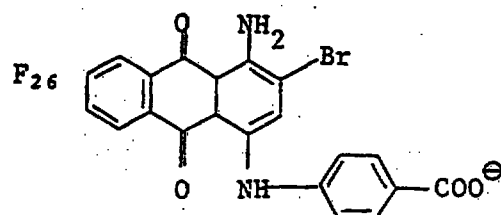
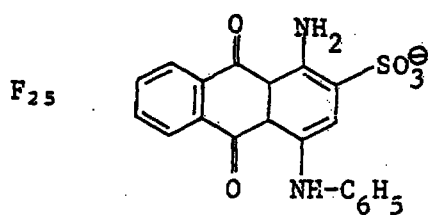
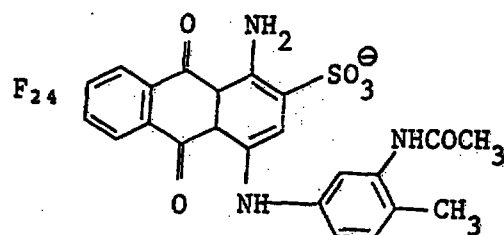
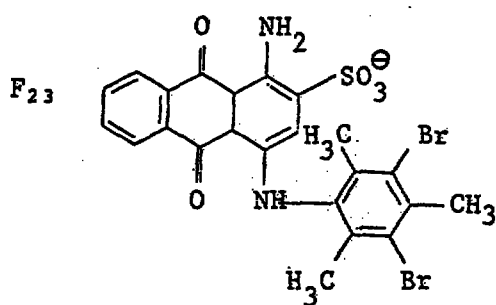
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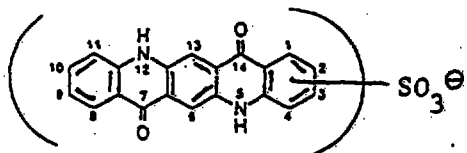
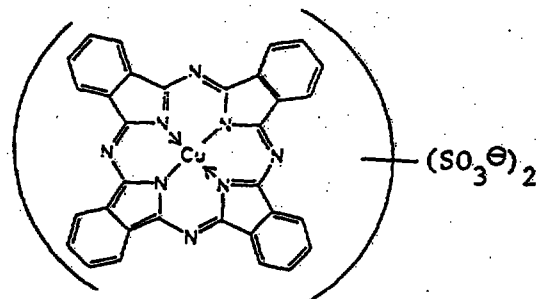
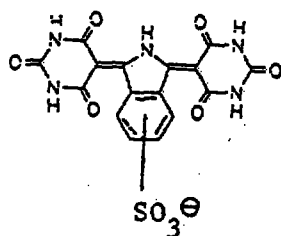
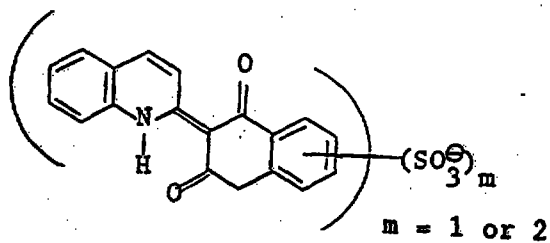


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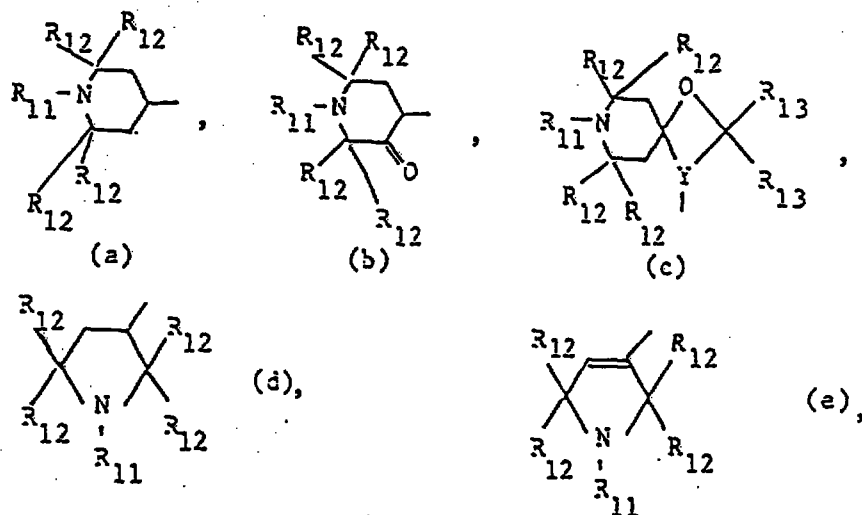


in which R₉ = Chloro, Bromo,
C₁₋₃alkyl or C₁₋₄alkoxy
and m=1, 2 or 3,

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F₄₀F₄₁F₄₂F₄₃

Preferably any sterically hindered group present is selected from formula (a) to (e) below:



in which

R_{11} is hydrogen or C_{1-4} alkyl, preferably hydrogen or methyl, more preferably hydrogen;

each R_{12} independently is C_{1-6} alkyl, preferably methyl;

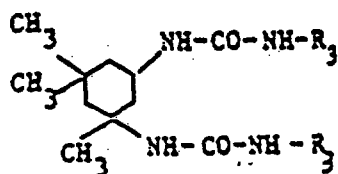
both groups R_{13} independently are hydrogen, methyl or ethyl or one group R_{13} is phenyl or both groups R_{13} together form a group of (CH_2) and Y is a group of the formula $-NCO-$ or $-CO-N-$.

Preferably A is A' where A' is a cationic group derived from a compound selected from A1 to A 29

- A1 1,3,5-Tri-(2',2',6',6'-tetramethylpiperidyl-4')-trimesic-acid-triamide,
- A2 2,4-Bis-(2',2',6',6',-tetramethylpiperidyl-4' amino)-6-chloro-triazine

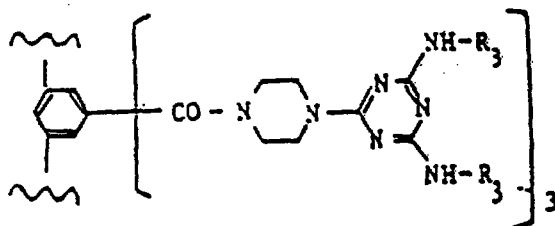
- A3 2,4,6-Tri-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-triazine,
- A4 Bis-(2',2',6',6'-tetramethylpiperidyl-4'-aminocarbonyl-para-phenylene)-terephthalic acid diamide,
- A5 Bis-(2',2',6',6'-tetramethylpiperidyl-4')-terephthalic acidamide,
- A6 2,4-Bis-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-qinazoline,
- A7 2,3-Bis-(2',2',6',6'-tetramethylpiperidyl-4'-amino)qinoxaline,
- A8 1,4-Bis-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-phthalazine,
- A9 2-Chloro-4,6-Bis-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-pyrimidine,
- A10 2,5-Dichlor-4,6-Bis-(2',2',6',6',-tetramethylpiperidyl-4'-amino) pyrimidine,
- A11 2-Fluor-5-chlor-4,6-Bis-(2',2',6',6-tetramethylpiperidyl-4'-amino)-pyrimidine,
- A12 2,4,6-Tri-(2',2',6',6'-teramethylpiperidyl-4'-amino)-pyrimidine,
- A13 2,4,6-Tri-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-5-chlor-pyrimidine,

A14

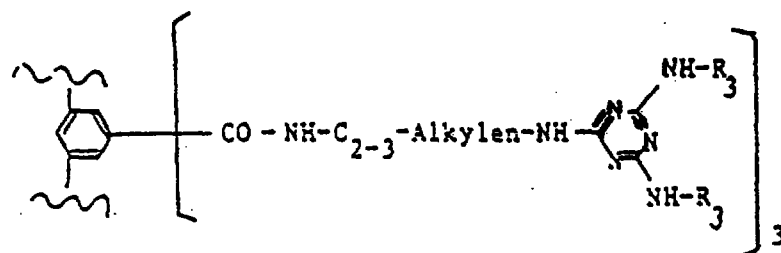


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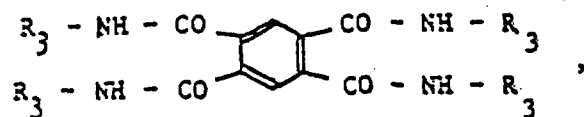
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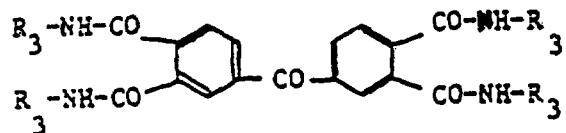
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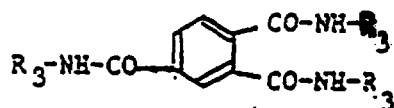
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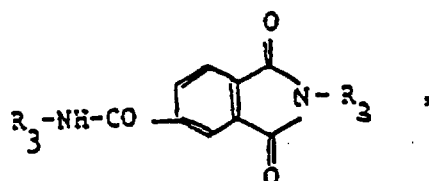
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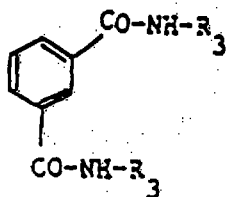
A19



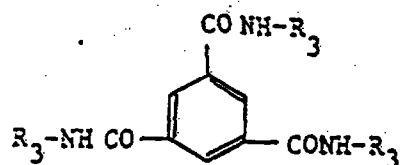
A20



A21

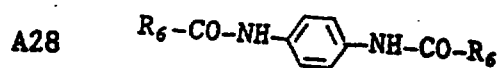
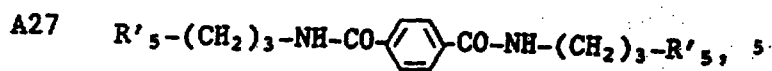
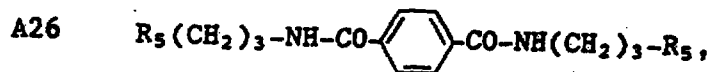
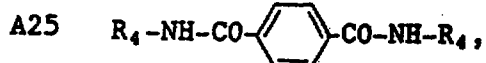


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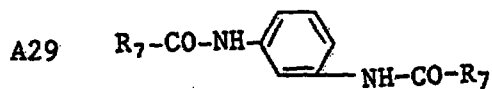


A23 Bis-(1,2,2,6,6-pentamethylpiperidyl-4)-terephthalic acidamide,

A24 Bis-1,2,2,6,6-pentamethylpiperidyl-4)-isophthalic acidamide,



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in which R_3 is 2,2,6,6-tetramethylpiperidyl-4-;

R_4 is a group of formula b) defined above;

R_5 is a group of formula c) as defined above, wherein Y is
- $\ast N-CO-$;

R_5' is a group of formula c) as defined above, wherein Y is
- $\ast CO-N-$;

where the $\ast$ atom is attached to the piperidyl group;

R_6 is a group formula d) defined above and

R_7 is a group of formula e) defined above

The production of the compounds of formula A1 to A29 can be carried out by known methods; preferably through condensation of the corresponding amine with the corresponding carboxylic acid (or carboxylic acid chloride) or, for example the condensation of the corresponding amine with trichlorotriazine, dichloroquinazoline, dichloroquinoxaline, dichlorophthalazine, tri or tetrachloropyrimidine. Corresponding compounds containing the groups of formulae a) to e) are known.

The production of the new pigments can be carried out by salting the appropriate dyestuff with a basic compound A by known methods. For example, acid dyestuffs as obtained after production i.e. in the form of sodium salts, can be reacted in the presence of an adequate amount of mineral acid (for example HCl) with the basic components A

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to form a salt of formula I.

The compounds of formula I are very strong in color, either when they are used in small amounts or when they are used in the usual amounts for other organic pigments. Normal amounts used are from 0.02 to 5% more preferably 0.06 to 3%, by weight of the substrate to be pigmented. The colorings using the compounds of formula I show excellent light fastness. Furthermore the substrates to which the compounds of formula I have been applied show excellent stability against the detrimental effects of UV light, heat and oxidation.

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The following examples illustrate the invention, in which all parts and percentages are by weight and all temperatures given are in °C.

Example 1

- a) 10.15 parts of terephthalic acid dichloride are stirred into 70 parts of toluene and 19.5 parts of triacetone diamine are added at room temperature over 3 hours. The resulting suspension is diluted with a further 30 parts of toluene and then boiled under reflux for 18 hours continually stirring. The resulting precipitate is then filtered, washed with acetone, stirred in 50 parts of water, brought to a pH of about 13 with sodium hydroxide, filtered again, washed with water again and dried under vacuum. The resulting white powder melts at temperatures over 300°.
- b) 4.84 parts of 3,4-dichloranilin-6-sulphonic acid are dissolved in 11 parts of 15% hydrochloric acid, the solution is cooled to 0 to 4° and then it diazotised with 6 parts of 4N NaNO₂, the NaNO₂ excess being destroyed with amino sulphonic acid. A solution of 3.48 parts of 1-phenyl-3-methyl-5pyrazolone in 20 parts of water and 2.2 parts of 30% sodiumhydroxide while keeping the mixture at 0 to 4° the addition being carried out slowly and under stirring. This is then stirred for 18 hours at room temperature, then heated while stirring for 2 hours to 60°, filtered and the residue is washed with water. It is then dried then taken up in water again and the pH is brought to about 8.5 using dilute NaOH.
- c) 4.42 parts of the product of a) above is brought into solution in 30 parts water and 1.9 parts of 33% hydrochloric acid. The mixture of part b) is added slowly over 30 minutes while stirring, and to improve the stirrability further water is added to the mixture. The mixture is then heated for 2-1/2 hours to 60°, cooled to room temperature and the residue is

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filtered, washed with water and dried, the melting point of the resulting yellow-orange powder is over 300°.

By a method analogous to that of Example 1, further pigments of the formula

$$F_n-A$$

in which the symbols defined in the Table below can be prepared from known compound. The nuance of the pigmented substrate is given in the last column.

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TABLE

Example Number	n	F	A	Variation of Coloration
2	1	F ₆	A ₁	yellow
3	1	F ₆	A ₂₁	do.
4	1	F ₆	A ₅	do.
5	1	F ₆	A ₄	do.
6	1	F ₁	A ₂₁	red
7	1	F ₇	A ₂₁	yellow
8	1	F ₁	A ₅	red
9	1	F ₇	A ₅	yellow
10	1	F ₁	A ₄	red
11	1	F ₇	A ₄	yellow
12	1	F ₁	A ₁	red
13	1	F ₇	A ₁	yellow
14	2	F ₂	A ₅	red
15	2	F ₃	A ₅	do.
16	2	F ₈	A ₅	yellow
17	2	F ₁₅	A ₅	do.
18	2	F ₁₅	A ₂	yellow
19	2	F ₅	A ₅	red
20	2	F ₂	A ₂	orange-red
21	1	F ₂	A ₂	red
22	2	F ₅	A ₂	do.
23	2	F ₄	A ₂	do.
24	2	F ₄	A ₅	orange-red
25	2	F ₁₆	A ₄	red
26	2	F ₁₇	A ₅	blue
27	2	F ₂₆	A ₅	do.
28	2	F ₂₉	A ₅	do.
29	2	F ₉	A ₂₄	red
30	2	F ₁₀	A ₂₄	do.
31	2	F ₁₁	A ₂₄	do.

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32	2	F_{12}	A_{23}	do.
33	1	F_{13}	A_{23}	do.
34	2	F_{14}	A_{22}	do.
35	2	F_{16}	A_{23}	do.
36	2	F_{18}	A_3	blue
37	2	F_{19}	A_8	do.
38	2	F_{20}	A_9	do.
39	2	F_{21}	A_{11}	do.
40	2	F_{22}	A_{17}	do.
41	2	F_{23}	A_{20}	do.
42	2	F_{24}	A_{19}	do.
43	2	F_{25}	A_{14}	do.
44	2	F_{31}	A_{23}	red
45	1	F_{33}	A_{23}	do.
46	1	F_{35}	A_2	do.
47	1	F_{35}	A_5	do.
48	1	F_{36}	A_5	violet
49	1	F_{36}	A_6	do.
50	1	F_{41}	A_7	blue
51	1	F_{37}	A_8	red-violet
52	2	F_{42}	A_9	yellow
53	2	F_{42}	A_{10}	do.
54	1	F_{41}	A_{14}	blue
55	2	F_{41}	A_{17}	do.
56	2	F_{39}	A_{18}	red
57	1	F_{38}	A_6	orange
58	1	$F_{43}(m=2)$	A_6	yellow
59	2	F_{40}	A_{22}	red

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Application Example A:

4 parts of the pigment of Example 1 are grounded together with 96 parts of a mixture of

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

for 24 hours in a ball mill. The resulting dispersion is then sprayed onto an aluminum sheet, dried for 30 minutes in air and then stoved for 30 minutes at 120°. A brilliant reddish yellow film with very good light and weathering properties results.

Application Example B

A 0.1% dye colored PVC sheet (colored pigment to white pigment ratio being 1:5) can be made as follows;

16.5 parts of a mixture of equal parts of dioctylphthalate and dibutylphthalate are mixed +

0.05 parts of the pigment of Example 1 and
0.25 parts of titanium dioxide.

33.5 parts of polyvinylchloride are added. The mixture is then rolled between two rollers to produce a sheet that is cut up with a spatula and rolled together again. One of the rollers is kept at a temperature of 40° the other at a temperature of 140°. Finally the mixture is then taken off as a sheet and pressed between to polishing metal plates 160° for 5 minutes.

A reddish yellow colored PVC folio having a high brilliance and very good migration and light fastness properties result.

Application Examples A & B can be repeated using instead of the pigment of Example 1, an equivalent amount of any one of the products of Examples 2-59 inclusive.

CLAIMS:

1. A salt of formula I

$$F_n \cdot A$$

$$(I)$$

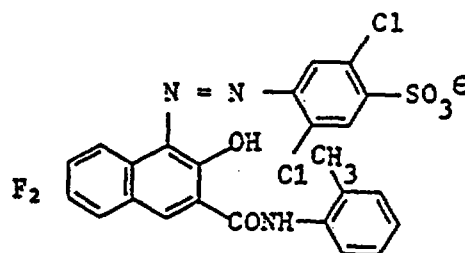
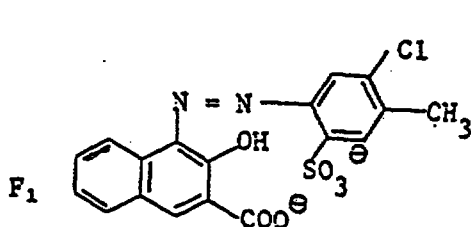
in which F is the residue of a metal free anionic dyestuff having 1 to 4 acids groups,

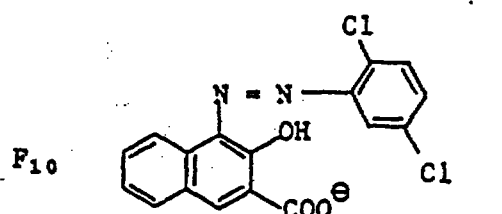
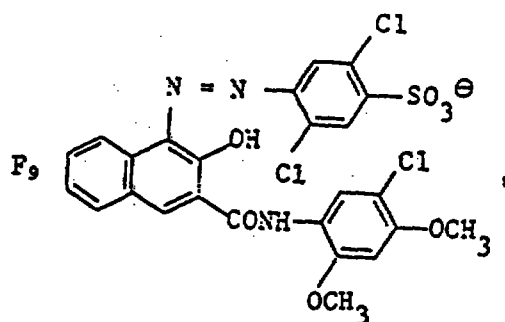
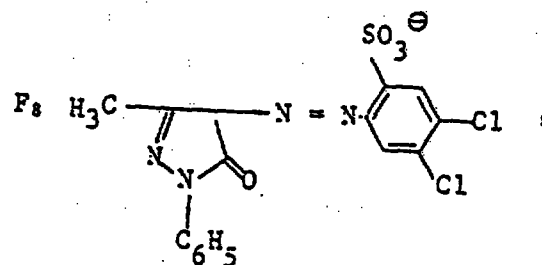
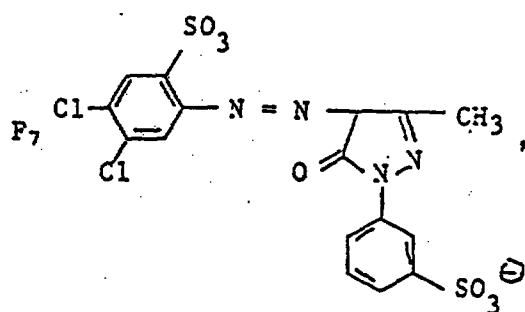
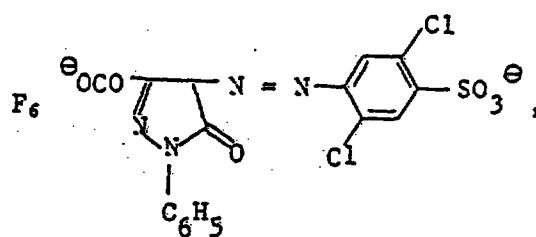
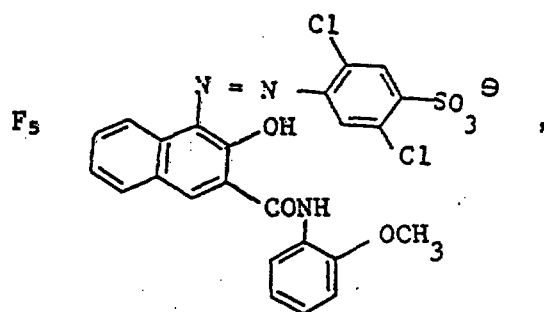
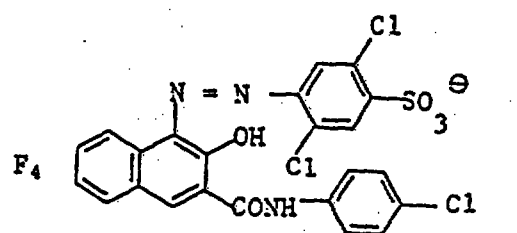
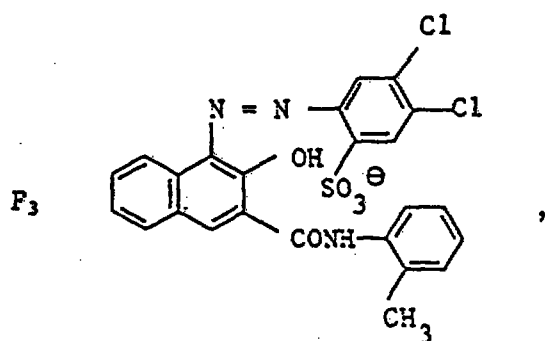
n is 1 to 2; and

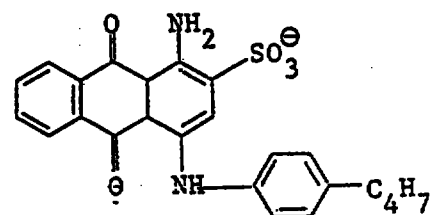
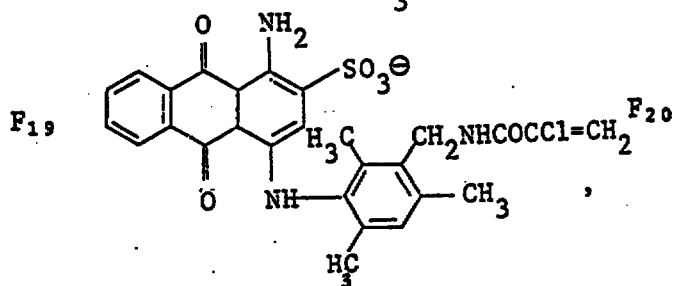
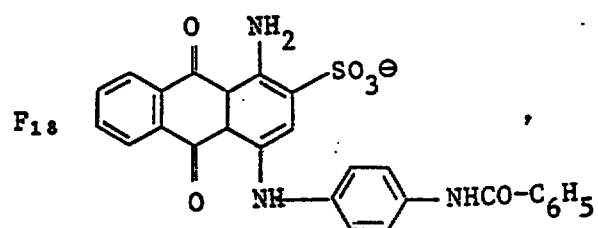
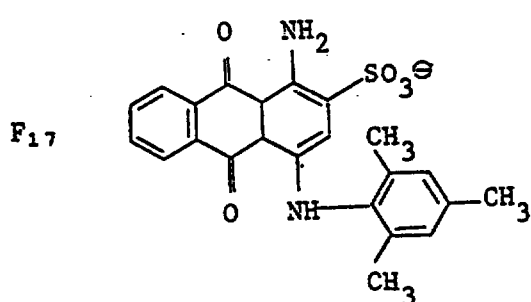
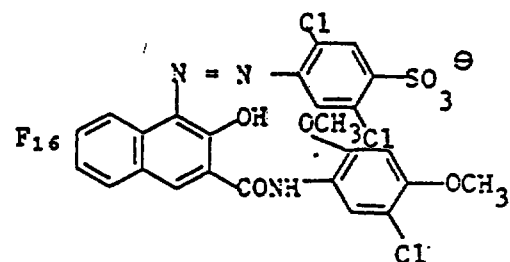
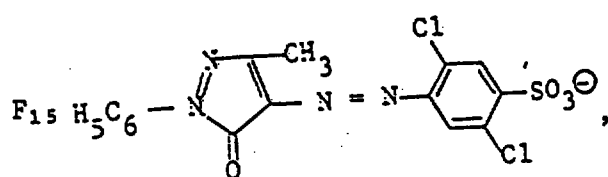
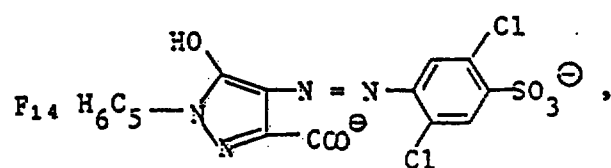
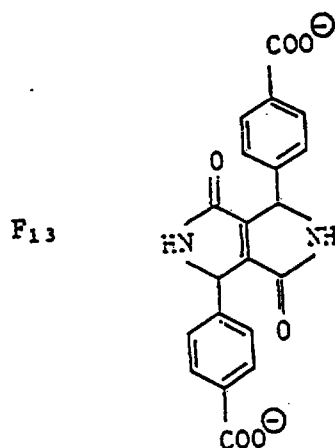
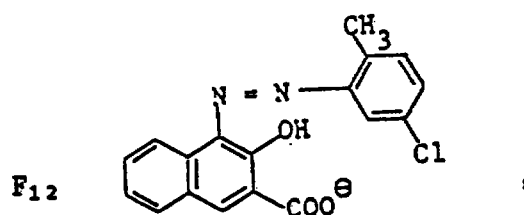
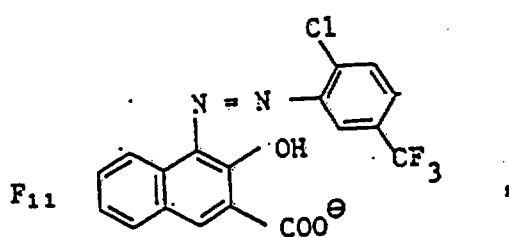
A is a group containing 1 to 4 sterically hindered amine groups and at least n ammonium or immonium groups.

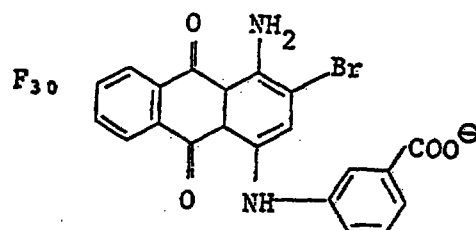
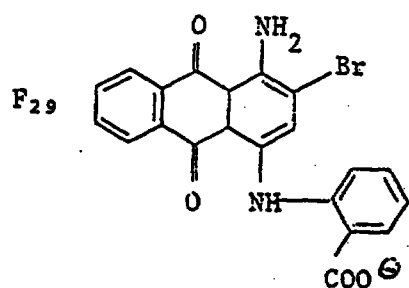
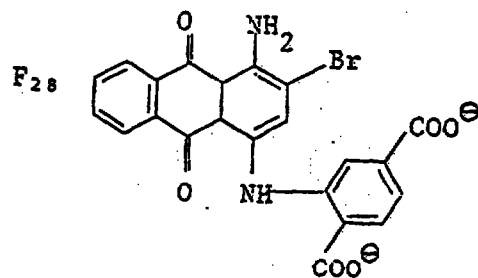
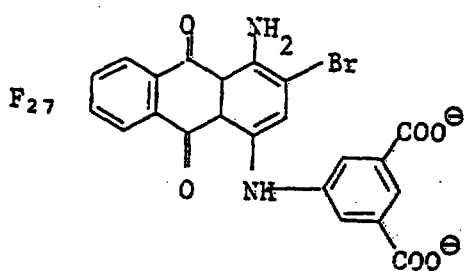
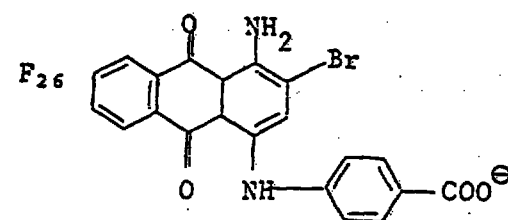
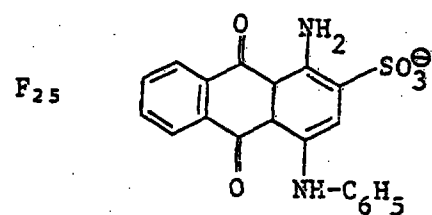
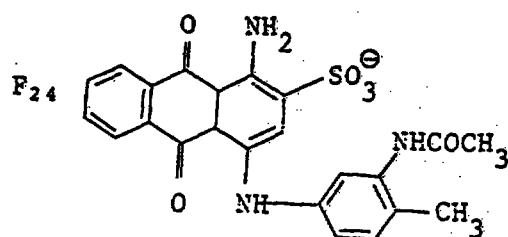
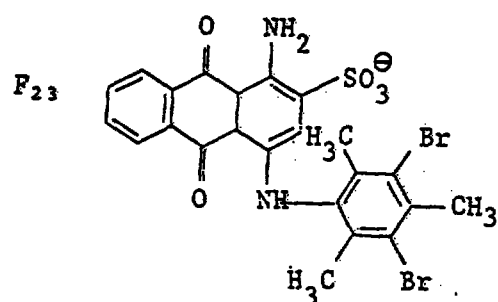
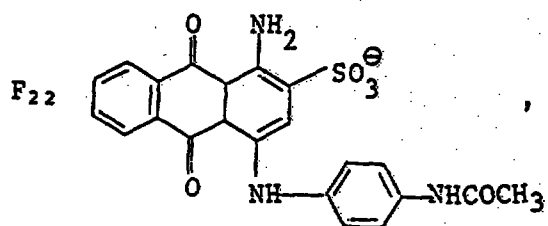
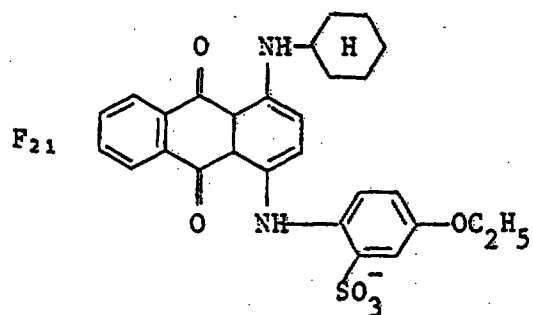
2. A compound according to Claim 1 or Claim 2 in which F is F' where F' is a group derived from an acid group containing non-metallised dyestuff, of the azo series, of the phthalocyanine series, of the anthraquinone series, of the perylene series, of the indigo series, of the thioindigo series, of the perinone series, of the quinacridone series, of the dioxazine series, of the isoindoline series, of the isoindolinone series, of the diketopyrrole series or of the pyrrole series, especially of the azo, the phthalocyanine, the indigo, the anthraquinone, the dioxazine and the isoindoline series.

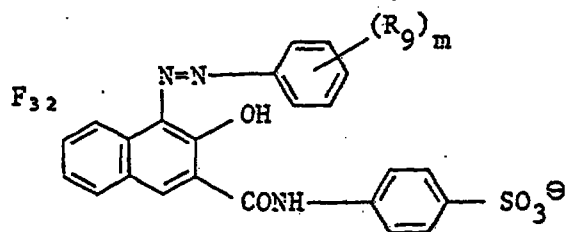
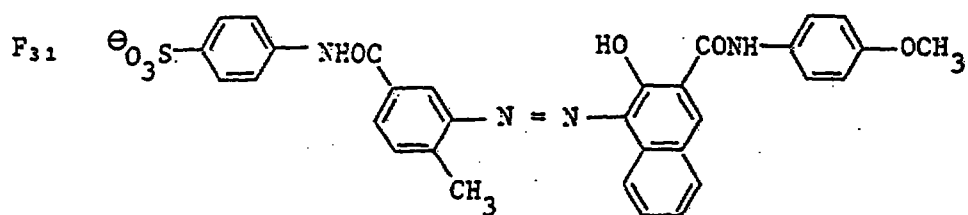
3. A compound according to any one of the preceding Claims in which F is F'', where F'' is a compound of formula F1 to 43



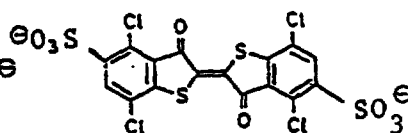
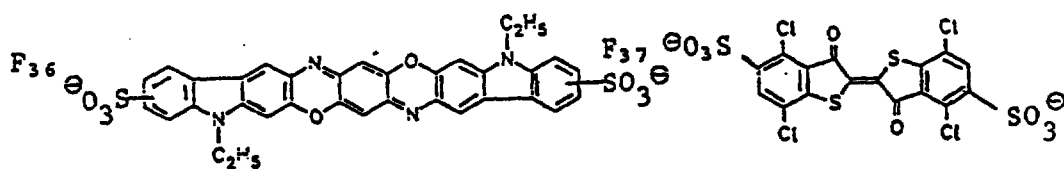
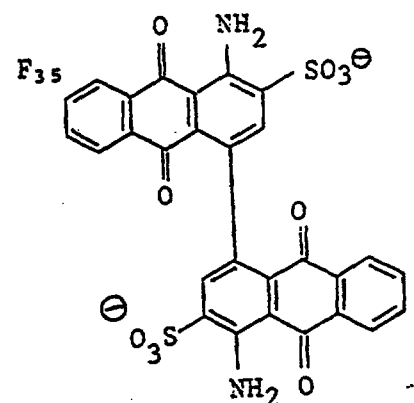
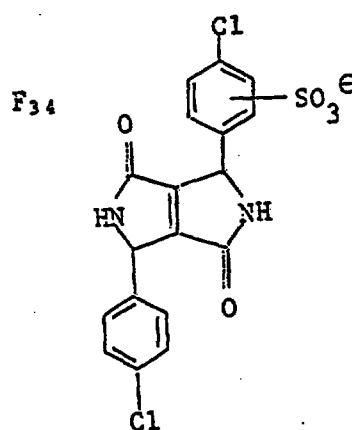
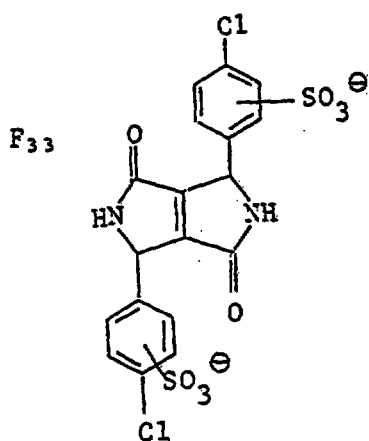


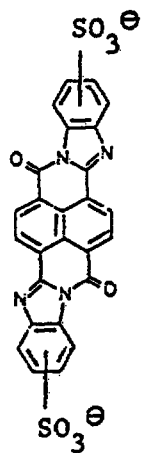
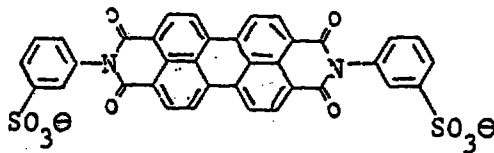
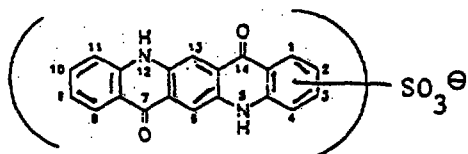
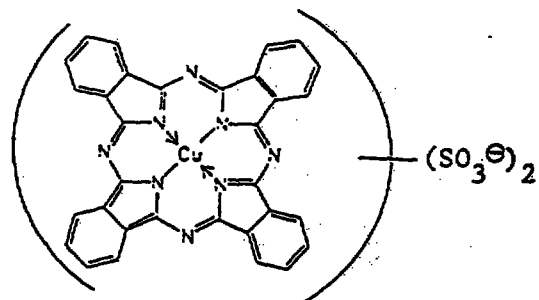
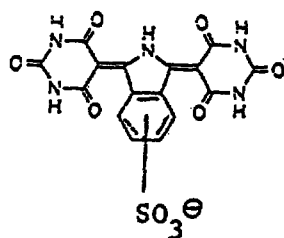
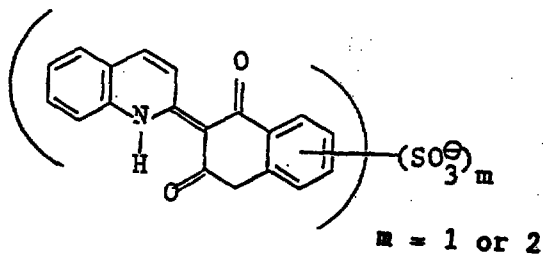






in which R_9 = Chloro, Bromo,
 C_{1-3} alkyl or C_{1-4} alkoxy
and $m=1, 2$ or 3 ,



F₃₈F₃₉F₄₀F₄₁F₄₂F₄₃

m = 1 or 2



4. A compound according to any one of the preceding claims in which A is A' where A' is a cationic group derived from a compound selected from A1 to A29 below

A1 1,3,5-Tri-(2',2',6',6'-tetramethylpiperidyl-4')-trimesic-acid-triamide,

A2 2,4-Bis-(2',2',6',6',-tetramethylpiperidyl-4' amino)-6-chloro-triazine

A3 2,4,6-Tri-(2',2',6',6'-tetramethylpiperidyl-4' amino)-triazine,

A4 Bis-(2',2',6',6'-tetramethylpiperidyl-4'-aminocarbonyl-para-phenylene)-terephthalic acid diamide,

A5 Bis-(2',2',6',6'-tetramethylpiperidyl-4')-terephthalic acidamide,

A6 2,4-Bis-(2',2',6',6'-tetramethylpiperidyl-4' amino)-qinazoline,

A7 2,3-Bis-(2',2',6',6'-tetramethylpiperidyl-4' amino)qinoxaline,

A8 1,4-Bis-(2',2',6',6'-tetramethylpiperidyl-4' amino)-phthalazine,

A9 2-Chloro-4,6-Bis-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-pyrimidine,

A10 2,5-Dichlor-4,6-Bis-(2',2',6',6',-tetramethylpiperidyl-4'-amino) pyrimidine,

A11 2-Fluor-5-chlor-4,6-Bis-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-pyrimidine,

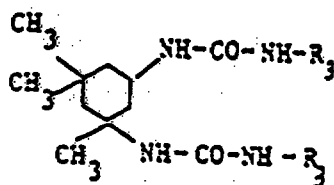
A12 2,4,6-Tri-(2',2',6',6'-teramethylpiperidyl-4'-amino)-pyrimidine,

A13 2,4,6-Tri-(2',2',6',6'-tetramethylpiperidyl-4'-amino)-5-chlor-pyrimidine,

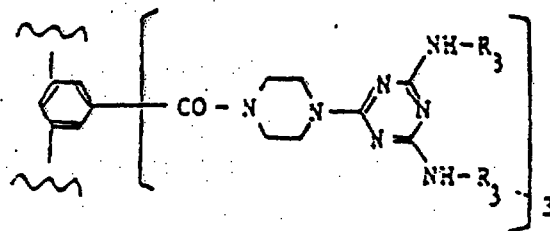
-27-



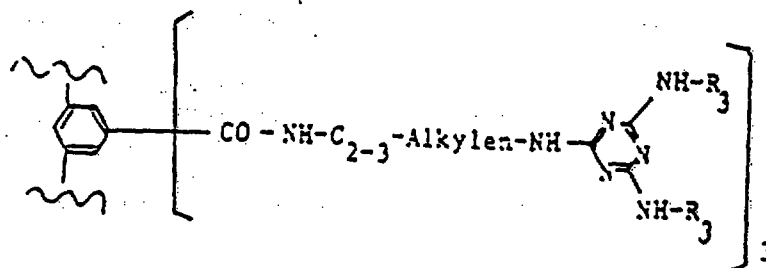
A14



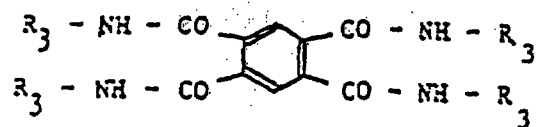
A15



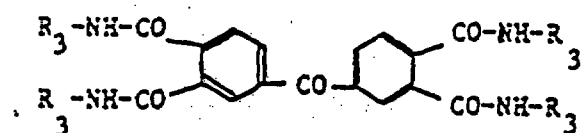
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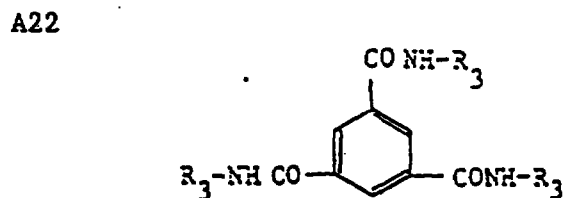
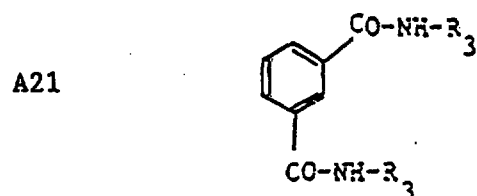
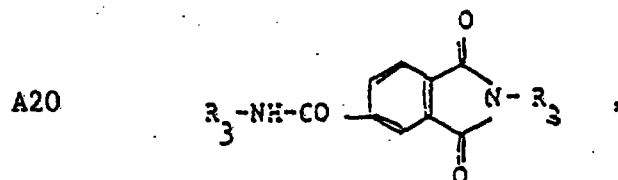
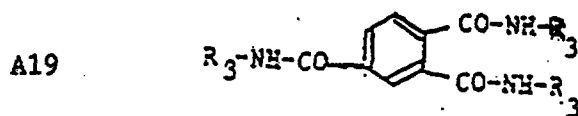


A17



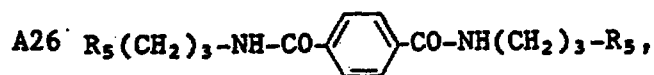
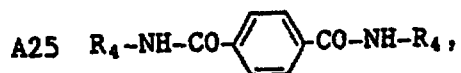
A18

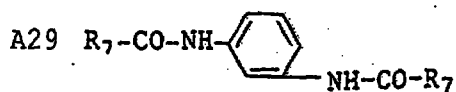
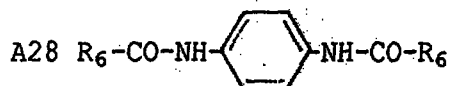
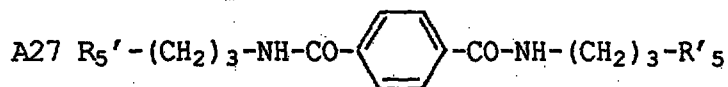




A23 Bis-(1,2,2,6,6-pentamethylpiperidyl-4)-terephthalic acidamide,

A24 Bis-1,2,2,6,6-pentamethylpiperidyl-4)-isophthalic acidamide,





in which R_3 is 2,2,6,6-tetramethylpiperidyl-4-;

R_4 is a group of formula b) defined above;

R_5 is a group of formula c) as defined above, wherein Y is $-*N-CO-$;

R_5' is a group of formula c) as defined above, wherein Y is $-*CO-N-$;

where the * atom is attached to the piperidyl group;

R_6 is a group formula d) defined above and

R_7 is a group of formula e) defined above.

5. A compound of formula I defined in Claim 1 substantially as herein described with reference to any one of Examples 1-59.

6. A process of coloring a substrate comprising applying to that substrate a compound of formula I.