THE PATENT OFFICE

(12) UK Patent (19) GB (11) 2 210 053 (13) B

(54) Title of Invention

Process for mass dyeing of synthetic polyamides

(51) INT CL^5; **C09B 53/00 57/12 // C08L 77/00**

(21) Application No
8822309.4

(22) Date of filing
22.09.1988

(30) Priority Data

(31) **3731929**

(32) **23.09.1987**

(33) **DE**

(43) Application published
01.06.1989

(45) Patent published
19.02.1992

(52) Domestic classification
(Edition K)
C4P PAE PAE01Q PAE02
PAE04 PAE07 PAE08 PAE12
PAE17 PAE18 PAE20 PAE41
PAE43 PBE PBE1A PBE2B
PBE4B PBE6C PT07 PT11
PT12 PT17 P104 P126
C3K KAA K336
C3W W310
U1S S1399 S1565 S3071

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GB1522683 A
GB1513168 A
GB1488981 A
GB1413510 A
CH0561763 A
GB1413510 A is equivalent to
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GB1413510 A is equivalent to
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(continued on next page)

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2 210 053 B – continuation

(58) Field of search

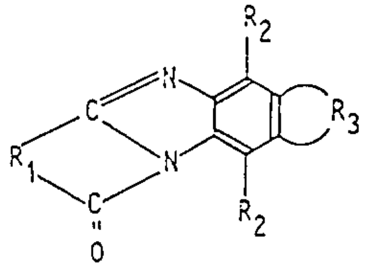
As for published application
2210053A *viz:*
UK CL(Edition J) **C3K KAA, C4P**
PAE PBP
updated as appropriate

2210053

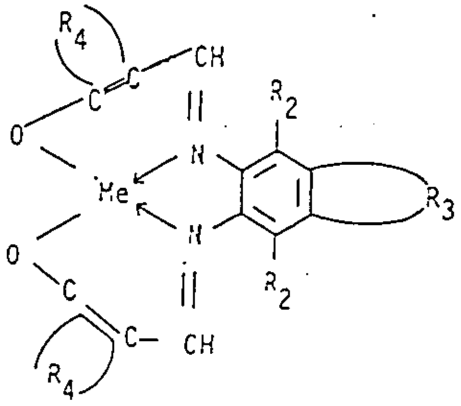
A PROCESS FOR MASS DYEING OF SYNTHETIC POLYAMIDES

The invention relates to a process for mass dyeing of synthetic polyamides.

According to the invention, there is provided a process for pigmenting synthetic polyamide comprising pigmenting in the mass the polyamide with a compound of formula I or II



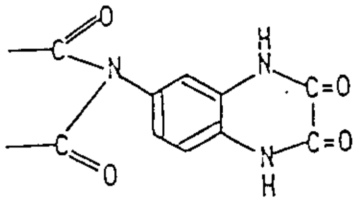
(I)

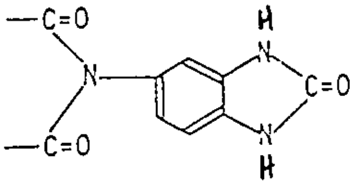


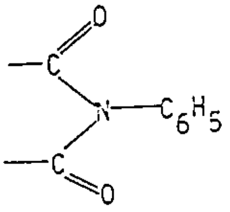
(II),

in which R_2 is hydrogen, trifluoromethyl, halogen, C_{1-4}alkyl, C_{1-4}alkoxy, cyano, nitro, hydroxyl, amino, C_{1-4}alkylamino, di-(C_{1-4})alkylamino, phenylamino, N-C_{1-4}alkyl-N-phenylamino; acyl, acyloxy or acylamino, Me is a divalent metal atom;

R_1 is 1,2-phenylene, 1,2-, 2,3- or 1,8-naphthylene or 2,2′-diphenylene, the phenylene and naphthylene groups of R_1 being unsubstituted or mono- or di-substituted by R_{2a} where R_{2a} has a significance of R_2 other than hydrogen or by 3 or 4 halogen atoms; or in the naphthylene group two adjacent carbon atoms can be bridged by $-NH-CO-NH-$, $-N{=}C(CH_3)-NH-$, $-N{=}C(C_6H_5)-NH-$, $-CO-N(C_6H_5)-CO-$, $-CO-NH-CO-$,







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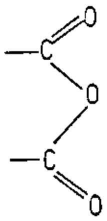
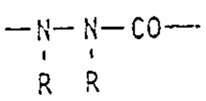
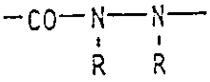


;

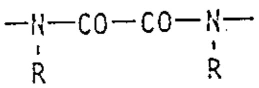
R_3 is



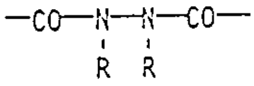
$-\underset{R}{N}-\underset{R}{N}-CO-$;



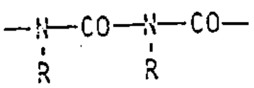
$-CO-\underset{R}{N}-\underset{R}{N}-$;



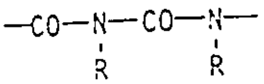
$-\underset{R}{N}-CO-CO-\underset{R}{N}-$;



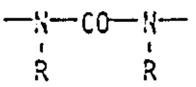
$-CO-\underset{R}{N}-\underset{R}{N}-CO-$;



$-\underset{R}{N}-CO-\underset{R}{N}-CO-$;

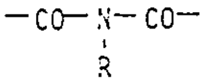


$-CO-\underset{R}{N}-CO-\underset{R}{N}-$



$-\underset{R}{N}-CO-\underset{R}{N}-$.

or



$-CO-\underset{R}{N}-CO-$

where R is hydrogen or C_{1-4}alkyl unsubstituted or substituted by 1 to 4 groups selected from halogen, cyano, C_{1-4}alkoxy, phenyl, phenoxy, acyl, acyloxy or acylamino; and

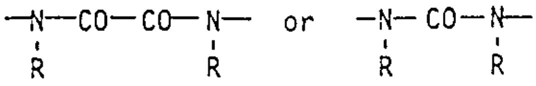
R_4 together with the two carbon atoms to which it is attached form a 5 or 6-membered carbocyclic or heterocyclic group or form a 9- or 10-membered bicyclic carbocyclic or heterocyclic group, the rings of R_4 being unsubstituted or substituted by 1, 2 or 3 groups R_{2a} when R_{2a} has a significance of R_2 other than hydrogen, or R_4 is $-NH-COC(CN)=C(CH_3)-$, $N(CH_3)-CO-C(CN)=C(CH_3)-$, $-N(C_6H_5)-CO-C(CN)=C(CH_3)-$ or $-N(C_3H_7)-CO-C(CN)=C(CH_3)-$.

In this Specification, where a symbol appears more than once in a formula, its significances are independent of one another unless indicated to the contrary.

In this Specification preferably any acyl group is a $-CO-R_{10}$, $-SO_2-C_6H_5$ or SO_2C_{1-4}alkyl group where R_{10} is selected from C_{1-4}alkyl, phenyl C_{2-4}alkenyl; C_{1-4}alkoxy, hydrogen or phenoxy. Any acyloxy group is preferably $-O-CO-R_{10}$ or $-O-SO_2-C_6H_5$ or $-O-SO_2C_{1-4}$alkyl and any acylamino is preferably $-N(R_{10a})COR_{10}$ or $-N(R_{10a})SO_2C_{1-4}$alkyl or $-N(R_{10a})SO_2-C_6H_5$ where R_{10a} is hydrogen, C_{1-4}alkyl or phenyl.

Preferably any halogen present is chloro or bromo.

Preferably R_3 is R_3' where R_3' is

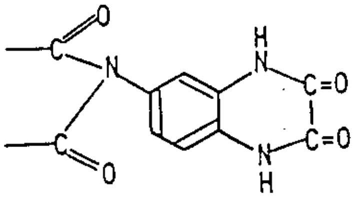


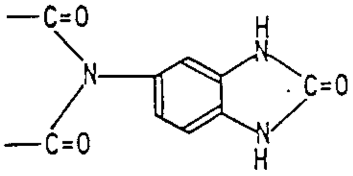
$$-\underset{R}{N}-CO-CO-\underset{R}{N}- \quad \text{or} \quad -\underset{R}{N}-CO-\underset{R}{N}-$$

where R is defined above.

Preferably R is hydrogen.

Preferably R_1 is R_1' where R_1' is 1,2-phenylene unsubstituted or substituted by 1 to 4 halogen atoms, 1,8-naphthylene, unsubstituted or substituted by 1 to 4 halogen atoms or mono- or di-substituted by amino, nitro, methoxy, phenylamino, acetylamino or benzoylamino or bridged in the 4,5-position by -NH-CO-NH-, $-N=C(CH_3)-NH-$, $-N=C(C_6H_5)-NH$, $-CO-N(C_6H_5)-CO-$, -CO-NH-CO-





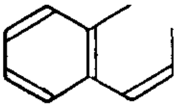
More preferably R_1 is R_1'' where R_1'' is a 1,8-naphthylene unsubstituted or substituted by 1 to 4 halogen atoms or mono- or di-substituted by methoxy or mono-substituted by nitro, acetylamino or benzoylamino.

Preferably R_2 is hydrogen.

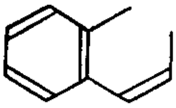
Preferably Me is Me' where Me' is chromium, copper, manganese, iron, zinc, nickel or cobalt.

More preferably Me is Me" where Me" is copper, zinc, nickel or cobalt.

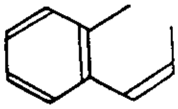
Preferably R_4 is R_4' where R_4' is $-CH=CH-CH=CH-$, $-CH=C(Cl)-CH=C(Cl)-$, $-CH=CH-C(OCH_3)=CH-$, $-CH=CH-CH=C(OCH_3)-$, $-NH-CO-C(CN)=C(CH_3)-$, $-N(CH_3)-CO-C(CN)=C(CH_3)-$, $-N(C6H_5)-CO-C(CN)=C(CH_3)-$, $-N(C_6H_5)-CO-C(CN)=C(CH_3)-$ or



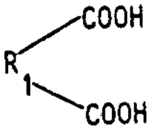
More preferably R_4 is R_4'' where R_4'' is $-CH=CH-CH=CH-$, $-CH=C(Cl)-CH=C(Cl)-$ or



Most preferably R_4 is

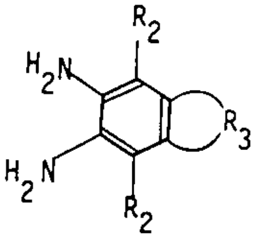


Compounds of formula I and II are known or can be made from known compounds by known methods. For example, compounds of formula I can be prepared by condensing one mole of a compound of formula III



(III)

(or its acid halide or acid anhydride) with one mole of a compound of formula IV



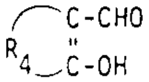
(IV)

(or its salt form), in which the symbols R_1 to R_3 are as defined above.

The condensation can take place without solvent in molten form at temperatures of 150-300°C inclusive (preferably at 250°C) or in inert solvent at temperatures from 250-300°C inclusive, preferably 100-250°C optionally in the presence of a catalyst.

Preferred solvents are high boiling aliphatic or aromatic hydrocarbons (e.g. xylene, diphenyl, nitrobenzene, chlorobenzene, chloronaphthalene, glycol ether, organic acids and acid amides). If the compound of formula III is used in free acid form, water can also be used as solvent.

Compounds of formula II can be prepared by condensing 2 moles of a compound of formula V (or a mixture thereof)



(V)

where R_4 is as defined above;

with one mole of a compound of formula IV above (or its salt form); and metallising (either at the same time or after the condensation process) with one mole of the salt of a divalent metal.

Such metal salts include the chloride, formate and acetate.

The condensation reaction of the compounds of formula V with that of formula IV will generally take place in water or in a solvent system miscible with water, or for example a low molecular weight C_{1-4}alcohol, dimethylformamide, N-methylpyrrolidone, dimethylacetamide, a glycol, dioxane or a glycol ether. The temperature of the reaction is from 20 to 250°C, more preferably 30 to 150°C. Compounds of formulae I and II and their preparation are disclosed in CH 561,763 and US Patent 3,896,113, the disclosures of which are incorporated herein by reference.

The pigments used in a process according to the invention are excellent for mass pigmenting of synthetic polyamides (e.g. all types of nylon). Such polyamides are those resulting from the condensation or polymerisation of dicarboxylic acids and diamines - for example the condensation products of adipic acid and hexamethylene diamine, of lactams (e.g. ε-caprolactam) or of aminocarboxyclic acids (e.g. ω-aminoundecanoic acid). These products are mixed with the pigment and can be formed into fibres and textile articles by known methods, e.g. melt spinning, injection dye casting, injection extrusion or film blowing.

Mass pigmentation of polyamides is disclosed, for example, in DOS 1,670,238, DOS 3,504,143 and DOS 3,439,045, the disclosures of which are incorporated herein by reference. Preferably, the mass pigmentation process comprises mixing the pigment with molten polymer prior to molding the resulting mixture into the desired form. More preferably the pigment and polymer are premixed in finely divided solid form followed by melting of the polymer and further mixing. According to a further preferred technique, the pigment is added to the polymer in the form of a masterbatch, i.e. previously formed mixture of a relatively high concentration of pigment, i.e. 1.5 to 50 %, by weight, in a relatively small amount of the same polymer that is to be pigmented. Typically, the masterbatch is prepared by extruding a mixture of pigment and polymer in the form of strands, which are cooled and then cut into particles of suitable size for mixing with additional polymer.

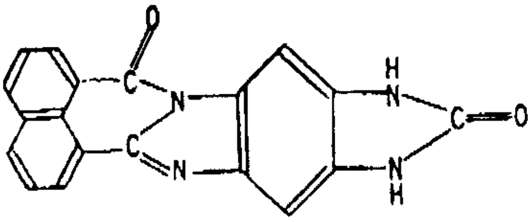
Preferably, the pigment is of a particle size less than 5 microns for mass pigmentation, more preferably about 1 to 2 microns. Size reduction of the pigment can, if necessary, be carried out during the preparation of a masterbatch, e.g. by shearing forces in the extruder.

The pigments used in a process according to the invention are not only heat stable at the formation temperatures of the synthetic polyamide, but also form light stable pigmentations.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight and all temperatures are in degrees Centigrade.

Example 1

100 Parts of poly-ε-caprolactam in powder form are mixed with 1.0 part of the dyestuff of formula 1a



(1a)

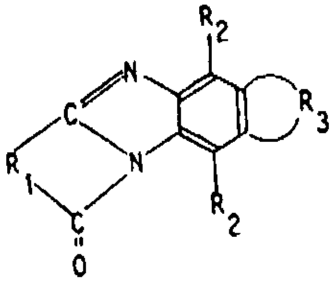
(prepared according to Example 1 of Swiss Patent 561,763) in granulate powder form in a tumble mixer. The powder mixes well in a short time and agglomerate with the granulate. After mixing for about 10 minutes the mixture is taken for drying at 120°C for 16 hours, after which it is placed in a melt spinning machine and after standing in the spinning machine (Fourne spinning machine spinning rate 1 kg/hr) for about 8 minutes at 275-280° under a nitrogen atmosphere the resulting molten polymeric product is spun into fibres followed by stretching at room temperature (stretching ratio 1:4) on a Dienes tenser. The resulting yellow dyed fibres have good light fastness properties.

In a similar fashion, other synthetic polyamide fibres (e.g. Nylon or Perlon) can be mass-dyed.

Examples 2 to 74

Example 1 is repeated using 1 part of a compound of any one of Compounds 2 to 74 in place of the compound of formula 1a.

Compounds 2 to 74 are compounds of the formula



in which R_1 [illegible] and R_3 are defined in Table 1 below.

TABLE 1

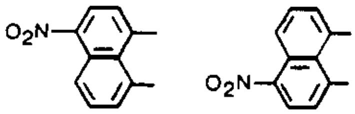
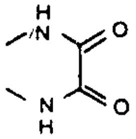
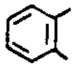
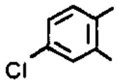
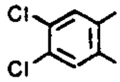
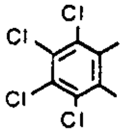
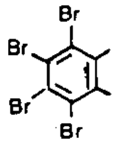
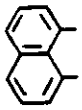
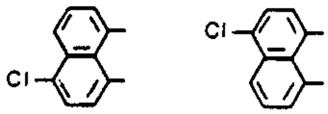
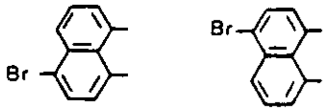
Compound No.	R_1	R_3	Shade on Nylon 6,6
2			reddish-yellow
3		do.	yellow
4		do.	do.
5		do.	do.
6		do.	orange
7		do.	do.
8		do.	yellow
9		do.	do.
10		do.	do.

Table 1 (cont.)

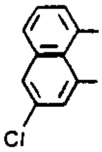
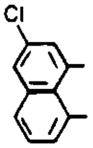
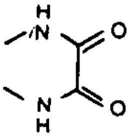
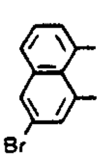
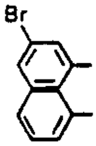
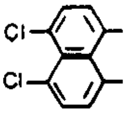
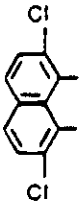
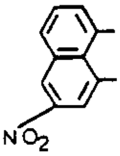
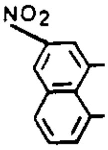
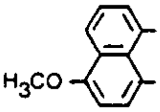
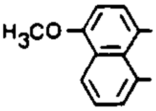
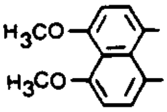
Compound No.	R1	R3	Shade on Nylon 6,6
11	 		yellow
12	 	do.	yellow
13		do.	orange
14		do.	red
15		do.	red
16	 	do.	yellow
17	 	do.	orange
18		do.	orange-red

Table 1 (cont.)

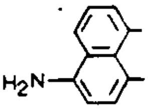
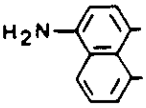
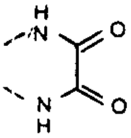
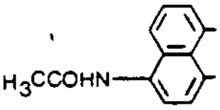
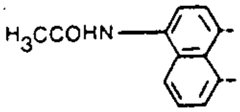
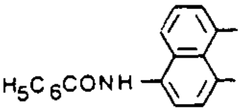
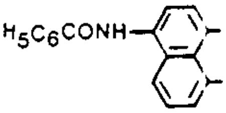
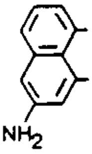
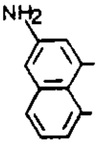
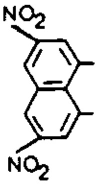
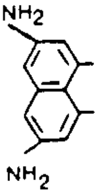
Compound No.	R_1	R_3	Shade on Nylon 6,6
19	  		red
20	  	do.	yellowish-orange
21	  	do.	yellow
22	  	do.	red
23	 	do.	yellow
24	 	do.	red

Table 1 (cont.)

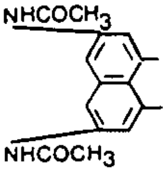
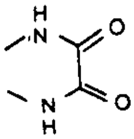
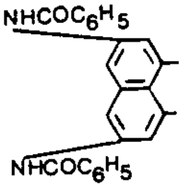
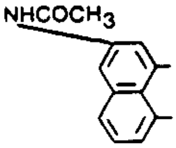
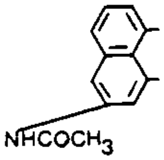
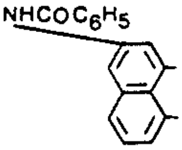
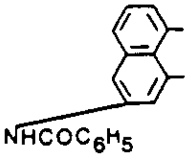
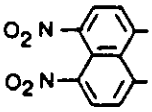
Compound No.	R_1	R_3	Shade on Nylon 6,6
25			orange
26		do.	do.
27	 	do.	do.
28	 	do.	do.
29		do.	brown

Table 1 (cont.)

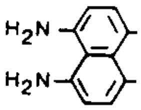
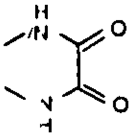
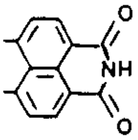
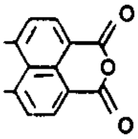
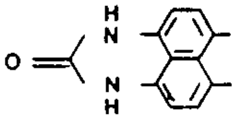
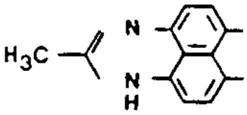
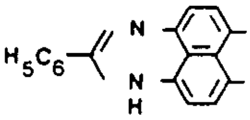
Compound No.	R_1	R_3	Shade on Nylon 6,6
30			red
31		do.	yellowish-orange
32		do.	do.
33		do.	yellow
34		do.	yellowish-orange
35		do.	yellowish-orange

Table 1 (cont.)

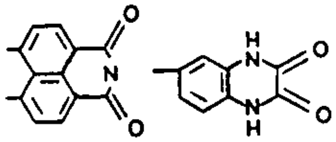
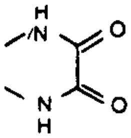
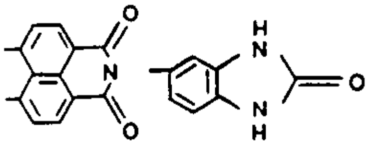
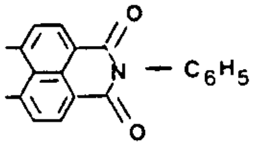
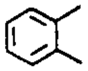
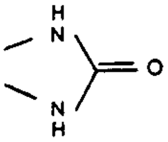
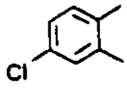
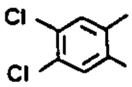
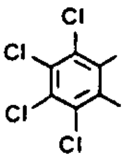
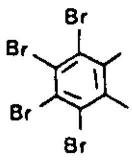
Compound No.	R_1	R_3	Shade on Nylon 6,6
36			yellowish-orange
37		do.	do.
38		do.	do.
39			yellow
40		do.	do.
41		do.	do.
42		do.	orange
43		do.	do.

Table 1 (cont.)

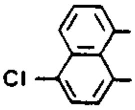
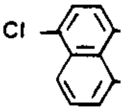
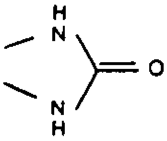
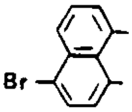
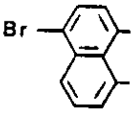
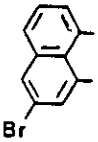
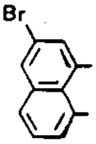
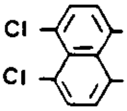
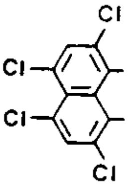
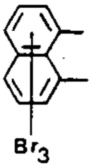
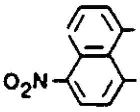
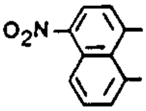
Compound No.	R_1	R_3	Shade on Nylon 6,6
44	 		orange
45	 	do.	do.
46	 	do.	do.
47		do.	orange-red
48		do.	red
49		do.	red
50	 	do.	brown

Table 1 (cont.)

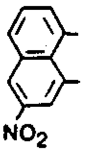
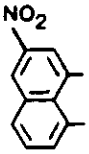
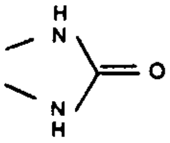
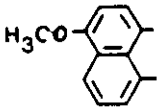
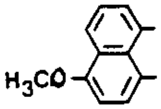
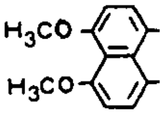
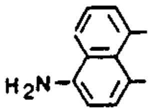
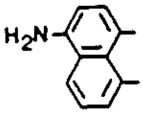
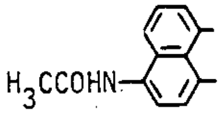
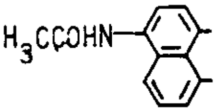
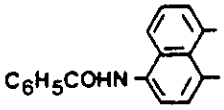
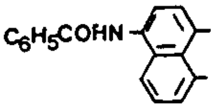
Compound No.	R_1	R_3	Shade on Nylon 6,6
51	 		orange
52	 	do.	do.
53		do.	reddish- violet
54	 	do.	orange
55	 	do.	do.
56	 	do.	do.

Table 1 (cont.)

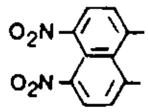
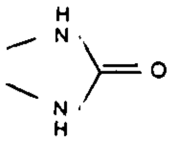
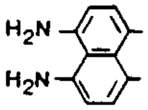
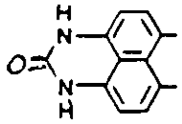
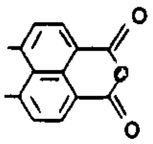
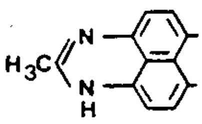
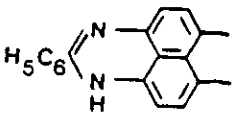
Compound No.	R_1	R_3	Shade on Nylon 6,6
57			brown
58		do.	reddish-violet
59		do.	orange
60		do.	do.
61		do.	do.
62		do.	do.

Table 1 (cont.)

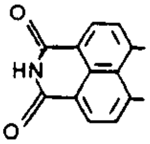
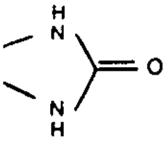
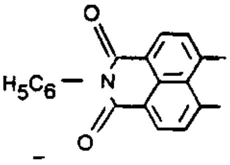
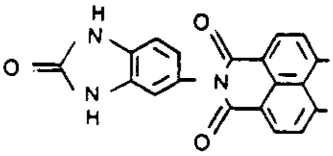
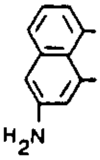
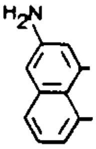
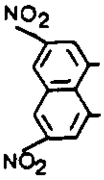
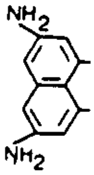
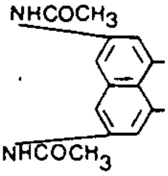
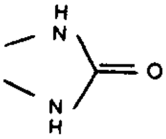
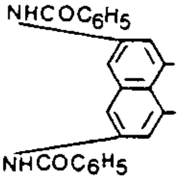
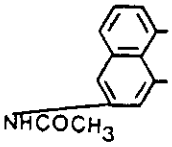
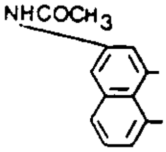
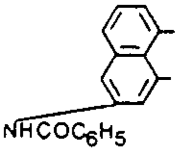
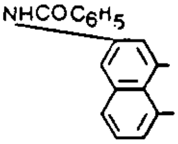
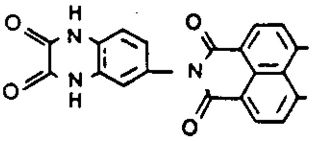
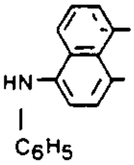
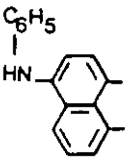
Compound No.	R_1	R_3	Shade on Nylon 6,6
63			orange-red
64		do.	do.
65		do.	do.
66	 	do.	red
67		do.	orange
68		do.	red

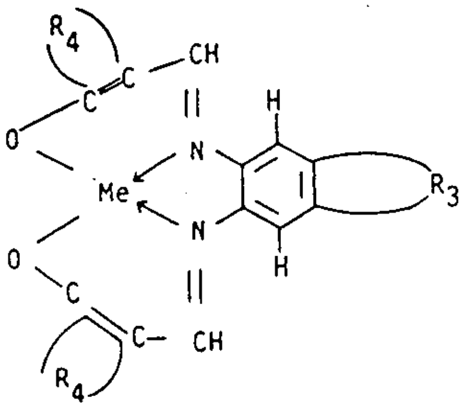
Table 1 (cont.)

Compound No.	R_1	R_3	Shade on Nylon 6,6
69			orange-red
70		do.	do.
71	 	do.	orange
72	 	do.	do.
73		do.	orange-red
74	 	do.	red

EXAMPLES 75 to 95

Example 1 can be repeated using 1 part of Compounds 75 to ~~96~~ 95 in place of the compound of Example 1.

Compounds 75 to ~~96~~ 95 are compounds of the formula



where R_3 and R_4 are as defined in Table 2 below. The compounds of Examples 76 to 97 an be made analogously to those of Example 1 of DOS 2263235 from suitable reactants.

TABLE 2

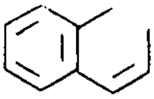
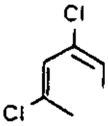
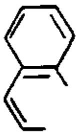
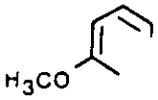
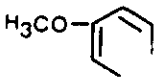
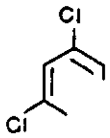
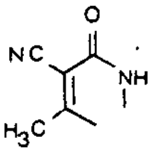
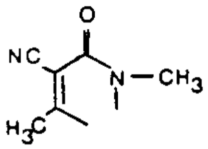
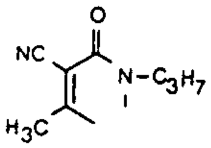
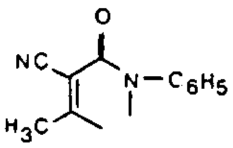
Compound No.	R_4	R_3		Shade on Nylon 6,6
75		-NH-CO-CO-NH-	Ni	yellowish-red
76	do.	-NH-CO-NH-	do.	orange
77		-NH-CO-CO-NH-	do.	yellowish-orange
78	do.	do.	Co	brown
79		do.	Ni	brown
80	do.	do.	Cu	yellow
81		do.	Cu	orange
82	do.	-NH-CO-NH-	Zn	yellowish-orange
83	do.	do.	Cu	brownish-orange
84		do.	Cu	brownish-yellow
85	do.	do.	Co	yellowish-orange

Table 2 (cont.)

Compound No.	R_4	R_3	Me	Shade on Nylon 6,6
85		-NH-CO-NH-	Zn	yellow
86		do.	Cu	yellow
87		do.	Ni	orange
88	do.	do.	Zn	yellow
89		do.	Cu	yellowish-orange
90	do.	do.	Ni	orange
91	do.	do.	Zn	yellow
92		do.	Zn	do.
93		do.	Ni	reddish-orange
94		do.	Zn	do.
95		do.	Cu	brownish-orange

Example 96

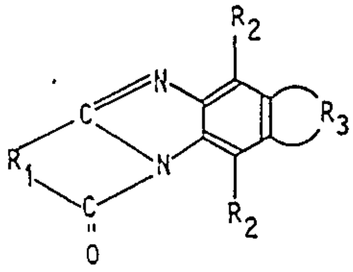
Example 1 is repeated, using instead of the 100 parts of poly-ε-caprolactam and 1.0 parts of the dyestuff of formula 1a, of the following

1.0 parts of the dyestuff of formula 1a (particle size 5 μ) defined in Example 1 is mixed well with 4.0 parts of poly-ε-caprolactam in powder form. This is then extruded at about 200°C in a Werner Pfleider extrusiometer (at a ratio of 100 kg /hr) and then granulated in a Werner Pfleider granulator. This granulate is then added to 96 parts of poly-ε-caprolactam powder and is mixed well.

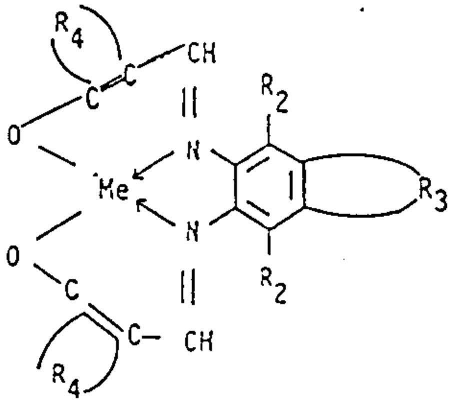
Instead of the dyestuff of Example 1, Example 96 can be repeated using any one of compounds 2 to 95 of Examples 2 to 95 respectively.

CLAIMS: -

1. A process for pigmenting synthetic polyamide comprising pigmenting in the mass the polyamide with a compound of formula I or II



(I)

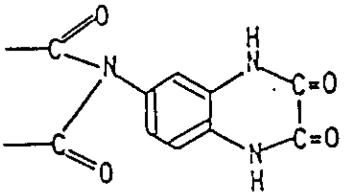


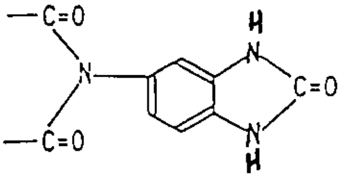
(II),

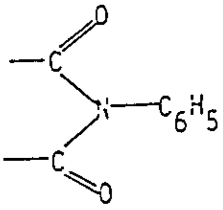
in which R_2 is hydrogen, trifluoromethyl, halogen, C_{1-4}alkyl, C_{1-4}alkoxy, cyano, nitro, hydroxyl, amino, C_{1-4}alkylamino, di-(C_{1-4})alkylamino, phenylamino, N-C_{1-4}alkyl-N-phenylamino; acyl, acyloxy or acylamino,

Me is a divalent metal atom;

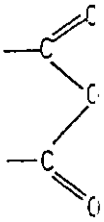
R_1 is 1,2-phenylene, 1,2-, 2,3- or 1,8-naphthylene or 2,2'-diphenylene, the phenylene and naphthylene groups of R_1 being unsubstituted or mono- or di-substituted by R_{2a} where R_{2a} has a significance of R_2 other than hydrogen or by 3 or 4 halogen atoms; or in the naphthylene group two adjacent carbon atoms can be bridged by -NH-CO-NH-, -N=C(CH_3)-NH-, -N=C(C_6H_5)-NH-, -CO-N(C_6H_5)-CO-, -CO-NH-CO-,





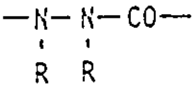


or

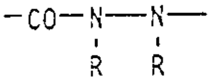


;

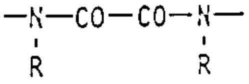
R$_3$ is



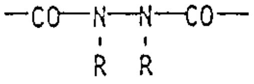
$-\underset{R}{N}-\underset{R}{N}-CO-$;



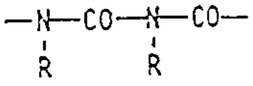
$-CO-\underset{R}{N}-\underset{R}{N}-$;



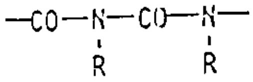
$-\underset{R}{N}-CO-CO-\underset{R}{N}-$;



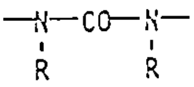
$-CO-\underset{R}{N}-\underset{R}{N}-CO-$;



$-\underset{R}{N}-CO-\underset{R}{N}-CO-$;

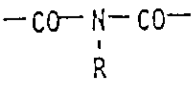


$-CO-\underset{R}{N}-CO-\underset{R}{N}-$



$-\underset{R}{N}-CO-\underset{R}{N}-$

or



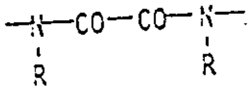
$-CO-\underset{R}{N}-CO-$

where R is hydrogen or C$_{1-4}$alkyl unsubstituted or substituted by

1 to 4 groups selected from halogen, cyano, C_{1-4}alkoxy, phenyl, phenoxy, acyl, acyloxy and acylamino; and

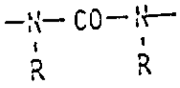
R_4 together with two carbon atoms to which it is attached form a 5 or 6-membered carbocyclic or heterocyclic group or form a 9- or 10-membered bicyclic carbocyclic or heterocyclic group, the rings of R_4 being unsubstituted or substituted by 1, 2 or 3 groups R_{2a} when R2a has a significance of R_2 other than hydrogen or R_4 is $-NH-CO-C(CN)=C(CH_3)-$, $N(CH_3)-CO-C(CN)=C(CH_3)-$, $-N(C_6H_5)-CO-C(CN)=C(CH_3)-$ or $-N(C_3H_7)-CO-C(CN)=C(CH_3)-$.

2. A process according to Claim 1, in which R_3 is R_3' where R_3 is



$-\underset{R}{N}-CO-CO-\underset{R}{N}-$

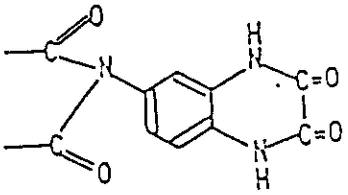
or



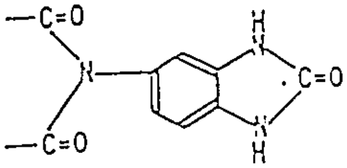
$-\underset{R}{N}-CO-\underset{R}{N}-$

in which R is as defined in Claim 1.

3. A process according to Claim 1, in which R_1 is R_1' where R_1' is 1,2-phenylene unsubstituted or substituted by 1 to 4 halogen atoms, 1,8-naphthylene, unsubstituted or substituted by 1 to 4 halogen atoms or mono- or di-substituted by amino, nitro, methoxy, phenylamino, acetylamino or benzoylamino or bridged in the 4,5-position by $-NH-CO-NH-$, $-N=C(CH_3)-NH-$, $-N=C(C_6H_5)-NH$, $-CO-N(C_6H_5)-CO-$, $-CO-NH-CO-$



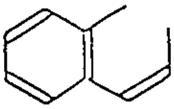
or



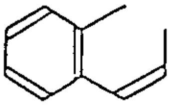
4. A process according to Claim 3, in which R_1 is R_1'' where R_1'' is 1,8-naphthylene, unsubstituted or substituted by 1 to 4 halogen atoms or mono- or di-substituted by methoxy or mono-substituted by nitro, acetylamino or benzoylamino.

5. A process according to Claim 1, in which Me is Me′ where Me′ is chromium, copper, manganese, iron, zinc, nickel or cobalt.

6. A process according to Claim 1, in which R_4 is R_4' where R_4' is $-CH=CH-CH=CH-$, $-CH=C(Cl)-CH=C(Cl)-$, $-CH=CH-C(OCH_3)=CH-$, $-CH=CH-CH=C(OCH_3)-$, $-NH-CO-C(CN)=C(CH_3)-$, $-N(CH_3)-CO-C(CN)=C(CH_3)-$, $-N(C_6H_5)-CO-C(CN)=C(CH_3)-$, or



7. A process according to Claim 6, in which R_4 is R_4'' where R_4'' is $-CH=CH-CH=CH-$, $-CH=C(Cl)-CH=C(Cl)-$ or



8. A process according to Claim 1 substantially as herein described with reference to Example 1.

9. Synthetic polyamide to which a compound of formula I or formula II as defined in Claim 1 has been applied in the mass.

3700/DH/KC

REGISTER ENTRY FOR GB2210053

Form 1 Application No GB8822309.4 filing date 22.09.1988

Priority claimed:
23.09.1987 in Federal Republic of Germany - doc: 3731929

Title PROCESS FOR MASS DYEING OF SYNTHETIC POLYAMIDES

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Classified to
C4P C3K C3W U1S
C09B

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Publication No GB2210053 dated 01.06.1989

Examination requested 22.09.1988

Patent Granted with effect from 19.02.1992 (Section 25(1)) with title PROCESS FOR MASS DYEING OF SYNTHETIC POLYAMIDES

**** END OF REGISTER ENTRY ****

0A80-01 OPTICS - PATENTS 19/10/94 08:22:52
FG PAGE: 1

RENEWAL DETAILS

PUBLICATION NUMBER	GB2210053

PROPRIETOR(S)

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DATE FILED	22.09.1988
DATE GRANTED	19.02.1992
DATE NEXT RENEWAL DUE	22.09.1995
DATE NOT IN FORCE	
DATE OF LAST RENEWAL	26.08.1994
YEAR OF LAST RENEWAL	07
STATUS	PATENT IN FORCE