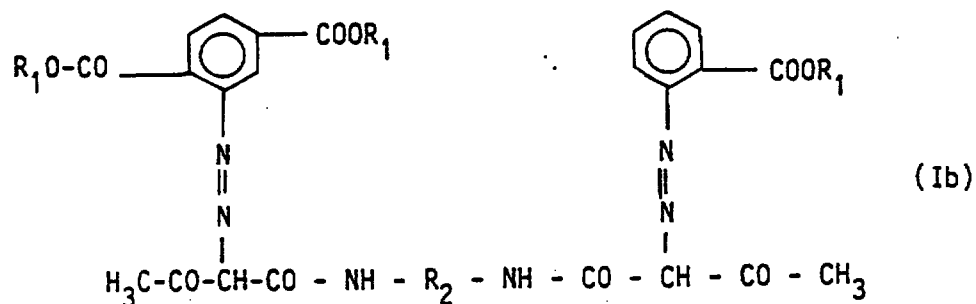
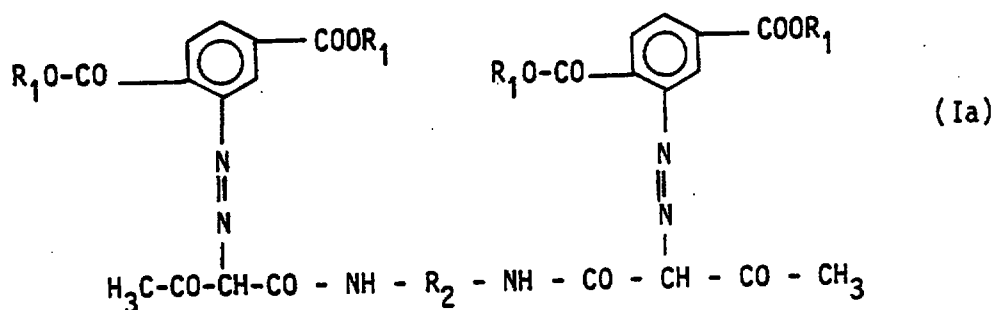


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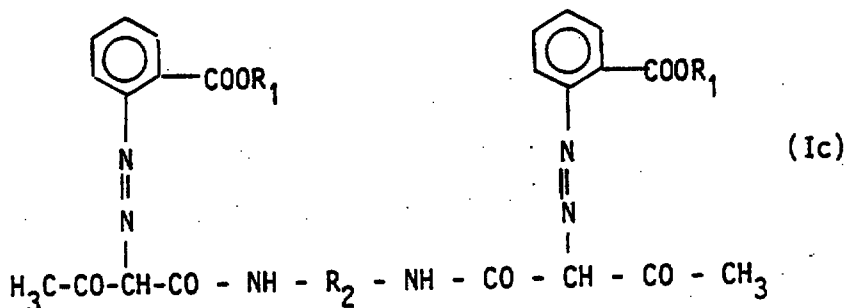
DISAZO PIGMENT MIXTURES

The invention relates to mixtures of azo pigments, particularly for mass pigmenting polymeric material.

According to the invention there is provided a mixture
5 comprising the following azo pigments of formulae



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in which each R_1 , independently, is C_{1-4} alkyl
each R_2 , independently, is 1,4-phenylene; 1,4-phenylene substituted by up to two substituents selected from one or two chlorine, bromine, methyl and methoxy and one trifluoromethyl and nitro;
4,4'-diphenylene substituted in the 3 and/or 3' positions by up to two substituents selected from chlorine, bromine, methyl and methoxy; or 1,4- or 1,5-naphthylene

the mixture containing from 8 to 20% mole of benzoic acid ester residues and from 92 to 80% mole of terephthalic acid ester residues.

Any alkyl as R_1 may be linear or branched. Preferably R_1 is methyl or ethyl.

When R_2 is substituted 1,4-phenylene, it is preferably substituted by up to two substituents selected from chlorine, methyl and methoxy.

When R_2 is substituted 4,4'-diphenylene, it is preferably a radical in which each phenyl ring bears a substituent. Preferred substituents are chlorine, methyl and methoxy. More preferably, the 4,4'-diphenylene group as R_2 bears 2 identical substituents located in the positions 3 and 3'.

R_2 is preferably R_2' , where R_2' is unsubstituted 1,4-phenylene; 1,4-phenylene substituted by up to two substituents selected from

chlorine, methyl and methoxy; 3,3'-dichloro-4,4'-diphenylene; 3,3'-dimethyl-4,4'-diphenylene, 3,3'-dimethoxy-4,4'-diphenylene; and unsubstituted 1,5-naphthylene. More preferably R_2 is R_2'' , where R_2'' is 1,4-phenylene.

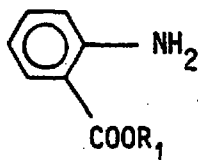
5 In the mixture of the invention, the groups R_1 and the groups R_2 , respectively, may be identical or different. Preferably all groups R_1 are identical and all groups R_2 are identical.

10 Preferably the mixture of the invention contains from 8 to 12% mole benzoic acid ester residues and from 92 to 88% mole terephthalic acid ester residues.

15 Preferred mixtures of the invention are those containing compounds of formulae Ia, Ib and Ic in which the R_1 's are either methyl or ethyl and the R_2 's have one of the significances given above for R_2' , the % mole ratios of the benzoic acid ester residues and of the terephthalic acid ester residues being as already indicated.

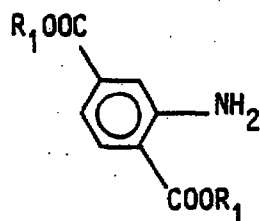
20 More preferred mixtures of the invention are those containing compounds of formulae Ia, Ib and Ic in which the R_1 's are either methyl or ethyl and the R_2 's are R_2'' , said mixtures containing from 8 to 12% mole benzoic acid ester residues and from 92 to 88% mole terephthalic acid ester residues.

The mixtures of the invention may be prepared by coupling a mixture of the diazo derivatives of an amine of formula IIa



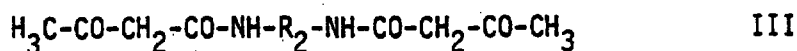
IIa

and of an amine of formula IIb



IIb

in which each R₁, independently, is as defined above,
with a compound of formula III



in which R₂ is as defined above
or a mixture thereof

5 in a mole ratio IIa:IIb:III of from 0.8-2:8-9.2:5.

Diazotization and coupling may be carried out according to known methods.

The compounds of formulae IIa, IIb and III are known.

10 Before use, the mixture of the invention can be after-treated according to known methods, e.g. treated in an organic solvent having a high boiling point such as dimethylformamide or 1,2-dichlorobenzene.

15 The mixture of the invention is useful for pigmenting in the mass synthetic polymers or synthetic resins such as polyethylene, polypropylene, polystyrene, polyvinyl chloride, synthetic leather and rubber latices, in the presence or absence of solvents. The resulting pigmentations have good all-round fastness properties, more particularly good light fastness.

20 The mixture of the invention has a high tinctorial depth. In addition to these properties, the mixture of the invention is characterized by a high dispersibility. Owing to this dispersion ability in polymeric materials, the mixture is particularly useful for spin dyeing in the mass of synthetic polymers, preferably polypropylene. Of particular interest is that the re-
25 sulting mass-pigmented shaped articles, particularly poly-



propylene fibres, have an improved tensile strength.

5 The mass pigmenting of polymeric materials with the mixture of the invention, particularly spin dyeing may be carried out according to known methods. Spin dyeing in the mass is preferably effected using the master-batch procedure.

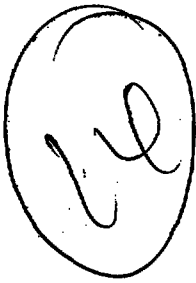
In the following Examples which illustrate the invention, the parts and percentages are by weight so far as not otherwise indicated and the temperatures in degrees Centigrade.

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Example 1

- 5 a) 76.0 Parts 2-aminoterephthalic acid dimethyl ester and 6.1 parts anthranilic acid methyl ester are stirred with 100 parts water and 100 parts (by volume) concentrated hydrochloric acid for 4 hours. After cooling to 0° by the addition of 125 parts ice and using a water/ice cooling bath, 105 parts (by volume) of a 4N sodium nitrite solution are added to the mixture and the whole is further stirred for one hour at 0-5°. Thereafter the excess nitrous acid is destroyed with a small amount of amino-sulphonic acid. The mixture is then filtered to remove the small amounts of impurities which are present.
- 10
- b) 55.2 Parts 1,4-bis-(acetoacetylamino)-benzene are dissolved at approx. 50° in 400 parts water and 60 parts (by volume) 30% sodium hydroxide and the resulting mixture is then filtered.
- 15
- c) The diazo solution obtained in a) is diluted with 1000 parts water and 600 parts ice and adjusted to pH 4.0 with a sodium acetate solution. To this solution there is added the solution obtained in (b), over the course of approx. 30 minutes. The resulting lemon yellow suspension is further stirred for 2 hours at 5-10°, one hour at 40-45° and one hour at 80-85°. The mixture is then filtered and the filtration cake is washed salt free with water, dried and ground.
- 20
- 25 The resulting pigment mixture gives yellow pigmentations with good fastness properties.

30 When replacing in the above procedure the 1,4-bis-(acetoacetylamino)-benzene by an equivalent amount of a corresponding derivative substituted in the benzene nucleus either by methyl, methoxy or chlorine, pigments are obtained which give reddish, orange or yellow-greenish pigmentations, respectively.



Example 2

5 A pigment concentrate is formed in an extruder with 70 parts commercially available low molecular weight polyethylene and 30 parts of the pigment mixture obtained in c) above. This concentrate is then added at a ratio of 1:50 to commercially available polypropylene and the resulting pigmented mass is spun according to known methods.

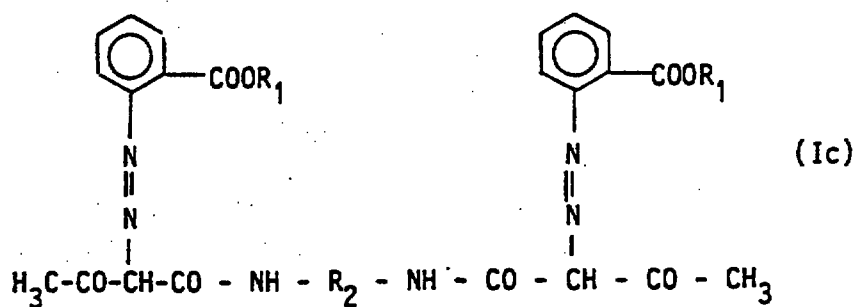
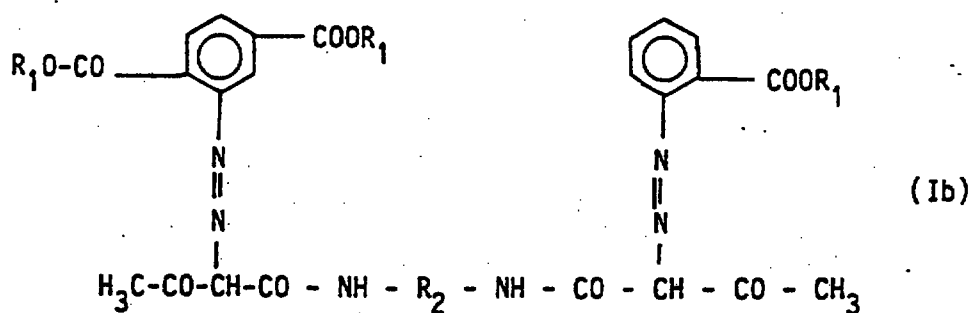
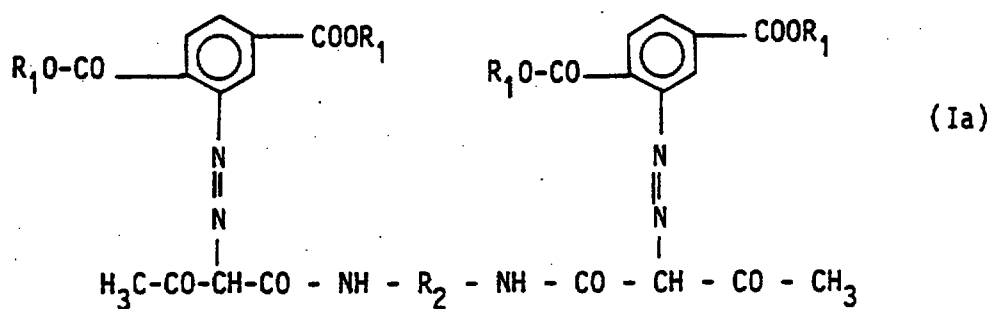
The resulting fibres have a good tensile strength.

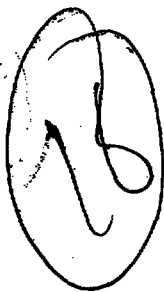
10 The pigment concentrate can also be added at a ratio of 1:50 to polyethylene and the resulting pigmented mass is then formed into blown films which have a good tensile strength.

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Claims

1. A mixture of azo pigments of formulae





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in which each R_1 , independently, is C_{1-4} alkyl

each R_2 , independently, is 1,4-phenylene; 1,4-phenylene substituted by up to two substituents selected from one or two chlorine, bromine, methyl and methoxy and one trifluoromethyl and nitro; 4,4'-diphenylene substituted in the 3 and/or 3' positions by up to two substituents selected from chlorine, bromine, methyl and methoxy; or 1,4- or 1,5-naphthylene

5

10 the mixture containing from 8 to 20% mole of benzoic acid ester residues and from 92 to 80% mole of terephthalic acid ester residues.

2. A mixture of azo pigments according to Claim 1, in which each R_1 is methyl or ethyl.

15

3. A mixture of azo pigments according to Claim 1 or 2, in which each R_2 is R'_2 , where R'_2 is unsubstituted 1,4-phenylene; 1,4-phenylene substituted by up to two substituents selected from chlorine, methyl and methoxy; 3,3'-dichloro-4,4'-diphenylene; 3,3'-dimethyl-4,4'-diphenylene, 3,3'-dimethoxy-4,4'-diphenylene; and unsubstituted 1,5-naphthylene.

20

4. A mixture of azo pigments according to any one of the preceding claims, containing from 8 to 12% mole benzoic acid ester residues and 92 to 88% mole terephthalic acid ester residues.

25

5. A mixture of azo pigments according to Claim 1, in which the R_1 's are methyl or ethyl and the R_2 's have one of the significances given for R'_2 in Claim 3, the mixture containing from 8 to 12% mole benzoic acid ester residues and 92 to 88% mole terephthalic acid ester residues.

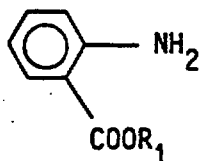
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6. A mixture of azo pigments according to Claim 5, in which the R_1 's are methyl or ethyl and the R_2 's are 1,4-phenylene, the mixture containing from 8 to 12% mole benzoic acid ester residues

and 92 to 88% mole terephthalic acid ester residues.

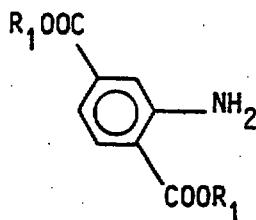
7. A mixture of azo pigments substantially as described hereinbefore with reference to Example 1.

8. A process for the production of a mixture of azo pigments of formulae Ia, Ib and Ic as stated in Claim 1, comprising coupling
5 a mixture of the diazo derivatives of an amine of formula IIa



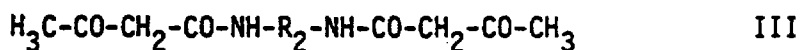
IIa

and of an amine of formula IIb



IIb

in which each R_1 , independently, is as defined above,
with a compound of formula III



10 in which R_2 is as defined above

or a mixture thereof

in a mole ratio IIa:IIb:III of from 0.8-2:8-9.2:5.

9. A process for pigmenting in the mass synthetic polymers or resins, in the presence or absence of solvents, comprising
15 using a mixture of compounds of formulae Ia, Ib and Ic according to any one of Claims 1 to 7.

10. A process according to Claim 9 in which the polymer is polypropylene which is spun in the mass.



11. A process for pigmenting synthetic polymers or resins in the mass, substantially as described hereinbefore with reference to Example 2.

12. A synthetic polymer or resin whenever pigmented by a mixture according to any one of Claims 1 to 7 or by a process according to any one of Claims 9 to 11.

