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(71) Applicant *(for all designated States except US)*: **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **RUIZ GOMEZ, Gloria** [ES/FR]; 3, rue des Violettes de Tassigny, F-68220 Hésingue (FR). **VEITH, Ulrich** [DE/CH]; Saffretweg 7b, CH-4143 Dornach (CH). **CUONY, Bruno** [CH/CH]; Kaspar Pfeifferstr. 15, CH-4142 Münchenstein (CH). **POWELL, Jon** [GB/DE]; Fridolinsgasse 4, 79540 Lörrach (DE). **BOEHRINGER, Guillaume** [FR/FR]; 46 rue de Blotzheim, F-68220 Hésingue (FR). **EWALD, Raymond** [US/US]; 205 St. James Street, Newport, DE 19804 (US). **BUGNON, Philippe** [CH/CH]; Impasse des Rosiers 4, Essert, CH-1724 Le Mouret (CH).

(74) Agent: **LINDNER, Dr. Anton**; BASF Schweiz AG, - IP Department -, P.O. Box, CH-4002 Basel (CH).

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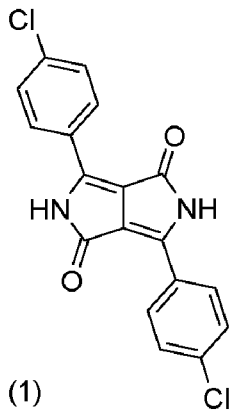
(54) **Title**: PIGMENT COMPOSITION FOR MASS COLOURATION OF ALIPHATIC POLYAMIDE



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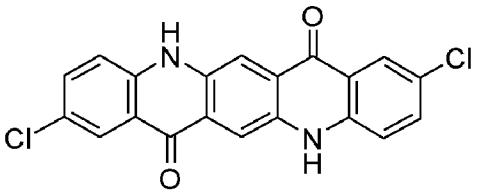

(2)

(57) **Abstract**: Pigment composition for mass colouration of aliphatic polyamide Abstract The invention relates to a process for mass colouration of a composition containing an aliphatic polyamide, which process comprises - incorporation of a pigment mixture containing a pigment of formula (1), (1), and a pigment of formula (2), (2), wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, and - heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C.

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Pigment composition for mass colouration of aliphatic polyamide

Description

Pigments are used in mass colouration of polymers. Mass colouration of thermoplastic polymers is typically performed at elevated temperatures above 180°C, when the polymer softens and a homogenous distribution of the pigments in the viscous polymer melt is facilitated.

EP-A-0794235 discloses a physical mixture of 3,6-di-(4'-chlorophenyl)-1,4-diketopyrrolo-[3,4-c]-pyrrole and 2,9-dichloroquinacridone.

US 5529623 discloses a ternary solid solution of 3,6-di-(4'-chlorophenyl)-1,4-diketo-pyrrolo-[3,4-c]-pyrrole, 3,6-diphenyl-1,4-diketo-pyrrolo-[3,4-c]-pyrrole and 2,9-dichloroquinacridone.

EP-A-0277914 discloses solid solution mixtures of 1,4-diketo-pyrrolo-[3,4-c]-pyrroles with quinacridones, which are applied inter alia for mass colouration of high molecular weight organic material.

US 4810304 is a continuation-in-part, which is related to EP-A-0277914, and discloses solid solution mixtures of 1,4-diketo-pyrrolo-[3,4-c]-pyrroles with quinacridones, which are applied for mass colouration of high molecular weight organic material.

EP-A-0737723 discloses the application of a physical mixture of 3,6-di(4-biphenyl)-1,4-diketopyrrolo-[3,4-c]-pyrrole and 2,9-dichloroquinacridone, which is applied for mass colouration of high molecular weight organic material.

US 6494947 discloses the application of a physical mixture of 3,6-di(4'-chlorophenyl)-1,4-diketopyrrolo-[3,4c]-pyrrole and 2,9-dichloroquinacridone in a printing ink and refers inter alia also to mass colouration of high molecular weight organic material.

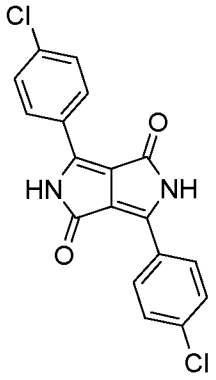
Some specific polymers are known to be critical substrates in regard to mass colouration. For example at polyamide, the chemical stability of many pigments suffers, which is believed to be caused by the strongly reducing conditions in heated polyamide. Accordingly, the mass-colouration of polyamide is still a problem in regard to the stability of the colouration during the heating of the polyamide, which is required for processing polyamide from pellets into articles like fibres.

It has now been found that the process for mass colouration according to the invention surprisingly meet the above-mentioned heat stability criteria during processing of aliphatic polyamide to a larger extent.

The present invention relates to a process for mass colouration of a composition containing an aliphatic polyamide, which process comprises

- incorporation of a pigment mixture containing

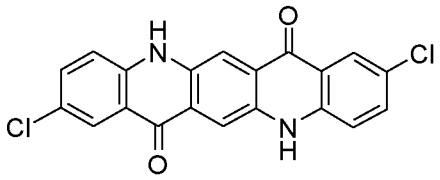
a pigment of formula (1)



(1)

and

a pigment of formula (2)



(2)

,

wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, and

- heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C.

Aliphatic polyamide is obtainable from a polycondensation reaction.

In contrast, there are many polymers, which are obtainable by radical polymerisation of ethylenic unsaturated derivatives. Examples are polyolefins, such as polyethylene, polypropylene, polybutene, polystyrene, polyacrylates, such as polymethylacrylate, polymethacrylates, such as polymethylmethacrylate, polyvinylchloride, polyvinylalcohol, polybutadiene and polyacrylonitrile. Co-polymers are also comprised, i.e. poly(ethylene-co-vinylacetate), poly(ethylene-co-hex-1-ene), poly(styrene-co-butadiene) and poly(styrene-co-butylacrylate).

Preferred is a process for mass colouration of a composition, wherein the composition is free of polypropylene.

Preferred is a process for mass colouration of a composition, wherein the composition is free of polyvinylchloride.

Preferred is a process for mass colouration of a composition, wherein the composition is free of polypropylene and polyvinylchloride.

Preferred is a process for mass colouration of a composition, wherein the composition is free of polymers, which are obtainable by radical polymerisation of ethylenic unsaturated derivatives.

The aliphatic polyamide as defined herein can have for example a molecular weight in the range from 10^4 g/mol to 10^8 g/mol, in particular from 10^5 g/mol to 10^7 g/mol and especially from $3x10^5$ g/mol to 10^7 g/mol.

An aliphatic polyamide, which transforms at elevated temperatures from a solid into a viscous liquid state and solidifies again once cooled down, is defined herein as a thermoplastic aliphatic polyamide. Under the application of pressure, the heated aliphatic polyamide can be formed, for example in an extruder.

Preferred is a process for mass colouration of a composition, wherein the aliphatic polyamide is thermoplastic.

An aliphatic polyamide is for example obtainable

from polycondensation of a diamine of formula (aI)

$$H_2N-X-NH_2 \quad (aI),$$

wherein

X is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

and of a dicarboxylic acid of formula (aII)

$$HOOC—Y-COOH \quad (aII),$$

wherein

X is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1;

from polycondensation of an aminocarboxylic acid of formula (aIII),

$$H_2N-Z-COOH \quad (aIII)$$

wherein

Z is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

or

from polycondensation of a diamine of formula (aI), a dicarboxylic acid of formula (aII) and an aminocarboxylic acid of formula (aIII);
wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1.

A molar ratio close to 1 as defined herein is for example in a range from 0.9 to 1.1, in particular from 0.95 to 1.05 and especially from 0.97 to 1.03.

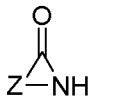
C_2-C_{12}-alkylene is for example ethylene, 1,3-propylene, 1-methylethyl-1,2-diyl, 1,4- butylene, 1,2-butylene, 2-methylpropyl-1,3-diyl, 1,5-pentylene, 1,6-hexylene [= hexamethylene], 1,7-heptylene, 1,8-octylene, 1,9-nonylene, 1,10-decylene, 1,11-undecylene and 1,12-dodecylene.

C_5-C_{12}-cycloalkylene is for example cyclopentane-1,2-diyl, cyclopentane-1,3-diyl, cyclohexane-1,2-diyl, cyclohexane-1,3-diyl, cyclohexane-1,4-diyl, cycloheptane-1,2-diyl and cyclo-octane-1,2-diyl.

C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene) is for example 1,2-bis(methylene)cyclopentane [= 1,2-dimethylcyclopentane-1',1''-diyl], 1,2-bis(methylene)cyclohexane [= 1,2-dimethylcyclohexane-1',1''-diyl], 1,3-bis(methylene)cyclohexane [= 1,3-dimethylcyclohexane-1,1''-diyl], 1,4-bis(methylene)cyclohexane [= 1,4-dimethylcyclohexane-1',1''-diyl], 1,2-bis(methylene)cycloheptane, 1,5-bis(methylene)cyclooctane.

Dicarboxylic acids can also be partly or completely in their cyclic anhydride form, if a 5- or 6-atom ring formation is sterically possible.

Aminocarboxylic acids of formula (aIII) can also be partly or completely in the form of their corresponding lactam form of formula (aIII-r), if a 3-, 4-, 5-, 6- or 7-atom ring formation is possible.



(aIII-r)

An aliphatic polyamide can be defined herein as a polyamide, which is obtainable from a polycondensation, wherein
- in a compound of formula (aI), X is free of an aromatic moiety and in a compound of formula (aII), Y is free of an aromatic moiety,
- in a compound of formula (aIII), Z is free of an aromatic moiety, or
- in the case of an aliphatic polyamide, which is obtainable from polycondensation of a compound of formula (aI), a compound of formula (aII) and a compound of formula (aIII), X, Y and Z are free of an aromatic moiety.

An aromatic polyamide can be defined herein as a polyamide, which is obtainable from a polycondensation, wherein
- in a compound of formula (al), X contains an aromatic moiety or in a compound of formula (all), Y contains an aromatic moiety,
- in a compound of formula (alll), Z contains an aromatic moiety, or
- in the case of an aromatic polyamide, which is obtainable from polycondensation of a compound of formula (al), a compound of formula (all) and a compound of formula (alll), at least one of X, Y or Z contains an aromatic moiety.

Preferred is a process for mass colouration of a composition, wherein the composition is free of an aromatic polyamide.

Examples for aliphatic polyamides are

- polyamide-4 (polycondensation of a compound of formula alll with Z = 1,3-propylene), polyamide-6 (polycondensation of a compound of formula alll with Z = 1,5-pentylene), polyamide-10 (polycondensation of a compound of formula alll with Z = 1,9-nonylene), polyamide-11 (polycondensation of a compound of formula alll with Z = 1,10-decylene), polyamide-12 (polycondensation of a compound of formula alll with Z = 1,11-undecylene),
- polyamide-4.6 (polycondensation of a compound of formula al with X = 1,4-butylene and of a compound of formula all with Y = 1,4-butylene), polyamide-6.6 (polycondensation of a compound of formula al with X = 1,6-hexylene and of a compound with formula all with Y = 1,4-butylene) [= polyhexamethyleneadipinamide], polyamide-6.10 (polycondensation of a compound of formula al with X = 1,6-hexylene and of a compound of formula all with Y = 1,8-octylene) [= polyhexamethylenesebacinamide], polyamide-6.12 (polycondensation of a compound of formula al with X = 1,6-hexylene and of a compound of formula all with Y = 1,10-decylene) [= polyhexamethylenedodecanamide], polyamide-12.12 (polycondensation of a compound of formula al with X = 1,12-dodecylene and of a compound of formula all with Y = 1,10-decylene),
- polyamide-6.6/6 (polycondensation of a compound of formula al with X = 1,6-hexylene [= hexane-1,6-diamine], of a compound of formula all with Y = 1,4-butylene [= adipic acid] and of a compound of formula alll with Z = 1,5-pentylene [= ε-caprolactam]), polyamide-6.10/6 (polycondensation of a compound of formula al with X = 1,6-hexylene [= hexane-1,6-diamine], of a compound of formula all with Y = 1,8-octylene [= decanedioic acid] and of a compound of formula alll with Z = 1,5-pentylene [= ε-caprolactam]), polyamide-6.12/6 (polycondensation of a compound of formula al with X = 1,6-hexylene [= hexane-1,6-diamine], of a compound of formula all with Y = 1,10-decylene [= 1,12-dodecanedioic acid] and of a compound of formula alll with Z = 1,5-pentylene [= ε-caprolactam]), polyamide-6.6/6 (80:20) (polycondensation of a compound of formula al with X = 1,6-hexylene [= hexane-1,6-diamine], of a

compound of formula aII with Y = 1,4-butylene [= adipic acid] and of a compound of formula aIII with Z = 1,5-pentylene [= ε-caprolactam], wherein the molar ratio of compound of formula I : compound of formula II : compound of formula III = 80 : 80 : 20).

Preferred is a process for mass colouration, wherein the aliphatic polyamide is obtainable

from polycondensation of a diamine of formula (aI)

$$H_2N-X-NH_2 \quad (aI),$$

wherein

X is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

and of a dicarboxylic acid of formula (aII)

$$HOOC—Y-COOH \quad (aII),$$

wherein

X is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1;

from polycondensation of an aminocarboxylic acid of formula (aIII),

$$H_2N-Z-COOH \quad (aIII)$$

wherein

Z is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

or

from polycondensation of a diamine of formula (aI), a dicarboxylic acid of formula (aII) and an aminocarboxylic acid of formula (aIII);

wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1.

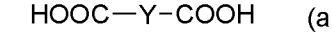
Preferred is a process for mass colouration, wherein the aliphatic polyamide is obtainable

from polycondensation of a diamine of formula (aI)

$$H_2N-X-NH_2 \quad (aI),$$

wherein

X is 1,6-hexylene;
and of a dicarboxylic acid of formula (aII)



(aII),

wherein
X is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);
wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1;

from polycondensation of an aminocarboxylic acid of formula (aIII),

(aIII)

wherein
Z is 1,6-hexylene;

or

from polycondensation of a diamine of formula (aI), a dicarboxylic acid of formula (aII) and an aminocarboxylic acid of formula (aIII);
wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1.

Preferred is a process for mass colouration of a composition, wherein the aliphatic polyamide is selected from the group consisting of polyamide-6, polyamide-6.6, polyamide-6.10, polyamide-6.12, polyamide-6.6/6, polyamide-6.10/6 and polyamide-6.12/6.

The pigment mixture containing a pigment of formula (1) and a pigment of formula (2) can be incorporated into the composition containing an aliphatic polyamide for example by mixing the pigment mixture into the composition containing the aliphatic polyamide using roll mills or mixing or grinding instruments. As a result, the pigments are finely distributed in the composition containing the aliphatic polyamide. The composition containing the aliphatic polyamide and the pigment mixture is then heated to a temperature in the range from 180°C to 350°C. It can be further processed by methods known *per se*, such as calendering, compression moulding, extrusion, melt-spinning, casting or by injection moulding, whereby the composition acquires typically its final shape as an article. Admixture of the pigment mixture can also be effected immediately prior to the actual heating step, for example by continuously feeding a solid, for example pulverulent pigment mixture and, at the same time, a granulated or powdered composition containing the aliphatic polyamide. Optionally, additional ingredients such as, for example, additives, can be fed directly into the intake zone of the processing equipment, where mixing takes place immediately before or during heating. The heating and the

processing can occur at the same time. A crosslinking of the aliphatic polyamide in the composition may also be effected or completed at this stage. Generally, however, it is preferable to mix the pigment mixture into the composition containing the aliphatic polyamide beforehand, since more uniformly mass-coloured articles can be achieved.

It is also possible that the process for mass colouration includes two heating steps with processing. For example, in a first step, the composition is heated and processed, for example extruded, to obtain pellets or granules. In a second step, these pellets or granules are heated again and processed, for example extruded, into the desired final article. Typically, the second step occurs under higher thermal and mechanical stress. A typical second heating and processing step is example melt extrusion, for example injection moulding and melt fibre spinning.

Preferred is a process for mass colouration of a composition, wherein the heated composition with the pigment mixture containing compounds of formulae (1) and (2) is extruded.

Preferred is a process for mass colouration of a composition, wherein the heated composition is extruded at injection moulding or at melt fibre spinning.

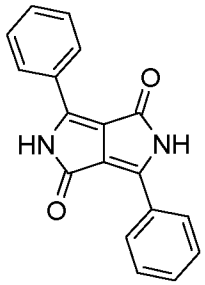
Typically, the composition with the pigment mixture is heated to a temperature in the range from 180°C to 350°C, in particular in the range of 200°C to 330°C and especially in the range of 240°C to 320°C. A range of 240°C to 300°C, in particular from 240°C to 290°C, can be preferable.

Preferred is a process for mass colouration of a composition, wherein the temperature is in the range from 200°C to 330°C.

Preferred is a process for mass colouration of a composition, wherein the temperature is in the range from 200°C to 330°C and the composition with the pigment mixture is extruded.

The weight ratio of the pigment of formula (1) and of the pigment of formula (2) is from 9 to 1, i.e. in the range from 9 parts pigment of formula (1) and 1 part pigment of formula (2) to 1 part pigment of formula (1) and 1 part of pigment of formula (2). Preferable, the weight ratio of the pigment of formula (1) and of the pigment of formula (2) is from 4 to 1, especially from 2 to 1 and very especially from 2.0 to 1.3.

Preferred is a process for mass colouration of composition, wherein the pigment mixture, which is incorporated, contains pigments of formulae (1) and (2) and a further pigment of formula (3)



(3)

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wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 4 to 1, and

wherein a pigment of formula (3) is present in a range of 5 to 35% based on the combined weight of the pigments of formulae (1) and (2).

Preferred is a range of 15 to 25% of a pigment of formula (3) based on the combined weight of the pigments of formulae (1) and (2).

Preferred is a process for mass colouration of a composition, wherein the pigment mixture, which is incorporated, contains pigments of formulae (1) and (2) and a further pigment of formula (3),

wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 2 to 1, and

wherein a pigment of formula (3) is present in a range of 15 to 25% based on the combined weight of the pigments of formulae (1) and (2).

Preferred is a process for mass colouration of a composition containing an aliphatic polyamide, which comprises

- incorporation of a pigment mixture containing
  a pigment of formula (1) and a pigment of formula (2),
  wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, and
- heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C,

wherein the composition with the pigments of formulae (1) and (2) is free of a further pigment.

The overall amount of pigments incorporated into the composition, which is mass-coloured, can be from 0.01% to 60% based on the weight of the aliphatic polyamide, in particular from 0.05% to 30%. Preferred is a range from 0.05% to 10% in the case of a mass-coloured final article, especially from 0.05% to 1%.

A masterbatch is employed as a pigment concentrate foreseen for pigment dilution during a further processing step. Preferred is a range for the overall amount of pig-

ments from 30% to 60% by weight of the aliphatic polyamide in the case of a masterbatch.

Preferred is a process for mass colouration of a composition, wherein the overall amount of pigments is from 0.05% to 30% based on the weight of the aliphatic polyamide.

Glass fibres or other reinforcing agents can be incorporated to increase the rigidity and / or solidity of the shaped article. Typically, they can be present in the composition containing an aliphatic polyamide prior to the incorporation of the pigment mixture. Glass fibres or other reinforcing agents can be present in a range from 5% to 75% based on the weight of the aliphatic polyamide, in particular from 10% to 65% and especially from 10% to 45%.

Preferred is a process for mass colouration of a composition, wherein the composition contains glass fibres in a range from 5% to 75% based on the weight of the aliphatic polyamide.

In order to produce non-rigid articles, for example by moulding, or to reduce their brittleness, it is possible to incorporate so-called plasticisers into the composition, which is mass-coloured by the process. Typically, the plasticisers may be incorporated into the composition before or after incorporation of the pigment mixture. Examples for plasticisers are esters of phosphoric acid, phthalic acid or sebacic acid.

Further pigments, which are different to those of formulae (1), (2) or (3), or other colourants can be added to the composition in order to achieve a different colour shade. Preferably, the amount of such a further shading dye is below 10% based on the combined weight of the pigments of formulae (1) and (2), in particular below 4% and especially below 2%.

Optionally, the composition, which is mass-coloured by the process, contains further additional ingredients such as, for example, siccatives (drying agents), waxes, carboxylic acid metal salts like magnesium stearate, stabilizers like antioxidants or a copper-containing stabilizer system.

Typically, the weight content of the aliphatic polyamide prior to the incorporation of pigments of formula (1) and (2) is in the range from 60% to 100% based on the weight of the composition less the weight content of optional glass fibres or other reinforcing agents. In particular, the range is from 80% to 100% and especially from 90% to 100%.

Preferred is a process for mass colouration of a composition containing an aliphatic polyamide,

wherein the content of the aliphatic polyamide prior to the incorporation of the pigment mixture containing a pigment of formula (1) and a pigment of formula (2) is in the range from 60% to 100% based on the weight of the composition less the weight content of optional glass fibres or other reinforcing agents.

In general, if a mixture of pigments, after a special treatment or a special preparation, shows an X-ray diffraction pattern that differs form the X-ray diffraction pattern of a mere physical mixture of its single components, said special pigment mixture is called a solid solution. There are mainly two types of clearly-defined solid solutions, a 'guest-host' type solid solution and a 'solid compound' type solid solution. The concept is explained in more detail in EP-A-0704496, especially at page 2, columns 1, line 55 to column 2, line 26.

Quinacridone solid solutions and compounds are described in US 3160510.

Solid solutions containing a pigment of the 1,4-diketo-pyrrolo-[3,4-c]-pyrrole type and a pigment of another class, for example a pigment of the quinacridone type, are described in US 4783540.

A ternary solid solution of a pigment of formula (1), formula (2) and formula (3) is described in EP-A-0704496 at example 5.

The special treatment to obtain a solid solution from a physical mixture can be an intensive milling process, an acidic or basic re-precipitation or sometimes a special synthetic process. In any case, this means an additional effort.

It has been surprisingly found, that in the case of an aliphatic polyamide, it does not matter whether the applied mixture of a pigment of formula (1) and a pigment of formula (2) is in the form of a physical mixture or in the form of a solid solution. Equally, it does not matter for the mixture of a pigment of formula (1), a pigment of formula (2) and a pigment of formula (3).

Preferred is a process for mass colouration of a composition containing an aliphatic polyamide, which process comprises
- incorporation of a pigment mixture containing a pigment of formula (1) and a pigment of formula (2),
wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, and
- heating of the composition with the pigment mixture to a temperature in the range form 180°C to 350°C,
wherein the pigment of formula (1) and the pigment of formula (2) are not in the form of a solid solution, when they are incorporated into the composition.

Preferred is a process for mass colouration of a composition containing an aliphatic polyamide, which process comprises
- incorporation of a pigment mixture containing a pigment of formula (1), a pigment of formula (2) and a pigment of formula (3),
wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 4 to 1,
wherein a pigment of formula (3) is present in a range of 5 to 35% based on the combined weight of the pigments of formulae (1) and (2), and
- heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C,
wherein the pigment of formula (1), the pigment of formula (2) and the pigment of formula (3) are not in the form of a solid solution, when they are incorporated into the composition.

In an aliphatic polyamide, a copper-containing stabilizer system can be present.

A copper-containing stabilizer system contains a copper compound soluble in the aliphatic polyamide and an alkali metal halide. In particular, the stabilizer system consists essentially of a copper-(I) salt, for example cuprous acetate, cuprous stearate, a cuprous organic complex compound such as copper acetylacetonate, a cuprous halide or the like, and an alkali metal halide. Preferably, the stabilizer system consists essentially of a copper halide selected from copper iodide and copper bromide and an alkali metal halide selected from the group consisting of the iodides and bromides of lithium, sodium and potassium. The weight ratio of the alkali metal halide to copper-(I) halide is preferably in the range from 2.5 to 20, in particular in the range from 8 to 10.

The amount of the copper-containing stabilizer system, i.e. the combined weight of the copper compound and the alkali metal halide can be from 0.01 to 2% based on the weight of the aliphatic polyamide, in particular from 0.01 to 1%.

Copper-(I) iodide and potassium iodide can be used as a copper-containing stabilizer system for aliphatic polyamide, especially if the aliphatic polyamide is selected from the group consisting of polyamide-6, polyamide-6.6, polyamide-6.10, polyamide-6.12, polyamide-6.6/6, polyamide-6.10/6 and polyamide-6.12/6.

A composition containing an aliphatic polyamide is defined herein as containing a copper-containing stabilizer system, if the amount of copper atoms is between 50 and 1000 ppm based on the weight of the aliphatic polyamide, in particular between 50 and 400 ppm and especially between 100 and 200 ppm.

A composition containing an aliphatic polyamide is defined herein as free of a copper-containing stabilizer system, if the amount of copper atoms is below 10 ppm based on the weight of the aliphatic polyamide.

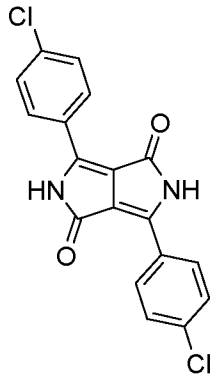
In the presence of a copper-containing stabilizer system in aliphatic polyamide, the combination of a pigment of formula (1) and a pigment of formula (2) can result in a very preferable heat stability at the process of mass-colouration of the composition, which contains the aliphatic polyamide.

An example is a process for mass colouration of a composition containing an aliphatic polyamide and a copper-based stabilizer system, which process comprises
- incorporation of a pigment mixture containing pigment of formula (1) and a pigment of formula (2),
wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, and
heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C,
wherein the heated composition is free of a pigment of formula (3).

An example is a process for mass colouration of a composition containing an aliphatic polyamide, which process comprises
- incorporation of a pigment mixture containing a pigment of formula (1), a pigment of formula (2) and a pigment of formula (3),
wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 4 to 1,
wherein a pigment of formula (3) is present in a range of 5 to 35% based on the combined weight of the pigments of formulae (1) and (2), and
- heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C,
wherein the composition is free of a copper-containing stabilizer system.

The invention as defined herein comprises further embodiments, for which the above described preferences for a process for mass colouration of a composition apply equally.

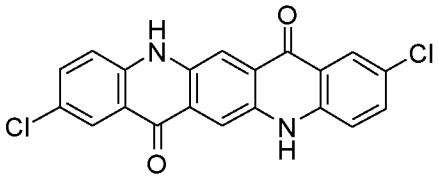
A further embodiment of the invention is a composition, which is mass-coloured by a process, which process comprises
- incorporation of a pigment mixture containing a pigment of formula (1) and (2), and
- heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C, comprising
(a) an aliphatic polyamide,
(b) a pigment of formula (1)



(1)

, and

(c) a pigment of formula (2)



(2)

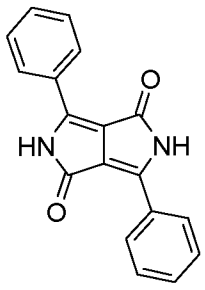
,

wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1.

A further embodiment of the invention is a composition, which is mass-coloured by a process, which process comprises

- incorporation of a pigment mixture containing a pigment of formula (1) and (2), and
- heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C, comprising

(a) an aliphatic polyamide,
(b) a pigment of formula (1),
(c) a pigment of formula (2), and
(d) a pigment of formula (3)



(3)

,

wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 4 to 1, and

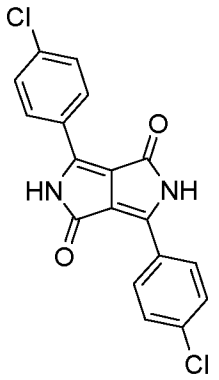
wherein a pigment of formula (3) is present in a range of 5% to 35% based on the combined weight of the pigments of formulae (1) and (2).

A further embodiment of the invention is an article made of a composition, which is mass-coloured by a process as defined above. Examples for articles are on one side

pellets, granules and powder. On the other side, examples of articles are fibres for carpets or yarns, which result from melt-spinning. Or the articles are for example consumer durable electricals & electronics (E&E), power tools and automotive parts, which result for example from injection-moulding.

A further embodiment of the invention is a method for heat stabilisation of a pigmented mass-coloured composition containing an aliphatic polyamide, which comprises the incorporation of a pigment mixture containing a pigment of formula (1) and a pigment of formula (2),
wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1,
into the composition and the heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C.

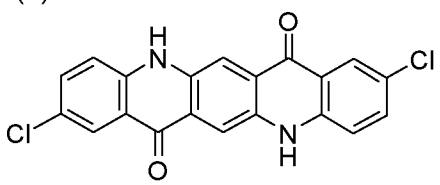
A further embodiment of the invention is a composition comprising
(a) an aliphatic polyamide,
(b) a pigment of formula (1)



(1)

, and

(c) a pigment of formula (2)

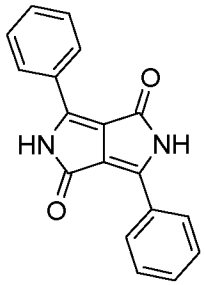


(2)

,

wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1.

Preferred is a composition comprising
(a) an aliphatic polyamide,
(b) a pigment of formula (1),
(c) a pigment of formula (2), and
(d) a pigment of formula (3)



(3)

,

wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 4 to 1, and

wherein a pigment of formula (3) is present in a range of 5% to 35% based on the combined weight of the pigments of formulae (1) and (2).

A further embodiment is an article made of a composition, which contains

(a) an aliphatic polyamide,

(b) a pigment of formula (1), and

(c) a pigment of formula (2),

wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1.

A further embodiment of the invention is the use of a pigment mixture containing a pigment of formula (1) and a pigment of formula (2), wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, for a heat-stable mass-coloration of a composition containing an aliphatic polyamide.

In the examples, the following materials are used.

Commercially available C.I. Pigment Red 254 of formula (1) without other additives, i.e. Irgazin Red 2030 (RTM, BASF), is used.

Commercially available C.I. Pigment Red 202 of formula (2) without other additives is used.

A solid solution of C.I. Pigment Red 254 (48% by weight), C.I. Pigment Red 255 (32% by weight) and C.I. Pigment Red 202 (20% by weight) is used. The solid solution can be prepared according to example 5 at US 5529623.

Measurement of colour

dE* is a measure for colour difference in the CIELAB system and is described for example in 'Industrial colour testing, fundamentals and techniques', Hans G. Voelz, Wiley-VCH, Weinheim, Germany, 2001 (2nd edition).

Plaques for colour testing

All plaques for colour testing have been moulded in a 30mm x 55 mm x 1.5 mm injection tool equipped with a film gate.

Example 1

- comparative -

2 g of Irgazin Red 2030 and 1000 g of Ultramid B3K (polyamide-6, RTM, BASF) are dry-mixed in a tumble mixer for 20 minutes. The mixture is extruded in a twin-screw extruder at 220ºC. The resultant pellets are processed on an injection moulding machine at 240°C, 260°C, 280°C and 300 ºC to give plaques measuring 55 mm x 30 mm x 1.5 mm. Following injection moulding, the plaques are thermally conditioned in an oven at 75ºC for one week and stored at room temperature for at least 15 hours. Finally, the colours of the plaques are precisely measured.

The plaques processed at 260°C, 280°C and 300ºC lose progressively the vibrant red coloration measured at 240ºC with dE* values relative to the colour at 240°C of 9.1, 27.7 and 42.0 respectively.

Example 2

- according to the invention -

2 g of a solid solution of C.I. Pigment Red 254 (48% by weight), C.I. Pigment Red 255 (32% by weight) and C.I. Pigment Red 202 (20% by weight) and 1000 g of Ultramid B3K (polyamide-6, RTM BASF) are dry-mixed in a tumble mixer for 20 minutes. The mixture is extruded in a twin-screw extruder at 220ºC. The resultant pellets are processed on an injection moulding machine at 240°C, 260°C, 280°C and 300ºC to give plaques measuring 55 mm x 30 mm x 1.5 mm. Following injection moulding, the plaques are thermally conditioned in an oven at 75ºC for one week and stored at room temperature for at least 15 hours. Finally, the colours of the plaques are precisely measured.

The plaques processed at 260°C, 280°C and 300ºC keep the vibrant red colour measured at 240ºC, with dE* values of only 2.3, 1.0 and 2.0 respectively.

Example 3

- according to the invention –

3.5 g of C.I. Pigment Red 254 and 1.5 g of C.I. Pigment Red 202 are dry-mixed with 5 steatite balls of 1 cm diameter in a tumble mixer for 20 minutes. 2 g of this blend and 1000 g of Ultramid B3K (polyamide-6, RTM BASF) are dry-mixed in a tumble mixer for 20 minutes. The mixture is extruded in a twin-screw extruder at 220ºC. The resultant pellets are processed on an injection moulding machine at 240°C, 260°C, 280°C and 300ºC to give plaques measuring 55 mm x 30 mm x 1.5 mm. Following injection moulding, the plaques are thermally conditioned in an oven at 75ºC for one week and stored at room temperature for at least 15 hours. Finally, the colours of the plaques are precisely measured.

The plaques processed at 260°C, 280°C and 300ºC keep the vibrant red colour measured at 240ºC, with dE* values of only 2.0, 1.8 and 4.5 respectively.

Example 4

- according to the invention –

2 g of a solid solution of C.I. Pigment Red 254 (48% by weight), C.I. Pigment Red 255 (32% by weight) and C.I. Pigment Red 202 (20% by weight), and 1000 g of Ultramid A3SK (polyamide-6.6, RTM BASF) are dry-mixed in a tumble mixer for 20 minutes. The mixture is extruded in a twin-screw extruder at 260ºC. The resultant pellets are processed on an injection moulding machine at 280°C, 290°C and 300 ºC to give plaques measuring 55 mm x 30 mm x 1.5 mm. Following injection moulding, the plaques are thermally conditioned in an oven at 75ºC for one week and stored at room temperature for at least 15 hours. Finally, the colours of the plaques are measured precisely.

The plaques processed at 290ºC keep the vibrant red colour measured at 280ºC, with a dE* value in relation to the colour at 280°C of only 2.2.

Example 5

- according to the invention –

2 g of a solid solution of C.I. Pigment Red 254 (48% by weight), C.I. Pigment Red 255 (32% by weight) and C.I. Pigment Red 202 (20% by weight), and 1000 g of Ultramid A3EG6 (RTM BASF, glass fibre reinforced polyamide-6.6 with a glass fibre content of 30%) are dry-mixed in a tumble mixer for 20 minutes. The mixture is extruded in a twin-screw extruder at 260ºC. The resultant pellets are processed on an injection moulding machine at 280°C, 290°C, 300°C and 310°C to give plaques measuring 55 mm x 30 mm x 1.5 mm. No thermal conditioning is applied. The colours of the plaques are precisely measured.

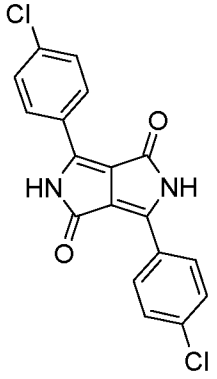
The plaques processed at 290°C, 300°C and 310ºC keep the vibrant red colour measured at 280ºC with dE* values in relation to the colour at 280°C of only 2.2, 2.4 and 4.9 respectively.

Claims

1. A process for mass colouration of a composition containing an aliphatic polyamide, which process comprises

- incorporation of a pigment mixture containing

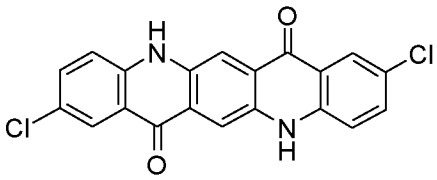
a pigment of formula (1)



(1)

and

a pigment of formula (2)



(2)

,

wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, and

- heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C.

2. A process according to claim 1, wherein the aliphatic polyamide is obtainable

from polycondensation of a diamine of formula (aI)

$$H_2N-X-NH_2 \quad (aI),$$

wherein

X is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

and of a dicarboxylic acid of formula (aII)

$$HOOC—Y-COOH \quad (aII),$$

wherein

X is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1;

from polycondensation of an aminocarboxylic acid of formula (aIII),

$H_2N-Z-COOH$ (aIII)

wherein
Z is C_2-C_{12}-alkylene, C_5-C_{12}-cycloalkylene or C_5-C_{10}-cycloalkane-bis-(C_1-C_3-alkylene);

or

from polycondensation of a diamine of formula (aI), a dicarboxylic acid of formula (aII) and an aminocarboxylic acid of formula (aIII);
wherein the molar ratio between a diamine of formula (aI) and a dicarboxylic acid of formula (aII) is close to 1.

3. A process according to claims 1 or 2, wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 4 to 1.

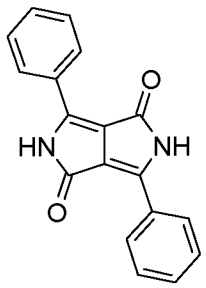
4. A process according to anyone of claims 1 to 3, wherein the aliphatic polyamide is selected from the group consisting of polyamide-6, polyamide-6.6, polyamide-6.10, polyamide-6.12, polyamide-6.6/6, polyamide-6.10/6 and polyamide-6.12/6.

5. A process according to anyone of claims 1 to 4, wherein the heated composition with the pigment mixture is extruded.

6. A process according to anyone of claims 1 to 5, wherein the temperature is in the range from 200°C to 330°C.

7. A process according to anyone of claims 1 to 6, wherein the composition contains glass fibres in a range from 5% to 75% based on the weight of the aliphatic polyamide.

8. A process according to claims 1 to 7, wherein the pigment mixture, which is incorporated, contains a further pigment of formula (3)



(3)

,

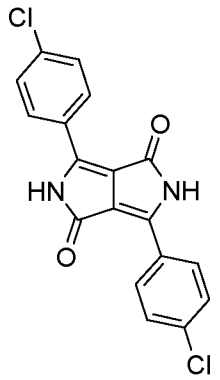
wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 4 to 1, and
wherein the pigment of formula (3) is present in a range of 5% to 35% based on the combined weight of the pigments of formulae (1) and (2).

9. A process according to claims 1 to 8, wherein the overall amount of pigments is from 0.05% to 30% based on the weight of the aliphatic polyamide.

10. A composition, which is mass-coloured by a process as defined in claim 1, comprising

(a) an aliphatic polyamide,

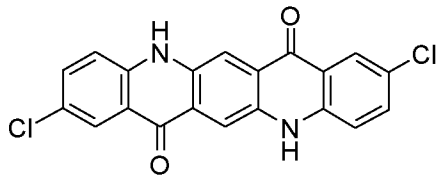
(b) a pigment of formula (1)



(1)

, and

(c) a pigment of formula (2)



(2)

,

wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1.

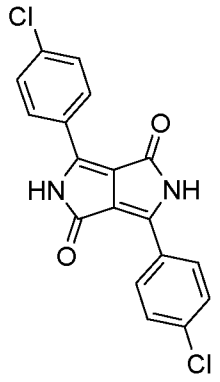
11. An article made of a composition as defined in claim 10.

12. A method for heat stabilisation of a pigmented mass-coloured composition as defined in claim 10, which comprises the incorporation of a pigment mixture containing a pigment of formula (1) and a pigment of formula (2), wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1, into the composition and the heating of the composition with the pigment mixture to a temperature in the range from 180°C to 350°C.

13. A composition comprising

(a) an aliphatic polyamide,

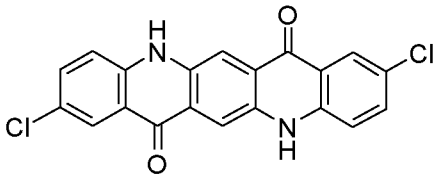
(b) a pigment of formula (1)



(1)

, and

(c) a pigment of formula (2)

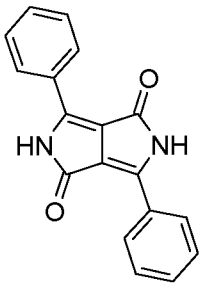


(2)

,

wherein the weight ratio between the pigment of formula (1) and the pigment of formula (2) is from 9 to 1.

14. A composition according to claim 13, which comprises as a further component
(d) a pigment of formula (3)



(3)

,

wherein the weight ratio of a pigment of formula (1) to a pigment of formula (2) is from 4 to 1, and
wherein a pigment of formula (3) is present in a range of 5% to 35% based on the combined weight of the pigments of formulae (1) and (2).

15. The use of a pigment mixture as defined in claim 1 for a heat-stable mass-coloration of a composition containing an aliphatic polyamide.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/067245

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/00 C08J3/20
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K C08J C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 200739 Thomson Scientific, London, GB; AN 2007-408498 XP002616681, -& JP 2007 094270 A (CASIO COMPUTER CO LTD) 12 April 2007 (2007-04-12) abstract claim 1; compounds (1),(4) paragraph [0021] - paragraph [0022] examples 3,9 ----- -/--	1-15

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 October 2011	03/11/2011

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Russell, Graham

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/067245

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 810 304 A (JAFFE EDWARD E [US] ET AL) 7 March 1989 (1989-03-07) cited in the application column 7, line 21 - line 32 column 6, line 57 - line 68 example 4 claims 9,10	1-15
A	US 6 494 947 B1 (HAUSER HANSPETER [CH] ET AL) 17 December 2002 (2002-12-17) page 8, line 10 - line 38 column 8, line 44 - line 52 column 9, line 9 - line 30 examples 1-3,5-8 claims 1-6,8,9	1-15
A	EP 0 737 723 A1 (CIBA GEIGY AG [CH] CIBA SC HOLDING AG [CH]) 16 October 1996 (1996-10-16) cited in the application examples 14,18,19 claims 1,12	1-15
A	US 5 095 056 A (BAEBLER FRIDOLIN [US] ET AL) 10 March 1992 (1992-03-10) claims 1,4,6-9,11,13,14	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/067245

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2007094270 A	12-04-2007	JP 4475213 B2	09-06-2010
US 4810304 A	07-03-1989	NONE	
US 6494947 B1	17-12-2002	AT 225385 T	15-10-2002
		AU 4106400 A	09-10-2000
		BR 0009269 A	26-12-2001
		CA 2362088 A1	28-09-2000
		CN 1354772 A	19-06-2002
		DE 50000604 D1	07-11-2002
		DK 1163294 T3	27-01-2003
		WO 0056819 A1	28-09-2000
		EP 1163294 A1	19-12-2001
		ES 2181652 T3	01-03-2003
		JP 4489974 B2	23-06-2010
		JP 2003526703 A	09-09-2003
EP 0737723 A1	16-10-1996	CA 2174062 A1	15-10-1996
		DE 69605838 D1	03-02-2000
		DE 69605838 T2	03-08-2000
		JP 3897374 B2	22-03-2007
		JP 8295816 A	12-11-1996
		TW 448214 B	01-08-2001
		US 5641351 A	24-06-1997
US 5095056 A	10-03-1992	DE 69114827 D1	04-01-1996
		DE 69114827 T2	04-07-1996
		EP 0495338 A1	22-07-1992
		JP 3062328 B2	10-07-2000
		JP 4311769 A	04-11-1992