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(54) TONER COMPOSITION

(57) A toner composition containing a color developing agent and at least one kind of polymer selected from the groups A and B, having excellent melt fluidity, fixability, offset resistance and blocking resistance and capable of imparting positive electric charge, wherein A is a non-crosslinked polyester imide containing a specific ester unit E and a specific imide unit I, and B is a crosslinked polyester imide containing the above units E and I and a crosslinking unit C.

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Description

Detailed Description of the Invention

Technical Field

[0001] The present invention relates to a toner composition useful for a high speed copy machine and a full-color printer. More particularly, this invention relates to a toner composition having excellent blocking resistance, low-temperature fixability and melt-fluidity and useful for the development of electrostatic image or magnetic latent image in electrophotography or magnetic transfer printing, and to a polyester imide resin giving said toner composition.

Background Arts

[0002] In an electrostatic photography, i.e. a process for producing a permanent sensible image by electrostatic charge, the electrostatic image formed on a photoconductive semiconductor or an electrostatic recording material is developed with a toner charged by frictional electrification and the developed image is fixed. In a magnetic latent image, a latent image on a magnetic drum is developed with a toner containing magnetic material and fixed. The fixation is carried out by directly fusing the toner image developed on a photoconductive photosensitive material or on an electrostatic recording material or transferring the toner image on a paper or a film and fusing the transferred image on a transfer sheet. The fusion of the toner image is usually performed by the application of pressure and heat. The heating process comprises a non-contact heating process using an electric oven or flash light and a pressure-heating process using a pressurising roller, and the latter process is being mainly employed in recent years requiring the speed-up and simplification of the fixing step. The above methods are generally called as "dry developing process".

[0003] The toner composition to be used in the dry developing process is produced by sufficiently dispersing a binder resin as a base, a coloring agent, a charge-controlling agent, magnetic powder and necessary other additives by kneading the components in molten state and pulverizing the kneaded mixture. The resin is a main component of the toner and exerts substantial influence on the performance required for a toner. The binder resin for toner is required to have good dispersibility of the coloring agent and other additives in the melt-kneading process, pulverizability in the crushing process and various properties such as fixability, offset resistance, blocking resistance and electrical properties in the case of using as a toner. Resins generally used as the binder resins are epoxy resins, polyester resins, polystyrene resins, acrylic resins, etc., and polyester resins among the above resins are attracting attention because the resins are fixable at lower temperature, give fixed toner image having excellent resistance to plasticizers for polyvinyl chloride resin and have high transparency to cope with the development of color copying technique.

[0004] JP-A 6-128367 (hereunder, JP-A means "Japanese Unexamined Patent Publication)], JP-B 59-11902 (hereunder, JP-B means "Japanese Examined Patent Publication) and JP-B 5-85901 describe polyester resins having crosslinked structure introduced by using a tri- or higher-functional monomer or a monomer having an unsaturated group as a component for improving the offset resistance in the fixing step. However, these polyester resins having branched or crosslinked structure have lowered fluidity and are unsuitable for high-speed copying and color copying use.

[0005] A polyester resin having a linear structure has been proposed as a toner resin having high melt fluidity. Linear polyesters generally have a problem that the Tg is lowered to deteriorate the storage stability and the blocking resistance of the toner when the fluidity of the resin is improved by lowering the melt-viscosity. Polyesters produced by using ethylene oxide or propylene oxide adduct of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) as a diol component are described in the JP-A 2-269364, JP-A 4-42161, JP-A 5-9278 and JP-A 5-107805. These resins have relatively high Tg and excellent melt-fluidity. However, ethylene oxide or propylene oxide adduct of bisphenol A usually contains an adduct having a structure containing two or more molecules of ethylene oxide or propylene oxide based on the OH group of bisphenol A, and the Tg-improving effect is not sufficient because the aliphatic ether structure results in the lowering of Tg. Furthermore, the polyester easily releases the alkylene oxide by the acid treatment condition used in a sewage treatment or by acid rain when the polyester is wasted and left outdoors to bring dangers of the release of bisphenol A which has recently been attracting attention as a troublesome "environmental hormone".

[0006] Accordingly, there is no polyester resin free from environmental problems as a binder resin for toner and satisfying the required melt-fluidity, low-temperature fixability, offset resistance and blocking resistance at present.

[0007] JP-B 8-10358 discloses an attempt to introduce an imide structure into a resin for toner taking consideration of an aliphatic imide and a positive-charge imparting property introduced by the imide, however, the compound is added or copolymerised to a conventional resin in a small amount as an agent for controlling the electric charge.

[0008] JP-A 7-160046 and JP-A 8-62896 describe a toner containing a polyester imide resin produced by the melt-polycondensation of a flexible diaminoalkane (Jeffamin, product of Texaco Chemical Co.) and trimellitic anhydride.

[0009] A polyester imide resin prepared by the polycondensation of Jeffamin and pyromellitic anhydride is described in JP-A 7-181738.

[0010] In addition to the above, crosslinked polyester imide resins produced by introducing an unsaturated group together with Jeffamin and optionally reacting with a free radical initiator are disclosed in JP-A 7-160047, JP-A 7-219273 and JP-A 7-333907.

[0011] All of these resins have poor handling performance in the manufacture of the resins because of the use of the diamine (Jeffamin) which is viscous at ordinary temperature. Furthermore, since a polyester imide resin produced by the polycondensation of Jeffamin and an acid anhydride has extremely high hygroscopicity, electric charge accumulation is insufficient under high temperature and humidity conditions to cause fixability problem in the case of evaluating the resin as a toner, supposedly, because of the presence of ether bond in the imide-constituting component. Further, the synthesis of Jeffamin necessitates a considerably large number of steps to raise the production cost in comparison with the performance improvement as a toner, and the use of the resin as a toner resin meeting the cost is difficult.

[0012] An object of the present invention is to provide a new toner composition.

[0013] Another object of the present invention is to provide a toner composition having excellent melt-fluidity, fixability, offset resistance and blocking resistance and capable of applying positive static charge.

[0014] A further object of the present invention is to provide a polyester imide as a binder resin for toner for giving the above toner composition.

[0015] Still another object of the present invention is to provide a toner composition containing a polyester imide having high glass transition temperature (Tg) and low melt-fusion temperature.

[0016] Still further object of the present invention is to provide a new binder resin for toner having improved characteristics of a polyester resin as a binder resin for toner.

[0017] Still further object of the present invention is to provide a toner composition useful as a dry-type toner applicable to hot-roll fixing process, flash fixing process, etc.

[0018] The other objects and advantages of the present invention will be clarified by the following descriptions.

Disclosure of the Invention

[0019] According to the present invention, the objects and advantages of the present invention can be attained by a toner composition comprising a coloring agent and at least one kind of polymer selected from the group consisting of A and B.

A: a non-crosslinked polyester imide

(i) comprising mainly an ester unit E represented by the following formula (1) below and at least one kind of imide unit I selected from the group consisting of units represented by the following formulas (2) and (3) below, E and I are bonded through ester bond;

(ii) having physical properties of

(a) a number-average molecular weight of from 2,000 to 10,000,

(b) a glass transition temperature of from 50 to 90°C and

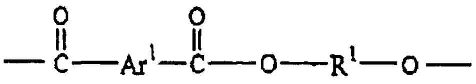
(c) a softening temperature of from 90 to 160°C ;

(iii) satisfying the following formula (A-1)

$$0.01 \leqq a_2/a_1 \leqq 0.60 \qquad \text{(A-1)}$$

(wherein a_1 is the mol% of the ester unit E and a_2 is the mol% of the imide unit I based on the all units constituting the non-crosslinked polyester imide A)

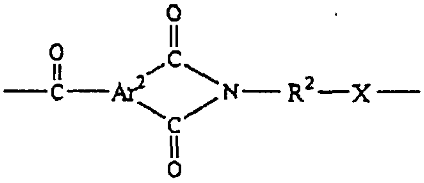
formula (1)



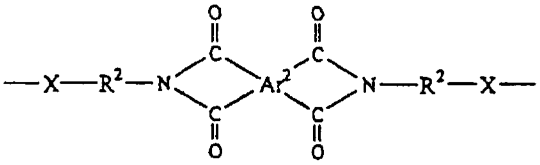
$$-\overset{\overset{\displaystyle O}{\|}}{C}-Ar^1-\overset{\overset{\displaystyle O}{\|}}{C}-O-R^1-O- \qquad (1)$$

(wherein Ar^1 is a bivalent aromatic hydrocarbon group having a carbon number of from 6 to 12, and R^1 is at least one kind of group selected from the group consisting of an alkylene group, an oxyalkylene

group and a polyoxyalkylene group each having a carbon number of from 2 to 20)
formula (2) and (3)



(2)



(3)

(wherein Ar^2 is a tri- or tetravalent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^2 is an alkylene group

having a carbon number of from 2 to 12, and X is -CO- or -O-)
B : a crosslinked polyester imide

(iv) comprising mainly the above ester unit E, the above imide unit I and at least one kind of crosslinking unit C selected from the group consisting of units represented by the following formulas (4) and (5) below, the above three units (E, I and C) are bonded together through ester bond,
(v) having physical properties of

(d) a glass transition temperature of from 50 to 90°C and
(e) a softening temperature of from 90 to 190°C,

(vi) satisfying the following formulas (B-1) and (B-2)

$$0.01 \leqq b_2/b_1 \leqq 0.60 \quad \text{(B-1)}$$

$$0.01 \leqq b_3/b_1 \leqq 0.40 \quad \text{(B-2)}$$

(wherein b_1 is the mol% of the ester unit E, b_2 is the mol% of the imide unit I, and b_3 is the mol% of the crosslinking unit C based on the all units constituting the crosslinked polyester imide B).
formulas (4) and (5)

$$Ar^3\text{-(-CO-)}_r\text{-} \quad (4)$$

$$R^3\text{-(-O-)}_q\text{-} \quad (5)$$

(wherein Ar^3 is an r-valent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^3 is a q-valent aliphatic group having a carbon number of from 3 to 8, and r and q are each 3 or 4)

Best Mode for Carrying out the Invention

[0020] The toner composition of the present invention contains a coloring agent and a polymer selected from the group of A and B.

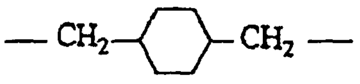
[0021] The polymer A is a polyester imide resin composed mainly of an ester unit E expressed by the above formula (1) and an imide unit I selected from the group consisting of the units expressed by the above formulas (2) and (3). These units are not bonded through ether bond but bonded through ester bond.

[0022] In the above formula (1), Ar^1 is an aromatic hydrocarbon group having a carbon number of from 6 to 12. Such aromatic hydrocarbon groups are, for example, 1,4-phenylene group, 1,3-phenylene group, 1,2-phenylene group, 2,6-naphthylene group, 2,7-naphthylene group and 4,4'-biphenylene groups. Two or more kinds of these groups may be used in combination. 1,4-Phenylene group and 1,3-phenylene group are preferable among the above exemplified groups. These are groups usually derived from aromatic dicarboxylic acid components.

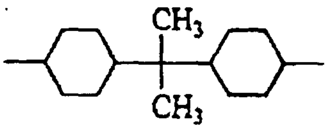
[0023] In the case of using 1,4-phenylene group in combination with 1,3-phenylene group, the amount of 1,4-phenylene group is 50 to 80 mol%, preferably 60 to 70 mol% based on the total groups.

[0024] The group R^1 is selected from the group consisting of alkylene groups, oxyalkylene groups and polyoxyalkylene groups each having a carbon number of from 2 to 20.

[0025] Examples of such alkylene groups are ethylene group, 1,2-propylene group, trimethylene group, tetramethylene group, hexamethylene group, neopentylene group (2,2-dimethyl-1,3-propylene group) and the groups expressed by the following formulas (R1-1) and (R1-2).



(R1-1)



(R1-2)

[0026] Two or more kinds of these groups may be used in combination. Alkylene groups having a carbon number of from 2 to 6 are preferable, and ethylene group, 1,2-propylene group and neopentylene group are especially preferable among the above groups.

[0027] Such oxyalkylene groups are, for example, oxydiethylene group and trioxyethylene group. Oxydiethylene group is preferable between the exemplified groups.

[0028] Such polyoxyalkylene groups are, for example, a polyoxyethylene group and a polyoxypropylene group. The molecular weight of the polyoxyalkylene group is usually from 500 to 10,000.

[0029] Two or more kinds of the above alkylene groups, oxyalkylene groups and polyoxyalkylene groups each having a carbon number of from 2 to 20 may be used in combination. These groups are usually derived from diol components.

[0030] The ester groups E expressed by the above formula (1) are preferably those of the formula (1) wherein, e.g. Ar^1 is 1,4-phenylene group, 1,3-phenylene group or their combination and R^1 is ethylene group, 1,2-propylene group, neopentylene group, oxydiethylene group or their combination.

[0031] Especially, when R^1 is an oxyalkylene group, it is preferably used in combination with an alkylene group. In this case, the content of such oxyalkylene group is preferably 10 to 99 mol%, more preferably 20 to 85 mol%, especially 30 to 80 mol%, based on the alkylene group.

[0032] The groups Ar^1 may be those, in addition to the above-mentioned groups, derived from a relatively small amount of other carboxylic acid component. The following acids are examples of these other dicarboxylic acid components.

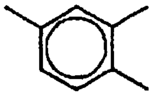
[0033] Aromatic dicarboxylic acid such as phthalic acid, phthalic anhydride, diphenyl ether dicarboxylic acid and diphenylsulfone dicarboxylic acid; aliphatic dicarboxylic acid such as succinic acid, fumaric acid and adipic acid; alicyclic dicarboxylic acid such as cyclohexanedicarboxylic acid and norbornene-2,3-dicarboxylic acid. The ratio of these other dicarboxylic acid components is preferably 30 mol% or less, more preferably 20 mol% or less, especially 10 mol% or less based on the total acid component constituting the ester unit E.

[0034] The group R^1 may contain groups derived from diol components other than the groups cited above to an extent not to deteriorate the physical properties of the product. Examples of such other diol component are bisphenol A, bisphenol S, bisphenol Z, hydroquinone, 1,4-benzenediol and 1,3-benzenediol. The addition amount of such other diol component is preferably 40 mol% or less, more preferably 30 mol% or less based on the diol components constituting the ester unit E.

[0035] The above ester unit E may contain a small amount of unit derived from hydroxycarboxylic acids such as hydroxybenzoic acid and ε - hydroxycaproic acid. The ratio of such unit is preferably 30 mol% or less, more preferably 20 mol% or less, especially 10 mol% or less based on the ester unit E.

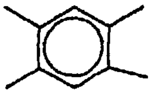
[0036] In the formulas (2) and (3), the group Ar^2 is a tri- or tetravalent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^2 is an alkylene group having a carbon number of from 2 to 12, and X is -CO- or -O-.

[0037] Examples of the group Ar^2 consisting of a tri- or tetravalent aromatic hydrocarbon group having a carbon number of from 6 to 12 are a benzene ring bonded to other atoms at 1,2 and 4 positions and expressed by the following formula (Ar2-1)



(Ar2-1)

and a benzene ring bonded to other atoms at 1,2,4 and 5 positions and expressed by the following formula (Ar2-2).



(Ar2-2)

These groups are derived from trimellitic acid or its anhydride and pyromellitic acid or its anhydride, respectively.

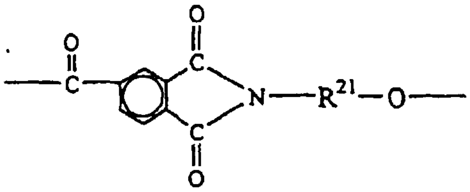
[0038] Examples of the group R^2 consisting of an alkylene group having a carbon number of from 2 to 12 are ethylene group, 1,2-propylene group, 1.3-propylene group, 1,4-tetramethylene group and hexamethylene group. Among the above groups, an alkylene group having a carbon number of from 2 to 6 such as ethylene group and 1,3-propylene group is preferable and ethylene group is especially preferable. These are groups usually derived from aliphatic amino alcohol or aliphatic aminocarboxylic acid.

[0039] The group X is -CO- or -O-.

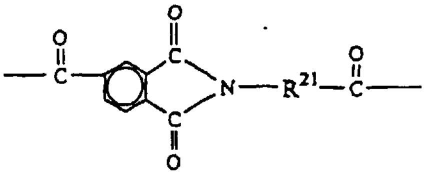
[0040] Preferable examples of the imide unit I expressed by the above formula (2) are those of the formula (2) wherein Ar^2 is a benzene ring bonded to other atoms at 1, 2 and 4 positions, R^2 is an alkylene group having a carbon number of from 2 to 6 and X is -O- or -CO-.

[0041] Preferable examples of the imide unit I expressed by the above formula (3) are those of the formula (3) wherein Ar^2 is a benzene ring bonded to other atoms at 1,2,4 and 5 positions, R^2 is an alkylene group having a carbon number of from 2 to 6 and X is -O-or-CO-.

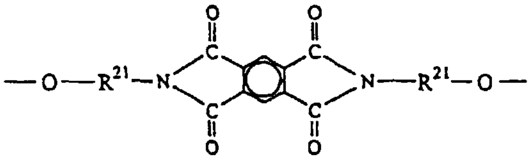
[0042] Concrete examples of the imide unit I are those expressed by the following formulas.



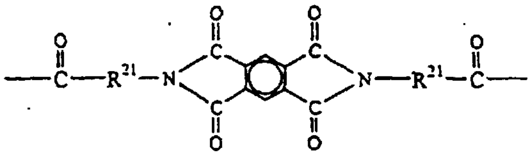
(2-1)



(2-2)



(3-1)



(3-2)

[0043] In the above formulas, R^{21} is an alkylene group having a carbon number of from 2 to 6, especially preferably ethylene group.

[0044] Especially preferable imide unit I is composed solely of the unit expressed by the above formula (2-1).

[0045] Introduction of the above imide unit I randomly or in the form of blocks into a polymer chain containing the above ester unit E by ester bond gives an amorphous polymer and contributes to the improvement of the storage stability by raising the Tg which is insufficient by the single use of a polyester resin composed solely of the above ester unit while keeping excellent melt-fluidity of the polyester resin composed solely of the above ester unit. Furthermore, the obtained polymer can be applied to a positive-charge developing process which is difficult to be achieved by the use of conventional polyesters.

[0046] The above polyester imide resin A preferably has a Tg of 50 to 90°C and a softening temperature of 90 to 160°C for the use of the resin as a binder resin for toner. The Tg is the rise temperature of the inflection point determined by differential scanning calorimetry at a temperature increasing rate of 20°C/min. The softening temperature is measured by charging 1 gram of a sample into a Koka flow tester under a load of 30 kg, slowly raising the temperature from room temperature at a temperature increasing rate of 3°C/min and determining the temperature when 50% of the charged sample is extruded in molten state through a nozzle having a diameter of 1 mm and a land length of 10 mm.

[0047] When the Tg of the above polyester imide A is lower than 50°C, the blocking resistance becomes insufficient, and a Tg higher than 90°C results in poor low-temperature fixability. The value of Tg is preferably between 55°C and 85°C. When the softening temperature is lower than 90°C , the offset resistance becomes insufficient, and a softening temperature higher than 160°C causes the lowering of the fluidity of the resin. The softening temperature is preferably between 90°C and 150°C. The polyester imide A having the above-mentioned thermal characteristics gives the toner composition of the present invention producible at a low cost, having excellent fixability caused by the low melt-fluidity and excellent blocking resistance even at a high temperature, and exhibiting excellent storage stability compared with conventional binder resins for toner.

[0048] The molecular weight of the above polyester imide A is preferably adjusted to give the polymer satisfying the above thermal characteristics. The number-average molecular weight is preferably in the range of from 2,000 to 20,000, more preferably from 2,000 to 10,000, particularly from 2,000 to 8,000, and especially preferably from 2,500 to 5,000 depending upon the kinds of the constituent units.

[0049] The above polyester imide resin A satisfies the following formula (A-1).

$$0.01 \leqq a_2/a_1 \leqq 0.60 \qquad \text{(A-1)}$$

wherein a_1 is the mol% of the ester unit E and a_2 is the mol% of the imide unit I based on the total unit constituting a non-crosslinked polyester imide A.

[0050] When the value of a_2 in the above formula (A-1) is smaller than 0.01, the Tg becomes low and blocking trouble is liable to occur in the case of using the resin as a toner. Conversely, the a_2 value larger than 0.60 gives high softening temperature to cause poor fixability in the case of evaluating as a toner and shifts the non-offset region to a high temperature side. The preferable ratio of a_1 to a_2 satisfies the following formula (A-2), more preferably the following formula (A-3).

$$0.05 \leqq a_2/a_1 \leqq 0.50 \qquad \text{(A-2)}$$

$$0.10 \leqq a_2/a_1 \leqq 0.40 \qquad \text{(A-3)}$$

[0051] The polymer B is a crosslinked polyester imide resin composed mainly of the ester unit E expressed by the above formula (1), the imide unit I selected from the group consisting of the units expressed by the above formulas (2) and (3), and a crosslinking unit C selected from the group consisting of the above formulas (4) and (5). These units are bonded not through ether bond but through ester bond.

[0052] The units same as the above-mentioned units can be used as the ester unit E and the imide unit I.

[0053] The crosslinking unit C is selected from the group consisting of the above formulas (4) and (5).

[0054] In the above formula (4), the group Ar^3 is an r-valent aromatic hydrocarbon group having a carbon number of from 6 to 12. Examples of such aromatic hydrocarbon group are the benzene ring bonded to other atoms at 1, 2 and 4 positions and expressed by the above formula (Ar2-1) and a benzene ring bonded to other atoms at 1, 2, 4 and 5 positions and expressed by the above formula (Ar2-2). These groups are derived from trivalent or tetravalent aromatic polybasic carboxylic acids or their anhydrides.

[0055] The value of r is 3 or 4.

[0056] In the above formula (5), the group R^3 is a q-valent aliphatic group having a carbon number of from 3 to 9. These groups are usually derived from polyhydric aliphatic alcohols having 3 or more valences. Examples of polyhydric aliphatic alcohol component giving such aliphatic groups are glycerol, pentaerythritol, trimethylolpropane, trimethylolethane and tris(2-hydroxyethyl) isocyanurate. Two or more kinds of the above compounds may be used in combination. Among the above examples, aliphatic groups having a carbon number of from 3 to 6 such as glycerol, pentaerythritol and trimethylolpropane are preferable and, above all, glycerol and pentaerythritol are more preferable.

[0057] The value of q is 3 or 4.

[0058] The crosslinking unit C is preferably composed of the unit expressed by the above formula (5).

[0059] The above polyester imide satisfies the following formula (B-1).

$$0.01 \leqq b_2/b_1 \leqq 0.60 \qquad \text{(B-1)}$$

In the formula, b_1 is the mol% of the ester unit E and b_2 is the mol% of the imide unit I based on the total unit constituting the crosslinked polyester imide B.

[0060] When the ratio b_2/b_1 is smaller than 0.01, the Tg of the polymer becomes low and blocking trouble is liable to occur in the case of using the resin as a toner. Conversely, the ratio b_2/b_1 larger than 0.60 gives high softening temperature to cause poor fixability in the case of evaluating as a toner and shifts the non-offset region to a high temperature side. The ratio of b_1 to b_2 preferably satisfies the following formula (B-1-1), more preferably the following formula (B-1-2).

$$0.05 \leqq b_2/b_1 \leqq 0.50 \qquad \text{(B-1-1)}$$

$$0.10 \leqq b_2/b_1 \leqq 0.40 \qquad \text{(B-1-2)}$$

[0061] Furthermore, the above polyester imide B satisfies the following formula (B-2).

$$0.01 \leqq b_3/b_1 \leqq 0.40 \qquad \text{(B-2)}$$

In the formula, the definition of b_1 is same as above and b_3 is the mol% of the crosslinking unit C.

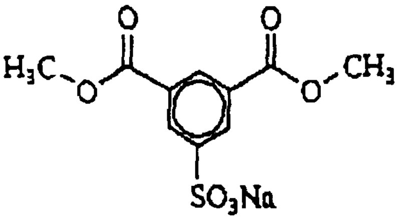
[0062] The ratio of b_3/b_1 smaller than 0.01 lowers the softening temperature of the polymer, decreases the storage modulus G' within the temperature range of from 150 to 200°C measured by using a rheometer while varying the temperature from the softening temperature of the resin to 200°C, and causes offset-resistance problem in the case of evaluating the resin as a toner. When the ratio is larger than 30%, the softening temperature is raised to deteriorate the fixability in the evaluation of the resin as a toner and the production of the resin becomes difficult. The ratio of b_3 to b_1 preferably satisfies the following formula (B-2-1), more preferably the following formula (B-2-2).

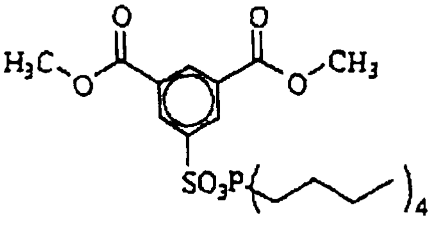
$$0.03 \leqq b_3/b_1 \leqq 0.20 \qquad \text{(B-2-1)}$$

$$0.05 \leqq b_3/b_1 \leqq 0.15 \qquad \text{(B-2-2)}$$

[0063] The above polyester imide preferably has a Tg of 50 to 90°C and a softening temperature of 90 to 190°C for the use of the polymer as a binder resin for toner. The influence of Tg in this case is same as the case of the above polyester imide A. The offset resistance becomes insufficient when the softening temperature is lower than 90°C, and the fluidity of the resin is lowered when the temperature is higher than 190°C. The softening temperature is preferably from 100 to 180°C, more preferably from 110 to 160°C. The polyester imide B having the above thermal characteristics gives the toner composition of the present invention producible at a low cost, having excellent fixability caused by low melt-fluidity and excellent blocking resistance even at a high temperature and exhibiting excellent storage stability compared with conventional binder resin for toner.

[0064] The above polymers A and B may contain other units functioning as a thermal stabilizer, oxidation stabilizer, photo-stabilizer, pigment dispersing agent, dye-fixing improving agent, flame-retardant, etc., in the polymer chain in small amounts, e.g. not more than 20 mol% based on the total polymer. For example, the compounds shown as the following formulas (Other-1), (Other-2) and (Other-3) can be used as the fixation improving agent and a dispersing agent for coloring agent, and a flame-retardant. The above polymer can be imparted with the objective performance of each agent by adding and reacting the agent in the production of the polymer.


(Other-1)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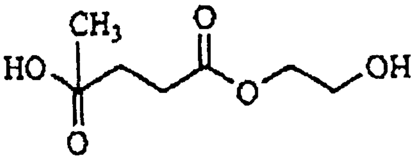

(Other-3)

[0065] There is no particular restriction on the method for producing the polyester imides A and B in the present invention, and conventional production processes in the field can be used.

[0066] For example, the polymer may be produced by reacting the imide-constituting raw materials, synthesizing an imide unit and subjecting the unit to the esterification to form the ester unit E and the simultaneous dehydrative condensation; or reacting the raw materials of the imide unit to form an amidocarboxylic acid as an imide precursor and subjecting the acid to the esterification to form the ester unit E simultaneously with dehydrative condensation; or charging the raw materials for the ester unit and the raw materials for the imide unit into a single reaction system and carrying out the formation of the imide unit I simultaneously with the formation of the ester unit E. These methods can be properly used in the present invention.

[0067] The esterification process for the production of the ester unit E can be carried out, for example, by the direct polymerization process using the dicarboxylic acid component and each glycol component as raw materials, the transesterification polymerization process to use a dicarboxylic acid ester and each glycol component as raw materials, etc.

[0068] The imide unit I can be produced by the reaction of an aromatic polybasic carboxylic acid component with an amino alcohol component or an aminocarboxylic acid component. Examples of such aromatic polybasic carboxylic component are trimellitic anhydride and pyromellitic anhydride. Trimellitic anhydride is preferable between the above compounds because of the formation of a polyester imide having higher amorphousness.

[0069] The amino alcohol component is, for example, ethanolamine, 2-aminopropanol and 3-aminopropanol. Ethanolamine is preferable among the above compounds because it has high reactivity, gives a polyester imide having higher amorphousness similar to the above and is easily removable at the latter stage of polymerization owing to its low boiling point even if the compound is left in the system as an unreacted material.

[0070] The aminocarboxylic acid component is, for example, β - aminocarboxylic acids, γ -aminocarboxylic acids, δ - aminocarboxylic acids and ε -aminocarboxylic acids. ε -Aminocarboxylic acids are preferable among the above compounds owing to good handleability to enable the use as a toner resin at a low cost.

[0071] The ester unit E can be produced by reacting an aromatic dicarboxylic acid component with a diol component. The aromatic dicarboxylic acid component is, for example, terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid and their alkyl esters. Terephthalic acid and isophthalic acid are preferable among the above compounds to enable the use as a toner resin at a low cost.

[0072] The diol component is, for example, alkylene glycols such as ethylene glycol, propylene glycol and 2,2-dimethyl-1,3-propylene glycol; oxyalkylene glycols such as diethylene glycol and triethylene glycol; and polyoxyalkylene glycols such as polyoxyethylene glycol, polyoxypropylene glycol and polytetraethylene glycol. Among the above compounds, ethylene glycol and 2-dimethyl-1,3-propylene glycol are preferable because these compounds do not lower the Tg of the resultant toner, and diethylene glycol is also preferable because it gives a toner having improved melt-fluidity.

[0073] A concrete example of the process for producing the polymer A comprises the mixing of a trivalent or tetravalent aromatic polybasic carboxylic acid component such as trimellitic anhydride and an aliphatic amino alcohol such as ethanolamine as raw materials for constructing the imide unit I and a diol component such as ethylene glycol which is a raw material for constructing the ester unit E, the reaction of the above components at 100°C or below to form an amidocarboxylic acid, the incorporation of the system with an aromatic dicarboxylic acid component such as terephthalic acid as the remaining raw material component for constructing the ester unit E optionally together with an oxyalkylene glycol component and/or a polyalkylene glycol component, and the dehydration and polycondensation of the components. The amounts of the diol component and the tri- or tetravalent polybasic aromatic carboxylic acid component are usually 0.01 to 0.90 mol% and 0.99 to 0.10 mol% based on the aromatic dicarboxylic acid component, respectively, and the amount of the amino alcohol is equivalent to the polybasic aromatic carboxylic acid component.

[0074] The imide unit I and the ester unit E of the polymer B can be produced by the methods described above.

[0075] The crosslinking unit C can be derived from a trivalent or tetravalent aromatic polybasic carboxylic acid component and a trivalent or tetravalent polyhydric aliphatic alcohol component.

[0076] A concrete example of the production process of the polymer B comprises the preparatory charging and mixing of a trivalent or tetravalent aromatic polybasic carboxylic acid component such as trimellitic anhydride and an aliphatic amino alcohol such as ethanolamine as raw materials for constructing the imide unit I and a diol component such as ethylene glycol which is a raw material for constructing the ester unit E, the reaction of the above components at 100°C or below, the incorporation of the system with an aromatic dicarboxylic acid component as the remaining raw material component for constructing the ester unit E and an aromatic polybasic carboxylic acid or a polyhydric aliphatic alcohol component constructing the crosslinking unit C optionally together with an oxyalkylene glycol component and/or a polyalkylene glycol component, and the polycondensation of the components.

[0077] In the case of using the trivalent or tetravalent aromatic polybasic carboxylic acid component such as trimellitic anhydride as a crosslinking unit C, it may be mixed in the stage of charging.

[0078] In the case of using trimellitic anhydride in the imide unit I and the crosslinking unit C, trimellitic anhydride is used in excess of ethanolamine in terms of charging ratio (molar ratio), and the molar amount of trimellitic anhydride is preferably 1 to 3 times, more preferably 1 to 2 times that of ethanolamine.

[0079] The polyester imides A and B can be used as a mixture with other crosslinked or non-crosslinked binder resin for toner in the present invention. The other binder resin for toner to be used by mixing with the polymer A is, for example, the above polymer B, a bisphenol-type polyester resin, a polyester resin free from bisphenol component and a crosslinked styrene-acrylic resin. The other binder resin for toner to be used by mixing with the polymer B is, for example, the above polymer A, a bisphenol-type polyester resin, a polyester resin other than the bisphenol-type resin and a non-crosslinked styrene-acrylic resin. The use of the polymers as a mixture with other resins is effective for increasing the physical properties of the above polymers A and B such as Tg and storage modulus and further improving the physical properties as a binder resin. Accordingly, the physical properties such as offset resistance is further improved in the case of evaluating the resin as a toner. The amount of the polymer A or B is preferably 10 to 90% by weight, more preferably 20 to 80% by weight based on the total binder resin.

[0080] For example, when the above polymer B is to be used by blending with other binder resin consisting of a polypropylene terephthalate having a molecular weight of 2,500 and a molecular weight distribution of 2.0, the ratio of the polymer B is preferably 10 to 50% by weight, more preferably 20 to 40% by weight, especially 25 to 35% by weight. The resultant mixture (composition) has a number-average molecular weight of 3,000 to 5,000 and a molecular weight distribution of 10 to 20, and exhibits balanced properties as a binder resin for toner, i.e. a Tg of 60 to 70°C and a softening temperature of 115 to 125°C.

[0081] The polyester imide A and B in the present invention is properly mixed as a binder resin for toner with additives such as a color developing agent, a static charge regulator, a wax and a surface-treating agent to form a toner composition.

[0082] The amount of the binder resin in the toner composition depends upon the process for forming the latent image such as the electrophotographic process or magnetic process and is about 40 to 99% by weight, preferably 50 to 99% by weight.

[0083] The color-developing agent is e.g. a coloring agent such as pigment and dye. The pigment is, for example, a carbon black such as furnace black Raven 5250, Raven 5750, Raven 1250 and Raven 1255 manufactured by Columbian Carbon Japan Ltd. and a magnetite such as MAPICO BLACKS manufactured by Columbian Magnetite Co., or other equivalent black pigment. The amount of the color-developing agent is generally 1 to 50% by weight, preferably 1 to 30% by weight based on the toner.

[0084] Conventional cyan, magenta, blue, red, green, brown or yellow pigment or their mixture can be used as the color pigment other than black pigment in an amount same as the above-mentioned amount of the black pigment.

[0085] Conventional charge controlling agent can be used as the charge controlling agent. Representative examples of the agent are azo-based metal complex, nigrosine pigment, ammonium salt-based agent and fatty acid metal salt agent and the amount of the agent is generally 1 to 15% by weight, preferably 1 to 10% by weight based on the toner.

[0086] Conventional surface-treating agent can be used as the surface-treating agent. Representative examples of the agent are hydrophobic silica, alumina, titanium oxide and ultrafine resin particles and the amount of the agent is generally 0.1 to 10% by weight, preferably 0.1 to 7% by weight.

[0087] Conventional wax can be used as the wax. Representative examples of the wax are polypropylene, polyethylene (molecular weight: 1,000 to 10,000) and higher fatty acid salt. The amount of the wax is generally 0.5 to 10% by weight, preferably 1 to 5% by weight based on the toner.

[0088] The above toner composition can be prepared in the form of toner particles having an average particle diameter of from 7 to 20 μ m measured by a Coulter counter by the conventional crushing, pulverization and classification processes after the addition of the above additives.

[0089] The toner composition of the present invention may further contain a small amount, e.g. not more than 20% by weight (based on the total composition) of a heat-stabilizer, an oxidation stabilizer, a light stabilizer, a pigment dispersing agent, a dye-fixing promoting agent, a flame-retardant and a dye as necessary.

Effect of the Invention

[0090] The toner composition of the present invention has especially excellent melt-fluidity, fixability and offset resistance and high blocking resistance because of the use of the above polyester imide resin having high Tg and low softening temperature as the binder resin. Accordingly, the toner composition is extremely useful for electrophotographic printer, magnetic printer, etc.

[0091] Especially, the polyester imide to be used in the present invention has a characteristic feature to enable the use as a binder resin of a toner for a positively charged printing system in contrast with conventional polyester resins restricted to the use in negatively charged printing system owing to the characters of the polymer. Since the polyester imide to be used in the present invention contains a specific imide unit, it is easily imparted with positively charging property compared with conventional polyester resins and is usable as a toner for a positively charged printing system.

[0092] The present invention is explained in more details by the following examples, which do not restrict the scope of the invention. The term "part" in the examples means "parts by weight".

[0093] The reduced viscosity (η sp/C) of the polymer was measured by using a phenol/1,1,2,2-tetrachloroethane mixture (weight ratio: 6/4) at 35°C and a polymer concentration of 1.2 g/dl.

[0094] The Tg of the polymer was determined by the following method using a differential scanning calorimeter DSC220 (product of Seiko Instruments Inc.). The polymer was heated to 200°C at a temperature increasing rate of 20°C/min, quenched with dry ice and measured by the differential scanning calorimeter at a temperature increasing rate of 20°C /min. The temperature at the intersection of the base line and the tangential line of the heat-absorption curve near the Tg was determined on the chart and defined as Tg.

[0095] The softening temperature was measured by "KOKA FLOW TESTER" (manufactured by Shimadzu Corp.) using a nozzle of 1mm ∅ × 10mm under a load of 30 kgf. The sample was heated at a temperature increasing rate of 3 °C /min and the temperature was defined as the softening temperature when 1/2 of 1 gram of the sample was melted and flowed out through the nozzle.

[0096] The average molecular weights (Mw and Mn) were determined in terms of standard polystyrene by dissolving 20 mg each of the samples in 10 ml of THF and measuring the molecular weights by Shodex "GPC system-11" having four columns "Shodex KF-80M" for GPC connected in series using THF as the developing solvent.

[0097] The polyester imide resin was subjected to the following toner tests (1) to (3) and evaluated as a resin for toner binder.

(1) Simplified fixability test

[0098] The generation of offset phenomenon consisting of the adhesion of a resin or a toner composition to a roller was examined by using a conventional hot-roller-type fixability tester. The examination was carried out on two cases, i.e. the generation of print blot caused by the deposition of the toner on a hot roller in the form of toner powder without melting the polymer at a roller temperature of 160°C (cold offset) and the generation of print blot caused by the adhesion of molten polymer to the hot roller without being fixed to a test printing paper at a roller temperature of 200°C (hot offset). The generation of offset phenomenon is shown by the mark X and the absence of the phenomenon is shown by ○ .

(2) Fixing ratio test

[0099] The printing density of a printed matter obtained by the simplified fixability test was measured beforehand. A piece of Sekisui cellophane adhesive tape was applied to the measured part of the printed matter and rubbed 20 strokes with a roller under a load of 1 kg. The tape was peeled off, the printing density of the peeled part was measured and the ratio of the printing densities before and after the application of the tape was defined as the fixing ratio (%). The printing density was measured by using a reflection densitometer.

(3) Blocking property test

[0100] A powdery specimen was filled in a container, left at rest for 1 week in an atmosphere of 45°C and dropped from the container on a 20 mesh sieve. The case absolutely free from powdery specimen on the sieve is shown by the mark ○ , the mark △ shows the case that the lump of the powdery specimen left on the sieve is crushed and passed through the sieve by knocking the sieve, and the mark X is the case that the lump of the powdery specimen is left on the sieve even by knocking the sieve.

Examples 1 to 3 and Comparative Example 1

[0101] Aminoethanol, trimellitic anhydride and propylene glycol were charged into a reaction vessel provided with a stirring apparatus and a distillation system having a rectifying column in respectively specific amounts described in the Table 1, the atmosphere in the reaction vessel was substituted with nitrogen gas at ordinary temperature, and the vessel was heated at 50°C under atmospheric pressure. After reacting the components for 30 minutes, dimethyl terephthalate and diethylene glycol were added to the system in respectively specific amounts described in the Table 1, the system was further incorporated with 4 parts of tetrabutyl titanate and the reaction vessel was heated to 200°C under atmospheric pressure. After keeping the vessel at the reaction temperature (200°C) for 3 hours, the vessel was heated to 220°C and the reaction was continued for 1.5 hours. At the point, 36 parts of water and 560 parts of methanol were distilled out from the system. The reaction was further continued for 1 hour at 240°C under atmospheric pressure in nitrogen gas stream, for 15 minutes in low vacuum of about 20 mmHg and finally for 120 minutes in high vacuum of 1 mmHg or below to obtain a transparent pale-yellow non-crosslinked polyester imide resin.

[0102] The measured results of the number-average molecular weight, the Tg and the softening temperature of the polymer produced by the above method are shown in the Table 1.

[0103] Five (5) parts by weight of carbon black and 1 part of a charge-controlling agent were added to 94 parts by weight of the above polyester imide resin and the mixture was kneaded with a twin-screw extruder in molten state. The obtained pellets were crushed with a jet mill and classified with a classifier to obtain a toner composition having particle diameters of from 10 to 15 μ m.

[0104] The toner composition was evaluated by the above methods and the results are also described in the Table 1.

Table 1

	Example pts/mol	1	2	3	Comparative Example 1
Charged raw material	DMT	1940/100	1940/100	1940/100	1940/100
	TMA	384/20	192/10	384/20	-
	ethanolamine	122/20	61/10	122/20	-
	PG	1522 g	1522 g	1522 g	1522 g
	DEG	637/60	637/60	739/70	637/60
Resin properties	Mn	7900	7900	7500	8000
	Tg(°C)	65	59	61	48
	Softening temp. (°C)	148	144	138	150
Toner test	(1) Simplified fixability Cold offset	○	○	○	○
	(2) Fixing ratio(%	95	95	99	95
	(3) Blocking property	○	○	○	X
DMT: Dimethyl terephthalate TMA : Trimellitic anhydride PG : Propylene glycol DEG : Diethylene glycol					

[0105] The polyester imide resin to be used in the present Invention has low softening temperature for high Tg and excellent offset property, fixability and blocking resistance owing to the introduction of an aromatic imide group and exhibits balanced characteristics as a binder resin for toner.

Example 4

[0106] A reaction vessel furnished with a stirring apparatus and a distillation system having a rectifying column was charged with 122 parts (20 mol) of aminoethanol, 480 parts (25 mol) of trimellitic anhydride and 1522 parts of propylene glycol, the space in the reaction vessel was substituted with nitrogen gas at ordinary temperature and the vessel was heated at 50 °C under atmospheric pressure. After reacting the components for 30 minutes, the system was charged with 1940 parts (100 mol) of dimethyl terephthalate, 637 parts (60 mol) of diethylene glycol and 4 parts of tetrabutyl titanate and the reaction vessel was heated to 200°C under atmospheric pressure. The system was maintained at the reaction temperature (200°C) for 3 hours, heated to 220°C and reacted for 1.5 hours. At the point, 36 parts of water and 560 parts of methanol were distilled out from the system. The reaction was further continued for 1 hour at 240°C under atmospheric pressure in nitrogen gas stream, for 15 minutes in low vacuum of about 20 mmHg and finally for 120 minutes in high vacuum of 1 mmHg or below to obtain a transparent pale-yellow crosslinked polyester imide resin.

[0107] The measured results of the number-average molecular weight, the Tg and the softening temperature of the polymer produced by this process are shown in the Table 2.

Comparative Example 2

[0108] A reaction vessel furnished with a stirring apparatus and a distillation system having a rectifying column was charged with 1522 parts of propylene glycol, 1940 parts of dimethyl terephthalate and 4 parts of tetrabutyl titanate, the space in the reaction vessel was substituted with nitrogen gas at ordinary temperature and the vessel was heated at 200°C under atmospheric pressure. The system was maintained at the reaction temperature (200°C) for 3 hours, heated to 220°C and reacted for 1.5 hours. At the point, 36 parts of water and 560 parts of methanol were distilled out from the system. The reaction was further continued for 1 hour at 240°C under atmospheric pressure in nitrogen gas stream, for 15 minutes in low vacuum of about 20 mmHg and finally for 120 minutes in high vacuum of 1 mmHg or below to obtain a colorless transparent non-crosslinked polyester resin.

[0109] The measured results of the number-average molecular weight, the Tg and the softening temperature of the polymer produced by this process are shown in the Table 2.

Example 5

[0110] A transparent yellow blend polymer was produced by the melt extrusion kneading of 40 parts of the polyester imide resin obtained by the Example 4 and 60 parts of the polyester resin obtained by the Comparative Example 2 using a twin-screw extruder (PCM30 manufactured by Ikegai Corp.) at a cylinder temperature of 170°C.

[0111] The measured results of the number-average molecular weight, the Tg and the softening temperature of the blend polymer produced by this process are shown in the Table 2.

[0112] Pellets were produced by adding 5 parts by weight of carbon black and 1 part of a charge controlling agent to 94 parts by weight of polyester (imide) resins of the above Examples 4 and 5 and the Comparative Example 2 and kneading the mixture by a twin-screw extruder in molten state. The obtained pellets were crushed with a jet mill and classified with a classifier to obtain toners having particle diameter of 10 to 15 μ m.

[0113] The toners were evaluated by the above methods and the results are shown in the Table 2.

Table 2

	Example pts/mol	4	Comparative Example 2	5
Charged raw material	DMT	1940/100	1940 g	Mixture of 40 pts. of the polymer of Example 4 and 60 pts. of the polymer of Comparative Example 2
	TMA	480/25	-	
	ethanolamine	122/20	-	
	PG	1522 g	1522 g	
	DEG	637/60	-	

Table 2 (continued)

	Example pts/mol	4	Comparative Example 2	5
Resin properties	Mn	6800	2500	3500
	Tg(°C)	65	61	63
	Softening temp. (°C)	146	110	123
Toner test	(1) Simplified fixability Cold offset	○	○	○
	Hot offset	○	X	○
	(2) Fixing ratio(%)	95	95	95
	(3) Blocking property	○	X	○

[0114] The polyester imide resin for toner to be used in the present invention has low softening temperature for high Tg and excellent offset property, fixability and blocking resistance owing to the introduction of an aromatic imide group and exhibits balanced characteristics as a binder resin for toner.

Examples 6 to 13

[0115] Aminoethanol, trimellitic anhydride and propylene glycol were charged into a reaction vessel provided with a stirring apparatus and a distillation system having a rectifying column in respectively specific amounts described in the Table 3, the atmosphere in the reaction vessel was substituted with nitrogen gas at ordinary temperature and the vessel was heated at 50°C under atmospheric pressure. After reacting for 30 minutes, dimethyl terephthalate, diethylene glycol and a polyhydric diol were added to the system in respectively specific amounts described in the Table 3, the system was further incorporated with 60 parts of tetrabutyl titanate and the reaction vessel was heated to 200°C under atmospheric pressure. After keeping the vessel at the reaction temperature (200°C) for 8 hours, the vessel was heated to 230°C and the reaction was continued for 2 hours. At the point, 550 parts of water and 9120 parts of methanol were distilled out from the system. The system was evacuated from 760 mmHg to 5 mmHg spending 1 hour and the reaction was further continued for 1.5 hour in high vacuum of 3 mmHg or below to obtain a crosslinked polyester imide resin.

[0116] The obtained polymer was a transparent pale-yellow polymer insoluble in THF and the measurement of the molecular weight was impossible.

[0117] The measured results of the number-average molecular weight, the Tg and the softening temperature of the produced polymer are shown in the Table 3 and the Table 4.

Table 3

	Example parts/mol	6	7	8	9
Charged raw material	DMT	29100/100	29100/100	29100/100	29100/100
	TMA	5910/20.5	8790/30.5	5910/20.5	5910/20.5
	ethanolamine	1830/20	2745/30	1830/20	1830/20
	PG	22830 g	22830 g	22830 g	22830 g
	DEG	9550/60	9550/60	9550/60	9550/60
	glycerol	1380/10	1380/10	2072/15	-
	trimethylol propane	-	-	-	1006/5
	pentaerythritol	-	-	-	-
Resin properties	Tg (°C)	63	67	61	62
	Softening temperature (°C)	179	158	158	150

Table 4

	Example parts/mol	10	11	12	13
Charged raw material	DMT	29100/100	29100/100	29100/100	29100/100
	TMA	5910/20.5	5910/20.5	5910/20.5	5910/20.5
	ethanolamine	1830/20	1830/20	1830/20	1830/20
	PG	22830 g	22830 g	22830 g	22830 g
	DEG	9550/60	9550/60	9550/60	9550/60
	glycerol	-	-	-	691/5
	trimethylol propane	2013/10	-	-	-
	pentaerythritol	-	2021/5	2042/10	511/2.5
Resin properties	Tg (°C)	59	57	57	57
	Softening temperature (°C)	144	151	157	153

Reference Example 1

[0118] A reaction vessel furnished with a stirring apparatus and a distillation system having a rectifying column is charged with 1522 parts of propylene glycol, 1940 parts of dimethyl terephthalate and 4 parts of tetrabutyl titanate, the atmosphere in the reaction vessel was substituted with nitrogen gas at ordinary temperature and the vessel was heated to 200°C under atmospheric pressure. The vessel was maintained at the reaction temperature (200°C) for 3 hours and heated at 220°C and the reaction was continued for 1.5 hours. At the point, 36 parts of water and 560 parts of methanol were distilled out from the system. The reaction was further continued for 1 hour at 240°C under atmospheric pressure in nitrogen gas stream, for 15 minutes in low vacuum of about 20 mmHg and for 120 minutes in high vacuum of 1 mmHg or below to obtain a non-crosslinked polyester resin as the final product.

[0119] The obtained polymer was colorless and transparent and had a number-average molecular weight of 2500, a Tg of 61°C and a softening temperature of 110°C.

Examples 14 to 17

[0120] The polyester imide resins obtained by the Examples 6 to 8 and the polyester resin obtained by the Reference Example 1 were subjected to the extrusion kneading under melting at specific compositional ratios shown in the following Table 5 using a twin-screw extruder (PCM30 manufactured by Ikegai Corp.) at a cylinder temperature of 230°C to obtain a composition.

[0121] The obtained blend polymer (composition) was yellow and transparent. The number-average molecular weights, the glass transition temperatures and the softening temperatures are shown in the Table 5.

[0122] Five (5) parts by weight of carbon black and 1 part of a charge controlling agent were added to 94 parts by weight of each of the above compositions and the mixture was kneaded with a twin screw extruder in molten state. The obtained pellets were crushed with a jet mill and classified with a classifier to obtain toners having particle diameters of from 10 to 15 μ m.

[0123] The toners were evaluated by the aforementioned methods. The results are shown in the Table 5.

Table 5

Example pts/mol		Reference Example 1	14	15	16	17
Polymer of Example 6		-	30	40	-	-
Polymer of Example 7		-	-	-	40	-
Polymer of Example 8		-	-	-	-	40
Polymer of Reference Example 1		100	70	60	60	60

Table 5 (continued)

Example pts/mol		Reference Example 1	14	15	16	17
Resin properties	Mn	2500	3020	-	-	-
	Tg(°C)	61	61	61	63	61
	Softening temp. (°C)	110	119	124	125	123
Toner test	(1) Simplified fixability Cold offset	○	○	○	○	○
	Hot offset	X	○	○	○	○
	(2) Fixing ratio(%)	99	95	95	95	95
	(3) Blocking property	X	○	○	○	○

Examples 18 to 20

[0124] Aminoethanol, a polybasic carboxylic acid anhydride and ethylene glycol were charged into a reaction vessel provided with a stirring apparatus and a distillation system having a rectifying column in respectively specific amounts described in the Table 6, the atmosphere in the reaction vessel was substituted with nitrogen gas at ordinary temperature and the vessel was heated at 50 °C under atmospheric pressure. After reacting for 30 minutes, dimethyl terephthalate, diethylene glycol or neopentyl glycol and glycerol were added to the system in respectively specific amounts described in the Table 6, the system was further incorporated with 60 parts of tetrabutyl titanate and the reaction vessel was heated to 200°C under atmospheric pressure. After keeping the vessel at the reaction temperature (200°C) for 8 hours, the vessel was heated to 230°C and the reaction was continued for 2 hours. Water and methanol were distilled out at the point. The system was evacuated from 760 mmHg to 5 mmHg spending 1 hour and the reaction was further continued for 1.5 hours in high vacuum of 3 mmHg or below to obtain a crosslinked polyester imide resin as the final product.

[0125] The obtained polymer was pale yellow and transparent and insoluble in THF and the measurement of the molecular weight was impossible.

[0126] The measured results of the number-average molecular weight, the Tg and the softening temperature of the produced polymer are shown in the Table 6.

Table 6

	Example parts/mol	18	19	20
Charged raw material	DMT	29100/100	388/100	388/100
	TMA	5910/20	79/20	-
	PMA	-	-	45/10
	ethanolamine	1830/20	24/20	24/20
	EG	13950 g	186 g	186 g
	DEG	9550/60	-	127/60
	neopentyl glycol	-	42/20	-
	glycerol	2763/20	18/10	18/10
Resin properties	Tg (°C)	58	76	55
	Softening temperature (°C)	143	137	146
PMA : Pyromellitic anhydride				

Examples 21 and 22

[0127] Aminoethanol, trimellitic anhydride and ethylene glycol were charged into a reaction vessel provided with a stirring apparatus and a distillation system having a rectifying column in respectively specific amounts described in the

Table 7, the atmosphere in the reaction vessel was substituted with nitrogen gas at ordinary temperature and the vessel was heated at 50°C under atmospheric pressure. After reacting for 30 minutes, dimethyl terephthalate, dimethyl isophthalate and diethylene glycol or neopentyl glycol were added to the system in respectively specific amounts described in the Table 7, the system was further incorporated with 4 parts of tetrabutyl titanate and the reaction vessel was heated to 200°C under atmospheric pressure. After keeping the vessel at the reaction temperature (200°C) for 3 hours, the vessel was heated to 220°C and the reaction was continued for 1.5 hours. At the point, 36 parts of water and 560 parts of methanol were distilled out from the system. The reaction was further continued for 1 hour at 240°C in nitrogen gas stream under atmospheric pressure, for 15 minutes in low vacuum of about 20 mmHg and then for 120 minutes in high vacuum of 1 mmHg or below to obtain a pale yellow transparent non-crosslinked polyester imide resin as the final product.

[0128] The measured results of the number-average molecular weight, the Tg and the softening temperature of the polymers obtained by the above process are shown in the Table 7.

Table 7

	Example parts/mol	21	22
Charged raw material	DMT	20370/70	272/70
	DMI	8730/30	116/30
	TMA	3030/10	20/5
	ethanolamine	915/10	6/5
	EG	13950 g	186 g
	DEG	1590/10	-
	neopentyl glycol	-	21/10
Resin properties	Tg (°C)	55	63
	Softening temperature (°C)	110	119
DMI : Dimethyl isophthalate			

Claims

1. A toner composition comprising a coloring agent and at least one kind of polymer selected from the group consisting of A and B.

   A : a non-crosslinked polyester imide

   (i) comprising mainly an ester unit E represented by the following formula (1) below and at least one kind of imide unit I selected from the group consisting of-units represented by the following formulas (2) and (3) below, E and I are bonded through ester bond;
   (ii) having physical properties of

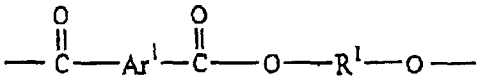
   (a) a number-average molecular weight of from 2,000 to 10,000,
   (b) a glass transition temperature of from 50 to 90°C and
   (c) a softening temperature of from 90 to 160°C ;

   (iii) satisfying the following formula (A-1)

$$0.01 \leqq a_2/a_1 \leqq 0.60 \qquad \text{(A-1)}$$

   (wherein a_1 is the mol% of the ester unit E and a_2 is the mol% of the imide unit I based on the all units constituting the non-crossed polyester imide A)

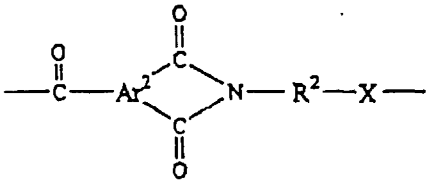
   formula (1)



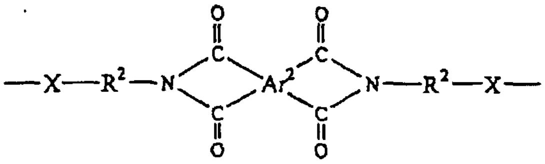
$$-\overset{O}{\overset{\|}{C}}-Ar^1-\overset{O}{\overset{\|}{C}}-O-R^1-O- \qquad (1)$$

(wherein Ar^1 is a bivalent aromatic hydrocarbon group having a carbon number of from 6 to 12, and R^1 is at least one kind of group selected from the group consisting of an alkylene group, an oxyalkylene group and a polyoxyalkylene group each having a carbon number of from 2 to 20)

formula (2) and (3)



(2)



(3)

(wherein Ar^2 is a tri- or tetravalent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^2 is an alkylene group having a carbon number of from 2 to 12, and X is -CO- or -O-)

B : a crosslinked polyester imide

(iv) comprising mainly the above ester unit E, the above imide unit I and at least one kind of crosslinking unit C selected from the group consisting of units represented by the following formulas (4) and (5) below, the above three units (E, I and C) are bonded together through ester bond,
(v) having physical properties of

(d) a glass transition temperature of from 50 to 90°C and
(e) a softening temperature of from 90 to 190°C,

(vi) satisfying the following formulas (B-1) and (B-2)

$$0.01 \leqq b_2/b_1 \leqq 0.60 \qquad (B\text{-}1)$$

$$0.01 \leqq b_3/b_1 \leqq 0.40 \qquad (B\text{-}2)$$

(wherein b_1 is the mol% of the ester unit E, b_2 is the mol% of the imide unit I, and b_3 is the mol% of the crosslinking unit C based on the all units constituting the crosslinked polyester imide B).
formulas (4) and (5)

$$Ar^3\text{-}(\text{-CO-})_r\text{-} \qquad (4)$$

$$R^3\text{-}(\text{-O-})_q\text{-} \qquad (5)$$

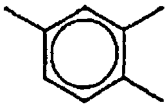
(wherein Ar^3 is an r-valent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^3 is a q-valent aliphatic group having a carbon number of from 3 to 9, and r and q are each 3 or 4)

2. A toner composition according to Claim 1, wherein the group R^1 in the above formula (1) is at least one kind of group selected from the group consisting of an alkylene group and an oxyalkylene group each having carbon number of from 2 to 6.

3. A toner composition according to Claim 1, wherein the group Ar^1 in the above formula (1) is at least one kind of group selected from 1,4-phenylene group and 1,3-phenylene group.

4. A toner composition according to Claim 1, wherein the group R^2 in the above formula (2) is an alkylene group having a carbon number of from 2 to 6 and the group X is -O-.

5. A toner composition according to Claim 1, wherein the group Ar^2 in the above formula (2) is a benzene ring bonded to other atoms at 1,2 and 4 positions which is represented by the following formula (Ar2-1).



(Ar2-1)

6. A toner composition according to Claim 1, wherein the non-crosslinked polyester imide A satisfies the following formula (A-2)

$$0.05 \leqq a_2/a_1 \leqq 0.50 \quad \text{(A-2)}$$

(wherein the definitions of the terms a_1 and a_2 are same as those described above).

7. A toner composition according to Claim 1, wherein the crosslinking unit C is represented by the following formula (5-1)

$$R^{31}\text{-(-O-)}_3\text{-} \quad \text{(5-1)}$$

(wherein R^{31} is a trivalent aliphatic group having a carbon number of from 3 to 6).

8. A toner composition according to Claim 1, wherein the crosslinked polyester imide B satisfies the following formulas (B-1-1) and (B-2-1)

$$0.05 \leqq b_2/b_1 \leqq 0.50 \quad \text{(B-1-1)}$$

$$0.03 \leqq b_3/b_1 \leqq 0.20 \quad \text{(B-2-1)}$$

(wherein the definitions of the terms b_1, b_2 and b_3 are same as those described above).

9. A toner composition according to Claim 1, wherein the non-crosslinked polyester imide A has a number-average molecular weight of from 2,500 to 8,000.

10. A toner composition according to Claim 1, wherein the ratio of the polymer in the toner composition is from 40 to 99% by weight.

11. A toner composition comprising a coloring agent and at least one kind of polymer selected from the group consisting of A and B.

A : a non-crosslinked polyester imide

(i) comprising mainly an ester unit E represented by the following formula (1-1) below and an imide unit I represented by the following formula (2-1) below, E and I are bonded through ester bond;
(ii) having physical properties of

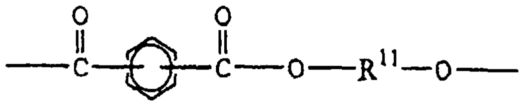
(a) a number-average molecular weight of from 2,000 to 10,000,
(b) a glass transition temperature of from 55 to 85°C and
(c) a softening temperature of from 90 to 150°C ;

(iii) satisfying the following formula (A-2)

$$0.05 \leqq a_2/a_1 \leqq 0.50 \qquad \text{(A-2)}$$

(wherein a_1 is the mol% of the ester unit E and a_2 is the mol% of the imide unit I based on the all units constituting the non-crosslinked polyester imide A)

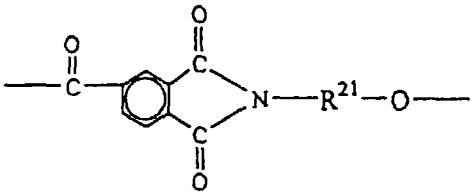
formula (1-1)



(1-1)

(wherein R^{11} is at least one kind of group selected from the group consisting of an alkylene group and an oxyalkylene group each having a carbon number of from 2 to 6)

formula (2-1)



(2-1)

(wherein R^{21} is an alkylene group having a carbon number of from 2 to 5)

B: a crosslinked polyester imide

(iv) comprising mainly the above ester unit E represented by formula (1-1), the above imide unit I represented by the formula (2-1) and a crosslinking unit C represented by the following formula (5-1) below, the above three units (E, I and C) are bonded through ester bond,
(v) having physical properties of

(d) a glass transition temperature of from 55 to 85°C and
(e) a softening temperature of from 110 to 160°C,

(vi) satisfying the following formulas (B-1-1) and (B-2-1)

$$0.05 \leqq b_2/b_1 \leqq 0.50 \qquad \text{(B-1-1)}$$

$$0.03 \leqq b_3/b_1 \leqq 0.20 \qquad \text{(B-2-1)}$$

(wherein b_1 is the mol% of the ester unit E, b_2 is the mol% of the imide unit I, and b_3 is the mol% of the crosslinking unit C based on the all units constituting the crosslinked polyester imide B).

formula (5-1)

$$R^{31}\text{-(-O-)}_3\text{-} \qquad \text{(5-1)}$$

(wherein R^{31} is an aliphatic group having a carbon number of from 3 to 6)

12. A toner composition according to Claim 11, wherein the ratio of the above polymer in said toner composition is from 40 to 99% by weight.

13. A non-crosslinked polyester imide suitable for toner,

(i) comprising mainly an ester unit E represented by the following formula (1) below and at least one kind of imide unit I selected from the group consisting of units represented by the following formulas (2) and (3) below, E and I are bonded through ester bond;
(ii) having physical properties of

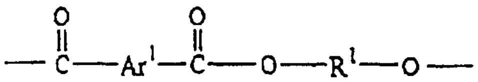
(a) a number-average molecular weight of from 2,000 to 10,000,
(b) a glass transition temperature of from 50 to 90°C and
(c) a softening temperature of from 90 to 160°C ;

(iii) satisfying the following formula (A-1)

$$0.01 \leqq a_2/a_1 \leqq 0.60 \qquad \text{(A-1)}$$

(wherein a_1 is the mol% of the ester unit E and a_2 is the mol% of the imide unit I based on the all units constituting the non-crosslinked polyester imide A)

formula (1)

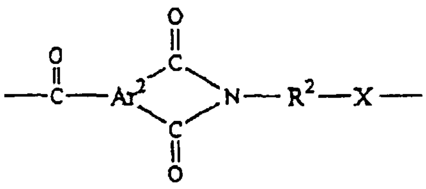


$$-\overset{\overset{\displaystyle O}{\|}}{C}-Ar^{1}-\overset{\overset{\displaystyle O}{\|}}{C}-O-R^{1}-O-$$

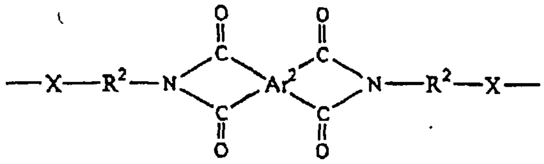
(1)

(wherein Ar^1 is a bivalent aromatic hydrocarbon group having a carbon number of from 6 to 12, and R^1 is at least one kind of group selected from the group consisting of an alkylene group, an oxyalkylene group and a polyoxyalkylene group each having a carbon number of from 2 to 20)

formula (2) and (3)



(2)

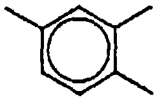


(3)

(wherein Ar^2 is a tri- or tetravalent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^2 is an alkylene group having a carbon number of from 2 to 12, and X is-CO-or -O-)

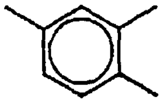
14. A non-crosslinked polyester imide according to Claim 13, wherein the group R^1 in the above formula (1) is at least one kind of group selected from the group consisting of an alkylene group and an oxyalkylene group each having a carbon number of from 2 to 6 and the group Ar^1 is at least one kind of group selected from 1,4-phenylene group and 1,3-phenylene group.

15. A non-crosslinked polyester imide according to Claim 13, wherein the group R^2 in the above formula (2) is an alkylene group having a carbon number of from 2 to 5, X is -O- and Ar^2 is a benzene ring bonded to other atoms at 1, 2 and 4 positions which is represented by the following formula (Ar2-1).



(Ar2-1)

16. A non-crosslinked polyester imide suitable according to Claim 13, wherein the group R^1 in the above formula (1) is at least one kind of group selected from the group consisting of an alkylene group and an oxyalkylene group each having a carbon number of from 2 to 6, the group Ar^1 is at least one kind of group selected from 1,4-phenylene and 1,3-phenylene group, the group R^2 in the above formula (2) is ethylene group, X is -O- and Ar^2 is a bensene ring bonded to other atoms at 1, 2 and 4 positions which is represented by the following formula (Ar2-1)



(Ar2-1)

provided that the non-crosslinked polyester imide has a number-average molecular weight of from 2,500 to 8,000, a glass transition temperature of from 55 to 85°C and a softening temperature of from 95 to 130°C and satisfies the following formula (A-2)

$$0.05 \leqq a_2/a_1 \leqq 0.50 \quad \text{(A-2)}$$

(wherein the definitions of the terms a_1 and a_2 are same as those described above).

17. A non-crosslinked polyester imide according to Claim 16, wherein the alkylene group R^1 having a carbon number of from 2 to 6 is ethylene group, 1,2-propylene group or neopentylene group.

18. A crosslinked polyester imide suitable for toner,

(iv) comprising mainly an ester unit E represented by the following formula (1) below, at least one kind of imide unit I selected from the group consisting of units represented by the following formulas (2) and (3) below, and at least one kind of crosslomking unit C selected from the group consisting of units represented by the following formulas (4) and (5) below, the above three units (E, I and C) are bonded together through ester bond,
(v) having physical properties of

(d) a glass transition temperature of from 50 to 90°C and
(e) a softening temperature of from 90 to 190°C,

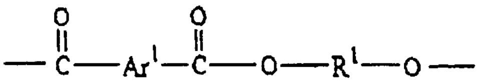
(vi) satisfying the following formula (B-1) and (B-2)

$$0.10 \leqq b_2/b_1 \leqq 0.60 \quad \text{(B-1)}$$

$$0.01 \leqq b_3/b_1 \leqq 0.40 \quad \text{(B-2)}$$

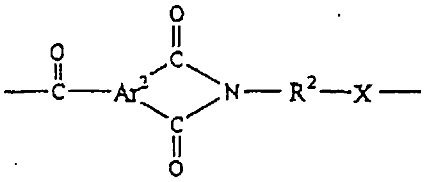
(wherein b_1 is the mol% of the ester unit E, b_2 is the mol% of the imide unit I, and b_3 is the mol% of the crosslinked unit C based on the all units constituting the crosslinked polyester imide B)

formula (1)

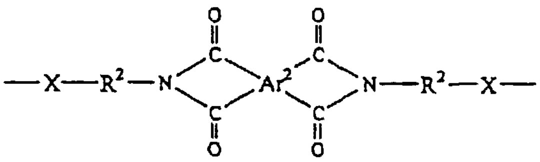


$$-\overset{O}{\overset{\|}{C}}-Ar^1-\overset{O}{\overset{\|}{C}}-O-R^1-O- \qquad (1)$$

(wherein Ar^1 is a bivalent aromatic hydrocarbon group having a carbon number of from 6 to 12, and R^1 is at least one kind of group selected from the group consisting of an alkylene group, an oxyalkylene group and a polyoxyalkylene group each having a carbon number of from 2 to 20)
formula (2) and (3)



(2)



(3)

(wherein Ar^2 is a tri- or tetravalent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^2 is an alkylene group having a carbon number of from 2 to 12, and X is -CO- or -O-)
formulas (4) and (5)

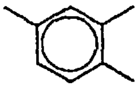
$$Ar^3(\text{-CO-})_r\text{-} \qquad (4)$$

$$R^3\text{-}(\text{-O-})_q\text{-} \qquad (5)$$

(wherein Ar^3 is an r-valent aromatic hydrocarbon group having a carbon number of from 6 to 12, R^3 is a q-valent aliphatic group having a carbon number of from 3 to 9, and r and q are each 3 or 4)

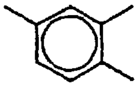
19. A crosslinked polyester imide according to Claim 18, wherein the group R^1 in the above formula (1) is at least one kind of group selected from the group consisting of an alkylene group and an oxyalkylene group each having a carbon number of from 2 to 6 and Ar^1 is at least one kind of group selected from 1,4-phenylene group and 1,3-phenylene group.

20. A crosslinked polyester imide according to Claim 18, wherein the group R^2 in the above formula (2) is an alkylene group having a carbon number of from 2 to 5, X is -O- and Ar^2 is a benzene ring bonded to other atoms at 1,2 and 4 positions which is represented by the following formula (Ar2-1).



(Ar2-1)

21. A crosslinked polyester imide according to Claim 18, wherein the group R^1 in the above formula (1) is at least one kind of group selected from the group consisting of an alkylene group and an oxyalkylene group each having a carbon number of from 2 to 6, and the group Ar^1 is at least one kind of group selected from 1,4-phenylene group and 1,3-phenylene group, the group R^2 in the above formula (2) is ethylene group, X is -O- and Ar^2 is a benzene ring bonded to other atoms at 1, 2 and 4 positions which is represented by the following formula (Ar2-1),



(Ar2-1)

the crosslinking unit C is represented by the following formula (5-1)

$$R^{31}\text{-(-O-)}_3\text{-} \quad (5\text{-}1)$$

(wherein R^{31} is an aliphatic group having a carbon number of from 3 to 6), provided that the polymer has a glass transition temperature of from 55 to 85°C and a softening temperature of from 110 to 160°C and satisfies the following formulas (B-1-1) and (B-2-1)

$$0.05 \leqq b_2/b_1 \leqq 0.50 \quad (B\text{-}1\text{-}1)$$

$$0.03 \leqq b_3/b_1 \leqq 0.20 \quad (B\text{-}2\text{-}1)$$

(wherein the definitions of the terms b_1, b_2 and b_3 are same as those described above).

22. A crosslinked polyester imide according to Claim 21, wherein the alkylene group R^1 having a carbon number of from 2 to 6 is ethylene group, 1,2-propylene group or neopentylene group.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/03474

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^6 G03G9/087

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)
Int.Cl^6 G03G9/087

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

Jitsuyo Shinan Koho	1963-1996	Toroku Jitsuyo Shinan Koho	1994-1997
Kokai Jitsuyo Shinan Koho	1971-1998	Jitsuyo Shinan Toroku Koho	1996-1998

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 7-219273, A (Xerox Corp.), 18 August, 1995 (18. 08. 95), Claim 1 & US, 5427881, A & EP, 666508, A1	1-22
A	JP, 7-134446, A (Sanyo Chemical Industries, Ltd.), 23 May, 1995 (23. 05. 95), Claim 1 (Family: none)	1-22

☐ Further documents are listed in the continuation of Box C. ☐ 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
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"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
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"&" document member of the same patent family

Date of the actual completion of the international search 21 October, 1998 (21. 10. 98)	Date of mailing of the international search report 4 November, 1998 (04. 11. 98)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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