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(71) Applicant: **SANYO CHEMICAL INDUSTRIES LTD.**
Kyoto 605 (JP)

(72) Inventors:
• **Taguchi, Takayuki**
Yasu-gun, Shiga-ken (JP)

- **Hasegawa, Kenichi,**
Kinkitochi Oike Bildg. No. 308
Nakagyo-ku, Kyoto (JP)
- **Baba, Sohkiichi**
Osaka (JP)
- **Takai, Yoshitsugu,**
Famille Fushimi A-302
Fushimi-ku, Kyoto (JP)

(74) Representative: **Gaunt, Robert John**
London EC4Y 1LL (GB)

(54) **Releasing composition and binder resin composition for electrophotographic toner, and toner containing the same**

(57) A releasing composition, comprising

- (A) a low molecular weight polypropylene, and
(B) a modified polyolefin, such as a low molecular weight polypropylene or polyethylene modified with ethylenically unsaturated carboxylic acid, such as (meth)acrylic or maleic acid or anhydride thereof,

is used with a thermoplastic binder resin, such as a polyester resin, for electrophotographic toners, whereby resin compositions of improved flowability are attained without reducing offset temperature of toners.

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DescriptionBACKGROUND OF THE INVENTION5 1. Field of the Invention

This invention relates to a releasing composition suitable for electrophotographic toner (hereinafter referred to as toner). More particularly, it relates to a releasing composition for toner, particularly suitable for that used in copy machines or printers of heat fixation type.

10 2. Description of the Prior Art

Toners, in heat fixation methods, are fixed on a substrate with a heated roller. In these methods, it is desired that the minimum temperature for fixing (hereinafter referred to as MF) is low and the hot offset temperature (the temperature causing offset to the heated roller) (hereinafter referred to as HO) is high. In order to meet these two requirements, it has been heretofore proposed to add a releasing agent such as low molecular weight polypropylene during the preparation of toners to attain an elevated HO. In these techniques, there are drawbacks, that use of such a releasing agent as low molecular weight polypropylene results in poor toner flowability (hereinafter referred to as TF), and that sufficiently high HO is not always obtained. In order to remedy these drawbacks, there have been made researches, such as modifying it with carboxylic acid or anhydride thereof. Such modified low molecular weight polypropylenes, however, are not put to practical use because of drawback reducing HO, though they can suppress reduction of TF.

SUMMARY OF THE INVENTION

25 It is an object of the present invention to provide a releasing composition capable of providing improved TF.

It is another object of the present invention to provide a releasing composition capable of providing high HO together with improved TF.

It is still another object of the present invention to provide such a toner binder composition capable of providing high HO without reducing TF.

30 It is yet another object of the present invention to provide such a toner binder composition, which can reduce filming or adhere of toner onto carrier particles.

Briefly, these and other objects of the present invention as hereinafter will become more readily apparent have been attained broadly by a releasing composition suitable for electrophotographic toner, which comprises

- 35 (A) a low molecular weight polypropylene, and
(B) a modified polyolefin, selected from the group consisting of

(B1) a modified polypropylene, comprising a low molecular weight polypropylene (a1) having higher melt viscosity at 160°C than said polypropylene (A), modified with an acidic monomer (b1), and

40 (B2) a modified polyethylene, comprising a low molecular weight polyethylene (a2) having a melt viscosity of 10~ 8,000 cps at 140°C, modified with an acidic monomer (b2).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

45 (A) Low Molecular Weight Polypropylene

Suitable polypropylenes include propylene homopolymers, and copolymers of propylene with up to 25% (preferably up to 20%, more preferably up to 10%) of one or more other monomers copolymerizable therewith, for example, ethylene, and olefines containing 4 ~ 8 or more carbon atoms (such as butene and octene). (In the above and hereinafter, % represents % by weight, unless otherwise specified.) Copolymers containing less than 75% propylene units may result in lower HO.

Melt viscosity at 160°C of said polypropylene resin (A) is usually 10 ~ 3,000 cps (centipoises), preferably 15 ~ 2,000 cps. Polypropylenes of melt viscosity higher than 3,000 cps result in poor hot offset effects when used in toners. In case of melt viscosity lower than 10 cps, flowability of tonners becomes poor. Melt viscosity at 160°C is measured with a Brookfield rotational viscometer, under conditions in accordance with JIS-K1557-1970, except the measuring temperature. Temperature of the sample to be measured can be adjusted with an oil bath equipped with a temperature regulator.

Among these polypropylenes, preferred are thermally degraded products of high molecular weight polypropylene resins. Thermal degradation can be accomplished, for example, by passing a high molecular weight polypropylene resin through a reaction vessel, such as a tubular reactor, capable of applying heat homogeneously, at a temperature of 300

~ 450°C during 0.5 ~ 10 hours. The melt viscosity of thermally degraded products can be controlled by the degradation temperature and the degradation period. When the temperature is less than 300°C, longer period of time is required to attain low melt viscosity; while it is difficult to control the melt viscosity on account of too rapid degradation at the temperature exceeding 450°C.

(B) Modified Polyolefin

(B1) Modified Polypropylene

a) Base Polypropylene (a1)

Suitable low molecular weight polypropylenes (a1), constituting said modified polypropylene (B1) in this invention, include the same ones as the above-mentioned, which may be the same or different as (A) except that (a1) having a melt viscosity at 160°C higher than that of (A). Preferable ratio of the melt viscosity of at 160°C of said polypropylene (a1) to the melt viscosity at 160°C of said (A) is not more than 500/1, more preferably not more than 50/1, particularly not more than 5/1, and at least 1.1/1.

Melt viscosity at 160°C of said polypropylene (a1) is usually higher than 10 cps and not more than 5,000 cps, preferably 15 ~ 3,000 cps. When the melt viscosity is higher than 5,000 cps, hot offset of toners become poor. Suitable polypropylenes (a1) include, for example, thermally degraded polypropylenes, unmodified or modified with one or more monomers other than acidic monomers; and oxydates of these modified or unmodified, thermally degraded polypropylenes.

Suitable thermally degraded polypropylenes include ones obtainable by thermal degradation of high molecular weight polypropylene resins, usually having a melt index of 0.1 ~ 150 g/10min. or more, preferably 1 ~ 100 g/10min., as measured in accordance with JIS K6758. Such high molecular weight polypropylene resins are inclusive of propylene homopolymers, and copolymers of propylene with one or more other monomers copolymerizable therewith, for example, ethylene, and olefins containing 4 ~ 8 or more carbon atoms (such as butene and octene); as well as propylene (co)polymers modified with one or more monomers other than acidic monomers. Examples of suitable monomers, usable for modification of polypropylenes, before or after thermal degradation, include styrenic monomers, such as styrene, α -methylstyrene, p-methylstyrene and p-methoxystyrene; esters [such as alkyl ($C_1 \sim 18$) esters] of ethylenically unsaturated carboxylic acids [such as (meth)acrylic, maleic and itaconic acids], for instance, methyl, ethyl and butyl (meth)acrylates, and mono- or di-methyl, ethyl and butyl maleates; ethylenically unsaturated nitriles, such as (meth)acrylonitriles; ethylenically unsaturated organo silane compounds and ethylenically unsaturated organo fluorine compounds, as mentioned in US Patent No.5,238,767; and mixtures of two or more of these monomers.

Thermal degradation can be done in the same manner as described in the (A).

Modification may be carried out in the presence or absence of peroxide catalyst.

Oxydates of these modified or unmodified thermally degraded polypropylenes can be produced by partially oxidizing such polypropylenes with oxygen or oxygen-containing gas (air), or with ozone-containing oxygen or ozone-containing gas (air). The resulting oxydates have an acid value of usually at most 80, preferably at most 50.

The content of propylene units of these polypropylene (a1) is generally at least 75%, preferably at least 80%, more preferably at least 90%. Copolymers containing less than 75% propylene units may results in toners of lower HO.

Among these polypropylenes (a1), preferred are thermally degraded polypropylenes.

b) Acidic Monomer (b1)

Suitable acidic monomers (b1), for modification of said polypropylene (a1), include ethylenically unsaturated carboxylic acids and/or anhydrides thereof, for example, (meth)acrylic acids (acrylic acid and/or methacrylic acid; similar expressions are used hereinafter), maleic acid, fumaric acid and itaconic acid; anhydrides, such as maleic, itaconic, citraconic, allylsuccinic and nadic anhydrides; and mixtures of two or more of them. Among these, preferred are (meth)acrylic acids, maleic acid and anhydride thereof, particularly maleic acid and anhydride thereof.

The content of acidic monomer (b1), constituting said modified polypropylene (B1), is generally 0.1 ~ 50%, preferably 0.2 ~ 40%, more preferably 0.5 ~ 30%, based on the weight of (a1). Use of (b1) larger than 50% results in too hygroscopic modified polypropylene, which may make image concentration unstable when used in toners. When (b1) is less than 0.1%, sufficient effects of improving TF are not attained.

c) Preparation of Modified Polypropylene (B1)

Modified polypropylenes (B1) can be produced by carrying out grafting or addition reaction of one or more monomers comprising said acidic monomer (b1) onto said polypropylene (a1) in the presense of or in the absense of peroxide catalyst.

In addition to (b1), there may be used up to 30%, preferably up to 20% [based on the weight of (a1)] of one or more other monomers, as mentioned above [such as styreic monomers, alkyl (meth)acrylates, alkyl maleates; unsaturated nitriles, unsaturated organo silane and unsaturated organo fluorine compounds].

Modification is generally carried out within an atmosphere of inert gas, such as nitrogen. The reaction may be carried out at a temperature of usually between the melting point of polyolefin and 300 °C, preferably 140 ~ 250°C, for 1 ~ 20 hours. Suitable peroxide catalysts, optionally used in the reaction, include, for example, benzoyl peroxide, lauroyl peroxide, di-t-butyl peroxide, t-butylcumyl peroxide, dicumyl peroxide, t-butylperoxybenzoate, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, and the like.

d) Modified Polypropylene (B1)

Modified polypropylene (B1) usually has an acid number of 0.5 ~ 100, preferably 1 ~ 40, more preferably 1 ~ 20. Products having an acid number less than 0.5 provide toners of poor TF, while ones having an acid number higher than 100 may lower HO of toners.

Modified polypropylene (B1) generally has a number-average molecular weight (hereinafter referred to as $\overline{Mn}$) of usually 1,000~ 20,000, preferably 1,500 ~ 10,000, more preferably 2,000~ 8,000.

(B2) Modified Polyethylen

a) Base Polyethylene (a2)

Low molecular weight polyethylenes (a2), constituting said modified polyethylene (B2) in this invention, are low molecular weight polyethylenes having a melt viscosity of 10 ~ 8,000 cps, preferably 15 ~ 5,000 cps at 140°C, including low density ones, intermediate density ones and high density ones.

Suitable low molecular weight polyethylenes (a2) include, for example, polyethylenes obtainable by oligomerization; thermally degraded polyethylenes, unmodified or modified with one or more monomers other than acidic monomers; and oxydates of these modified or unmodified, thermally degraded polyethylenes.

Suitable thermally degraded polyethylenes include ones obtainable by thermal degradation of high molecular weight polyethylene resins, usually having a melt flow rate (MFR) of 0.1 ~ 300 or more, preferably 1 ~ 250, as measured in accordance with JIS K6760 (at 190 °C and 2.16kgf load). Such high molecular weight polyethylene resins are inclusive of ethylene homopolymers, and copolymers of ethylene with one or more other monomers copolymerizable therewith, for example, olefins containing 3 ~ 12 or more carbon atoms (such as propylene, 1-butene, 4-methyl-1-pentene, 1-pentene, 1-octene, 1-decene and 1-dodecene); as well as ethylene (co)polymers modified with one or more monomers other than acidic monomers. Examples of suitable monomers, usable for modification of polyethylenes before or after thermal degradation, include the same ones as mentioned above [such as styrenic monomers, alkyl (meth)acrylates, alkyl maleates, unsaturated nitriles, unsaturated organo silanes and unsaturated organo fluorine compounds].

Thermal degradation of polyethylene resins can be accomplished in the same manner as that of polypropylene resins described in the (A), except that the temperature may be 250 ~ 450°C. Modification and oxidation (production of oxidates) may be carried out in the same manner as polypropylenes.

The content of ethylene units of these polyethylenes is generally at least 75%, preferably at least 80%, more preferably at least 90%. Copolymers containing less than 75% ethylene units may results in toners of lower HO.

Low molecular weight polyethylenes (a2), such as thermally degraded ones, generally have a $\overline{Mn}$ of 800 ~ 20,000, preferably 1,000 ~ 10,000, as measured by GPC (gel permeation chromatography). Sufficient TF improving effects are not attained, when $\overline{Mn}$ is less than 800. Polyethylenes having $\overline{Mn}$ higher than 20,000 have a tendency to reduce HO.

Softening point of (a2) is usually 70 ~ 200°C preferably 90 ~ 180°C, which can be measured according to ring and ball method of JIS K2207. Sufficient improvement in TF is not attained, when softening point is less than 70°C. MF improving effects become insufficient in case of softening point exceeding 200°C.

Melt viscosity of (a2) is usually 10 ~ 8,000 cps, preferably 15 ~ 5,000 cps at 140°C. Flowability of toners becomes poor with lower melt viscosity than 10 cps. In case it exceeds 8,000 cps, there is a tendency of reducing HO.

Among low molecular weight polyethylenes (a1), preferred are thermally degraded polyethylenes.

Suitable thermally degraded polyethylenes include ones containing usually 1 ~ 10, preferably 2 ~ 7 terminal double bonds per 1,000 carbon atoms. Ones containing less than 1 terminal double bond per 1,000 carbon atoms cannot be reacted with sufficient amount of acidic monomer and provide toners of poor TF.

b) Acidic Monomer (b2)

Suitable acidic monomers (b2), for modification of said polyethylene (a2), include the same ones as the above-mentioned acidic monomers (b1). Among these, preferred are (meth)acrylic acids, maleic acid and anhydride thereof, particularly maleic acid and anhydride thereof.

The content of acidic monomer (b2), constituting said modified polyethylene (B2), is generally 0.1 ~ 50%, preferably 0.2 ~ 40%, more preferably 0.5 ~ 30%, based on the weight of (a2). Use of (b2) larger than 50% results in too hygroscopic modified polyethylene, which may make image concentration unstable when used in toners. When (b2) is less than 0.1%, sufficient effects of improving TF are not attained.

c) Preparation of Modified Polyethylene (B2)

Modified polyethylenes (B2) can be produced by carrying out grafting or addition reaction of one or more monomers comprising said acidic monomer (b2) onto said polyethylene (a2) in the presence of or in the absence of peroxide catalyst, in the same manner as modified polypropylene (B1). Similarly, up to 30% of one or more other monomers may be used in addition to (b2).

d) Modified Polyethylene (B2)

Modified polyethylene (B2) usually has an acid number of 0.5 ~ 100, preferably 1 ~ 50, more preferably 1 ~ 20. Products having an acid number less than 0.5 provide toners of poor TF, while ones having an acid number higher than 100 may lower HO of toners.

Modified polyethylene (B2) generally has a $\overline{Mn}$ of usually 1,000 ~ 20,000, preferably 1,500 ~ 10,000, more preferably 2,000 ~ 8,000. Products having $\overline{Mn}$ less than 1,000 provide toners of poor TF, while ones having $\overline{Mn}$ higher than 10,000 may lower HO of toners.

(I) Releasing composition

In releasing compositions of the present invention, comprising a low molecular weight polypropylene (A) and a modified polyolefin (B) [(B1) and/or (B2)], the content of (A) is generally 60 ~ 99.5%, preferably 70 ~ 99%, more preferably 80 ~ 98%, and the content of (B) is usually 0.5 ~ 40%, preferably 1 ~ 30%, more preferably 2 ~ 20%. Use of (B) less than 0.5% results in poor TF improving effects of toners, while (B) exceeding 60% may cause reduction of HO.

(II) Binder Resin

Suitable binders include thermoplastic resins, for example, polyester resins, styrenic and/or acrylic resin, epoxy resins, polyurethane resins, and the like.

Suitable polyesters include, for example, polycondensation products of a polycarboxylic acid component with a polyol component, and ring-opening polymers of a lactone. Examples of suitable polyols include aliphatic diols, such as ethylene glycol, 1,2- and 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and neopentyl glycol and diethylene glycol, and alcoholates (such as sodium alcoholate) of these diols; cycloaliphatic diols, such as cyclohexylene glycol, cyclohexane dimethanol and hydrogenated bisphenol A; aromatic diols, such as bisphenols (such as bisphenol A, bisphenol S and bisphenol F) and hydroquinone, and esters and alcoholates of these phenols (such as diacetylbisphenol A and bisphenol A disodium alcoholate); aliphatic polyols containing 3 ~ 8 hydroxyl groups, such as trimethylolpropane, glycerine, pentaerythritol and the like; as well as alkylene oxide ($C_2 \sim C_4$) (hereinafter referred to as AO) adducts of these diols and polyols, such as ethylene oxide (hereinafter referred to as EO) and/or propylene oxide (hereinafter referred to as PO) adducts of bisphenol A, and EO and/or PO adducts of bisphenol F; polyalkylene glycols, such as polyethylene glycol, polypropylene glycol and polytetramethyleneether glycol. Among these, preferred are AO adducts of aromatic diols, aliphatic diols and combinations of them, particularly AO adducts of aromatic diols (especially PO adducts of bisphenol A). Illustrative of suitable polycarboxylic acid components are $C_2 \sim C_{30}$ aliphatic dicarboxylic acids, such as malonic, succinic, adipic, sebacic and dodecane dicarboxylic acids, and esters and halides of these acids, such as dimethyl adipate and adipic dichloride; aromatic dicarboxylic acids, such as terephthalic, isophthalic, phthalic and naphthalene dicarboxylic acids, esters and halides of these acids, such as dimethyl terephthalate and terephthalic dichloride; and tribasic or higher carboxylic acids, such as trimellitic acid. Among these, preferred are aromatic dicarboxylic acid and combination thereof with aliphatic dicarboxylic acid. Suitable lactones include caprolactone. Polyesters may be hydroxyl-terminated or carboxyl-terminated. Illustrative of suitable polyester resins are polyesters of terephthalic acid with PO adducts of bisphenol A.

Suitable styrenic and/or acrylic resins include, for example, (co)polymers of one or more styrenic monomers [such as styrene; and styrene homologues or substituted styrenes, including alkyl($C_1 \sim C_8$)styrenes (such as α -methylstyrene, o-, m- and p-methylstyrenes, p-ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene, p-t-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, aryl-substituted styrenes (such as p-phenylstyrene), alkoxy-substituted styrenes (such as p-methoxystyrene), halogen-substituted styrenes (such as p-chlorostyrene, 3,4-dichlorostyrene); and mixtures of two or more of them (such as mixtures of styrene with one or more styrene homologues)]; copolymers of (1) one or more these styrenic monomers with (2) one or more (meth)acrylic monomers [for

example, esters of (meth)acrylic acids, for example, alkyl($C_1 \sim C_{18}$) (meth)acrylates, such as methyl, ethyl, n- and i-butyl, propyl, n-octyl, 2-ethylhexyl, dodecyl, lauryl and stearyl (meth)acrylates; aryl (meth)acrylates, such as phenyl (meth)acrylates; hydroxyl-containing (meth)acrylates, such as hydroxyethyl (meth)acrylates; amino-containing (meth)acrylates, such as dimethylaminoethyl, diethylaminoethyl and morpholinoethyl (meth)acrylates; epoxy-containing (meth)acrylates, such as glycidyl (meth)acrylates; (meth)acrylic acids, and derivatives thereof, such as (meth)acrylonitriles and (meth)acrylamides; and the like] and/or (3) one or more other monomers [for example, vinyl esters, such as vinyl acetate and vinyl propionate; aliphatic hydrocarbon monomers, such as α -olefins and butadiene; vinyl ethers, such as vinyl methyl ether, vinyl ethyl ether and vinyl isobutyl ether; vinyl ketones, such as vinyl methyl ketone, vinyl hexyl ketone and methyl isopropenyl ketone; N-vinyl compounds, such as N-vinylpyrrole, N-vinylcarbazole, N-vinylindole and N-vinylpyrrolidine; unsaturated carboxylic acids (such as maleic and itaconic acids) or derivatives thereof (such as anhydrides and esters); and the like], with or without (4) one or more one polyfunctional monomers containing at least two polymerizable double bonds [for example, aromatic di- or poly-vinyl compounds, such as divinylbenzene and divinyltoluene; di- or poly-(meth)acrylates of polyols, such as ethylene glycol di(meth)acrylates, 1,6-hexanediol di(meth)acrylates, di(meth)acrylates of EO adducts of bisphenol A; and so on]; and (co)polymers of one or more (meth)acrylic monomers (2), with or without one or more monomers (3) and/or (4). Among monomers (1), preferred is styrene. Among monomers (2), preferred are alkyl (meth)acrylates and (meth)acrylic acids, particularly methyl, ethyl, butyl and 2-ethylhexyl (meth)acrylates. Among monomers (3), preferred are vinyl esters and aliphatic hydrocarbon monomers, particularly vinyl acetate and butadiene. Among monomers (4), preferred are divinyl benzene and 1,6-hexanediol diacrylate. In styrenic and/or acrylic resins, the contents of these monomers (1), (2), (3) and (4) can be varied widely, but the usual ranges are as follows : [(1)+(2)] 70 ~ 100 %, preferably 80 ~ 100 %; (3) 0 ~ 30%, preferably 0 ~ 20%; and (4) 0 ~ 0.1 mole %, preferably at 0 ~ 0.05 mole %, based on the total monomers. Among these styrenic and/or acrylic resins, preferred are styrenic resin and styrene-acrylic resins, containing (1) 50 ~ 100 %, preferably 60 ~ 98 %; (2) 0 ~ 50 %, preferably 5 ~ 40 %. Styrenic and/or acrylic resins may be produced using any known polymerization techniques, such as solution, suspension, bulk and emulsion polymerizations, and combinations of them (such as solution polymerization followed by suspension or bulk polymerization, or suspension polymerization followed by solution or bulk polymerization). Polymerization can be carried out in the presence of one or more polymerization initiators, for example, azo compounds, such as azobis-iso-butyronitrile, azobis-iso-valeronitrile, and the like; peroxides, such as those mentioned above for modification; and so on. The amount of polymerization initiators can vary widely, but is generally 0.02 ~ 1.0 %, preferably 0.03 ~ 0.8 %, based on the total weight of the monomers. Polymerization is generally carried out within an atmosphere of inert gas, such as nitrogen atom, at a temperature of usually 50 ~ 250°C, preferably 70 ~ 230°C. Reaction period, which may be varied with other conditions, is usually 1 ~ 50 hours, preferably 2 ~ 15 hours.

Illustrative examples of styrenic polymers are styrene/(meth)acrylate copolymers, such as styrene/butyl acrylate copolymers and styrene/butyl acrylate/divinylbenzene terpolymers (molar ratio of styrene/butyl acrylate = about 7/3), and styrene/butadiene copolymers.

Suitable epoxy resins and polyurethanes are inclusive of those written in US Patent No.5,238,767.

Among these binder resins, preferred are styrenic resins [particularly styrene/(meth)acrylic copolymers] and especially polyester resins.

Molecular weight of binder resins may vary widely; but preferred are those having a $\overline{M}_n$ of about 2,000 ~ about 50,000 or higher, preferably about 3,000 ~ about 30,000. Weight-average molecular weight (hereinafter referred to as $\overline{M}_w$) of binder resins is usually about 100,000 ~ about 2,000,000, preferably about 150,000 ~ about 1,500,000. When $\overline{M}_w$ is less than 100,000, it is difficult to obtain sufficient HO; and $\overline{M}_w$ higher than 2,000,000 results in too high MF. Molecular weight distribution [represented by the ratio of $\overline{M}_w/\overline{M}_n$] of binder resins is generally at least about 20, preferably at least about 30. $\overline{M}_w/\overline{M}_n$ less than 20 results in poor balance of HO and MF. Glass transition temperature (T_g) of binder resins is generally about 40 ~ about 80°C, preferably about 45 ~ about 70°C. Resins of T_g less than 40°C provides toner of poor shelf stability; and when T_g is higher than 80°C, MF becomes too high to be used practically as toners.

(III) Resin Composition for Toner

Resin composition for electrophotographic toner comprises (I) a releasing composition, comprising a low molecular weight polypropylene (A) and a modified polyolefin (B) [(B1) and/or (B2)], and (II) a binder resin.

The amount of the releasing composition (I) [(A)+(B)] is generally 0.5 ~ 10%, preferably 1 ~ 5%, based on the total weight of (I) and (II), for final use as toners. Masterbatch containing (I) in a larger amount, for instance, 10 ~ 50%, preferably 20 ~ 40%, may be prepared, followed by adding the rest of (II) in producing toners.

In producing resin compositions, the components (A), (B) and (II) can be added at any order. (A) and (B) may be blended beforehand, or added separately to (II). Binder resin may be added beforehand to the releasing composition to obtain a resin composition for toners, or may be added together with the releasing composition during preparation of toners to obtain toners. The releasing composition can be mixed with the binder resin by any known methods. The releasing composition may be added during polymerization (preparation of binder resin), or may be blended with the binder resin

after polymerization, using a mixer. It is preferred that the releasing composition is homogeneously distributed in the resin composition, to obtain excellent release effects.

Resin compositions of the invention may contain optionally one or more of colorants and various additives to form toners.

- 5 Examples of suitable colorants and other additives include inorganic and organic pigments, such as carbon black, iron black, benzidine yellow, quinacridone pigments, rhodamine B, phthalocyanine pigments and the like; carrier particles, for example, magnetic powders, such as powders of ferromagnetic metals and compounds (such as iron, cobalt, nickel, magnetite, hematite, ferrite and the like), glass beads and the like; charge controllers, such as nigrosine, quaternary ammonium salts and metal complexes; lubricants (such as polytetrafluoroethylene, fatty acids and metal salts or amides thereof), plasticisers, hydrophobic colloidal silica powders, antioxidants (such as hindered phenols, sulphur compounds and phosphorus compounds, written in US Patent No.5,238,767), and so on.

In electrophotographic toners, the contents of these components can be varied widely. In general, the ranges may be approximately as follows:

- 15 colorant : usually 1 ~ 30%, preferably 3 ~ 20%
 magnetic powder : usually 0 ~ 60%, preferably 0 ~ 50%
 charge controller : usually 0 ~ 10%, preferably 0.5 ~ 5%
 other additives : usually 0 ~ 10%, preferably 0 ~ 5%

- 20 Electrophotographic toner can be prepared by any known methods, for instance, 1) by dry blending these toner components and then melted under kneading, followed by crushing, and then finely pulverizing with a grinder (such as jet grinder), thereafter classifying to obtain particles (usually 2 ~ 20 μ diameter); or 2) by suspension-polymerizing monomers (precursors for the binder component) in the presence of the other toner components to obtain particles (usually 2 ~ 20 μ diameter).

- 25 Said toner can be optionally mixed with one or more carrier particles, such as iron powder, glass beads, nickel powder and ferrite, and used as a developer for electrical latent images. Besides, hydrophobic colloidal silica powder may be used to improve TF.

- Said toner can be fixed on substrates (such as paper, polyester film and the like) to be used as recording materials. Fixation may be accomplished by any known fixation means, for example, heat roll fixation of copy machines, such as heat-fixation type copiers or printers.

Having generally described the invention, a more complete understanding can be obtained by reference to certain specific examples, which are included for purposes of illustration only and not intended to be limiting unless otherwise specified.

In the followings, parts represent parts by weight.

- 35 In the following examples, $\overline{M}_n$ and $\overline{M}_w$ of polyolefins and modified polyolefins, were measured with GPC under following conditions :

Equipment : 150CV, produced by Waters.
 Columns : Shodex KF-80M, 2 columns, and Shodex AT-800P, 1 column.
 40 Temperature : 135°C .
 Sample solution : 0.3 % o-dichlorobenzene solution.
 Amount of solution : 100 microliters.
 Detector : Refractometer.

- 45 Binder resins used in the following examples are as follows:

- (1) Binder (i) : a thermoplastic styrene-acrylic resin, having Tg of 53°C, $\overline{M}_n$ of 11,000 and $\overline{M}_w$ of 70,000, prepared by thermally polymerizing 660 parts of styrene and 340 parts of butyl acrylate at 130 ~ 180°C without using any solvent and any polymerization initiator, followed by removing volatile matters (such as unreacted monomers) under reduced pressure not more than 5 mmHg at 180°C .

$\overline{M}_n$ and $\overline{M}_w$ of Binder (i) were measured with GPC under following conditions :

- Equipment : HCL-802A, produced by Toyo Soda Manuf.
 55 Columns : TSK gel GMH6, 2 columns, produced by Toyo Soda Manuf.
 Temperature : 25°C ;
 Sample solution : 0.5 % THF solution.
 Amount of solution : 200 microliters.

Detector : Refractometer.

Calibration curve was prepared using standard polystyrenes.

(2) Binder (ii) : a thermoplastic polyester, having T_g of 63°C, an acid number of 45 and a hydroxyl number of 1.5, prepared by polycondensing 302 parts of isophthalic acid with 480 parts of an adduct of 2 moles EO to bisphenol A at 220°C in the presence of 1.6 parts of dibutyltin oxide.

[Preparation of Low Molecular Weight Polypropylenes (A)]

Example A-1

A high molecular weight polypropylene resin (J130G, produced by Ubekosan; MFR=30) was thermally degraded by introducing the resin continuously into a tubular reaction vessel equipped with a static mixer under heating to 355 ~ 360°C for 80 minutes to obtain a polypropylene (A-1) having an isotactic content of 96%, $\overline{M}_n$ of 3,000 and a melt viscosity of 70 cps at 160°C.

Example A-2

A high molecular weight ethylene-propylene copolymer (J609H, produced by Ubekosan; MFR=9, ethylene content=about 7 mol.%) was thermally degraded in the same manner as Example A-1 to obtain a polypropylene (A-2) having an isotactic content of 90% and a melt viscosity of 72 cps at 160°C.

[Preparation of Modified Polyolefins (B)]

Example B1-1

1) Example A-1 was repeated except that heating period was 50 minutes to obtain a thermally degraded polypropylene (a1-1) having a melt viscosity of 300 cps at 160°C.

2) Then, 400 parts of (a1-1) and 12 parts of maleic anhydride were charged into a reaction vessel, equipped with a nitrogen inlet, a thermometer, a condensor and a stirrer, and heated under stirring within an atmosphere of nitrogen to 195°C for 10 hours. After the reaction, volatile matters (such as unreacted maleic anhydride) were removed under reduced pressure of 5 mmHg maintaining the temperature to 195°C for an hour to obtain a modified polypropylene (B1-1) having an acid number of 13 and a melt viscosity of 430 cps at 160°C.

Example B1-2

Into an autoclave, were charged 400 parts of (a1-1) and 40 parts of maleic anhydride, and heated under stirring within an atmosphere of nitrogen to 180°C. Then, 100 parts of 2% xylene solution of di-t-butyl peroxide were added thereto continuously dropwise over 4 hours. Then, the product after cooling was removed into a vessel equipped with a thermometer and a stirrer, and volatile matters (such as xylene and unreacted maleic anhydride) were removed under reduced pressure not more than 5 mmHg at 195°C for 2 hours to obtain a modified polypropylene (B1-2) having an acid number of 42 and a melt viscosity of 2200 cps at 160°C.

Example B2-1

1) A high molecular weight polyethylene resin (J5019, produced by Ubekosan; MFR=50) was thermally degraded by introducing the resin continuously into a tubular reaction vessel equipped with a static mixer under heating to 300 ~ 305°C for 50 minutes to obtain a thermally degraded polyethylene (a2-1) having $\overline{M}_n$ of 3,000 and a melt viscosity of 290 cps at 140°C.

2) Then, 400 parts of (a2-1) and 12 parts of maleic anhydride were charged into a reaction vessel, equipped with a nitrogen inlet, a thermometer, a condensor and a stirrer, and heated under stirring within an atmosphere of nitrogen to 200 ~ 230°C for 10 hours. After the reaction, volatile matters (such as unreacted maleic anhydride) were removed under reduced pressure of 5 mmHg maintaining the temperature to 230°C for 2 hours to obtain a modified polyethylene (B2-1) having an acid number of 15, $\overline{M}_n$ of 3,200 and a melt viscosity of 500 cps at 140°C.

Example B2-2

Into an autoclave, were charged 300 parts of (a2-1), 20 parts of maleic anhydride and 400 parts of xylene, and heated under stirring within an atmosphere of nitrogen to 180°C. Then, 20 parts of 10% xylene solution of di-t-butyl

peroxide were added thereto continuously dropwise over 15 minutes. Then, the product after cooling was removed into a vessel equipped with a thermometer and a stirrer, and volatile matters (such as xylene and unreacted maleic anhydride) were removed under reduced pressure not more than 5 mmHg at 180°C for 2 hours to obtain a modified polyethylene (B2-2) having an acid number of 28, $\overline{Mn}$ of 3,100 and a melt viscosity of 3,800 cps at 140°C.

[Preparation of Releasers]

Examples 1 ~ 8 and Comparative Examples 1 ~ 4

In accordance with the formulations (parts) written in Table 1, a polypropylene (A) and a modified polyolefin (B) were charged into a vessel equipped with a thermometer and a stirrer, and heated under stirring to 180°C for an hour to obtain releasing compositions (Releasers R1 ~ R8).

For comparison, releasing compositionS (ReleaserS R9 and R10) containing (A) and (B) in a ratio beyond the scope of the invention was prepared in the same manner. Releasing compositions (Releasers R11 and R12) consisting of (A) or (B) alone are also used for comparison.

Table 1

Example No.		Example								Comparative Example			
		1	2	3	4	5	6	7	8	1	2	3	4
(A)	(A-1)	480	480	425	-	440	440	375	-	150	140	500	-
	(A-2)	-	-	-	480	-	-	-	440	-	-	-	-
	(B1-1)	20	-	75	20	-	-	-	-	-	-	-	-
(B)	(B1-2)	-	20	-	-	-	-	-	-	350	-	-	-
	(B2-1)	-	-	-	-	60	-	125	60	-	-	-	500
	(B2-2)	-	-	-	-	-	60	-	-	-	360	-	-
Releaser No.		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12

[Preparation of Resin Compositions]

Example 9

Into a vessel equipped with a thermometer and a stirrer, 450 parts of Binder (i) and 50 parts of Releaser R1 were charged, and heated under stirring to 190°C for 2 hours to prepare a resin composition (C-1).

Example 10

In the same manner as Example 9, using Releaser R5, was prepared a resin composition (C-2).

[Preparation of Toners and Developers, and Evaluation]

Examples I ~ XII and Comparative Examples I ~ IV

Using each releaser or resin composition and binder, toners for electrophotography and an electrophosographic developers were produced and evaluated as follows :

[1] Preparation of toners

In accordance with the formulations (parts) written in Table 2, the ingredients was powder dryblended, and kneaded with a laboplast mill at 140°C at 30 rpm for 10 minutes, followed by finely pulverizing the kneaded mixture with a jet mill (PJM100, produced by Nippon Pneumatic Mfg.Co.,Ltd.) and then classifying with a dispersion separator (MSD, produced by Nippon Pneumatic Mfg.Co.,Ltd.) to cut fine powders of less than 2 microns diameter. To 1000 parts of the resulting powder, 3 parts of a colloidal silica powder (Aerosil R972, produced by Japan Aerosil Co.) were added and homogene-

ously mixed to obtain a toner.

Table 2

Example No.	E x a m p l e												Comparative Example			
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	I	II	III	IV
Releaser	R1	R2	R3	R4		R1	R5	R6	R7	R8		R5	R9	R10	R11	R12
	4	4	4	4	—	4	4	4	4	4	—	4	4	4	4	4
Resin					C1						C2					
Compn.	—	—	—	—	40	—	—	—	—	—	40	—	—	—	—	—
Binder	(i)	(i)	(i)	(i)	(i)	(ii)	(i)	(i)	(i)	(i)	(i)	(ii)	(i)	(i)	(i)	(i)
	87	87	87	87	51	87	87	87	87	87	51	87	87	87	87	87
CB ^{*1}	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
CC ^{*2}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

*1 : Carbon black, MA-100, produced by Mitsubishi-kasei Co.

*2 : Charge controller, Spiron black TRH, produced by
Hodogaya Chemical Co.

[2] Preparation of developer

To 25 parts of each toner as above, 1000 parts of a iron powder carrier (F-100, produced by Nippon Seihun Co.) were added and mixed to obtain a developer.

[3] Evaluation

1) HO : using a commercially available electrophotographic copy machine of heat fixation type, HO (the temperature causing offset to the heated roller) was measured, or occurrence of hot offset at heat roll temperature of 230°C was observed with eyes.

2) Flowability : Flow index (FI) was measured with a powder tester, produced by Hosokawa Micron, Co.

3) Filming to carrier : after mixing developer with a turbula shaker mixer at 100 r.p.m. for 3 hours, the amount of toner adhered on the surface of carrier was observed with a microscope.

4) MF : using a commercially available electrophotographic copy machine of heat fixation type, MF (the temperature of the heated roller providing printed image density of solid part remained at least 70 % after 5 times reciprocating rubbing of black solid part of printed image density 1.2 with a Gakushin fastness tester (rabbed part=paper).

The results were as shown in Table 3.

Table 3

Example No.		Releaser (Compn.)	HO, °C	FI	Filming	MF, °C
Example	I	R1	≥ 240	≥ 80	little	< 130
	II	R2	≥ 240	≥ 80	little	<130
	III	R3	≥ 240	≥ 80	little	<130
	IV	R4	≥ 240	≥ 80	little	<130
	V	R1(C1)	≥ 240	≥ 80	little	<130
	VI	R1	≥ 240	≥ 85	little	<130
	VII	R5	≥ 240	≥ 80	little	<130
	VIII	R6	≥ 240	≥ 80	little	<130
	IX	R7	≥ 240	≥ 80	little	< 130
	X	R8	≥ 240	≥ 80	little	<130
	XI	R5(C2)	≥ 240	≥ 80	little	<130
	XII	R5	≥ 240	≥ 80	little	<130
Comparative Example	I	R9	<220	≥ 85	little	<130
	II	R10	<220	≥ 80	little	<130
	III	R11	≥ 240	<70	much	≥ 150
	IV	R12	<220	≥ 80	little	<130

Releasing compositions, comprising (A) and (B), according to the present invention, can provide toners having improved anti-hot offset properties without reducing flowability. Besides, the releasing compositions can prevent effectively toner adhesion (filming) towards carrier to attain toners having low tendency of filming towards carrier. In addition, improved low temperature fixability can be attained.

Claims

1. A releasing composition for electrophotographic toner, which comprises
60~ 99.5%, preferably 70~ 99% by weight of a low molecular weight polypropylene (A), and
0.5~ 40%, preferably 1~ 30% by weight of at least one modified polyolefin (B), selected from
(B1) a modified polypropylene, comprising a low molecular weight polypropylene (a1) having a melt viscosity at 160°C higher than that of said polypropylene (A), modified with an ethylenically unsaturated carboxylic acid or an anhydride thereof (b1), and
(B2) a modified polyethylene, comprising a low molecular weight polyethylene (a2) having a melt viscosity of 10~ 8,000 cps at 140°C, modified with an ethylenically unsaturated carboxylic acid or an anhydride thereof (b2).
2. A composition according to Claim 1, wherein (A) has a melt viscosity of 10~ 3,000 cps, preferably 15~ 2,000 cps at 160°C, (a1) has a melt viscosity of higher than 10 cps and upto 5,000 cps at 160°C, and the ratio of the melt viscosity of at 160°C of (a1) to the melt viscosity at 160°C of (A) is not more than 500/1 and preferably at least 1.1/1.
3. A composition according to Claim 1 or 2, wherein (a1) and/or (A) is obtainable by thermal degradation of a high molecular weight polypropylene.
4. A composition according to any one of Claims 1 to 3, wherein (b1) and/or (b2) is (meth)acrylic acid, maleic acid or anhydride thereof.
5. A composition according to any one of Claims 1 to 4, wherein (B) has an acid number of 0.5~ 100, preferably 0.5~ 40, and preferably has a number-average molecular weight of 1,000~ 20,000.

6. A composition according to any one of Claims 1 to 5, wherein (A) and/or (a1) is a propylene homopolymer, or a copolymer of propylene with up to 20 % by weight of at least one other olefin, preferably selected from ethylene, butene and octene.

5 7. A resin composition for electrophotographic toner, which comprises a releasing composition of any one of Claims 1 to 6, and a thermoplastic binder resin, preferably selected from a polyester, styrenic resin, acrylic resin, polyolefin resin, polyurethane and epoxy resin.

10 8. A composition according to Claim 7, comprising 0.5~ 10% by weight of said releasing composition and 90~ 99.5% by weight of said binder resin.

9. A composition according to Claim 7 or 8, wherein said binder resin comprises a polyester, particularly a polycondensate of a polycarboxylic acid with a polyol comprising an oxyalkylene ether of a bisphenol.

15 10. An electrophotographic toner, which comprises a toner binder resin, a colorant, and a releasing composition according to any one of Claims 1 to 6, the weight ratio of said releasing composition to said binder resin being preferably 0.5/99.5~ 10/90.

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European Patent
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EUROPEAN SEARCH REPORT

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EP 94 30 4892

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 17, no. 184 (P-1519) 9 April 1993 & JP-A-04 337 737 (RICOH) 25 November 1992 * abstract *	1,2,4, 7-10	G03G9/087
Y	& DATABASE WPI Section Ch, Week 9302, Derwent Publications Ltd., London, GB; Class G06, AN 93-011853 & JP-A-4 337 737 (RICOH) 25 November 1992 * abstract *	3,5,6	
X	--- DATABASE WPI Section Ch, Week 8735, Derwent Publications Ltd., London, GB; Class G06, AN 87-245442 & JP-A-62 166 358 (HITACHI) 22 July 1987 * abstract *	1	
X	--- PATENT ABSTRACTS OF JAPAN vol. 10, no. 132 (P-456) 16 May 1986 & JP-A-60 254 149 (KONISHIROKU) 14 December 1985 * abstract *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
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Y	--- US-A-5 116 713 (M.UCHIDA) * claim 1; table 2 *	5	
A	--- EP-A-0 421 416 (CANON) * claims 1,2; example 3; table 1 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 November 1994	Examiner Vanhecke, H
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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