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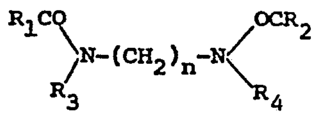
(54) Toner for developing electrostatic latent image.

(57) A toner suitable for developing an electrostatic latent image is described comprising (a) a polyester containing not less than 5% by weight of chloroform-insoluble component as binder resin and either (b) at least one of a first mold release agent which has the general formula;



wherein R_1 and R_2 are independently a saturated or unsaturated aliphatic hydrocarbon group having not less than 10 carbon atoms, R_3 and R_4 are independently a hydrogen atom or a group represented by $-OCR^5$ wherein R_5 is a saturated or unsaturated hydrocarbon group and n is a positive integer, or (c) a mixture of a second mold release agent which contains at least 20% by weight of ester component, the needle penetration degree of said mold releasing agent being not more than 4, and a third mold release agent which is a polyolefin was or a compound of the general formula given above.

2. A toner according to claim 1 in which in component (b) n is from 1 to 5.

3. A toner according to claim 1 or 2 in which in component (b) R_1 and/or R_2 contains 10 to 23 carbon atoms.

4. A toner according to any one of claims 1 to 3 which contains 1 to 10% by weight of mold release agent.

5. A toner according to any one of claims 1 to 4 in which the second mold release agent is a wax having a melting point of 60 to 110°C.

6. A toner according to any one of claims 1 to 5 in which in component (c) the weight ratio of the . . .

Croydon Printing Company Ltd

TONER FOR DEVELOPING ELECTROSTATIC LATENT IMAGE

FIELD OF THE INVENTION

The present invention relates to a toner for developing an electrostatic latent image formed in electrophotography, electrostatic recording, electrostatic printint, etc.

BACKGROUND OF THE INVENTION

Development process of electrostatic latent images generally comprises a step in which an electrostatically charged fine toner particles are attracted to and adsorbed onto the surface of an electrostatic latent image-bearing support by electrostatic attractive force.

The image forming process making use of the electrostatic latent image should preferably be performed as quick as possible, and in this view, the heat roll fixing process, which has better heat efficiency and other advantages in comparison with other fixing processes of the art, has been widely applied in this field.

Recently, however, further speed-up of the total image formation process is strongly demanded, and for the attainment of this purpose, it is essential for the fixing step to be speeded up. For the fixing of toner to be carried out at higher speed in the heat roll fixing method, the toner for the development is required to have a fixability at lower temperature, and for this purpose, the binder resin to be used should necessarily have a lower softening point.

However, in general when the softening point of the binder resin of a toner is lowered, a part of the toner image tends to be transferred to the surface of the heat roll and thus transferred toner is re-transferred to the surface of the subsequent transfer sheet, which is so-called an off-set phenomenon, to cause deterioration in the toner image. In addition, in the heat roll fixing method there is a tendency that a transfer sheet easily winds round the surface of the heat roll, which is so-called a winding penomenon.

Thus in order for a rapid fixing to be possible, toner should be fixable at lower temperature, having good off-set prevention and winding prevention properties.

As for the binder for the toner, vinyl-type polymers have widely been used, and for the purpose of enhancing high off-set prevention property, it has been proposed to incorporate high molecular component into the binder resin.

However, if sufficent off-set prevention property is to be obtained by this technique, since a resin having high softening point has to be used, the minimum temperature necessary to fix the toner (hereinafter referred to as " minimum fixing temperature") generally rises, and the advantages of the heat roll fixing method are often lost or reduced.

On the contrast thereto, by the use of a polyester resin, low molecular weight resin being readily obtainable, it is possible to obtain a toner having relatively low softening point. The toner using the polyester resin as a binder has, in comparison with the toner in which vinyl-type polymer is used, such an advantage that it has better wetting property against a transfer sheet such as paper and, therefore, fixing at lower temperature is possible comparing with the case where a vinyl-type polymer having approximately the same softening point.

However, toner using a polyester resin as a binder generally has had such an disadvantage that the minimum temperature, at which off-set phenomenon takes place is low. For the purpose of elevating the minimum off-set occurring temperature, it is effective to incorporate a high molecular weight component into the binder resin. However, in order to obtain sufficient off-set prevention property by this way, the softening point of the binder resin as a whole is elevated, and, therefore the minimum fixing temperature rises and, again, the advantage of the heat roll fixing method comes to be lost.

It is, as a matter of course, preferable that toner has a low minimum fixing temperature, and especially, in order to form a visual image on both sides of the parer it is almost essential that the toner for the development can be fixed at low temperature.

From such background of the art, a technique for lowering the minimum fixing temperature and for improving off-set and winding-up prevention properties of the toner was developed by incorporating a mold releasing agent selected from polyolefin waxes, such as polyethylene waxes or polypropylene waxes, into the toner particles. This technique is intended to confer a fixability at low temperature and mold releasing property on the toner itself, and is advantageous compared with such fixing sistem, in which fixing is carried out while providing and coating a heat roller with a mold releasing oil such as silicone oil, in the view that there is no need for the fixing unit to be provided with a coating device of silicone oil and that the structure of the fixing unit may be made simpler.

However, according to this technology, in order to sufficiently enjoy the advantage of lowering the minimum fixing temperature, the prportion of such wax to be incorporated should often be considerably high and, as the result thereof, fluidity of the toner particles becomes lowered and the toner comes to bear a tendency to easily aggregate and to contaminate carrier particles, when used in a so-called two-component developer, sleeve in the developing unit and a support for the electrostatic latent image (photoreceptor) by forming a thin film of such wax component by adhesion, thus to jeopardise the function of these components in the electrophotograpgic copying machine.

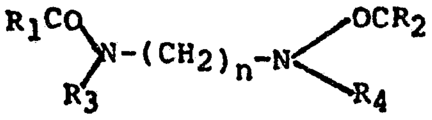
Further if such toner is used, for the purpose of making efficient use thereof, in a so-called re-cycling system, wherein toner provided for development but not used for the image formation is brought back to the developing unit to be re-used for the development, there is observed such drawback that the fluidity of the toner remakably lowers, or that the durability of the toner becomes degraded.

OBJECT OF THE INVENTION

The present invention has been made under such circumstances and the object of the invention is to provide a toner for developing an electrostatic latent image which has a low minimum fixing temperature, sufficient off-set prevention property, good fluidity and durability, and which is capable of giving a number of visual images with high quality at high speed.

SUMMARY OF THE INVENTION

The present invention specifically relates to toner for developing an electrostatic latent image which comprises (a) a binder resin consisting essentialy of a polyester containing not less than 5% by weight of chloroform-insoluble component and (b) at least one of a first mold releasing agent selected from compounds represented by the general formula;



$$(R_1CO)(R_3)N-(CH_2)_n-N(OCR_2)(R_4)$$

wherein R_1 and R_2 are independently selected from saturated or unsaturated aliphatic hydrocarbon groups having not less than 10 carbon atoms, R_3 and R_4 are independently selected from a hydrogen atom and a group represented by $-OCR_5$ wherein R_5 is a saturated or unsaturated hydrocarbon group and n is a positive integer, or (c) a combination of mold releasing agents selected from a secon mold releasing agent containing more than 20 % by weight of ester component, the needle penetration degree of said mold releasing agent being not more than 4, and a third mold releasing agent selected from polyolefin waxes and compounds of the general formula given above.

DETAILED DESCRIPTION OF THE INVENTION

The polyester resin used in the present invention can be obtained by condensation polymerization of a composition containing an alcohol monomer and a carboxylic acid monomer.

As for example of alcohols which constitutes the polimeric composition, diols including ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butane diol, neopentyl glycol, 1,4-butene diol; 1,4-bis(hydroxymethyl)cyclohexane; etherified bisphenols including bisphenol A, hydrogenated bisphenol A, a polyoxy-ethylenified bisphenol A, a polyoxypropionized bisphenol and other divalent alcoholic monomer may be mentioned.

As for carboxylic acid monomers for example, maleic acid, fumaric acid, metaconic acid, citraconic acid, itaconic acid, glutaconic acid, phthalic acid, iso-phthalic acid, terephthalic acid, cyclohexane-di-carboxylic acid, succinic acid, adipic acid, sebacic acid, malonic acid and an anhydride thereof, a dimer of a lower alkylester and linolenic acid and other dibasic organic acid may be mentioned.

As for the polyester resin used in the present invention, in addition to those polymers obtained from above mentioned di-functional monomers, polymers containing a component derived from multi-functional monomers are also preferable.

As for polyhydric alcohol monomers as for multi-functional monomers, for example, sorbitol, sorbitol, 1,2,3,6-hexanetetraol, 1,4-sorbitan, pentaerythritol, dipentaerythritol, tri-pentaerythritol, saccharose, 1,2,4-butanetiol, 1,2,5-pentanetiol, glycerol, 2-methylpropane-triol, 2-methyl-1,2,4-butanetriol, trimethylol ethane, trimethylol propane and 1,3,5-tri-hydroxymethyl benzene and the like can be mentioned.

As for poly-basic acids, for example, 1,2,4-benzenetricarboxylic acid, 1,2,5-benzene tricarboxylic acid, 1,2,4-cyclohexanetricarboxylic acid, 2,5,7-naphthalenetri-carboxylic acid, 1,2,4-naphthalenetricaboxylic acid, 1,2,4-butanetricaboxylic acid, 1,2,4-haxanetricaboxylic acid, 1,3-dicarboxyl-2-methyl-2-methylenecarboxylic-propane, tetra(methylenecalboxylic)methane, 1,2,7,8-octane-tetracarboxylic acid, empol trimer acid, and acid anhydride of heretofore-mentioned organic acids can be mentioned.

It is preferable in the present invention that the component of multi-functional monomer of not less than tri-function is incorporated into the composition at a proportion of from 30 to 80 % by mole relative to the total of alcohol component and acid component respectively to be contained in the final polymer.

The polyester resin used in the present invention contains a chloroform-insoluble component at a proportion of not less than 5% by weight. Herein, the chloroform-insoluble component in the present invention means a component which does not permeates through a filter paper when a sample is dissolved in chloroform and this is obtained by the following method.

5.00 g of sample powder, which has been prepared by finely pulverising a sampl resin and passed though a sieve of 40 meshes, together with 5.00g of Radiolite(#700) are put in a 150ml container and hereto 100g of chloroform is poured. The sample is thoroughly dissolven in chloroform by being rotated for more than 5 hours on the rotatable table. A filter paper(No.2) is placed in a pressure filter and thereon is coated uniformely 5.00g of Radiolite and after the filter paper is subjected to close contact with the pressure filter by the addition of small amount of chloroform, the solution in the container is pored into the pressure filter. After washing thoroughly inside the container with 100ml of chloroform so that no precipitation is left on the wall, which chloroform is then put into the pessure filter. Thereafter the upper lid of the pressure filter is closed and filtration is carried out. The filtration is carried out under pressure of 4Kg/cm^2, and after flowing out of chloroform from the pressure filter, the residuals on the filter paper is washed with 100ml of chloroform and, again, pressure filtration is carried out. After completion of the above-mentioned operation, the filter paper, residuals left thereon and Radiolite are placed on a aluminium foil and put into a vacuum drier and dried for 10 hours at a temperature of 80 to 100 °C under a pressure of 100mmHg. The total weight of the thus obtained solid substance a(g) and the content of chloroform-insoluble component x(% by weight) is obtained by the following expression.

$$x(\%\text{ by weight}) = \frac{a(g) - \text{Weight of Radiolite } (10.00g)}{\text{Sampling Weight } (5.00g)}$$

The chloroform-insoluble component thus obtained is a high molecular weight polymer component or a cross-linked polymer component and the molecular weight thereof is assumed to be more than about 200,000.

The chloroform-insoluble component of the present invention can be formed to in a controlled manner to a considerable extent by selecting the conditions for the polymerization of the hereinbefore mentioned alcohol and carboxylic acid, or by presenting an appropriate crosslinking agent in the reaction system.

In the present invention it is essential that the chloroform-insoluble component is contained at a proportion not less than 5% by weight in the polyester resin. In the case where a polyester resin containing chloroform-insoluble component of less than 5% by weight is used the minimum offset occurring temperature will be insufficiently low.

The representative examples of the alkykene-bis-aliphatic acid amide represented by the general formula, which is used in the present invention as a first mold releasing agent are showb below:

1. $C_{10}H_{21}CO\text{-}NH\text{-}(CH_2)_5\text{-}NH\text{-}OCC_{10}H_{21}$

2. $C_{11}H_{23}CO\text{-}NH\text{-}(CH_2)_4\text{-}NH\text{-}OCC_{11}H_{23}$

3. $C_{13}H_{27}CO\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}OCC_{13}H_{27}$

4. $C_{10}H_{21}CO\text{-}NH\text{-}(CH_2)_3\text{-}NH\text{-}OCC_{14}H_{29}$

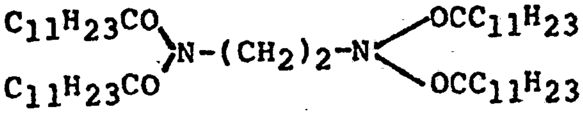
5. $C_{15}H_{31}CO\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}OCC_{15}H_{31}$

6. $C_{17}H_{35}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}OCC_{15}H_{31}$

7. $C_{17}H_{35}CO-NH-(CH_2)_2-NH-OCC_{15}H_{31}$

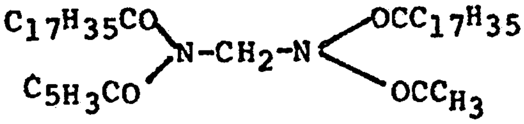
8. $C_{23}H_{47}CO-NH-CH_2-NH-OCC_{15}H_{31}$

9.



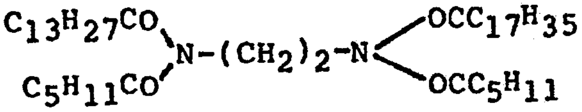
$$\begin{matrix}C_{11}H_{23}CO\\C_{11}H_{23}CO\end{matrix}\!\!>N-(CH_2)_2-N<\!\!\begin{matrix}OCC_{11}H_{23}\\OCC_{11}H_{23}\end{matrix}$$

10.



$$\begin{matrix}C_{17}H_{35}CO\\C_5H_3CO\end{matrix}\!\!>N-CH_2-N<\!\!\begin{matrix}OCC_{17}H_{35}\\OCCH_3\end{matrix}$$

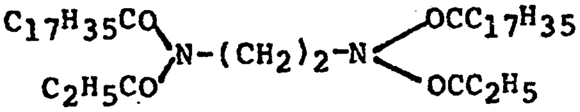
11.



$$\begin{matrix}C_{13}H_{27}CO\\C_5H_{11}CO\end{matrix}\!\!>N-(CH_2)_2-N<\!\!\begin{matrix}OCC_{17}H_{35}\\OCC_5H_{11}\end{matrix}$$

12. $C_{21}H_{41}CO-NH-CH_2-NH-OCC_{21}H_{41}$

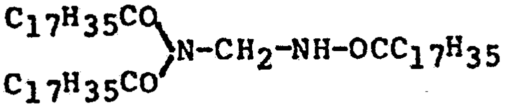
13.



$$\begin{matrix}C_{17}H_{35}CO\\C_2H_5CO\end{matrix}\!\!>N-(CH_2)_2-N<\!\!\begin{matrix}OCC_{17}H_{35}\\OCC_2H_5\end{matrix}$$

14. $C_{17}H_{35}CO-NH-(CH_2)_2-NH-OCC_{17}H_{31}$

15.



$$\begin{matrix}C_{17}H_{35}CO\\C_{17}H_{35}CO\end{matrix}\!\!>N-CH_2-NH-OCC_{17}H_{35}$$

As for alkylenebisamide compounds available in the market, the followings may be mentioned.

"BISAMIDE" (Nitto Chemical Ind., Co., Ltd.),
"PLASTFLOW" (Nitto Chemical Ind., Co., Ltd),
"DIADD 200BIS" (Nippon Hygrogen Co., Ltd.),
"LUBRON E" (Nippon Hydrogen Co., Ltd.),
"ALFLOW H50S" (Nippon Oil and Fats Co., Ltd.),

"ALFLOW V-60" (Nippon Oil and Fats Co., Ltd.),
"AMIDE 6-L" (Kawaken Fine Chemical Co.),
"AMIDE 7-S" (Kawaken Fine Chemicak Co.),
"ARMOWAX-EBS" (Lion-Armer Co.,)'
"Hoechst Wax C" (Hoechst),
"Nobuko Wax-22DS" (Nobuko Chemical Co.,),
"Adva Wax-280" (Advance Co.,),
"Kao Wax-EB" (Kao Soap Co., Ltd.),
"Parycin-285" (Baker-Caster Oil Co.,)

The mold releasing agent represented by the aforementioned formula generally has an increased softening point with the increase of the number of carbon atoms in the hydrocarbon group or of the length of the alkylene chain contained in the molecule. In view of the heating temperature to be applied during the manufacture of the toner and intended lowering of the fixing temperature thereof, those having the softening point of 100 to 180°C, and more preferably, those having the softening temperature of 130 to 160°C are advantageously used in the present invention. For this reason, it is preferred that n in the general formula be not more than 5.

The preferable proportion of the amount of the mold releasing agent of this type to be contained in the toner conposition is within the range of 1 to 20% by weight relative to the binder resin and, more preferably, within the range of 1 to 10% by weight. When the proportion to be con-

tained is less than 1%, the effect as the mold releasing agent is hardly exerted and, accordingly, off-set prevention effect as well as winding prevention effect will be weakened. And good fixability of the toner at low temperature may not be obtained. When, on the other hand, the proportion exceeds 20% by weight, the fluidity of the toner is likely to degrade, causing degrading of goog developability and transferability of the toner, thus to make the good image formation difficult.
Further, excess addition of the mold releasing tends to cause adhesion of it to the sleeve in the developing unit or to the electrostatic latent image-bearing support(i.e., photoreceptor, etc.), and thus to hinder the exertion of the normal function thereof.

The mold releasing agent which is also used in the present invention is a combination of two kinds of releasing agents selected from a second mold releasing agent which is a wax containing therein as a component thereof an ester at a proportion of more than 20% by weight, together with other component such as higher fatty acids, higher alcohols or hydrocarbons, which may optionally be contained therein, and the needle penetration degree of which is not more than 4, and a third mold releasing agent selected from polyolefin waxes and compounds represented by the general formula given hereinbefore.

It is preferable in the present invention that the first mold releasing agent is selected from a wax having a melting point of between 60 and 110°C.

In the present invention the needle penetration degree is a value obtained in accordance with the measuring method described in JIS K2235-1980. That is to say, a sample wax which is heated and melted is taken in a sample container and, after the sample is left and cooled down, the sample is kept constant in its temperature at 25°C in a water bath. A needle the total mass of which is fixed to be 100g is then penetrated vertically into the sample wax for 5 minutes, and the depth of the needle thus penetrated is measured to the precision of 0.1mm. The value of the needle penetration degree of the invention is defined as the value obtained by multiplying the depth by 10.

The melting point of the wax can be obtained by Differential Scanning Calorimetory(DSC), i.e., the peak fusion value of the sample, when a few mg of sample was heated at a constant temperature rising rate of 10°C/min, is taken as the melting point.

Some representative examples of the mold releasing agent are given below:

Mold Releasing Agent	Ester Component Kind	Ester Component Content (% by weight)	Needle Penetration Degree	Melting Point (°C)
Carnauba Wax No.1 (Noda Wax Co.)	Ester of Fatty Acid	80-85	below 1	84
Candelilla Wax (Special) (Noda Wax Co.)	Ditto	24-30	1	66
Candelilla Wax No.1 (Noda Wax Co.)	Ditto	24-30	2	64
Candelilla Wax No.2 (Noda Wax Co.)	Ditto	24-30	2	64
Hoechst Wax E (Hoechst Japan Co.)	Ethylene Glycol Ester of Montanic Acid	above 50	1	78
Hoechst Wax OP(Hoechst Japan Co.)	Partially Saponified Butylene Glycol Ester of Montanic Acid	above 50	1	79
Kao Wax 85P (Kao Soap Co.)	Glycerol-tri12-hydroxy Stearate	above 80	2	83
Hohoba Solid Wax (Noda Wax Co.)	Ester of Unsaturated Alcohol and Unsaturated Acid	97	2	68-78

One of the third mold releasing agent used in the present invention is a polyolefin wax.

As the polyolefin wax preferably used in the present invention, either unmodified polyolefins or modified

polyolefins,
wherein a modification component is blocked or grafted to an unmodified polyolefin wax or an olefin component, may be used. the olkefin wax of the invention includes homopolymers or copolymers of the olefin which connsists of at least two olefin monomer components, copoymers containing as its monomer component an olefin monomer and another monomer other than olefin.

As for olefin monomers, any kinds of olefin may be used, for example, ethylene, propylene, butene-1, pentene-1, 3-methyl-1-butene, 3-methyl-2-pentene, etc. As for nonomer components other than olefins, which form copolymers together with olefins, for example, vinyl-ethers such as vinyl methyether; vinyl esters such as vinyl acetate; halo-olefins such as vinyl fluoride; acrylic acid esters or methacrilic acid esters such as methyl acrylate or methyl methacrylate; acrylic acid derivatives such as acrylonitrile; organic acids such as acrylic acid and any othe monomer components which are coplymeriable with the olefin monomer.

As for olefin copolymers, such as ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-vinyl acetate copoly-mer, ethylene-vinyl methylether copolymer, ethylene-propylene-vinyl actate copolymer, etc. may be mentioned. When a monomer component other than olefin mononer is used to form an olefin copolymer, the proportion of the olefin part made of olefin monomer component in terms of molar % is preferably more than 50%.

Modifier component to form a modified polyolefin wax includes, for example, aromatic vinyl monomers such as 1-phenylpropene, styrene, methylstyrene, p-ethylstyrene, p-n-butylstyrene, etc., alpha-methylene aliphatic monocarbxylic acid esters such as methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, etc.

The proportion of the aromatic vinyl monomer component to be contained as a modifier component in the modified olefin coplymer is preferably within the range of from 0.1 to 15% by weight relative to the total modified polyolefin, and more preferably within the range of from 1 to 10% by weight.

The proportion of the alpha-methylene aliphatic monocarboxylic acid ester monomer component to be contained as a modifier component will be within the range of from 0.1 to 50% by weight, and more preferably 1 to 40% by weight relative to the total modified polyolefin.

The unmodified polyolefin or modified polymer thereof preferably used in the present invention advantageously has a low softening point of from 80 to 180°C, and more preferably 90 to 160°C, measured by the Ring and Ball method as defined in JIS K2531-1960.

As the preferable examples of the second mold releasing agente, "Viscol 660P" and "Viscol 550P", which are low molecular polypropylenes produced by Sanyo Chemical Industries Co., Ltd.; "Polyethylene 6A"(Product of Alide

Chemical Co.), "HI-WAX 400P", "HI-WAX 100P", "HI-WAX 200P", "HI-WAX 320P", "HI-WAX 220P", "HI-WAX 2203A", and "HI-WAX 4202E" (all produced by Mitsui Petrochemical Industries, Ltd.); "HOECHST WAX PE520", "HOECHST WAX PE 130", "HOECHST WAX PE190" , etc.(products of Hoechst Japan Co.) may be mentioned as ones available in the market. Further, for example, polyethylene waxes which have been subjected to block or graft polymerization by, for example, methyl methacrylate, butyl methacrylate or styrene may be mentioned.

The preferable proportion of the total amount of mold releasing agents to be contained in the toner conposition in this case is within the range of 1 to 20% by weight relative to the binder resin and, more preferably, within the range of 1 to 10% by weight. Further the ratio of the first mold releasing agent against the second mold releasing agents is preferably within the range from 0.5 : 1 to 10 : 1, and more preferably, from 0.5 : 1 to 5 : 1. When the proportion of the second mold releasing agent is too small, there is observed a tendency that the off-set prevention effect is weakened, and when the proportion of the first mold releasing agent is too small, the minimum fixing temperature of the toner increases and insufficient fixing is likely to occur.

In the present invention, as a matter of course, as the third mold releasing agents the polyolefin compound and the alkylene-bis-aliphatic acid amid compound may be incorporated into the toner composition altogether. Mixing ratio of the mold releasing agents in this case is optional provided that total proportion against the first mold releasing agent should preferably be within the range given hereinbefore with respect to the second or the third mold releasing agent.

The toner of the present invention is in a fine powder form prepared by incorporating into and dispersing in the above-mentioned binder resin the mold releasing agent and, if necessary, other additives for the improvment of the properties of the toner, such as, colorant, magnetic material and the like. The average particle size of the toner is generally 5 to 30 microns.

As for the colorant usable in the present invention, any conventionally known colorants and such colorant includes carbon black, Nigrosine(C.I. No. 50415B), Aniline Blue(C.I. No. 50405), Ultranarine Blue(C.I. No. 77103), Chrome Yellow(C.I. No. 14090), Quiniline Yellow(C.I. No. 47005), Rose Bengal(C.I. No. 45435), Du Pont Oil Red(C.I. No. 26105), Phthalocyanine Blue(C.I. No. 74160), Lamp Black(C.I. No. 77266), etc. and a mixture thereof may be used. The amount of the colorant to be incorporated into the toner of the present invention may not be limited but, in general, 1 to 20 parts by weight relative to 100 parts of the binder resin may be preferable.

In the case where toner of the present invention is applied to a so-called one-component toner, a magnetic material may be incorporated into the toner composition instead of, or together with the colorants. The magnetic material that may be used includes a compound or an alloy containing therein a ferromagnetic element such as iron, cobalt and nickel; ferrite, magnetite ; such an alloy as so-called Heusler's alloy which contains manganese and copper in the alloy, like Mn-Co-Al or Mn-Co-Sn, and whhich does not contain magnetic element but turns to show a ferromagnetic nature under suitable treatment by heat; or cromium dioxide, etc. may be mentioned.

These magnetic materials are usually incorporated into and uniformely dispersed in the the toner composition in the form of a fine powder of the avarage particle size of 0.1 to 1 micron. The amount of the magnetic material to be incorporated is generally 20 to 70 parts by weight relative to 100 parts by weight of toner and, preferably, at a proportion of 40 to 70 parts by weight relative to the same.

As for the other additives for improving other properties of the toner, for example, charge controlling agent, fluidity improving lubricants such as fine powdery silica and the like may be mentioned.

The toner of the present invention may be made as so-called two component developer, being mixed with carrier particles made of, for example, iron powder, glass beads, or so-called one component developer when the toner contains a magnetic material, both of which can be provided for the development of an electrostatic latent image.

EFFECTS OF THE PRESENT INVENTION

With the useof the toner of the present invention following technical advantages can be expected.

(i) Minimum fixing temperature can be lowered.

(ii) Improved off-set and winding prevention effects can be obtained.

(iii) Toner having improved fluidity and and copying durability can be obtained.

(iv) Even in the recycling system, toner image with a stable image quality can be obtained.

(v) Contamination due to the adhesion of the toner to carrier, photo-receptor or sleeve will be reduced.

(vi) Because of good fluidity of the toner the use of fluidity-improving agent such as powdery silica may be decreased or omitted and, therefore, disadvantages with the use of the silica such as the damage of the photoreceptor can be reduced or eliminated.

And thus according to the present invention toner images with sufficient high density will be obtainable at relatively low temperature, without causing off-set phenomenon, at high speed and stably when the copying is repeated for a long time.

The present invention is further explained with reference to Examples, however, the scope of the invention is not limited by them.

In the Examples the binder resins and the mold releasing agents used are as follows:

Binder Resin A (According to the present invention)

A round bottomed flask equipped with a thermometer, a stainless steel stirrer, a glass tube through which to introduce nitrogen and a condenser was charged with 299g of telephthalic acid, 211g of polyoxypropylene(2,2)-2,2-bis(4-hydroxy phenyl)propane and 82g of pentaerythritol. The flask was set in a mantle heater and heated while nitrogen gas was introduced into the flask to keek its interior under an inert atomosphere. Then, 0.05g of dibutyl tin oxide was added, and reduction was carried out at 200°C while the softening point was used as a parameter to monitor the progress of the reaction. As a result, a polyester resin A having a softening point of 131°C and containing 17 % by weight of chloroform-insoluble component was obtained. 4

Binder Resin B (For Comparison)

A copolymer obtained by copolymerizing strene, methyl methacrylate and n-butyl methacrylate at the proportion of 50 : 20 : 30 in terms of weight, containing a relatively high molecular component and relatively low molecular component at the ratio of 40 : 100 by weight.

Mw=130,000; Mn=8,000; Mw/Mn=16.25; Softening Point= 135°C

Mold Releasing Agent a1 (The First or the Third Wax)

"HOECHST WAX C" (HOECHST JAPAN Co.)

Mold Releasing Agent a2 (The First or the Third Wax)

"BISAMIDE" (Nitto Chemical Ind., Co., Ltd.)

Mold Releasing Agent a3 (The First or the Third Wax)

"ARMOWAX-EBS" (Lion-Armer Co.,)'

Mold Releasing Agent b1 (The Second Wax)

"Carnauba Wax No. 1" (Noda Wax Co.)

Mold Releasing Agent b2 (The Second Wax)

"Candelilla Wax" (Noda Wax Co.)

Mold Releasing Agent c1 (The Third Wax)

"Viscol 660P" (Sanyo Chemical Co.)

Polyolefin Wax, Needle Penetration Degree(N.P.D)=1.5;

Melting Point(m.p.)=142°C

Mold Releasing Agent c2 (The Third Wax)

"Hi-Wax 400P" (Mitsui Petrochemical Co.)

Polyethylene Wax

In the following Examples, the toner components shown in TABLE 1 were mixed and neaded in a extruder, the temperature of the inside thereof having been fixed to the one which is below the softening point of the resin used by 10°C. Then the mixture was cooled down by water, pulverized and classified to obtain a toner having the average particle size of 11 microns. Finally 0.8% by weight of hydrophobic silica was added to the thus prepared tone, to prepare the toner of the Examples. In TABLE 1 the numerals in the brackets are given in terms of parts by weight.

TABLE 1

Example No.	Binder Resin	First Wax	Second Wax	Third Wax	Carbon Black
1	A (100)	a1 (3)	-	-	MOGAL L (Cabbot Co.) (10)
2	A (100)	a1 (6)	-	-	ditto
3	A (100)	a2 (3)	-	-	ditto
4	A (100)	a3 (3	-	-	ditto
5	A (100)	-	b1 (2)	a1 (2)	ditto
6	A (100)	-	b1 (2)	a1 (6)	ditto
7	A (100)	-	b2 (2)	a2 (2)	ditto
8	A (100)	-	b1 (2)	c1 (2)	ditto
9	A (100)	-	b1 (2)	c2 (2)	ditto
Comparison					
1	B (100)	a1 (3)		-	ditto
2	A (100)	-	-	c1 (3)	ditto
3	A (100)	-	-	c2 (3)	ditto
4	A (100)	-	-	-	ditto
5	A (100)	-	b1 (2)	-	ditto
6	A (100)	-	b1 (4)	-	ditto

Thus obtained toners according to the present invention (Toners 1 to 9) and the toners for comparison (Comparative Toners 1 to 6) were subjected to various tests evplained below.

First, making use of the nature of the powder that the higher the fluidity of a powder is, the smaller is the condensation rate of the powder, the bulk density of the respective toners were measured in order to determine the fluidity of the toners. The respective toners were poured down into a container having a diameter of 28mm and the total volume of 100ml to its full through a sieve of 100 mesh and the weight was measured.

The respective toners were mixed with a resin coated carrier to prepare as many developers, of which toner content was 2% by weight respectively.

Thus prepared developer was subjected to an image formation test using a electrophotographic copying machine "U-Bix 4500"(product of Konishiroku Photo Industry Co., Ltd.), in which so-called toner recycling system is employed, and under the conditions of 33°C and relatitive humidity of 80%, 60000 times of repeated copying tests were carried out to determine developability of the electrstatic latent image, transferability of the developed toner image to the transfer sheet and fixability with the use of heat roll fixing unit of the toner, and the toner density of the copied image of the first and after 60000th copies were measured.

After 60000 times of copying test, the bulk density of the toner, extent of contamination on the surface of the carrier particles, photosensitive drum and developing sleave in the development unit were also observed.

Further the minimum fixing temperature, the minimum off-set occurring temperature and winding occurring temperature were measured.

As to the minimum fixing temperature, fixing test by the use of a heat roll fixing unit consisting of a heat roll, the surface of which is formed of TEFLON (polytetrafluoroethylene produced by du Pont), and a pressure roll, the surface of which is formed of a silicone rubber "KE-1300 RTV" (product of Shinetsu Chemical Industry Co., Ltd.), was carried out by passing through the fixing unit a sample transfer sheet, onto which 64 g/m^2 of toner has been adhered, at a line feeding speed of 200mm/sec, and this procedure was repeated while increasing stepwise the temperature of the heat roll by 5°C from 100°C. The fixed toner image thus obtained was subjected to rubbing test with KIM wiper and the minimum fixing temperature was determined as the lowest temperature at which the fixed toner image has a sufficient durability against rubbing.

Incidentally, the fixing unit used does not have a silicone oil providing device.

The the lowest temperature at which off-set phenomenon is first observed was determined in the similar manner as in the determination of the minimum fixing temperature, that is, the temperature at which the off-set phenomenon is first observed was measured by, first, developing an electrostatic image formed in an ordinary electrophotographic method with a developer and, transferring the toner image onto a plain paper sheet and fixing the transferred image in the above-mentioned fixing unit, and, thereafter, by passing a white paper through the fixing unit under the same conditions, to observe if any contamination is seen on the surface of the white paper due to the toner attached to the roll in the fixing unit. By repeating above-mentioned operation at various temperatures, the temperature, at which off-set phenomenon is first seen was obtained.

Still further, winding occurrence temperature was measured by the use of a uniformly black original, whereby toner was made attached to the whole surface of the transfer sheet by development and transfer processes, and by carrying out fixing test while lowering stepwise the temperature of the heat roll of the fixing unit.

TABLE 2

Sample No.	Minimum Fixing Temperature (°C)	Minimum Off-set Ocurring Temperature(°C)	Winding Occurrence Temperature (°C)
Toner of the Invention			
1	160	above 240	180
2	150	above 240	175
3	160	above 240	180
4	160	above 240	180
5	150	above 240	150
6	145	above 240	150
7	150	above 240	150
8	150	above 240	150
9	160	above 240	160
Comparative Toner			
1	above 240	180	210
2	190	above 240	190
3	160	above 240	180
4	230	above 240	200
5	160	-	160
6	150	-	150

TABLE 3

Sample No.	Bulk Density(g/cc)		Image Density		Degree of Contamination
	Initial	After 60000 copies)	Initial	After 60000 copies	
Toner of the Invention					
1	0.46	0.45	1.35	1.34	Without
2	0.45	0.45	1.34	1.33	Without
3	0.46	0.45	1.33	1.32	Without
4	0.46	0.44	1.34	1.32	Without
5	0.46	0.46	1.35	1.34	Without
6	0.46	0.46	1.35	1.33	Without
7	0.46	0.45	1.34	1.34	Without
8	0.45	0.45	1.34	1.32	Without
9	0.46	0.44	1.35	1.33	Without
Comparative Toner					
1	0.45	0.44	1.34	1.32	Without
2	0.39	0.36	1.17	0.90	Observed
3	0.38	0.34	1.15	0.78	Extensively Contaminated
4	0.46	0.45	1.34	1.32	Without
5	0.42	0.38	1.34	1.30	Without
6	0.39	0.36	1.30	1.02	Without

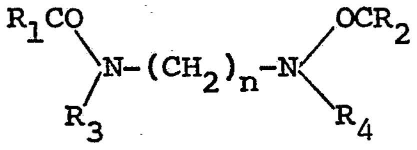
As apparent from TABLES 2 and 3, the toner of the present invention has higher off-set anf winding prevention ability, fixability at reduced temperature, excellent developability with sufficient density and excellent stability in image formation aafter long time repetition of copying in comparison with the toner of the prior art. Further no serious contamination in the sleeve of the developing unit or in the surface of the photoreceptor was observed even after 60000 times of copying.

In contrast thereto the comparative toner shows lower off-set coccurring temperature, inferior image quality and inferior stability in the image formation.

Further it is apparent from the TABLES that overall exellent copying performance can be obtained when the mold releasing agent of the present invention is used in combination with the case where the second or third molod releasing agent is used singly together with the resin of the present invention.

WE CLAIM:

1. A toner suitable for developing an electrostatic latent image comprising (a) a polyester containing not less than 5% by weight of chloroform-insoluble component as binder resin and either (b) at least one of a first mold release agent which has the general formula;



wherein R_1 and R_2 are independently a saturated or unsaturated aliphatic hydrocarbon group having not less than 10 carbon atoms, R_3 and R_4 are independently a hydrogen atom or a group represented by $-OCR_5$ wherein R_5 is a saturated or unsaturated hydrocarbon group and n is a positive integer, or (c) a mixture of a second mold release agent which contains at least 20% by weight of ester component, the needle penetration degree of said mold releasing agent being not more than 4, and a third mold release agent which is a polyolefin wax or a compound of the general formula given above.

2. A toner according to claim 1 in which in component (b) n is from 1 to 5.

3. A toner according to claim 1 or 2 in which in component (b) R_1 and/or R_2 contains 10 to 23 carbon atoms.

4. A toner according to any one of claims 1 to 3 which contains 1 to 10% by weight of mold release agent.

5. A toner according to any one of claims 1 to 4 in which the second mold release agent is a wax having a melting point of 60 to 110°C.

6. A toner according to any one of claims 1 to 5 in which in component (c) the weight ratio of the

second mold release agent to the third mold release agent is from 0.5:1 to 5:1.

7. A toner according to any one of claims 1 to 6 which is in the form of particles having an average particle size of 5 to 30 microns.