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(54) Method for forming fixed images.

(57) A method of forming fixed images of the present invention includes charging a photoconductor; exposing the photoconductor to light; applying a thermally dissociating encapsulated toner or an encapsulated toner whose shell is made of amorphous polyester to an electrostatic latent image formed on the photoconductor, thereby developing the electrostatic latent image to form a visible image; transferring the formed visible image to a recording medium; and fixing the transferred visible image onto the recording medium at a temperature of not more than 130 ° C. The fixing is carried out using a heat roller-type fixing apparatus including a heat roller having a conductive elastomer layer formed in a uniform thickness, a pressure roller and a current supplying means. The steps of the fixing include passing an electric current into the conductive elastomer layer; and thermally fixing the visible image by heat generated in the conductive elastomer layer.

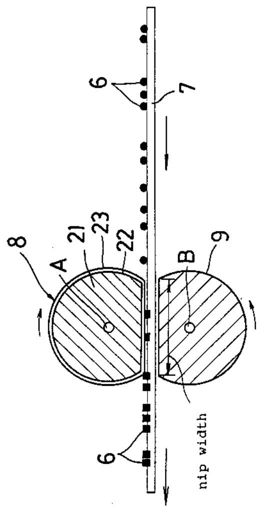


FIG. 2

EP 0 552 785 A2

Rank Xerox (UK) Business Services
(3.10/3.6/3.3.1)

The present invention relates to a method for forming fixed images used for plain paper copying machines, laser printers, plain paper facsimiles, etc.

Conventionally, when images are formed with copying machines, laser beam printers, etc., the Carlson Method has been generally used (U.S. Patent 2,221,776, 2,297,691 and 2,357,809, "Electrophotography," p22-p41, R.M. Shaffert, 1965, The Focal Press).

In a conventional method of forming fixed images, after the electrostatic latent image formed on a photoconductor by optical means is developed in a developing process, it is transferred to a recording medium such as a recording paper in a transfer process and then fixed into the final image generally with heat and pressure in a fixing process. Since the photoconductor is repeatedly used, a cleaning device is provided for cleaning the residual toner after the transfer process with its rotation.

In the conventional method of forming fixed images as described above, however, through the processes from the formation of the electrostatic latent image up to the transfer and then the fixing thereof onto the recording medium, the energy consumed in the fixing process is extremely large as compared to that of each of other processes. Therefore, the temperature of the heating element of the fixing apparatus has to remain at a very high level (usually around 200 °C) and further a high pressure is required (usually between 2.0 and 6.0 kg/cm).

On the other hand, since both the photoconductor and the developer device have to be maintained at around room temperature, a considerable distance has to be maintained between the fixing apparatus and the developer device, which necessitates making the machine larger. In addition, it is necessary to force the removal of the generated heat from the system, but the noise produced by the forced radiation device is not negligible.

Further, in the conventional method of forming fixed images, since the fixing process works independently and fixing is carried out at such a high temperature of around 200 °C, as mentioned above, expensive heat-resistant materials such as heat-resistant resins, heat-resistant rubbers, etc. have to be provided in the periphery of the fixing apparatus.

Since the fixing is carried out at a high temperature, problems as curling and jamming of the paper, etc. are likely to take place. In addition, when the fixing requires a high temperature, it takes more time to reach the set temperature so that a quick printing becomes impossible. In such a case, therefore, this method is unsuitable for devices such as a facsimile which requires quick printings.

As for solving these problems, a device for low temperature fixing using a cold pressing method carried out at a temperature of not more than 100 °C is known (Japanese Patent Laid-Open No. 159174/1984). In this reference, however, although the fixing temperature is low, the nip pressure has to be elevated normally to not less than 4 kg/cm in this method, making the machine heavier. Moreover, it poses problems in the gloss of the images, deformation of the paper copy sheets and an insufficient fixing strength. Also, some attempts for enabling quick printings and fixing with conserved energy by using heating sheets in place of the conventionally used quartz heaters, nichrome wires, etc. as heat sources for the heat rollers in thermally fixing apparatuses have been known (Japanese Patent Laid-Open Nos. 196562/1983, 150183/1989 and 260475/1989).

However, in these methods, since the fixing temperature is set at such a high temperature of about 200 °C, the heating element is inserted in a cylinder in order to avoid temperature unevenness, thereby delaying the rate of the temperature rise and making the energy efficiency of the fixing apparatus poor.

In order to solve such problems, it has been demanded to improve conducting effects by winding a heating layer in a helical structure to form a slit; or by providing a heat-resistant, protective layer made of expensive imide resins, fluororesins, etc. in the periphery of the heat roller when the releasing properties of the toner at a high temperature are insufficient. These may undesirably make the apparatuses complicated and also expensive.

In addition, in the conventional fixing apparatus, the relation between a radius of the elastic material roller and a nip width are such that the radius of the roller is from about 15 mm to at most 50 mm, and that the nip width thereof is from about 3 mm to at most 10 mm. Therefore, since the ratio of the nip width to the radius of the elastic material roller is usually from 0.05 to at most 0.20, those expensive elastic materials whose compression set at a temperature of 180 °C to 200 °C are extremely small have been used. The reasons for using elastic materials having such properties are as follows: The toner is usually fixed at a surface temperature of the heat roller of close to 200 °C, and a high nip pressure is applied thereto, so that the toner can be melted and adhered onto a recording paper, etc. Specifically, in order to thermally melt the toner using a heat roller and to adhere it onto the recording paper at a high nip pressure, it is preferred that the nip width is kept wide so that the time for heat conduction from the heat roller to the toner can be kept long. At the same time, however, it is more necessary to increase the nip pressure for the purpose of increasing the adhesion strength of the toner with the paper by pressing the thermally softened toners into the pulp fibers of the surface of the paper.

In the conventional methods, since the surface temperature of the heat roller is needed to be at a high temperature of close to 200 °C as described above, those having small compression set at a high temperature are chosen among various heat-resistant elastic materials. However, when a large plastic deformation takes place by applying such a high temperature and high nip pressure as described above, the compression set becomes large, and the nip pressure becomes uneven, resulting not only in poor fixing ability but also in the problems incurred due to large loads on the driving systems.

From these standpoints, the development of a novel compact fixing apparatus as well as a matching toner thereto is in demand.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for forming fixed images using a thermally dissociating encapsulated toner.

Another object of the present invention is to provide a method for forming fixed images using an encapsulated toner whose shell is made of amorphous polyester.

In the present invention, a heat roller-type fixing apparatus for forming fixed images is used at a temperature of not more than 130 °C, the apparatus comprising a heat roller, a pressure roller and a current supplying means, the rollers rotating in contact with each other to thermally fix a visible image onto the recording medium at the contacted surfaces, wherein a conductive elastomer layer is formed in a uniform thickness on a cylinder of the heat roller, and the electric current is passed into the layer by the current supplying means. In the present invention, excellent properties are fully exhibited under the conditions of the specific resistivity of the conductive elastomer layer of not more than 100 Ω•cm; the maximum heating temperature of not more than 150 °C; the nip width of a pair of rollers in the fixing apparatus of not less than 0.2 times the radius of the elastic material roller; and the rubber hardness of at least one of the rollers of not more than 90 degrees according to JIS A-type hardness.

The present invention essentially relates to a method for forming fixed images using the above fixing apparatus. Specifically, a method for forming fixed images formed by the encapsulated toner in the present invention using a heat roller-type fixing apparatus comprises the steps of passing a current into a conductive elastomer layer formed in a uniform thickness on a cylinder of the heat roller; and thermally fixing the toner by heat generated thereby at a temperature of not more than 130 °C.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of illustration only, and thus, are not limitative of the present invention, and wherein:

Figure 1 is a schematic view showing an electrophotographic process used in the present invention;

Figure 2 is a schematic view showing one example of a fixing apparatus as defined by the present invention;

Figure 3 is a schematic view showing one example of a fixing apparatus as defined by the present invention; and

Figure 4 is a schematic view showing one example of a fixing apparatus as defined by the present invention.

The reference numerals in Figures 1 through 4 denote the following elements:

Element 1 is a photoconductive drum, element 2 a charger, element 3 an exposure device, element 4 a developer device, element 5 a transfer device, element 6 a toner, element 7 a recording medium (a recording paper), element 8 a heat roller, element 9 a pressure roller, element 10 a radiator device, element 11 a cleaner device, element 12 an insulating layer, element 13 a heating layer, element 14 a developer sleeve, element 21 an elastic heating element, element 22 a conductive layer, element 23 a releasing layer, element 31 an elastic heating element, element 32 a releasing layer, element 41 an elastic heating element, element A a rotating shaft and element B a rotating shaft.

DETAILED DESCRIPTION OF THE INVENTION

The apparatuses for forming fixed images in the present invention are detailed below, referring to the drawings.

Figure 1 is a schematic view showing an electrophotographic process used in the present invention;

Element 1 is a photoconductive drum such as of amorphous selenium, amorphous silicon or organic photoconductor, etc., in which a photoconductive layer is provided on a conductive supporter.

Element 2 is a charger arranged opposite to the photoconductive drum 1. The charging means is not particularly restricted, and any of the ordinarily used chargers, for example, a charger by corotron, a roller charger using a conductive roller, a brush charger using a conductive brush, etc. can be used.

Element 3 is an exposure device arranged opposite to the photoconductive drum 1 for forming electrostatic latent images on the surface of the photoconductor. For an exposure device 3, light sources such as semiconductor laser beams, LED or EL arrays, etc. are used in combination with an image-forming optical system. Alternatively, a device based on optical systems projecting a reflected light of a document usually provided in the copying machine can be used.

Element 4 is a developer device for making visible the electrostatic latent image formed on the surface of the photoconductor with the toner. For a developer device, any of the commonly used two-component magnetic brush developer devices, the one-component magnetic brush developer devices, and the one-component non-magnetic developer devices, etc. can be used. The toner 6 charged inside the developer device passes through the developer sleeve 14 to visualize the electrostatic latent images formed on the surface of the photoconductor.

Element 5 is a transfer device which has the same function as that of the charger 2 with essentially the same mechanism. In the transfer process, the visualized images formed on the surface of the photoconductive drum 1 by using a developer is transferred onto the surface of the recording medium 7. Element 11 is a cleaner device, by which about 5% to 20% of the toners which remain untransferred in the transfer process are removed.

Element 8 is a heat roller, and element 9 is a pressure roller. The visible image is formed by transferring the toner onto the recording medium 7 and fixing thereonto by passing through a fixing apparatus comprising a pair of these rollers. Element 10 is a radiator device. Conventionally, driving systems or fans have been necessary in order to discharge forcefully high heat generated from the fixing apparatus from the printing machine. By contrast, when the fixing apparatus has a low heating temperature with low heat radiation as in the case of the present invention, a simple radiator device of a slit type or honeycomb type as shown in the figures serves its purposes.

Next, the individual processes of the method for forming fixed images of the present invention will be described.

In the charging process, a specified charge is uniformly supplied, e.g. by the corona charger to the photoconductor surface. A photoconductor sensitive to a positive charge is taken here for an example, and the surface of the conductive supporter is coated with the photoconductive layer to form the photoconductor. A uniform charge is applied by the corona charger to the photoconductive layer, thereby positively charging the surface of the photoconductive layer.

In the exposing process, a light from the exposure device is irradiated to the surface of the related photoconductor, so that a leakage of charges occurs only in the exposed parts to form an electrostatic latent image on the photoconductive layer.

In the developing process, the toner triboelectrically charged inside the developer device is transported by the developer sleeve, and developed onto the photoconductor surface in proportion to the charge on the photoconductor surface. The developing process is an assortment of normal development in which a reversely polarized toner adheres to the charges by the Coulomb's force and of reverse development in which the toner adheres to the charges lost due to exposure to the light. The development process in the present invention applies to either method.

In the transfer process, the toner image on the photoconductor body surface accepts the charges from the reverse side of the recording medium 7 such as a recording paper through a transfer-corotron or a transfer-roller, and it is then transferred to the recording medium 7. Part of the toner is left behind untransferred on the photoconductor surface, which is removed by the cleaning device 11 such as a cleaning web, which is arranged opposite to the photoconductor as shown in Figure 1.

In the fixing process, the following apparatus is used. Specifically, the fixing apparatus in the present invention is constituted by a heat roller 8, which has a conductive elastomer layer, and a pressure roller 9 made of an elastic material or a rigid material. Specifically, for example, as illustrated in Figure 1, the fixing apparatus of the present invention is constituted by a heat roller 8 comprising an insulating layer 12 formed in the periphery of the rotating shaft A and a conductive elastomer layer, which is a heating layer 13, formed thereon; and a pressure roller 9 made of an elastic material. In another embodiment, as illustrated in Figure 2, the fixing apparatus of the present invention is constituted by a heat roller 8 comprising a conductive elastomer layer, which is an elastic heating element 21, formed in the periphery of the rotating shaft A, a conductive layer 22 formed thereon and a releasing layer 23; and a pressure roller 9 made of an elastic material. In a further embodiment, as illustrated in Figure 3, the fixing apparatus of the present invention is constituted by a heat roller 8 comprising a conductive elastomer layer, which is an elastic heating element 31, formed in the periphery of the rotating shaft A and a releasing layer 32 formed thereon; and a pressure roller 9 made of an elastic material. In a still further embodiment, as illustrated in Figure 4, the fixing apparatus of the present invention is constituted by a heat roller 8 comprising a conductive elastomer layer, which is an elastic heating element 41 formed in the periphery of the rotating shaft A; and a pressure roller 9 made of a rigid material. As described above, although the heat roller is provided with a conductive elastomer layer having a thickness without being subject to limitation as long as it has a uniform thickness, the thickness is preferably about 0.5 to 3.0 mm.

In addition to conductive materials such as SUS steel and aluminum, insulating materials such as heat-resistant resins and insulating ceramics can be used as a roller base material for the heat roller 8.

Examples of the heat-resistant resins include polyamides, polyamide-imides, polyacetals, polycarbonates, denatured PPOs, polyethylene terephthalates, polybutylene terephthalates, polyarylates, polysulfones, polyether sulfones, polyether ether ketones, polyetherimides, aromatic polyesters, polyphenylene sulfides, fluorine polymers, ABS resins, AS resins, AAS resins, AES resins, ACS resins, methylpentene polymers, ultrahigh molecular polyethylenes, polypropylene resins, phenol resins, diallyl phthalate resins, unsaturated polyester resins, epoxy resins, polyimides, polyurethanes, cyclic polyolefins and liquid crystal polymers.

These resins may be used singly or in combination of two or more kinds. In addition, they may be supplemented with fillers such as glass fibers.

Examples of the insulating ceramic materials include metallic oxides such as alumina, magnesia, beryllia, zirconia, silica, forsterite, wollastonite, zircon, mullite, cordierite, spodumene, aluminum titanate, spinel and barium titanate, and non-oxide metallic compounds such as silicon nitride, sialon, aluminum nitride, titanium nitride, silicon carbide, boron carbide, titanium carbide, tungsten carbide, lanthanum borate, titanium borate and zirconium borate.

When these insulating ceramic materials are used as roller base materials, one or more kinds thereof are used in any structural form selected from the group consisting of sintered bodies, glass and crystallized glass.

In such a case of using an insulating material as the roller base material, the insulating layer 12 becomes unnecessary.

The specific resistivity of the conductive elastomer layer is not more than 100 Ω•cm, preferably 1 to 100 Ω•cm, and more preferably 2 to 50 Ω•cm. When the resistivity exceeds 100 Ω•cm, the heat roller may fail to reach the set fixing temperature because the elastomer layer is not sufficiently heated unless a high charge is applied, and, in many cases, it takes too much time to reach the set temperature. Also, when the resistivity is less than 1 Ω•cm, the temperature control of the heat roller is difficult due to excess heating speed, and the resulting high temperature may undesirably damage the fixing apparatus including the fixing roller. The maximum heating temperature of the conductive elastomer layer used in the present invention is not more than 150 ° C.

Examples of the conductive elastomers for the fixing apparatus of the present invention include tetrafluoroethylenepropylene, vinylidene fluoride, silicone, fluorosilicone and other fluorine-based or silicone-based heat-resistant elastomers; and acrylic elastomers, nitrile elastomers, epichlorohydrin elastomers, ethylene-propylene-non-conjugated diene terpolymer (EPDM) elastomers, and other general-purpose elastomers. Under certain conditions, neoprene, butadiene and isoprene elastomers are also usable. In the present invention, a preference is given to the fluorine-based and silicone-based heat-resistant elastomers and the acrylic elastomer.

The conductive elastomer used for the fixing apparatus of the present invention is prepared by dispersing a conductive material such as conductive carbon, conductive inorganic powder or conductive potassium titanate whisker in the above elastic material and shaping the dispersed mixture. Further, a conductive layer may be provided which comprises a dispersion of an organic polymer such as polypyrrole, polythiophene, polyparaphenylene or polyaniline or a charge transfer complex such as that of anthracene and tetracyanoquinoline or that of pyrene and tetracyanoethylene in the above elastic material. Moreover, in some cases, to prevent the toner adhesion to the heat roller, the heat roller may be provided with a releasing layer by coating silicone oil or by forming a film such as that of polyethylene terephthalate, polybutylene terephthalate, polycarbonate, nylon, Teflon or PFA. The thickness of the releasing layer is preferably not more than 200 µm, since thicknesses exceeding 200 µm result in decreased thermal conductivity. More preferably, the thickness of the releasing layer is not more than 100 µm, but it needs to be not less than 10 µm, since thicknesses under this level can result in pinholes, which in turn lead to leakages of electricity.

In the conventional fixing apparatuses, as described above, the ratio of the nip width to the roller radius is normally from 0.05 to at most 0.20. By contrast, in the fixing apparatus of the present invention, this ratio is remarkably larger than those of the conventional fixing apparatuses, and it is adjusted to not less than 0.2, preferably 0.25 to 0.8, relative to the radius of the roller made of the elastic material. By adjusting the ratio of the nip width to the roller radius to not less than 0.2, the amount of heat supplied to toner upon fixing is increased so that fixing can be carried out at a lower fixing temperature. This effect is highly remarkable when the roller radius is not more than 15 mm, particularly not more than 10 mm. In the present invention, a roller made of an elastic material means a roller comprising a roller base material in the form of a rod or cylinder made of SUS steel, aluminum or another material having an outer diameter of not less than 8 mm, and an elastic material coated thereon having a hardness of not more than 90 degrees as determined by using a JIS A-type rubber hardness tester.

In the conventional fixing apparatuses, the rubber hardness of pressure roller is 40 to 90 degrees, as determined by a JIS A-type rubber hardness tester, for the pressure rollers having a slow peripheral speed and a small roller radius, and it is 40 to 90 degrees as determined by a JIS C-type rubber hardness tester, for the pressure rollers having a high peripheral speed and a large roller radius. However, in the present invention, at least one of the pair of rollers has a rubber hardness of not more than 90 degrees, preferably 20 to 90 degrees as determined by the JIS A-type rubber hardness tester. When the rubber hardness of the roller made of an elastic material exceeds 90 degrees as determined by the JIS A-type rubber hardness tester, the nip pressure becomes too high in the case where the roller-to-roller nip width is set in a specified range, which in turn causes a nip pressure difference between the center and both ends of the roller due to rotating shaft torsion of the roller, resulting in uneven fixing in the case of a small roller radius. When the rubber hardness is not more than 20 degrees, a sufficiently high nip pressure cannot be achieved when the nip width is set at a specified range, thereby resulting in an unsatisfactory fixing of the toner onto the recording medium. When the nip pressure is raised to a specified level, the pressure deformation of the roller becomes too large, resulting in an increased load on the driving system during operation, which can interfere with the rotation of the roller of the fixing apparatus. Hardness is tested in accordance with JIS K6301-1975, which may also be tested using a Durometer in accordance with ASTM 2240-75.

As described above, in the present invention, at least one of the pair of rollers is made of a material having a low rubber hardness. However, as illustrated in Figure 2, both the heat roller and the pressure roller made of materials having a low rubber hardness may be used. Also, as illustrated in Figure 3, the heat roller may be made of an elastic material having a high rubber hardness from the aspect of deterioration due to thermal load, etc. In another embodiment, as illustrated in Figure 4, in order to widen the nip width by using a heat roller made of a material having a low rubber hardness and to lower the cost by using a pressure roller made of an inexpensive tough material, the heat roller is made of a material having a low rubber hardness, and the pressure roller is made of SUS steel or another steel material insulated with a PET film or the like. In this case, when the surface of the heat roller is conductive, it is necessary to form a protective film with an insulating sheet on the surface of the heat roller.

In the fixing apparatus of the present invention, the toner can be heated at a fixing temperature of not more than 130 ° C, a sufficiently wide nip width can be obtained even when the roller radius is smaller, and the fixing can be carried out at a remarkably low nip pressure so as not to cause permanent set even when the strain is large. Specifically, the nip pressure in the fixing apparatus of the present invention is 0.01 to 4.0 kg/cm, preferably 0.1 to 3.0 kg/cm.

The heat roller of the fixing apparatus of the present invention is heated by applying a voltage to a conductive brush in contact with both ends of the heat roller as current supplying means, when an insulating layer is provided in the periphery of the rotating shaft and a heating layer of conductive elastomer is formed thereon as illustrated in Figure 1. Examples of the conductive brushes include those formed in the periphery of a metal shaft in a brush-like manner with conductive resin fibers, such as nylon or rayon having conductive carbon dispersed therein, or with fibers having conductive carbon, conductive paint or the like adhered thereto. To enhance the effects of applying a voltage, both end surfaces of the roller may be coated with a conductive paint or the like having conductive carbon, tin oxide or copper powder dispersed therein. Also, in the case illustrated in Figure 2, the voltage may be applied between the rotating shaft and the conductive elastomer layer.

The fixing apparatus of the present invention is thus capable of thermally fixing a visible image onto a recording medium conveyed, by the pair of the heat roller and the pressure roller as described above, which rotate in contact with each other. The fixing is carried out at the contacted surfaces of the rollers at a fixing temperature of not more than 130 ° C by heat generated by passing the electric current into the conductive elastomer layer.

The heat roller and the pressure roller rotate in contact with each other by specified driving means not illustrated in the figures in the direction shown in the respective drawings at a constant peripheral speed. The peripheral speed is not particularly limitative, and it may be properly chosen.

In the conventional apparatuses, the fixing is usually carried out at a high temperature of about 200 °C because the softening point of the resin contained as the main component in the toner for forming the visible image is high. In order to eliminate this problem, various references proposing toners which can be fixed at low temperatures have been known.

The toner used in the present invention is an encapsulated toner wherein the function separation for the storage stability and the fixing ability, and the offset resistance can be achieved. Examples of these toners are not particularly limitative, but those comprising a shell having improved storage stability and chargeabiity and a core having improved coloring, fixing ability and offset resistance are suitably used (see Japanese Patent Laid-Open Nos. 176642/1983, 176643/1983, 56352/1986, 128357/1988, 128358/1988, 267660/1989, 51175/1990 and 212169/1992, and Japanese Patent Application No. 259088/1992).

The construction of the encapsulated toner are described in detail below.

For shell materials, styrene resins (Japanese Patent Laid-Open No.205162/1983), polyamide resins (Japanese Patent Laid-Open No.66948/1983), epoxy resins (Japanese Patent Laid-Open No.148066/1984), polyurethane resins (Japanese Patent Laid-Open No.179860/1982), polyurea resins (Japanese Patent Laid-Open No.150262/1987) and many others have been proposed. And as substances fixable under heat and pressure contained in the core material, those thermoplastic resins whose glass transition points (Tg) are not less than 10 °C and not more than 50 °C such as polyester resins, polyamide resins, polyester-polyamide resins and polyvinyl resins can be used.

Such encapsulated toners can be obtained usually by the following production method.

(1) A spray-drying method, wherein after the core material is dispersed in a non-aqueous solution of polymer or polymer-emulsion, the dispersed liquid is spray-dried.

(2) A phase separation method (coacervation method), wherein phase separation is conducted around the core material in a solution of ionic polymer colloids and the core material, so that a simple emulsion is first prepared, which in turn is converted to a complex emulsion, in which the core materials are micro-encapsulated.

(3) An interfacial polymerization method, wherein a core material solution or dispersion is dispersed in a water in oil or oil in water type emulsion system, while at the same time collecting the shell material monomers (A) around the surfaces, which in turn is followed by reacting monomers (A) with monomers (B) around the surfaces in the subsequent step.

(4) Other methods include an in situ polymerization method, a submerged cure coating method, an air suspension coating method, an electrostatic coalescing method, a vacuum vapor deposition coating method, etc.

In the present invention, the particularly preferred encapsulated toners include a thermally dissociating encapsulate toner produced by the interfacial polymerization method or the spray-drying method, and an encapsulated toner whose shell is made of amorphous polyester produced by the in situ polymerization method. The interfacial polymerization method and the in situ polymerization method not only have the merit of an easy function separation for the core material and shell material but also are capable of producing a uniform toner in an aqueous state. Moreover, substances of low softening points can be used for the core material in these polymerization methods, making it particularly suitable from the aspect of fixing ability of the toner.

The thermally dissociating encapsulated toner means a toner which comprises a shell whose structure is fragile to heat, and a thermoplastic core material containing at least a thermoplastic resin and a coloring agent which can be fixed at a low temperature by pressure. The shell structure of this toner changes with heat, and at the point where pressure is applied, the core material is discharged to effect the fixing of the toner.

As compared to the thermal properties of the core material, the structure and the thermal properties of the shell material concern themselves remarkably with the fixing ability of the whole toner. Since a particular polyurethane resin among the above-mentioned resins for the shell materials is thermally dissociating, having excellent storage stability and fixing ability at a low temperature, it is an extremely favorable shell material for the thermally dissociating encapsulated toner of the present invention.

The principal components of such a shell material include resins having at least one linkage selected from the group consisting of thermally dissociating urethane linkage, thiol urethane linkage and s-thiourethane linkage. Particularly, in the thermally dissociating urethane resin which is the principal components of the shell material, at least 30% of all of the linkages formed from the isocyanate and/or isothiocyanate groups are thermally dissociating linkages. For instance, resins obtainable from the reaction between an isocyanate compound and/or isothiocyanate compound and compounds containing a phenolic hydroxyl group and/or a thiol group are preferably used (EP0453857A).

The encapsulated toner whose shell is made of amorphous polyester means a toner coated on the surface of the thermoplastic core material containing at least a thermoplastic resin and a coloring agent, with amorphous polyester.

Such an amorphous polyester can be preferably obtained by condensation polymerization between at least one alcohol monomer selected from the group consisting of dihydric alcohol monomers and trihydric or higher polyhydric alcohol monomers and at least one carboxylic acid monomer selected from the group consisting of dicarboxylic acid monomers and tricarboxylic or higher carboxylic acid monomers, in which at least one of the monomers is trihydric or higher alcohol or tricarboxylic or higher carboxylic acid (Japanese Patent Application No. 259088/1992).

In the encapsulated toner obtained by coating the surface of the thermoplastic core material containing at least the thermoplastic resin and the coloring agent with such an amorphous polyester, the shell structure of these toners easily changes with heat, and at the point where pressure is applied, the core material is discharged to effect the fixing of the toner.

Although the encapsulated toner used in the present invention is not particularly limitative as described above, the thermally dissociating encapsulated toner and the encapsulated toner whose shell is made of amorphous polyester are described in detail below as the modes of preferred embodiments.

First, the thermally dissociating encapsulated toner is described in detail below.

The encapsulated toner in the present invention is composed of a heat-fusible core material containing at least a coloring agent and a shell formed thereon so as to cover the surface of the core material, wherein the main components of the shell are a resin prepared by reacting:

(A) an isocyanate and/or isothiocyanate compound comprising:
    (1) 0 to 30 mol % of a monovalent isocyanate and/or isothiocyanate compounds, and
    (2) 100 to 70 mol % of at least a divalent isocyanate and/or isothiocyanate compounds with
(B) an active hydrogen compound comprising:
    (3) 0 to 30 mol % of a compound having one active hydrogen atom reactive with the isocyanate and/or isothiocyanate groups and
    (4) 100 to 70 mol % of a compound having at least two active hydrogen atoms reactive with the isocyanate and/or isothiocyanate groups

at a molar ratio of the component (A) to the component (B) of between 1:1 and 1:20, and wherein at least 30% of all of the linkages formed from the isocyanate or isothiocyanate groups are thermally dissociating linkages.

According to the present invention, the thermally dissociating linkage is preferably one formed by the reaction between a phenolic hydroxyl and/or thiol group and an isocyanate and/or isothiocyanate group.

Examples of the monovalent isocyanate compounds to be used as the component (1) in the present invention include ethyl isocyanate, octyl isocyanate, 2-chloroethyl isocyanate, chlorosulfonyl isocyanate, cyclohexyl isocyanate, n-dodecyl isocyanate, butyl isocyanate, n-hexyl isocyanate, lauryl isocyanate, phenyl isocyanate, m-chlorophenyl isocyanate, 4-chlorophenyl isocyanate, p-cyanophenyl isocyanate, 3,4-dichlorophenyl isocyanate, o-tolyl isocyanate, m-tolyl isocyanate, p-tolyl isocyanate, p-toluenesulfonyl isocyanate, 1-naphthyl isocyanate, o-nitrophenyl isocyanate, m-nitrophenyl isocyanate, p-nitrophenyl isocyanate, p-bromophenyl isocyanate, o-methoxyphenyl isocyanate, m-methoxyphenyl isocyanate, p-methoxyphenyl isocyanate, ethyl isocyanatoacetate, butyl isocyanatoacetate and trichloroacetyl isocyanate.

Examples of the divalent or higher isocyanate compounds to be used as the component (2) in the present invention include aromatic isocyanate compounds such as 2,4-tolylene diisocyanate, 2,4-tolylene diisocyanate dimer, 2,6-tolylene diisocyanate, p-xylylene diisocyanate, m-xylylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,5-naphthylene diisocyanate, 3,3'-dimethyldiphenyl-4,4'-diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, m-phenylene diisocyanate, triphenylmethane triisocyanate and polymethylenephenyl isocyanate; aliphatic isocyanate compounds such as hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, lysine diisocyanate and dimer acid diisocyanates; alicyclic isocyanate compounds such as isophorone diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), methylcyclohexane-2,4(or 2,6)-diisocyanate and 1,3-(isocyanatomethyl)cyclohexane; and other isocyanate compounds such as an adduct of 1 mol of trimethylolpropane with 3 mol of tolylene diisocyanate.

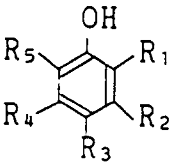
Examples of the isothiocyanate compounds include phenyl isothiocyanate, xylylene-1,4-diisothiocyanate and ethylidene diisothiocyanate.

Among these isocyanate and isothiocyanate compounds, compounds having an isocyanate group directly bonded to an aromatic ring are preferred, because they are effective in forming a urethane resin having a low thermal dissociation temperature.

According to the present invention, the monovalent isocyanate and/or isothiocyanate compound (1) also serves as a molecular weight modifier for the shell-forming resin and can be used in an amount of at most 30 mol % based on the isocyanate component and/or the isothiocyanate component. When the amount exceeds 30 mol %, the storage stability of the obtained encapsulated toner is undesirably poor.

Examples of compounds having one active hydrogen atom reactive with isocyanate and/or isothiocyanate groups to be used as component (3) in the present invention include aliphatic alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, tert-butyl alcohol, pentyl alcohol, hexyl alcohol, cyclohexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol, lauryl alcohol and stearyl alcohol; aromatic alcohols such as phenol, o-cresol, m-cresol, p-cresol, 4-butylphenol, 2-sec-butylphenol, 2-tert-butylphenol, 3-tert-butylphenol, 4-tert-butylphenol, nonylphenol, isononylphenol, 2-propenylphenol, 3-propenylphenol, 4-propenylphenol, 2-methoxyphenol, 3-methoxyphenol, 4-methoxyphenol, 3-acetylphenol, 3-carbomethoxyphenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2-bromophenol, 3-bromophenol, 4-bromophenol, benzyl alcohol, 1-naphthol, 2-naphthol and 2-acetyl-1-naphthol; and amides such as ϵ-caprolactam.

Particularly, a phenol derivative represented by the following formula (I) is preferably used:

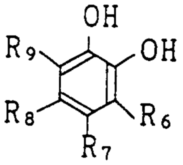


(I)

wherein R_1, R_2, R_3, R_4 and R_5 each independently represents a hydrogen atom, an alkyl group having 1 to 9 carbon atoms, an alkenyl group, an alkoxy group, an alkanoyl group, a carboalkoxy group or an aryl group or a halogen.

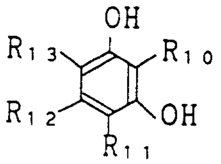
Examples of the dihydric or higher alcohols among the compounds having at least two active hydrogen atoms reactive with isocyanate and/or isothiocyanate groups to be used as the component (4) in the present invention include catechol, resorcinol, hydroquinone, 4-methylcatechol, 4-tert-butylcatechol, 4-acetylcatechol, 3-methoxycatechol, 4-phenylcatechol, 4-methylresorcinol, 4-ethylresorcinol, 4-tert-butylresorcinol, 4-hexylresorcinol, 4-chlororesorcinol, 4-benzylresorcinol, 4-acetylresorcinol, 4-carbomethoxyresorcinol, 2-methylresorcinol, 5-methylresorcinol, tert-butylhydroquinone, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, tetramethylhydroquinone, tetrachlorohydroquinone, methylcarboaminohydroquinone, methylureidohydroquinone, benzonorbornene-3,6-diol, bisphenol A, bisphenol S, 3,3'-dichlorobisphenol S, 2,2'-dihydroxybenzophenone, 2,4-dihydroxybenzophenone, 4,4'-dihydroxybenzophenone, 2,2'-dihydroxydiphenyl, 4,4'-dihydroxydiphenyl, 2,2'-dihydroxydiphenylmethane, 3,4-bis(p-hydroxyphenyl)hexane, 1,4-bis(2-(p-hydroxyphenyl)propyl)benzene, bis(4-hydroxyphenyl)methylamine, 1,3-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 1,5-dihydroxyanthraquinone, 2-hydroxybenzyl alcohol, 4-hydroxybenzyl alcohol, 2-hydroxy-3,5-di-tert-butylbenzyl alcohol, 4-hydroxy-3,5-di-tert-butylbenzyl alcohol, 4-hydroxyphenethyl alcohol, 2-hydroxyethyl 4-hydroxybenzoate, 2-hydroxyethyl 4-hydroxyphenylacetate, resorcinol mono-2-hydroxyethyl ether, hydroxyhydroquinone, gallic acid and ethyl 3,4,5-trihydroxybenzoate.

Among these dihydric or higher alcohols, catechol derivatives represented by the following formula (II) and resorcinol derivatives represented by the following formula (III) are preferably used:



(II)

wherein R_6, R_7, R_8 and R_9 each independently represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkenyl group, an alkoxy group, an alkanoyl group, a carboalkoxy group or an aryl group or a halogen.



(III)

wherein R_{10}, R_{11}, R_{12} and R_{13} each independently represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkenyl group, an alkoxy group, an alkanoyl group, a carboalkoxy group or an aryl group or a halogen.

Further, examples of the compounds having at least one isocyanate- or isothiocyanate-reactive functional group other than the hydroxyl group and at least one phenolic hydroxyl group include o-hydroxybenzoic acid, m-hydroxybenzoic acid, p-hydroxybenzoic acid, 5-bromo-2-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, 4-chloro-2-hydroxybenzoic acid, 5-chloro-2-hydroxybenzoic acid, 3,5-dichloro-4-hydroxybenzoic acid, 3-methyl-2-hydroxybenzoic acid, 5-methoxy-2-hydroxybenzoic acid, 3,5-di-tert-butyl-4-hydroxybenzoic acid, 4-amino-2-hydroxybenzoic acid, 5-amino-2-hydroxybenzoic acid, 2,5-dinitrosalicylic acid, sulfosalicylic acid, 4-hydroxy-3-methoxyphenylacetic acid, catechol-4-carboxylic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 3,4-dihydroxyphenylacetic acid, m-hydroxycinnamic acid, p-hydroxycinnamic acid, 2-amino-4-methylphenol, 2-amino-5-methylphenol, 5-amino-2-methylphenol, 3-amino-2-naphthol, 8-amino-2-naphthol, 1-amino-2-naphthol-4-sulfonic acid, 2-amino-5-naphthol-4-sulfonic acid, 2-amino-4-nitrophenol, 4-amino-2-nitrophenol, 4-amino-2,6-dichlorophenol, o-aminophenol, m-aminophenol, p-aminophenol, 4-chloro-2-aminophenol, 1-amino-4-hydroxyanthraquinone, 5-chloro-2-hydroxyaniline, α-cyano-3-hydroxycinnamic acid, α-cyano-4-hydroxycinnamic acid, 1-hydroxynaphthoic acid, 2-hydroxynaphthoic acid, 3-hydroxynaphthoic acid and 4-hydroxyphthalic acid.

Further, examples of the polythiol compounds having at least one thiol group in each molecule include ethanethiol, 1-propanethiol, 2-propanethiol, thiophenol, bis(2-mercaptoethyl)ether, 1,2-ethanedithiol, 1,4-butanedithiol, bis(2-mercaptoethyl) sulfide, ethylene glycol bis(2-mercaptoacetate), ethylene glycol bis(3-mercaptopropionate), 2,2-dimethylpropanediol bis(2-mercaptoacetate), 2,2-dimethylpropanediol bis(3-mercaptopropionate), trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), trimethylolethane tris(2-mercaptoacetate), trimethylolethane tris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(3-mercaptopropionate), dipentaerythritol hexakis(2-mercaptoacetate), dipentaerythritol hexakis(3-mercaptopropionate), 1,2-dimercaptobenzene, 4-methyl-1,2-dimercaptobenzene, 3,6-dichloro-1,2-dimercaptobenzene, 3,4,5,6-tetrachloro-1,2-dimercaptobenzene, xylylenedithiol and 1,3,5-tris(3-mercaptopropyl) isocyanurate.

In the thermally dissociating shell-forming resin used in the present invention, at least 30%, preferably at least 50% of all of the linkages formed from isocyanate or isothiocyanate groups are thermally dissociating linkages. When the content of the thermally dissociating linkages is less than 30%, the strength of the shell in the heat-and-pressure fixing cannot be sufficiently lowered, making it less likely to exhibit any advantageous fixing performance of the core material.

In the thermally dissociating encapsulated toner of the present invention, other compounds having an isocyanate-reactive functional group other than phenolic hydroxyl and thiol groups, which may be used as a shell-forming material in such an amount as not to lower the ratio of the linkages formed by the reaction of isocyanate and/or isothiocyanate groups with phenolic hydroxyl and/or thiol groups to the all of the linkages formed from isocyanate and/or isothiocyanate groups is less than 30%, include, for example, the following active methylene compounds such as malonate and acetoacetate, oximes such as methyl ethyl ketone oxime, carboxylic acid, polyol, polyamine, aminocarboxylic acid and aminoalcohol.

In the present invention, the compound having one active hydrogen atom reactive with isocyanate and/or isothiocyanate groups as the component (3) may be used in an amount of at most 30 mol % based on the active hydrogen component. When the amount exceeds 30 mol %, the storage stability of the resulting toner is undesirably poor.

Further, the molar ratio of (A) the isocyanate compound and/or isothiocyanate compound comprising the components (1) and (2) to (B) the active hydrogen compounds comprising the components (3) and (4) preferably lies between 1:1 and 1:20 in order to obtain a resin free from unreacted isocyanate groups.

In the production of the encapsulated toner, the shell is preferably formed by an interfacial polymerization or an in situ polymerization. Alternatively, it may be formed by a dry method comprising stirring in an air stream at a high rate matrix particles used as a core material together with particles used as a shell-forming material having a number-average particle size of one-eighth or less of that of the matrix particles.

The shell-forming resins can be produced in the presence of no catalysts. However, when the resins are produced in the presence of catalysts, those catalysts including tin catalysts such as dibutyltindilaurate, etc.; amine catalysts such as 1,4-diazabicyclo[2.2.2]octane, N,N,N-tris(dimethylaminopropyl)-hexahydro-S-triazine, etc.; and any known urethane catalysts can be used.

The resins used in the core materials of the thermally dissociating encapsulated toner of the present invention are thermoplastic resins having glass transition points (Tg) of 10 to 50 ° C, and examples thereof include polyester resins, polyester-polyamide resins, polyamide resins and vinyl resins, among which vinyl resins are particularly preferable. When the glass transition point (Tg) is less than 10 ° C, the storage stability of the resulting encapsulated toner is undesirably poor, and when it exceeds 50 ° C, the fixing strength of the encapsulated toner is undesirably poor.

Examples of the monomers constituting the vinyl resins include styrene and its derivatives such as styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, α-methylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-chlorostyrene and vinylnaphthalene; ethylenically unsaturated monoolefins such as ethylene, propylene, butylene and isobutylene; vinyl esters such as vinyl chloride, vinyl bromide, vinyl fluoride, vinyl acetate, vinyl propionate, vinyl formate and vinyl caproate; ethylenic monocarboxylic acids and esters thereof such as acrylic acid, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, amyl acrylate, cyclohexyl acrylate, n-octyl acrylate, isooctyl acrylate, decyl acrylate, lauryl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, methoxyethyl acrylate, 2-hydroxyethyl acrylate, glycidyl acrylate, 2-chloroethyl acrylate, phenyl acrylate, methyl α-chloroacrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, amyl methacrylate, cyclohexyl methacrylate, n-octyl methacrylate, isooctyl methacrylate, decyl methacrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, methoxyethyl methacrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate; substituted monomers with ethylenic monocarboxylic acids such as acrylonitrile, methacrylonitrile and acrylamide; ethylenic dicarboxylic acids and substituted monomers therewith such as dimethyl maleate; vinyl ketones such as vinyl methyl ketone; vinyl ethers such as vinyl methyl ether; vinylidene halides such as vinylidene chloride; and N-vinyl compounds such as N-vinylpyrrole and N-vinylpyrrolidone.

Among the above core material resin-constituting monomers of the present invention, the core material-forming resin contains, in the main chain of the resin, styrene or its derivatives preferably in an amount of 50 to 90 parts by weight, and the ethylenic monocarboxylic acid or an ester thereof preferably in an amount of 10 to 50 parts by weight to control the thermal properties of the resin, such as the softening point.

When the monomer composition constituting the core material-forming resin according to the present invention contains a crosslinking agent, which may be also used, if necessary, as a mixture of two or more of them, any known crosslinking agents may be properly used. When the amount of the crosslinking agent added is too large, the resulting toner is less likely to be heat-fused, thereby resulting in poor heat fixing ability and heat-and-pressure fixing ability. On the contrary, when the amount is too small, in heat-and-pressure fixing, a part of the toner cannot be completely fixed on a paper but rather adheres to the surface of a roller, which in turn is transferred to a subsequent paper which creates the so-called "offset" or "offset phenomenon." Accordingly, the amount of the crosslinking agent is preferably 0.001 to 15% by weight, more preferably 0.1 to 10% by weight, based on the polymerizable monomers used.

The core material of the thermally dissociating encapsulated toner according to the present invention may further contain, if necessary, one or more offset inhibitors of any known kind for the purpose of improving offset resistance in the heat-and-pressure fixing. These offset inhibitors are contained in an amount of 1 to 20% by weight based on the resin contained in the core material.

The core material of the thermally dissociating encapsulated toner according to the present invention contains a coloring agent, which may be any one of the dyes and pigments used in the conventional toners. The coloring agent is generally contained in an amount of 1 to 15 parts by weight based on 100 parts by weight of the resin contained in the core material.

In addition, in the shell-forming materials of the thermally dissociating encapsulated toner according to the present invention and in the core material, a metal-containing dye which has been used for toners, for example, a metal complex of an organic compound having a carboxyl or nitrogenous group, such as nigrosine, may be added in an effective amount as a charge control agent. Alternatively, such a charge control agent may be mixed with the toner.

The thermally dissociating encapsulated toner according to the present invention may contain, if necessary, a fluidity improver and/or a cleanability improver. Further, for the purpose of controlling the developability of the encapsulated toner, an additive, for example, finely powdered polymethyl methacrylate, etc. may be added. Furthermore, for the purposes of toning or resistance control, a small amount of carbon black may be used.

The thermally dissociating encapsulated toner of the present invention preferably has a softening point of 80 to 150 ° C. When the softening point is lower than 80 ° C, the offset resistance of the resulting encapsulated toner is undesirably poor, and when it exceeds 150 ° C, the fixing strength of the encapsulated toner is undesirably poor.

Although the particle size of the thermally dissociating encapsulated toner according to the present invention is not particularly limited, the average particle size thereof is generally 3 to 30 µm. The preferred thickness of the shell of the encapsulated toner is from 0.01 to 1 µm. When the thickness is less than 0.01 µm, the blocking resistance of the resulting encapsulated toner is poor, and when it exceeds 1 µm, the heat fusibility of the resulting encapsulated toner is undesirably poor.

Next, the encapsulated toner whose shell is made of amorphous polyester is described in detail below.

In the encapsulated toner whose shell is made of amorphous polyester, the amorphous polyester can be preferably obtained by condensation polymerization between at least one alcohol monomer selected from the group consisting of dihydric alcohol monomers and trihydric or higher polyhydric alcohol monomers and at least one carboxylic acid monomer selected from the group consisting of dicarboxylic acid monomers and tricarboxylic or higher carboxylic acid monomers, in which at least one of the monomers is trivalent or higher (Japanese Patent Application No. 259088/1992).

Examples of the dihydric alcohol components include bisphenol A alkylene oxide adducts such as polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene(3.3)-2,2-bis(4-hydroxyphenyl)-propane, polyoxypropylene(2.0)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene(2.0)-polyoxyethylene-(2.0)-2,2-bis(4-hydroxyphenyl)propane, and polyoxypropylene(6)-2,2-bis(4-hydroxyphenyl)propane; ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, neopentyl glycol, 1,4-butenediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, dipropylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, bisphenol A, a bisphenol A propylene adduct, a bisphenol A ethylene adduct, hydrogenated bisphenol A and other dihydric alcohols.

Examples of the trihydric or higher polyhydric alcohol components include sorbitol, 1,2,3,6-hexanetetrol, 1,4-sorbitan, pentaerythritol, dipentaerythritol, tripentaerythritol, 1,2,4-butanetriol, 1,2,5-pentanetriol, glycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane, 1,3,5-trihydroxymethylbenzene, and other trihydric or higher polyhydric alcohols.

In the present invention, these dihydric alcohol monomers and trihydric or higher polyhydric alcohol monomers may be used singly or in combination.

As for the acid components, examples of the dicarboxylic acid components include maleic acid, fumaric acid, citraconic acid, itaconic acid, glutaconic acid, phthalic acid, isophthalic acid, terephthalic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, malonic acid, n-dodecenylsuccinic acid, n-dodecylsuccinic acid, n-octylsuccinic acid, isooctenylsuccinic acid, isooctylsuccinic acid, and acid anhydrides thereof, lower alkyl esters thereof and other dicarboxylic acids.

Examples of the tricarboxylic or higher carboxylic acid components include 1,2,4-benzenetricarboxylic acid, 2,5,7-naphthalenetricarboxylic acid, 1,2,4-naphthalenetricarboxylic acid, 1,2,4-butanetricarboxylic acid, 1,2,5-hexanetricarboxylic acid, 1,3-dicarboxyl-2-methyl-2-methylenecarboxypropane, 1,2,4-cyclohexanetricarboxylic acid, tetra(methylenecarboxyl)methane, 1,2,7,8-octanetetracarboxylic acid, pyromellitic acid, Empol trimer acid and acid anhydrides thereof, lower alkyl esters thereof and other tricarboxylic or higher carboxylic acids.

In the present invention, these dicarboxylic acid monomers and tricarboxylic or higher carboxylic acid monomers may be used singly or in combination.

More particularly, the encapsulated toner whose shell is made of amorphous polyester suitably used in the present invention can be produced by any known methods such as in situ polymerization, and this encapsulated toner is composed of a heat-fusible core material containing at least a thermoplastic resin and a coloring agent, and a shell formed thereon so as to cover the surface of the core material.

The resins to be used as core materials of the encapsulated toner according to the present invention are thermoplastic resins having glass transition points (Tg) of 10 to 50 ° C, and examples thereof include polyester resins, polyester-polyamide resins, polyamide resins and polyvinyl resins, among which polyvinyl resins are particularly preferable. When the glass transition point (Tg) is less than 10 ° C, the storage stability of the resulting encapsulated toner is undesirably poor, and when it exceeds 50 ° C, the fixing strength of the encapsulated toner is undesirably poor.

The method of producing the encapsulated toner by the in situ polymerization is detailed below.

In this production method, a shell is formed based on the principle that the concentration of the shell material on the surface of the droplets takes place in a mixture solution containing a core material and a shell material comprising amorphous polyester, which mixture solution is dispersed in a dispersion medium. Specifically, the separation of the core material and the shell material takes place in the droplets of the mixture solution due to the differences in the indices of solubility. In this state, the polymerization progresses to form an encapsulated structure. By this method, since a shell is formed into a layer containing amorphous polyester in a substantially uniform thickness, the chargeability of the toner becomes uniform.

In the case of producing the encapsulated toner by the in situ polymerization method, a dispersion stabilizer is required to be contained in the dispersion medium in order to prevent agglomeration and incorporation of the dispersed substances.

Examples of the dispersion stabilizers include polyvinyl alcohol, sodium dodecylbenzenesulfonate, tricalcium phosphate, etc.

Examples of the dispersion media of the dispersion stabilizer include water, methanol, ethanol, propanol, butanol, ethylene glycol, glycerol, isopropyl ether, tetrahydrofuran, etc. These dispersion media can be used singly or in combination.

The addition amount of the amorphous polyester is normally 3 to 50 parts by weight, preferably 5 to 40 parts by weight, based on 100 parts by weight of the core material. When it is less than 3 parts by weight, the resulting shell becomes too thin, thereby making the storage stability of the toner poor, and when it exceeds 50 parts by weight, the resulting mixture becomes highly viscous, posing difficulty in making the powder fine, thereby leading to poor production stability of the toner.

The amorphous polyester suitably used in the present invention has a glass transition point of 50 to 80 °C, and an acid value of 3 to 50 KOH mg/g. The resins to be used as core materials of the encapsulated toner are thermoplastic resins having glass transition points of 10 to 50 °C.

According to the fixing method using the fixing apparatus in the present invention, since the toner adhered onto the recording medium while conveying is fixed at a fixing temperature of not more than 130 °C in the fixing process, it is no longer necessary to use expensive heat-resistant materials for the fixing apparatus and the periphery thereof, and inexpensive materials can be used. In addition, since the durability of the parts used become long, the service life of the overall apparatus becomes long, thereby making it possible to be low-cost printing machines. Further, since the fixing is carried out at a fixing temperature of not more than 130 °C and the nip pressure is also kept low, paper sheets are not likely to curl or jam, thereby conserving in its maintenance.

Since the fixing is carried out at a low temperature, the temperature of the heating element in the fixing device can be set low with only a small rise of the temperature in the printing machine. Accordingly, a forced radiation device such as an electric fan can be made smaller or is not required, thereby reducing the noise. Also, since the waiting time for the temperature rise in the fixing apparatus can be shortened, quick printing becomes possible, making it suitable in the field requiring quick printings such as facsimile. Further, since the fixing is carried out at a fixing temperature of not more than 130 °C, the fixing apparatus can be simplified, thereby making it possible to miniaturize and lower its overall cost.

EXAMPLES

The present invention is hereinafter described in more detail by means of the following production examples, test examples and comparative test examples, but the present invention is not limited by them.

Production Example 1 of Encapsulated Toner:

To a mixture comprising 70.0 parts by weight of styrene, 30.0 parts by weight of 2-ethylhexyl acrylate and 1.0 part by weight of divinylbenzene, 10.0 parts by weight of carbon black "#44" (manufactured by Mitsubishi Chemical Industries, Ltd.), 4.0 parts by weight of 2,2'-azobisisobutyronitrile, 9.5 parts by weight of 4,4'-diphenylmethane diisocyanate "Millionate MT" (manufactured by Nippon Polyurethane Industry Co., Ltd.) are added. The obtained mixture is introduced into an attritor (manufactured by Mitsui Miike Kakoki) and dispersed at 10 °C for 5 hours to give a polymerizable composition. This composition is added to 800 g of a 4% by weight aqueous colloidal solution of tricalcium phosphate which had been preliminarily prepared in a 2-liter separable glass flask, so as to give a concentration of 30% by weight. The obtained mixture is emulsified and dispersed with a TK homomixer (manufactured by Tokushu Kika Kogyo) at 5 °C and a rotational speed of 10000 rpm for 2 minutes. A four-necked glass cap is set on the flask, and a reflux condenser, a thermometer, a dropping funnel fitted with a nitrogen inlet tube and a stainless steel stirring rod are set thereon. The resulting flask is placed on an electric mantle heater. A solution of 22.0 g of resorcinol, 3.6 g of diethyl malonate and 0.5 g of 1,4-diazabicyclo [2.2.2] octane in 40 g of ion-exchanged water is prepared, and the resulting mixture is dropped into the flask in a period of 30 minutes through the dropping funnel while stirring. Thereafter, the contents are heated to 80 ° C and reacted for 10 hours in a nitrogen atmosphere while stirring. After cooling the reaction mixture, it is dissolved into 10%-aqueous hydrochloric acid. The resulting mixture is filtered and the obtained solid is washed with water, dried under a reduced pressure of 20 mmHg at 45 ° C for 12 hours and classified with an air classifier to give the thermally dissociating encapsulated toner with an average particle size of 9 μm having a shell made of a resin having a thermally dissociating urethane linkage. The glass transition point assignable to the resin contained in the core material is 30.2 ° C, and its softening point is 130.0 ° C.

Production Example 2 of Encapsulated Toner:

100 parts by weight of a copolymer consisting of 75 parts by weight of styrene and 25 parts by weight of n-butyl acrylate and having a softening point of 75.3 ° C and a glass transition temperature of 40.5 ° C, 6 parts by weight of copper phthalocyanine "Sumikaprint Cyanine Blue GN-O" (manufactured by Sumitomo Chemical Co., Ltd.), and 5 parts by weight of polypropylene wax "Biscol 550p" (manufactured by Sanyo Chemical Industries, Ltd.) are together premixed, kneaded in a twin-screw extruder, cooled and pulverized. 40 parts by weight of this kneaded mixture are mixed with 50 parts by weight of styrene, 15 parts by weight of n-butyl acrylate, 3 parts by weight of 2,2'-azobis-(2,4-dimethylvaleronitrile), 9.0 parts by weight of an adduct of 3 mol of 2,4-tolylene diisocyanate with 1 mol of trimethylolpropane "Takenate D-102" (manufactured by Takeda Chemical Industries, Ltd.), and 0.5 parts by weight of xylylene-1,4-diisothiocyanate to give a polymerizable composition. This composition is added to 800 g of a 4% by weight aqueous colloidal solution of tricalcium phosphate which is preliminarily prepared in a two-liter separable glass flask, so as to give a concentration of 30% by weight. The obtained mixture is emulsified and dispersed with a TK homomixer (manufactured by Tokushu Kika Kogyo) at 5 ° C and a rotational speed of 10000 rpm for 2 minutes.

A four-necked glass cap is set on the flask, and a reflux condenser, a thermometer, a dropping funnel fitted with a nitrogen inlet tube and a stainless steel stirring rod are attached thereto. The resulting flask is placed on an electric mantle heater. A solution of 27.4 g of 4-acetylcatechol, 4.0 g of dimethyl malonate, 0.8 g of 1,2-ethanedithiol and 0.5 g of 1,4-diazabicyclo[2.2.2]octane in 40 g of ion-exchanged water is prepared, and the resulting mixture is dropped into the flask in a period of 30 minutes through the dropping funnel while stirring. Thereafter, the contents are heated to 80 ° C and reacted for 10 hours in a nitrogen atmosphere while stirring. After cooling the reaction mixture, the dispersing agent is dissolved into 10%-aqueous hydrochloric acid. The resulting mixture is filtered, and the obtained solid is washed with water, dried under a reduced pressure of 20 mmHg at 45 ° C for 12 hours and classified with an air classifier to give the thermally dissociating encapsulated toner with an average particle size of 9 μm whose shell is made of a resin having a thermally dissociating urethane linkage. The glass transition temperature assignable to the resin contained in the core material is 35.4 ° C, and its softening point is 133.5 ° C.

Production Example 3 of Encapsulated Toner:

367.5 g of bisphenol A propylene oxide adduct, 146.4 g of bisphenol A ethylene oxide adduct, 126.0 g of terephthalic acid, 40.2 g of dodecenylsuccinic anhydride and 77.7 g of trimellitic anhydride are placed in a two-liter four-necked glass flask, and a thermometer, a stainless steel stirring rod, a condenser and a nitrogen inlet tube are attached thereto. The reaction is carried out in a nitrogen stream in a mantle heater at 220 ° C.

The degree of polymerization is determined based on the softening point measured according to ASTM E28-67, and the reaction is terminated when the softening point reaches 110 ° C.

When the glass transition point of the obtained resin is measured by a differential scanning calorimeter (manufactured by Seiko Instruments, Inc.), it is 65 ° C. In addition, its softening point and acid value are measured, and they are, respectively, 110 ° C and 18 KOH mg/g. The acid value is measured according to JIS K0070.

To a mixture comprising 69.0 parts by weight of styrene, 31.0 parts by weight of 2-ethylhexyl acrylate and 0.9 parts by weight of divinylbenzene, and 7.0 parts by weight of carbon black "#44" (manufactured by Mitsubishi Kasei Corporation), 20.0 parts by weight of the resin obtained as above and 3.5 parts by weight of 2,2'-azobisisobutyronitrile are added. The obtained mixture is introduced into an attritor (manufactured by Mitsui Miike Kakoki) and dispersed at 10 ° C for 5 hours to give a polymerizable composition. This composition is added to 800 g of a 4% by weight aqueous colloidal solution of tricalcium phosphate which had been preliminarily prepared in a 2-liter separable glass flask, so as to give a concentration of 30% by weight. The obtained mixture is emulsified and dispersed with a TK homomixer (manufactured by Tokushu Kika Kogyo) at 5 °C and a rotational speed of 12000 rpm for 5 minutes.

Next, a four-necked glass cap is set on the flask, and a reflux condenser, a thermometer, a nitrogen inlet tube and a stainless steel stirring rod are attached thereto. The resulting flask is placed on an electric mantle heater. Thereafter, the contents are heated to 85 °C and reacted for 10 hours in a nitrogen atmosphere while stirring. After cooling the reaction mixture, the dispersion medium is dissolved into 10%-aqueous hydrochloric acid. The resulting mixture is filtered and the obtained solid is washed with water, dried under a reduced pressure of 20 mmHg at 45 °C for 12 hours and classified with an air classifier to give the encapsulated toner with an average particle size of 8 µm whose shell is made of an amorphous polyester resin. The glass transition temperature assignable to the resin contained in the core material is 30.6 °C, and its softening point is 125.5 °C.

Test Example 1:

The thermally dissociating encapsulated toner obtained in Production Example 1 of Encapsulated Toner is surface-treated with 0.5% of silica "R972" (manufactured by Nippon Aerosil Co., Ltd.), and then 50 g of the toner is blended together with 1 kg of a commercially available ferrite carrier to obtain a developer.

Also, a commercially available copying machine is modified to produce an apparatus according to Figure 1, in which a fixing portion comprising a heat roller and a pressure roller is produced according to Figure 2. Specifically, each of the heat roller and the pressure roller has a diameter of 20 mm, the rubber hardness measured according to an A-type hardness tester is 60 degrees for the heat roller and 40 degrees for the pressure roller. The heat roller is obtained by coating the rotating shaft of the heat roller with a silicone resin as an insulating layer, and then forming a conductive elastomer layer thereon with a silicone resin dispersing a carbon black to provide the specific resistivity of 3 Ω•cm. The pressure roller is made of an elastic material using silicone foam rubber.

The nip pressure of the fixing apparatus is 0.3 kg/cm and the nip width is 3 mm, and voltage is supplied to both ends of conductive elastomer layer using a conductive brush. Here, the nip width is measured by a roll nip tester manufactured by Toshiba Silicone Co., Ltd. The ratio of the nip width to the roller radius is 0.30.

The obtained developer is used to carry out copying by using the modified copying machine to develop images. The fixing temperature is measured, and it has been found that a sufficient fixing strength is exhibited even at a temperature of 90 °C (lowest fixing temperature) at a peripheral speed of 25 mm/sec, and that it does not show any hot offsetting to the heat roller at a temperature of 150 °C. Further, a continuous copying test for 10,000 sheets is carried out at a fixing temperature of 90 °C, and substantially no failures caused on the formed images by the fixing apparatus are observed. Also, although no separation claw normally used in heat rollers and pressure rollers is used, substantially no deformation of paper sheets such as curling, jamming, wrinkling of the recording paper is observed, at the time of discharging of the recording medium from the fixing apparatus after fixing.

The lowest fixing temperature for the toner is the temperature of the paper surface at which the fixing rate of the toner exceeds 70%. This fixing rate of the toner is determined by placing a load of 500 g on a sand-containing rubber eraser having a bottom area of 15 mm x 7.5 mm which contacts the fixed toner image, placing the loaded eraser on a fixed toner image obtained in the fixing device, moving the loaded eraser on the image backward and forward five times, measuring the optical reflective density of the eraser-treated image with a reflective densitometer manufactured by Macbeth Co., and then calculating the fixing rate from this density value and a density value before the eraser treatment using the following equation.

$$\text{Fixing rate} = \frac{\text{Image density after eraser treatment}}{\text{Image density before eraser treatment}} \times 100$$

Test Example 2:

The thermally dissociating encapsulated toner obtained in Production Example 2 of Encapsulated Toner is surface-treated with 0.5% of silica "R972" (manufactured by Nippon Aerosil Co., Ltd.), and then 50 g of the toner is blended together with 1 kg of a commercially available ferrite carrier to obtain a developer.

The obtained developer is used to carry out copying by using the same apparatus and the same method as in Test Example 1 above, and the fixing temperature is measured. As a result, it has been found that a sufficient fixing strength is exhibited even at a temperature of 90 ° C (lowest fixing temperature) at a peripheral speed of 25 mm/sec, and that it does not show any hot offsetting to the heat roller at a temperature of 150 ° C. Further, a continuous copying test for 10,000 sheets is carried out at a fixing temperature of 90 ° C, and substantially no failures caused on the formed images by the fixing apparatus are observed. Also, although no separation claw normally used in heat rollers and pressure rollers is used, substantially no deformation of paper sheets such as curling, jamming, wrinkling of the recording paper is observed, at the time of discharging of the recording medium from the fixing apparatus after fixing.

Test Example 3:

The encapsulated toner whose shell is made of amorphous polyester obtained in Production Example 3 of Encapsulated Toner is surface-treated with 0.5% of silica "R972" (manufactured by Nippon Aerosil Co., Ltd.), and then 50 g of the toner is blended together with 1 kg of a commercially available ferrite carrier to obtain a developer.

The obtained developer is used to carry out copying by using the same apparatus and the same method as in Test Example 1 above, and the fixing temperature is measured. As a result, it has been found that a sufficient fixing strength is exhibited even at a temperature of 80 ° C (lowest fixing temperature) at a peripheral speed of 25 mm/sec, and that it does not show any hot offsetting to the heat roller at a temperature of 150 ° C. Further, a continuous copying test for 10,000 sheets is carried out at a fixing temperature of 90 ° C, and substantially no failures caused on the formed images by the fixing apparatus are observed. Also, although no separation claw normally used in heat rollers and pressure rollers is used, substantially no deformation of paper sheets such as curling, jamming, wrinkling of the recording paper is observed, at the time of discharging of the recording medium from the fixing apparatus after fixing.

Comparative Test Example 1:

The thermally dissociating encapsulated toner obtained in Production Example 1 of Encapsulated Toner is surface-treated with 0.5% of silica "R972" (manufactured by Nippon Aerosil Co., Ltd.), and then 50 g of the toner is blended together with 1 kg of a commercially available ferrite carrier to obtain a developer.

The fixing apparatus used in the commercially available copying machine is modified so as to make it variable in fixing temperature and roller rotating speed. The heat roller comprises an aluminum cylinder coated with a fluorine resin, which has a roller radius of 30 mm and a quartz heater disposed inside the cylinder. The pressure roller has a rubber hardness measured by the A-type tester of 80 degrees, a roller radius of 20 mm, and a nip pressure is 0.5 kg/cm and a nip width is 3 mm. The ratio of the nip width to the roller radius is 0.15.

The obtained developer is used to carry out copying using the copying machine to develop images, and the fixing temperature is measured. As a result, it has been found that although a sufficient fixing strength is exhibited even at a temperature of 90 ° C (lowest fixing temperature) at a peripheral speed of 25 mm/sec, a hot offsetting to the heat roller takes place at a temperature of 120 ° C.

Comparative Test Example 2:

The encapsulated toner whose shell is made of amorphous polyester obtained in Production Example 3 of Encapsulated Toner is surface-treated with 0.5% of silica "R972" (manufactured by Nippon Aerosil Co., Ltd.), and then 50 g of the toner is blended together with 1 kg of a commercially available ferrite carrier to obtain a developer.

The obtained developer is used to carry out copying by using the same apparatus and the same method as in Comparative Test Example 1 above, and the fixing temperature is measured. As a result, it has been found that although a sufficient fixing strength is exhibited even at a temperature of 80 ° C (lowest fixing temperature) at a peripheral speed of 25 mm/sec, a hot offsetting to the heat roller takes place at a temperature of 120 ° C.

The present invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

Claims

1. A method of forming fixed images comprising:
charging a photoconductor;
exposing said photoconductor to light;
applying a thermally dissociating encapsulated toner to an electrostatic latent image formed on said photoconductor, thereby developing said electrostatic latent image to form a visible image;
transferring said formed visible image to a recording medium; and
fixing said transferred visible image onto said recording medium at a temperature of not more than 130 °C, wherein said fixing is carried out using a heat roller-type fixing apparatus comprising a heat roller having a conductive elastomer layer formed in a uniform thickness, a pressure roller and a current supplying means, and said fixing comprises the steps of passing an electric current into the conductive elastomer layer; and thermally fixing the visible image by heat generated in the conductive elastomer layer.

2. The method according to claim 1, wherein the specific resistivity of the conductive elastomer layer is not more than 100 Ω•cm, and the maximum heating temperature thereof is not more than 150 °C.

3. The method according to claim 1 or 2, wherein the nip width of a pair of rollers in said fixing apparatus is not less than 0.2 times the radius of the elastic material roller.

4. The method according to claim 1, 2, or 3, wherein the rubber hardness of at least one of the rollers is not more than 90 degrees according to JIS A-type hardness.

5. The method according to any one of claims 1 to 4, wherein the thermally dissociating encapsulated toner contains a shell material whose main component is constituted by a resin containing at least one linkage selected from the group consisting of thermally dissociating urethane linkage, thiol urethane linkage and s-thiourethane linkage.

6. The method according to claim 5, wherein the thermally dissociating urethane resin contained as the main component of the shell material is those in which at least 30% of all of the linkages formed from the isocyanate and/or isothiocyanate groups is a linkage derived from reacting phenolic hydroxyl and/or thiol groups with the isocyanate and/or isothiocyanate groups.

7. The method according to any one of claims 1 to 6, wherein the softening point of said thermally dissociating encapsulated toner is 80 °C to 150 °C.

8. A method of forming fixed images comprising:
charging a photoconductor;
exposing said photoconductor to light;
applying an encapsulated toner whose shell is made of amorphous polyester to an electrostatic latent image formed on said photoconductor, thereby developing said electrostatic latent image to form a visible image;
transferring said formed visible image to a recording medium; and
fixing said transferred visible image onto said recording medium at a temperature of not more than 130 °C, wherein said fixing is carried out using a heat roller-type fixing apparatus comprising a heat roller having a conductive elastomer layer formed in a uniform thickness, a pressure roller and a current supplying means, and said fixing comprises the steps of passing an electric current into the conductive elastomer layer; and thermally fixing the visible image by heat generated in the conductive elastomer layer.

9. The method according to claim 8, wherein the specific resistivity of the conductive elastomer layer is not more than 100 Ω•cm, and the maximum heating temperature thereof is not more than 150 °C.

10. The method according to claim 8 or 9, wherein the nip width of a pair of rollers in said fixing apparatus is not less than 0.2 times the radius of the elastic material roller.

11. The method according to claim 8, 9, or 10, wherein the rubber hardness of at least one of the rollers is not more than 90 degrees according to JIS A-type hardness.

12. The method according to any one of claims 8 to 11, wherein said amorphous polyester has a glass transition point of 50 °C to 80 °C.

13. The method according to any one of claims 8 to 12, wherein said amorphous polyester is obtained by condensation polymerization between at least one alcohol monomer selected from the group consisting of dihydric alcohol monomers and trihydric or higher polyhydric alcohol monomers and at least one carboxylic acid monomer selected from the group consisting of dicarboxylic acid monomers and tricarboxylic or higher carboxylic acid monomers, in which at least one of the monomers is trihydric or higher alcohol or tricarboxylic or higher carboxylic acid.

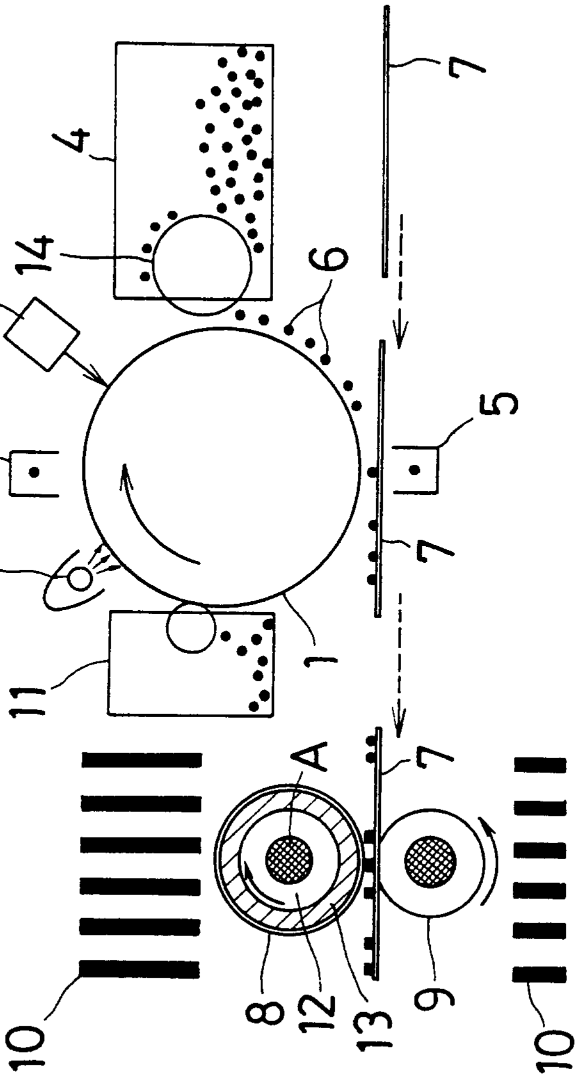


FIG. 1

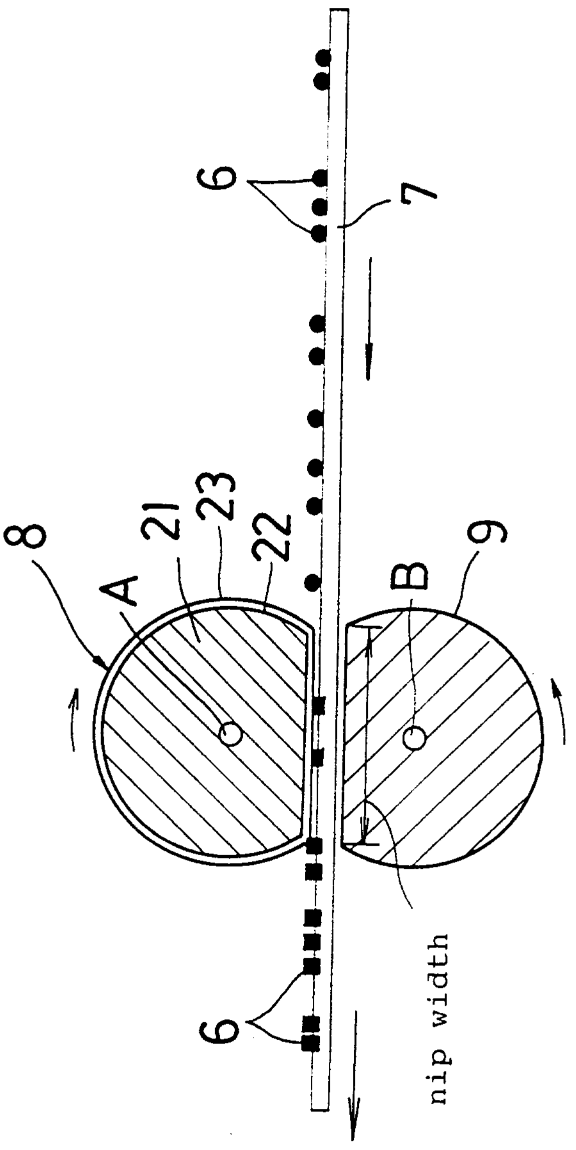


FIG. 2

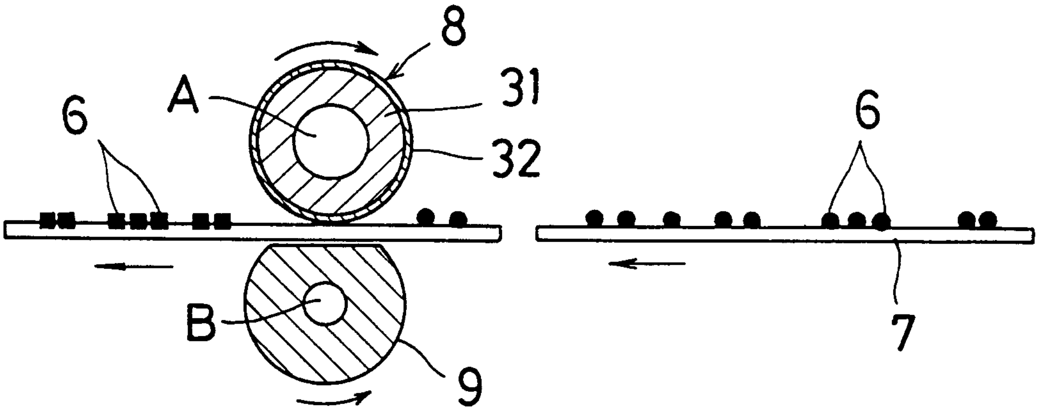


FIG. 3

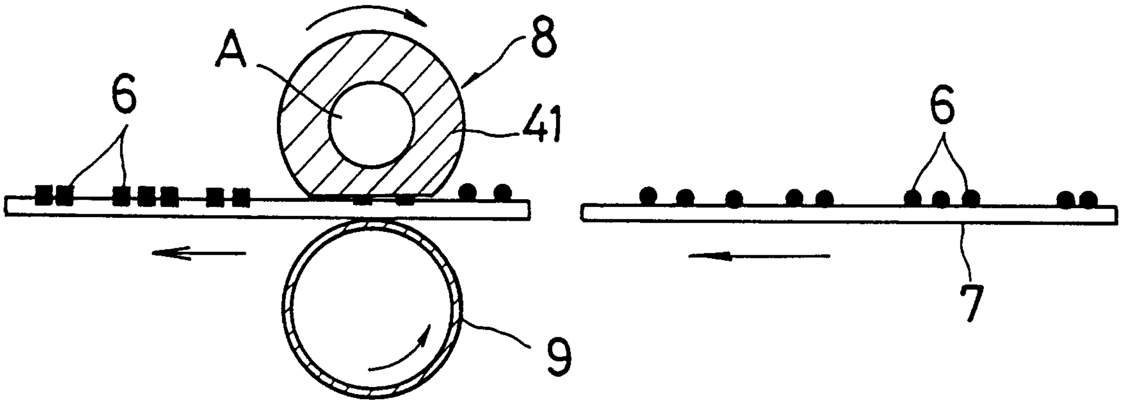


FIG. 4