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#### (54)ELECTROSTATIC LATENT IMAGE DEVELOPING TONER, IMAGE FORMING METHOD, AND **IMAGE FORMING APPARATUS**

(57)Provided is an electrostatic latent image developing toner capable of enhancing the application property and adhesion of a varnish even when a general-purpose varnish and a release agent. The electrostatic latent image developing toner of the present invention contain a binder resin, a release agent, and a saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms in the base particles. The content of the saturated hydrocarbon compounds is 1 ppm or more and 1000 ppm or less based on the total mass of the electrostatic latent image developing toner.

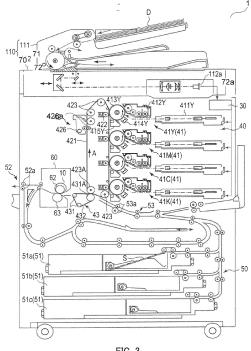


FIG. 3

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## Description

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#### **BACKGROUND OF THE INVENTION**

#### 5 1. Field of the Invention

**[0001]** The present invention relates to an electrostatic latent image developing toner, an image forming method, and an image forming apparatus.

#### 2. Description of Related Art

**[0002]** For the purpose of improving image quality and durability, an image formed with a toner may be subjected to varnish coating. On the other hand, the varnish used for varnish coating has a low affinity for wax contained in toner as a release agent. Therefore, there is a problem that the varnish coat is easily repelled at the time of coating, or the adhesion after coating is low.

**[0003]** In order to solve the above-described problem, Japanese Unexamined Patent Publication No. 2012-078565 uses a varnish in which a specific polymerizable compound is blended. It is described that this makes it possible to enhance the adhesiveness while suppressing repelling of the varnish. Japanese Unexamined Patent Publication No. 2012-078565 describes that when this varnish is used, it is preferable to use isoparaffin as a release agent for the toner.

**[0004]** In Japanese Unexamined Patent Publication No. 2011-191536, a wax having polar groups is used as a release agent for a toner. It is described that this makes it possible to enhance the adhesiveness while suppressing repelling of the varnish.

**[0005]** As described in Japanese Unexamined Patent Publication No. 2012-078565 and Japanese Unexamined Patent Publication No. 2011-191536, a method of suppressing the repelling of varnishes to enhance the application property and also enhance the adhesion of varnishes has been studied. However, according to the findings of the present inventors, in these methods, one or both of the application property and the adhesion of the varnish have not been sufficiently enhanced.

**[0006]** Furthermore, Japanese Unexamined Patent Publication No. 2012-078565 is premised on the use of specific varnishes, and when varnishes other than these are used, the application property and adhesion are not improved. In addition, Japanese Unexamined Patent Publication No. 2011-191536 is premised on the use of a specific release agent. Such a special release agent has a problem in that the offset resistance and the and releasability at the time of fixing, which are usually required for a release agent, are low.

#### **SUMMARY OF THE INVENTION**

**[0007]** The present invention has been made in view of the above problems, and an object of the present invention is to provide an electrostatic latent image developing toner capable of improving application property and adhesiveness of a varnish even when a general-purpose varnish and a release agent are used, an image forming method using the electrostatic latent image developing toner, and an image forming apparatus for forming an image using the electrostatic latent image developing toner.

**[0008]** An aspect of the present invention for achieving the above-described object relates to an electrostatic latent image developing toner according to the following [1] to [8].

- [1] An electrostatic latent image developing toner, containing:
- a saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms at a content of 1 ppm to 1000 ppm based on a total mass of the electrostatic latent image developing toner.
- [2] The electrostatic latent image developing toner according to [1], wherein the content of the saturated hydrocarbon compound is 100 ppm or more and 900 ppm or less based on the total mass of the electrostatic latent image developing toner.
- [3] The electrostatic latent image developing toner according to [1] or [2], further containing: a hydrocarbon wax having 36 or more and 76 or less carbon atoms as a release agent.
- [4] The electrostatic latent image developing toner according to any one of [1] to [3], further containing: a polyester resin as a binder resin.
- [5] The electrostatic latent image developing toner according to any one of [1] to [4], wherein the electrostatic latent image developing toner is a pulverized toner.
- [6] The electrostatic latent image developing toner according to any one of [1] to [5], further containing: strontium titanate as an external additive.
- [7] The electrostatic latent image developing toner according to [6], wherein the strontium titanate is in a form of a

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particle having a number-average primary particle diameter of 20 nm or more and 200 nm or less.

- [8] The electrostatic latent image developing toner according to [6] or [7], wherein the strontium titanate is in a form a particle having a number-average primary particle diameter of 30 nm or more and 150 nm or less.
- <sup>5</sup> **[0009]** Another aspect of the present invention for achieving the above-described object relates to the image forming methods of the following [9] to [13].
  - [9] An image forming method including:

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- attaching the electrostatic latent image developing toner according to any one of [1] to [8] to a recording medium; and
  - fixing the attached electrostatic latent image developing toner to the recording medium.
  - [10] The image forming method according to [9], wherein the fixing includes fixing the electrostatic latent image developing toner to the recording medium in two stages.
  - [11] The image forming method according to [9] or [10], wherein the fixing includes fixing the electrostatic latent image developing toner to the recording medium by causing the recording medium, to which the electrostatic latent image developing toner is attached, to pass through a planar nip portion formed by a non-rotating pad.
  - [12] The image forming method according to [11], wherein:

the nip portion is formed by the pad and a pressure roller pinching a rotating endless belt in between; and in the fixing, the endless belt is heated by a heating roller in contact with an inner peripheral surface of the endless belt.

[13] The image forming method according to any one of [9] to [12], further comprising: forming a varnish coat by applying a varnish to a surface of a toner image formed by fixing of the electrostatic latent image developing toner.

**[0010]** Another aspect of the present invention for achieving the above-described object relates to the image forming apparatus of the following [14].

An image forming apparatus, including:

an attacher that attaches the electrostatic latent image developing toner according to any one of claims 1 to 8 to a recording medium; and

a fixer that fix the attached electrostatic latent image developing toner to the recording medium.

## **BRIEF DESCRIPTION OF DRAWING**

- **[0011]** The advantageous features provided by one or more embodiments of the invention will become more fully understood from the detailed description given hereinbelow and the appended drawings which are given by way of illustration only, and thus are not intended as a definition of the limits of the present invention:
  - Fig. 1 is a schematic view showing an example of a surface treatment apparatus for performing a surface treatment with hot air;
- Fig. 2 is a schematic diagram illustrating an example of another surface treatment apparatus for performing surface treatment with hot air;
  - Fig. 3 is a schematic configuration diagram illustrating an example of an image forming apparatus; and
  - Fig. 4 is a schematic diagram illustrating a schematic configuration of a fixing device that forms a planar fixing nip with a non-rotating pressure pad.

### **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

- **[0012]** Hereinafter, one or more embodiments of the present invention will be described with reference to the drawings. However, the scope of the invention is not limited to the disclosed embodiments.
- 1. Electrostatic Latent Image Developing Toner
- [0013] One embodiment of the present invention relates to an electrostatic latent image developing toner for developing

an electrostatic charge image (electrostatic latent image) formed on an image bearing member such as a photoreceptor. Hereinafter, the electrostatic latent image developing toner is also referred to simply as "toner". The toner may be a one-component developer or a two-component developer containing toner base particles and carrier particles.

**[0014]** The toner contains, in toner base particles, a saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms (hereinafter, also referred to simply as "C16-35 saturated compound"). The content of the C16-35 saturated compound is 1 ppm or more and 1000 ppm or less based on the total mass of the toner. When the toner includes an external additive, the total mass is the total mass of the toner including the external additive. Note that the toner may contain an external additive.

**[0015]** On the surface of the image formed with the toner, a binder resin, a release agent precipitated during fixing, or other toner components are sparsely scattered. Due to the difference in these components, the image surface is in a state where portions having different surface energies are scattered. Due to this difference in surface energy between image parts, the varnish applied to the image surface does not tend to spread uniformly. Therefore, it is considered that the repelling of the varnish occurs.

**[0016]** Since the C16-35 saturated compound contained in the toner has a relatively small molecular weight, it is considered to be finely and uniformly dispersed in the toner base particles. Then, the C16-35 saturated compound finely and uniformly dispersed is precipitated little by little on the surfaces of the toner base particles at the time of fixing of the toner. Then, the compound is considered to uniformly coat the surface. In addition, since the C16-35 saturated compound has a small molecular weight, the viscosity at the time of melting is low, and the saturated compound is likely to be oriented and precipitated on the front side of the image. As a result, the surfaces of the images formed by fixing the toner are uniformly coated with the C16-35 saturated compound and the distribution of the surface energy is uniformized. Therefore, when an image is formed using the above-described toner, the varnish is likely to uniformly wet and spread over the surface of the image. Then, it is considered that the repelling of the varnish is less likely to occur, and the application property of the varnish becomes satisfactory.

**[0017]** On the other hand, the C16-35 saturated compound does not have a very high affinity for varnishes. Therefore, it is considered that when the amount of the C16-35 saturated compound in the toner is excessive and the image surfaces are densely covered with the C16-35 saturated compound, the varnish adhesion decreases.

**[0018]** As described above, there is a trade-off between the improvement of the application property of the varnish by the C16-35 saturated compound and the adhesion of the varnish. In order to satisfy both requirements, the content of the C16-35 saturated compound is 1 ppm or more and 1000 ppm or less based on the total mass of the toner.

[0019] Hereinafter, the toner of the present invention based on the above finding will be described in more detail.

## 1-1. Toner Base Particles

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[0020] The toner base particles include a C16-35 saturated compound.

[0021] The toner base particles preferably have a volume-based average particle diameter of 3.0  $\mu$ m or more and 10.0  $\mu$ m or less. The average particle diameter is more preferably 4.0  $\mu$ m or more and 8.0  $\mu$ m or less. The average particle diameter is more preferably 4.5  $\mu$ m or more and 7.0  $\mu$ m or less. When the average particle diameter is 4.0  $\mu$ m or more and 8.0  $\mu$ m or less, the state of migration of the C16-35 saturated compound to the surfaces of the toner base particles during fixing can be controlled more appropriately. As the particle diameter is increased, the separability of the toner can be enhanced. On the other hand, as the particle diameter becomes smaller, the C16-35 compound is more likely to ooze out, so that the varnish application property can be enhanced.

[0022] The volume-based average particle diameter of the toner base particles can be measured using a particle diameter distribution analyzer (Coulter Multisizer 3, manufactured by Beckman Coulter, Inc). The measurement device is connected to a computer system on which data-processing software Software V3.51 is mounted. To be specific, the sample of 0.02 g (toner base particles) is added to and mixed with 20 mL of the surfactant solution. This solution is, for example, a surfactant solution obtained by diluting a neutral detergent containing a surfactant component with pure water by 10 times for the purpose of dispersing the toner base particles. Ultrasonic dispersion treatment is performed for 1 minute to prepare a dispersion of toner base particles. This dispersion liquid is poured with a pipette into the beaker containing the electrolytic solution in the sample stand, until the concentration indicated on the measuring device becomes 8%. The electrolytic solution is ISOTONII manufactured by Beckman Coulter, Inc. By setting the concentration in this range, a reproducible measurement value can be obtained. Next, in the measurement device, the number of counted measurement particles is set to 25000, and the aperture diameter is set to 100  $\mu$ m. The frequency value is calculated by dividing the measurement range of 2 to 60  $\mu$ m into 256 parts. Based on this, the volume-based average particle diameter is calculated.

#### 1-1-1. C16-35 Saturated Compound

[0023] The C16-35 saturated compound enhances the application properties of the varnish by the action described

above. The C16-35 saturated compound has an effect of improving the application properties of the varnish as described above. On the other hand, the C16-35 saturated compound also has an effect of enhancing the releasability of the toner from a fixing member or the like to a predetermined extent. Therefore, the C16-35 saturated compound may be contained in the toner base particles as a release agent.

**[0024]** The content of the C16-35 saturated compound is 1 ppm or more and 1000 ppm or less based on the total mass of the toner. The content is preferably 50 ppm or more and 950 ppm or less. The content is more preferably 100 ppm or more and 900 ppm or less. The total mass of the toner is a mass including the toner base particles and the external additive. Thus, both the application property and adhesion of the varnish are achieved.

**[0025]** The content of the C16-35 saturated compound is measured by separating the C16-35 saturated compound from the toner using a solvent in which the saturated compound can dissolve. The hydrocarbons having these carbon numbers are qualified by gas chromatography-mass spectrometry (GC-MC). The amount of these hydrocarbons is quantified using a flame ionization detector as a detector for gas chromatography (GC-FID). Note that the extract extracted from the toner may also contain unsaturated hydrocarbons. Therefore, a polar group is added to the unsaturated bond after the extraction. Then, the separation of only of the saturated hydrocarbons is possible by column separation utilizing a polarity difference.

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**[0026]** At this time, a plurality of internal standard substances may be added to (dissolved in) the solvent to perform quantification or determine whether or not the pretreatment have been appropriately performed. Note that the concentration of the internal standard substance to be added may be set according to the amount of the C16-35 saturated compound (the estimated amount obtained by the preliminary measurement or the like).

**[0027]** The internal standard substance is preferably a saturated hydrocarbon compound which is not usually contained in the toner. For example, when N-undecane or N-tridecane is used, disappearance of the saturated hydrocarbon compound due to volatilization during the pretreatment is easily detected. In addition, it is easy to use as a guide for the elution time of a target saturated hydrocarbon compound at the time of solid-phase extraction or analysis by GC-FID. Furthermore, since the elution time of bicyclohexyl is less likely to overlap with that of the C16-35 saturated compound, the detection accuracy is likely to be improved.

**[0028]** The extraction from the toner can be performed by a conventionally known method. For example, a solid-liquid extraction method, a method in which the toner is dissolved or swollen and then separated by centrifugation, a Soxhlet extraction method, a high-speed solvent extraction method, or the like may be employed. The extraction method may be selected from the above methods in accordance with the predicted number of carbon atoms of the C16-35 saturated compound and the types of compounds acting as impurities in the binder resin and the like.

**[0029]** Solvents used for extraction are not particularly limited, but N-hexane, in which a C16-35 saturated compound is highly soluble is preferable. At this time, depending on the type of the binder resin and the like, a polar solvent such as dichloromethane and ethanol may be used in combination in order to swell the binder resin.

**[0030]** The method for introducing a polar group into the unsaturated hydrocarbon contained in the extract is also not particularly limited. Examples of the method include epoxidation with metachloroperbenzoic acid (mCPBA), addition of hydrogen halide, addition of water or alcohol with an acid catalyst, and derivation to alcohol by oxidation after hydroboration. Among these, the epoxidation reaction with mCPBA is preferred because of its high reactivity and reaction selectivity. At this time, by <sup>1</sup>H-NMR measurement, it is possible to confirm that the reaction has proceeded sufficiently, for example, by confirming the disappearance of the peak of the double bond. When sufficient detection accuracy can be secured depending on the type of the saturated hydrocarbon or the type of the unsaturated hydrocarbon, the addition of the polar group may be omitted.

**[0031]** The separation utilizing a polarity difference can be performed by a known method such as a method by solid-phase extraction or a method by online or offline GC. When a large amount of impurities is expected to be contained, separation is preferably performed by solid-phase extraction.

**[0032]** As the solvent used in the separation by solid-phase extraction, N-hexane is preferably used in both the conditioning and the extraction of saturated hydrocarbons. Also at this time, a polar solvent may be used in combination according to the type of expected impurities. After the fraction containing the C16-35 saturated compound is collected, the polarity of the eluent is increased to collect a fraction. Then, it is preferable to confirm that a saturated hydrocarbon component is not contained by qualitative analysis by GC/MS or the like.

**[0033]** As the solid phase for solid-phase extraction, a highly polar solid phase used for separation of a normal phase system that uses a polar interaction can be used. Examples of the solid phase include silica gel, silica gel activated with a polar substance such as anhydrous sodium sulfate and silver nitrate. Examples of the solid phase also include diols, cyanopropyl, magnesium silicate and the like. Of these, silica activated with silver nitrate is preferred. In order to specifically retain a long-chain N-alkane, alumina is preferably not used.

**[0034]** The fraction containing a saturated hydrocarbon extracted by the solid-phase extraction is preferably concentrated or diluted to have a concentration appropriate for qualitative and quantitative determination by gas chromatography. The concentration is performed by concentration under reduced pressure with an evaporator, concentration with a nitrogen stream, or the like. The concentration conditions at this time may be conditions under which disappearance of

the internal standard substance due to concentration of the low boiling point component does not occur.

**[0035]** The fraction after solid-phase extraction is subjected to, for example, GC-FID under the following conditions, thereby quantifying the C16-35 saturated compound.

5 (GC condition)

#### [0036]

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Device used: Shimadzu GC-2010 Plus

Injection amount: 1 µL, saturated hydrocarbon concentration 500 to 1000mg/l

Guard column: Restek MXT Siltek (10m  $\times$  0. 53 mm id) Column: Restek MTX-1 (15 m  $\times$  0. 25 mm id)  $\times$  0. 1  $\mu$ m df)

Carrier gas: Helium

**[0037]** At this time, the elution time of n-alkanes (number of carbon atoms: 10, 16, 24, 35 and 50) is measured in advance under the same conditions. In addition, only N-hexane is injected into the device in advance to prepare a blank chromatogram.

**[0038]** A blank chromatogram obtained by measuring only from the solvent in advance is subtracted from the chromatogram obtained for the toner to obtain a base line. At this time, it is preferable that the base line can be created with horizontal lines at the lowest points before and after the peak derived from the saturated hydrocarbon compound. In some cases, a horizontal base line cannot be created even by subtraction of the blank chromatogram due to column bleeding or the like. At this time, from the elution time of the compound having 10 carbon atoms to the elution time of the compound having 50 carbon atoms, a base line is set with a horizontal line from the lower signal intensity among the compound having 10 carbon atoms and the compound having 50 carbon atoms.

[0039] Then, perpendicular lines are drawn at positions corresponding to the elution times of 16 carbon atoms and 35 carbon atoms in the chromatogram. In the chromatogram above the base line, the area of the portion surrounded by these perpendicular lines is determined. Note that peaks that were confirmed not to be saturated hydrocarbon compounds are excluded from the calculation. From the obtained area, the masses of the C16-35 saturated compound can be determined. When an internal standard substance is used, the mass of the C16-35 saturated compound may be determined from the ratio of the obtained area to the area of the compound added as the internal standard. Next, the amount of the C16-35 saturated compound in the toner can be determined by dividing the obtained mass of the C16-35 saturated compound by the mass of the toner.

#### 1-1-2. Binder Resin

**[0040]** The binder resin binds the toner to a recording medium. The binder resin may be a thermoplastic resin or a thermosetting resin, but is preferably a thermoplastic resin.

**[0041]** Examples of the thermoplastic resin include styrene resins, vinyl resins, and polyester resins. Examples of the thermoplastic resin also include silicone resins, olefin resins, polyamide resins, epoxy resins, and the like. Examples of the vinyl resin includes acrylic resins and styrene-acrylic resins.

**[0042]** The binder resin may be an amorphous resin or a crystalline resin. Alternatively, a composite resin in which a crystalline resin and an amorphous resin are hybridized may be used.

**[0043]** As used herein, the term "crystalline resin" refers to a resin whose melting point is observed in measurement by differential scanning calorimetry (DSC). In addition, the amorphous resin means a resin whose melting point is not observed in measurement by DSC. In addition, in the present specification, the fact that a melting point is observed in a resin means that measurement is performed at a temperature increase rate of 10°C/min in DSC. Further, it also means that a peak having a half width of 15°C or less is observed.

[0044] Examples of the binder resin include styrene-based polymers, polyvinyl chloride, phenol resins, vinyl resins such as (meth) acrylic resins, polyvinyl acetate, silicone resins, and polyester resins. Polyurethane resins, polyamide resins, furan resins, epoxy resins, xylene resins, and polyvinyl butyral are also included. Also included are terpene resins, coumarone-indene resins, natural resins, modified natural resins (such as natural modified phenolic resins and natural resin-modified maleic acid resins). Examples of the binder resin also include other petroleum-based resins. The styrene-based polymer includes a styrene homopolymer and a homopolymer of a styrene substituent such as polyp-chlorostyrene and polyvinyltoluene. Styrene-p-chlorostyrene copolymers, styrene-vinyltoluene copolymers, and styrene-vinylnaphthalene copolymers are also included. Also included are styrene-based copolymers such as styrenebutadiene copolymers and styrene-isoprene copolymers. Styrene-(meth) acrylate copolymers, styrene- $\alpha$ -chloro (meth) acrylic acid methyl copolymers and styrene-(meth) acrylonitrile copolymers are also included. Styrene-vinyl methyl ether copolymers, styrene-vinyl ethyl ether copolymers, styrene-vinyl methyl ketone copolymers.

acrylonitrile-indene copolymers, and the like. Among these, vinyl resins and polyester resins are preferable, and polyester resins are more preferable. These preferable resins have polarities close to that of the varnish and easily improve the adhesion of the varnish.

[0045] Note that in the present specification, (meth) acrylic means acrylic or methacrylic. (Meth) acrylonitrile means acrylonitrile or methacrylonitrile. (Meth) acrylate means acrylate and methacrylate.

**[0046]** The binder resin preferably includes a crystalline polyester. This makes it difficult to make the C16-35 saturated compound compatible with the binder resin, and makes it easy to precipitate the C16-35 saturated compound at the time of fixing.

**[0047]** The crystalline polyester is usually obtained by subjecting a polyvalent carboxylic acid and a polyhydric alcohol to a dehydration condensation reaction by a known method.

**[0048]** The polyvalent carboxylic acid may be a carboxylic acid having a valency of 2 or more, and may be a carboxylic acid having a valency of 3 or more, such as trimellitic acid or pyromellitic acid. Among these, dicarboxylic acids are preferable from the viewpoint of increasing the crystallinity of the crystalline polyester. Examples of the dicarboxylic acid include oxalic acid, malonic acid, succinic acid, and glutaric acid. Also included are adipic, pimelic, suberic, azelaic, sebacic, 1,9-nonanedicarboxylic, 1,10-decanedicarboxylic acids. 1,11-undecanedicarboxylic acid, 1,12-dodecanedicarboxylic acid (dodecanedioic acid), 1,13-tridecanedicarboxylic acid, and 1,14-tetradecanedicarboxylic acid are also included. Also included are aliphatic carboxylic acids such as 1,16-hexadecanedicarboxylic acid and 1,18-octadecanedicarboxylic acid. Terephthalic, isophthalic, orthophthalic, t-butylisophthalic, and 2,6-naphthalenedicarboxylic acids are included. Aromatic dicarboxylic acids such as 4,4'-biphenyldicarboxylic acid and the like are also included. The crystalline polyester may contain only a constituent unit derived from one of these carboxylic acids. Alternatively, the crystalline polyester may contain constituent units derived from two or more types of carboxylic acids.

**[0049]** Of these, aliphatic carboxylic acids are preferred. This tends to increase the crystallinity of the crystalline polyester. Furthermore, it is easy to increase the affinity between the diol di(meth) acrylate that may be included in the varnish with the crystalline polyester. The aliphatic carboxylic acid preferably has a straight-chain hydrocarbon group having 6 or more and 16 or less carbon atoms. The aliphatic carboxylic acid more preferably has a linear hydrocarbon group having 10 or more and 14 or less carbon atoms. The hydrocarbon structure of the aliphatic carboxylic acid may be partially branched.

**[0050]** The polyhydric alcohol is an alcohol having a valence of 2 or more. The polyhydric alcohol may be any one of alcohols having 3 or more valences such as glycerin, pentaerythritol, trimethylolpropane, and sorbitol. Of these, dihydric alcohols are preferable from the viewpoint of increasing the crystallinity of the crystalline polyester. Examples of the divalent alcohol include aliphatic diols, diols having an unsaturated double bond, and diols having a sulfonic acid group. Examples of aliphatic diols include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, and 1,7-heptanediol. Examples of the aliphatic diol also include 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, and 1,11-undecanediol. Also included are 1,12-dodecanediol, 1,13-tridecanediol, 1,14-tetradecanediol, 1,18-octadecanediol, and 1,20-eicosanediol. Examples of the diol having an unsaturated double bond include 2-butene-1,4-diol, 3-hexene-1,6-diol and 4-octene-1,8-diol.

**[0051]** From the viewpoint of sufficiently exhibiting the above-described effect, the content of the crystalline polyester is preferably 5 parts by mass or more and 20 parts by mass or less with respect to 100 parts by mass of the total amount of the binder resin. The content is more preferably 8 parts by mass or more and 15 parts by mass or less.

**[0052]** From the viewpoint of sufficiently softening the toner base particles to enhance the low-temperature fixability of the toner, the melting point of the crystalline polyester is preferably 50°C or more and 85°C or less. The temperature is more preferably 60°C or more and 80°C or less.

**[0053]** The weight average molecular weight (Mw) of the crystalline polyester is preferably 5000 or more and 50000 or less. The crystalline polyester preferably has a number average molecular weight (Mn) of 2000 or more and 10,000 or less. When the weight average molecular weight (Mw) and the number-average molecular weight (Mn) of the crystalline polyester are within the above ranges, the low-temperature fixability becomes satisfactory.

**[0054]** The content of the binder resin is preferably 20% by mass or more and 99% by mass or less based on the total mass of the toner base particles. The content is more preferably 30 mass% or more and 95 mass% or less. The content is more preferably 40 mass% or more and 90 mass% or less. When the content of the binder resin is 20% by mass or more, the strength of an image to be formed can be further increased.

## 1-1-3. Release Agent

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**[0055]** The release agent increases releasability of the toner from a fixing member or the like. The release agent is preferably a wax.

**[0056]** Examples of the release agent as the wax include hydrocarbon waxes such as polyethylene wax, paraffin wax, microcrystalline wax, and Fischer-Tropsch wax, and dialkyl ketone waxes such as distearyl ketone. Examples of the release agent also include ester waxes such as carnauba wax, montan wax, behenic acid behenate, trimethylolpropane

tribehenate, pentaerythritol tetramyristate, pentaerythritol tetrastearate, pentaerythritol tetrabehenate, pentaerythritol diacetate dibehenate, glycerin tribehenate, 1,18-octadecanediol distearate, tristearyl trimellitate, and distearyl maleate; and amide waxes such as ethylenediamine dibehenylamide, and trimellitic acid tristearylamide. Of these, hydrocarbon waxes are preferred. This is because a hydrocarbon wax has a molecular structure similar to that of a C16-35 saturated compound, and thus the C16-35 saturated compound is easily compatible with the release agent. When the C16-35 saturated compound tends to be more finely and uniformly dispersed in the toner base particles. Furthermore, during fixing, the C16-35 saturated compound is more likely to precipitate from the toner base particles together with the wax, which tends to improve the application property of the varnish.

[0057] The release agent as the wax may be a C16-35 saturated compound, or may be a hydrocarbon wax having 36 or more and 76 or less carbon atoms different from the C16-35 saturated compound. The amount of the C16-35 saturated compound in the toner base particles is extremely small. Therefore, the toner base particles preferably contain the C16-35 saturated compound and another release agent. In addition, the toner base particles preferably contain both a C16-35 saturated compound and a hydrocarbon wax having 36 or more and 76 or less carbon atoms. Thus, both the effect of improving the application property of the varnish due to the C16-35 saturated compound and the effect of improving the releasability due to the release agent are achieved.

**[0058]** The hydrocarbon wax preferably has a melting point of 50°C or more and 95°C or less. When the melting point of the hydrocarbon wax is 50°C or higher, the hydrocarbon wax exuding from the toner particles tends to crystallize. Therefore, the releasing effect and the scratch resistance of the formed image are easily enhanced. When the melting point of the hydrocarbon wax is 95°C or lower, the hydrocarbon wax tends to exude from the toner base particles during fixing. Therefore, the releasing effect and the scratch resistance of the formed image are easily enhanced. In addition, when the melting point of the hydrocarbon wax is 95°C or less, the toner base particles are readily melted during fixing, and the low-temperature fixability of the toner is readily enhanced. From the above viewpoint, the melting point of the hydrocarbon wax (particularly, hydrocarbon wax having a carbon number of 36 or more and 76 or less) is more preferably 80°C or more and 90°C or less.

**[0059]** The content of the release agent is preferably 3% by mass or more and 20% by mass or less based on the total mass of the toner base particles. The content is more preferably 5 mass% or more and 15 mass% or less. When the content of the release agent is 3% by mass or more, the releasability of the toner from a fixing member is sufficiently enhanced. When the content of the release agent is 20% by mass or less, the toner base particles can contain a sufficient amount of the binder resin, so that the image fixability is sufficiently enhanced.

#### 1-1-4. Other Components

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[0060] The toner base particles may contain a colorant, a charge control agent, and the like.

**[0061]** The above colorantmay be a dye or a pigment. When the toner is a color toner, the toner base particles may contain a colorant such as yellow, magenta, cyan, or black. The toner base particles may contain only one colorant or a combination of two or more colorants.

**[0062]** Examples of a yellow colorant include yellow dyes such as C. I. Solvent Yellow 19, 44, 77, 79, 81, 82, 93, 98, 103, 104, 112, and 162. Yellow pigments such as C. I. Pigment Yellow 14, 17, 74, 93, 94, 138, 155, 180, and 185 are also included.

**[0063]** Examples of a magenta colorant include magenta dyes such as C.I Solvent Red 1, 49, 52, 58, 63, 111, and 122. Magenta pigments such as C. I. Pigment Red 5, 48:1, 53:1, 57:1, 122, 139, 144, 149, 166, 177, 178, and 222 are also included.

**[0064]** Examples of a cyan colorant include cyan dyes such as C.I. Solvent Blue 25, 36, 60, 70, 93, and 95. Cyan pigments such as C.I. Pigment Blue 1, 7, 15, 15:3, 60, 62, 66, and 76 are also included.

**[0065]** Examples of black colorants include carbon blacks such as channel black, furnace black, acetylene black, thermal black, and lamp black. In addition, a magnetic material including ferrite, magnesium, and the like, an iron-titanium composite oxide, and the like are also included.

**[0066]** The content of the colorant is preferably 0.5% by mass or more and 20% by mass or less and more preferably 2% by mass or more and 10% by mass or less based on the total mass of the toner base particles. Note that when the toner is a clear toner, the toner base particles preferably do not substantially contain a colorant, and the content of the colorant is preferably 0.1% by mass or less based on the total mass of the toner base particles.

[0067] The charge control agent can adjust the chargeability of the toner base particles.

**[0068]** Examples of the charge control agent include nigrosine dyes, metal salts of naphthenic acid or higher fatty acids, alkoxylated amines, quaternary ammonium salt compounds, azo metal complexes, metal salts of salicylic acid or metal complexes thereof, and the like.

**[0069]** The content of the charge control agent is preferably 0.1% by mass or more and 10% by mass or less, more preferably 0.5% by mass or more and 5% by mass or less based on the total mass of the binder resin. Note that when

an attempt is made to control the chargeability of the toner by a method such as adding an excessive amount of the charge control agent, other properties of the toner base particles may be significantly changed. On the other hand, in the present embodiment, the chargeability of the toner is adjusted by strontium titanate, and thus it is possible to adjust the chargeability of the toner to a desired degree while satisfying other required characteristics.

1-2. External Additives

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**[0070]** The toner base particles may include an external additive that is added as a post-treatment agent to the surfaces of the toner base particles in order to enhance the fluidity, the chargeability, and the cleanability of the toner.

1-2-1. Strontium Titanate

[0071] The external additive preferably includes particles of strontium titanate.

**[0072]** The strontium titanate can have any of a plurality of particle shapes such as a cubic shape, a rectangular parallelepiped shape, an irregular shape, or a shape of a cube with rounded corners, according to the manufacturing method or the composition thereof. The strontium titanate may have any of these particle shapes, but preferably has a cubic shape or a rectangular parallelepiped shape.

[0073] The shape of the strontium titanate particles can be confirmed by observation with a scanning electron microscope (SEM).

**[0074]** The strontium titanate having such a shape forms a planar exposed portion on the surface of the toner base particle. Thus, the proportion of the resin that tends to inhibit the wetting and spreading of the varnish on the surfaces of the toner base particles can be reduced, thereby improving the application property of the varnish. Similarly, the releasability of the toner from the fixing member can be enhanced by reducing the proportion of the resin in the surface of the toner base particle. In particular, when the strontium titanate has a rectangular parallelepiped shape, the area of the planar exposed portion from the surface of the toner base particle is more likely to increase, and thus the effect of improving the application property of the varnish and the releasability of the toner by the above-described action is more likely to be enhanced.

**[0075]** From the viewpoint of effectively exhibiting the above-described action, the number-average primary particle diameter of strontium titanate is preferably 20 nm or more and 200 nm or less, and more preferably 30 nm or more and 150 nm or less. From the above-described action, the larger the particle diameter of strontium titanate is, the better. However, by setting the upper limit of the particle diameter to a predetermined range, it is possible to suppress a decrease in the uniformity of the image surface due to exposed strontium titanate, and thus to suppress a decrease in the application property.

**[0076]** The number-average primary particle diameter of strontium titanate is determined by capturing image data of strontium titanate with a scanning electron microscope (SEM). Binarization processing is performed using an image processing analysis apparatus (LUZEX AP manufactured by Nireco Corporation). The average value of the Feret diameters in the horizontal direction measured for 100 particles is used as the number-average primary particle diameter.

**[0077]** The content of the strontium titanate is preferably 0.05% by mass or more and 2.0% by mass or less and more preferably 0.1% by mass or more and 1.0% by mass or less based on the total mass of the toner. When the content of the strontium titanate is 0.05% by mass or more, the effect of improving the application property of the varnish and the toner releasability due to the strontium titanate are easily obtained. When the content of the strontium titanate is 2.0 parts by mass or less, a decrease in application property due to a decrease in the uniformity of the image surface is less likely to occur.

**[0078]** Strontium titanate can be produced by a normal-pressure heating reaction method in which a titanium oxide source and a strontium oxide source are mixed, and then an alkaline aqueous solution is added while heating (warming) the mixture at normal pressure.

**[0079]** As the titanium oxide source, a mineral acid-peptized product of a hydrolysate of a titanium compound can be used. The titanium oxide source is preferably a compound obtained by peptizing metatitanic acid obtained by a sulfuric acid method and having a  $SO_3$  content of 1.0% by mass or less (preferably 0.5% by mass or less) by adjusting the pH to 0.8 or more and 1.5 or less with hydrochloric acid.

**[0080]** As the strontium oxide source, a nitrate or hydrochloride of the metal or the like may be used. For example, as the strontium oxide source, strontium nitrate, strontium chloride or like may be used.

[0081] As the aqueous alkaline solution, a caustic alkali can be used. An aqueous sodium hydroxide solution is preferred.

**[0082]** The particle diameter of the strontium titanate particles can be adjusted by the mixing ratio of the titanium oxide source and the strontium oxide source, the concentration of the titanium oxide source at the initial stage of the reaction, the temperature and the addition rate when the alkaline aqueous solution is added, and/or the like. Note that in order to prevent generation of a carbonate in the reaction process, it is preferable to prevent mixing of carbon dioxide gas at the

time of the reaction by reacting under a nitrogen gas atmosphere or the like.

[0083] The mixing ratio of the titanium dioxide source and the strontium oxide source is preferably 0.90 or more and 1.40 or less, and more preferably 1.05 or more and 1.20 or less in terms of  $SrO/TiO_2$  molar ratio. When the mixing ratio is within the above range, unreacted titanium oxide is less likely to remain. The concentration of the titanium dioxide source in the initial stage is preferably 0.05 mol/L or more and 1.3 mol/L or less, more preferably 0.08 mol/L or more and 1.0 mol/L or less, on the basis of  $TiO_2$ .

[0084] The temperature of the mixture when the alkaline aqueous solution is added is preferably 60°C or more and 100°C or less.

**[0085]** As the addition rate of the alkaline aqueous solution is lower, strontium titanate particles having a larger particle diameter are obtained, and as the addition rate is higher, strontium titanate particles having a smaller particle diameter are obtained. The addition rate of the alkaline aqueous solution is preferably 0.001 equivalent/h or more and 1.2 equivalent/h or less, and more preferably 0.002 equivalent/h or more and 1.1 equivalent/h or less with respect to the charged raw material. The addition rate of the alkaline aqueous solution can also be appropriately adjusted according to the particle diameter of the strontium titanate to be obtained.

**[0086]** The strontium titanate particles thus obtained are preferably further subjected to acid treatment. When the mixing ratio of the titanium dioxide source and the strontium oxide source is greater than 1.0 in terms of SrO/TiO<sub>2</sub> molar ratio, for example, unreacted sources of metals, other than titanium, that remain after completion of the reactions may react with carbon dioxide in the air to produce an impurity such as a metallic carbonate. In order to suppress a decrease in performance due to the impurities, an acid treatment for removing an unreacted metal source is preferably performed after the addition of the alkaline aqueous solution.

**[0087]** The acidic treatment is preferably performed using hydrochloric, nitric, acetic, or other acid at a pH2.5 or more and 7.0 or less, more preferably at a pH4 of 5 or more and 6.0 or less.

#### 1-2-2. Other External Additives

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[0088] The external additive may include particles containing, as a main component, an inorganic material other than strontium titanate. For example, silica particles, alumina particles, zirconia particles, zinc oxide particles, and chromium oxide particles are included. Also included are cerium oxide particles, antimony oxide particles, tungsten oxide particles, tin oxide particles, tellurium oxide particles, manganese oxide particles, boron oxide particles, and the like. The particles containing any of these inorganic materials as a main component may be subjected to hydrophobization treatment with a surface treating agent such as a silane coupling agent or silicone oil, if necessary. Regarding these particle diameter, number-average primary particle diameter, which is measured by the same method as those for strontium titanate, is preferably 20 nm or more and 200 nm or less, and more preferably 30 nm or more and 150 nm or less.

**[0089]** Furthermore, the external additive may contain particles containing, as a main component, an organic material such as a homopolymer of styrene, methyl methacrylate, or the like, a copolymer of these, or the like. Regarding these particle diameter, the particle diameter of the peak top measured by the same method as that for the strontium titanate is preferably 10 nm or more and 1000 nm or less.

**[0090]** The external additive may also include a lubricant, such as a metal salt of a higher fatty acid. Examples of the higher fatty acid include stearic, oleic, palmitic, linoleic, and ricinoleic acids. Examples of metals that constitute the above-mentioned metal salt include Zn, Mn, Al, Fe, Cu, Mg, and Ca.

**[0091]** The content of these external additives is preferably such that the total amount of the external additives in total with the strontium titanate is 0.05% by mass or more and 5.0% by mass or less based on the total mass of the toner base particles.

1-3. Toner Base Particle and Method for Producing Toner

**[0092]** The toner base particles can be produced in the same manner as known toners by a method such as a pulverization method, an emulsion polymerization aggregation method, an emulsion aggregation method, a suspension polymerization method, or a dissolution suspension method.

**[0093]** Of these, the pulverization method, the emulsion polymerization aggregation method, the emulsion aggregation method, and the suspension polymerization method are preferable, the pulverization method and the emulsion polymerization aggregation method are more preferable, and the pulverization method is still more preferable. The toner base particles of the pulverized toner prepared by a pulverization method are particles having an irregular shape and have a large number of minute recesses and projections randomly present in the entire particles, and therefore have a large surface area. Therefore, the C16-35 saturated compound is likely to be precipitated from the surfaces of the toner base particles produced by the pulverization method, and thus application property of the varnish and the toner releasability are more likely to be enhanced.

[0094] According to the pulverization method, the toner base particles can be obtained by pulverizing a solid resin

composition obtained by melting and kneading a mixture of binder resin, a release agent, a C16-35 saturated compound, and other materials until a predetermined particle diameter is obtained.

**[0095]** To be more specific, in the pulverization method, first, predetermined amounts of materials constituting the toner base particles (binder resin, release agent, C16-35 saturated compound, and other materials to be optionally added) are weighed, blended, and mixed. The mixing can be performed by a mixing apparatus such as a double-cone mixer, a V-type mixer, a drum-type mixer, a super mixer, a Henschel mixer, a Nauta mixer, or a mechanohybrid.

[0096] Next, the mixed materials are melted and kneaded. For the melt-kneading, a batch kneader such as a pressure kneader or a Banbury mixer, or a continuous kneader can be used. In continuous production, a single-screw extruder or a twin-screw extruder is preferably used. Examples of the twin-screw extruder include a KTK twin-screw extruder (manufactured by Kobe Steel, Ltd) and a TEM twin-screw extruder (manufactured by Toshiba Machine Co., Ltd). Other examples include a PCM kneader (manufactured by Ikegai Corporation), a twin-screw extruder (manufactured by K. C. K), a co-kneader (manufactured by Buss AG), and a Kneadex (manufactured by Nippon Coke & Engineering Co., Ltd). The temperature of the melt-kneading is preferably about 100 to 200°C. The resin composition obtained by melt-kneading is rolled with a two roll mill or the like, and rapidly cooled with water or the like to form a solid.

**[0097]** Next, the solid resin composition obtained by melt-kneading and cooling is pulverized to a desired particle diameter. The pulverization is performed by, for example, coarsely pulverizing with a pulverizer such as a crusher, a hammer mill, and a feather mill. Thereafter, the mixture may be finely pulverized with a pulverizer such as Kryptron System (manufactured by Kawasaki Heavy Industries, Ltd), Super Rotor (manufactured by Nisshin Engineering Inc), or Turbo Mill (manufactured by Freund -Turbo Corporation), or an air-jet pulverizer.

**[0098]** Thereafter, if necessary, the pulverized resin composition is classified. For the classification, an inertial classification system Elbow Jet (manufactured by Nittetsu Mining Co., Ltd) or a centrifugal classification system Turboplex (manufactured by Hosokawa Micron Corporation) is used. Alternatively, a classifier or a sifter, such as a TSP separator (manufactured by Hosokawa Micron Corporation) or Faculty (Hosokawa Micron Corporation), is used. In this way, the toner base particles can be produced by the pulverization method.

(Surface Treatment with Hot Air)

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**[0099]** The toner particles obtained by these methods, particularly the pulverization method, may be subjected to a surface treatment with hot air. By the surface treatment with hot air, the surface shape of the toner base particles can be adjusted (become spherical), and the physical properties of the surface can be adjusted. It is preferable that the hot air during the surface treatment has a temperature of about 100°C to 450°C.

**[0100]** The method of the surface treatment with hot air is not particularly limited, and the surface treatment can be performed by methods described in Japanese Unexamined Patent Publication No. S59-125743 and Japanese Unexamined Patent Publication No. 2022-96557, and the like. These publications describe a surface treatment method in which toner particles are dropped while being swirled by hot air in a heat treatment chamber, further cooled by cold air supplied to the inside of the heat treatment chamber, and then collected.

**[0101]** Fig. 1 is a schematic view showing an example of a surface treatment apparatus 100 for performing surface treatment with hot air. The toner particles supplied from a hopper 110 are mixed with the compressed air supplied from a nozzle 130 in a mixing chamber 120, and are ejected from a diffuser 150 into a heat treatment chamber 160 as a dispersion airflow 140. The hot air that has been supplied to a hot-air swirling chamber 170 and turned into a swirling flow is blown into the ejected dispersion airflow 140, thereby swirling the toner particles in the dispersion airflow 140 with the hot air. The toner particles subjected to the heat treatment by the swirling are cooled by cooling wind introduced along the side wall of the heat treatment chamber 160 from a cold air supplier 180, ejected from an ejector 190, and collected.

**[0102]** Fig. 2 is a schematic view showing an example of another surface treatment apparatus 200 for performing surface treatment with hot air. The toner particles mixed with the compressed gas are introduced into an introduction pipe 220 installed on the central axis of a heat treatment chamber 210. The toner base particles that have been introduced and passed through the introduction tube 220 are uniformly dispersed by a conical protrusion-shaped member 222 provided at the center of the introduction tube 220. Then, the powder particles pass through a radially extending supply tube 230, are guided to a powder particle supply port 240, and are guided from the powder particle supply port 240 to the heat treatment chamber 210. The hot air supplied from a hot-air supplying means 250 and introduced into the heat treatment chamber 210 from a hot-air introducing section 260 is swirled by a swirling member 270 including a plurality of blades and introduced into the heat treatment chamber 210 while swirling spirally. At this time, a substantially conical distribution member 280 uniformly distributes the swirled hot air in each direction. The toner base particles supplied to the heat treatment chamber 210 fall while swirling inside the heat treatment chamber 210 by spirally swirling hot air. In addition, cold air is introduced into the treatment chamber 6 from a plurality of cold air introducing sections 290, and the toner base particles falling while swirling are cooled by the cold air introduced from the cold air introducing sections 290.

(Addition of External Additive)

**[0103]** The toner base particles obtained through the above steps may be used as they are, or may be subjected to external addition treatment with an external additive, if necessary. The external addition treatment with an external additive can be performed by blending predetermined amounts of the toner base particles and the external additive, and stirring and mixing them with a mixing device. For example, a double-cone mixer, a V-type mixer, a drum mixer, a super mixer, a Henschel mixer, a Nauta mixer, Mechano Hybrid (manufactured by Nippon Coke & Engineering Co., Ltd), or Nobilta (manufactured by Hosokawa Micron Corporation) are used.

#### 1-4. Carrier

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**[0104]** The carrier is mixed with the toner base particles described above to form a two component magnetic toner. The carrier may be any known magnetic particle that can be contained in toner.

**[0105]** Examples of the magnetic particles include particles containing a magnetic material such as iron, steel, nickel, cobalt, ferrite, and ferromagnetic, and alloys thereof with aluminum, lead, and the like. The carrier may be a coated carrier in which the surface of particles composed of the magnetic material is coated with a resin or the like, or may be a resin-dispersed carrier in which the magnetic material is dispersed in a binder resin. Examples of the coating resin include olefin resins, styrene resins, styrene-acrylic resins, silicone resins, polyester resins, and fluororesins. Examples of the binder resin include acrylic resins, styrene-acrylic resins, polyester resins, fluororesins, and phenol resins.

[0106] The carrier has an average particle diameter of preferably 20  $\mu$ m or more and 100  $\mu$ m or less, more preferably 25  $\mu$ m or more and 80  $\mu$ m or less in terms of volume-based average particle diameter. The average particle diameter of the carrier can be measured by HELOS manufactured by SYMPATEC Co., which is a laser diffraction type particle diameter distribution measuring apparatus equipped with a wet type dispersing machine.

**[0107]** The content of the carrier is preferably 2% by mass or more and 10% by mass or less based on the total mass of the toner base particles and the carrier.

#### 2. Image Forming Method and Image Forming Apparatus

**[0108]** Another embodiment of the present invention relates to an image forming apparatus including: a toner image forming section that develops an electrostatic latent image with a toner to form a toner image.; and a fixing device that fixes the toner image onto a recording medium by transferring the toner image onto the recording medium. The present invention also relates to an image forming method using an image forming layer. In the present embodiment, the fixing device fixes the above-described toner onto the recording medium.

**[0109]** The image forming apparatus may be a four-cycle system image forming apparatus including four types of color developing devices of yellow, magenta, cyan, and black, and one electrophotographic photoreceptor. The image forming apparatus may be a tandem-system image forming apparatus including four types of color developing devices of yellow, magenta, cyan, and black, and four electrophotographic photoreceptors provided for the respective colors.

**[0110]** Fig. 3 is a schematic configurational view illustrating an example of the image forming apparatus 1 according to the present embodiment. The image forming apparatus 1 illustrated in Fig. 3 includes an image processor 30, an image former 40, a sheet conveyor 50, a fixing device 60, and an image reader 70.

**[0111]** The image former 40 includes image forming units 41Y, 41M, 41C, and 41K that form images with toners of respective colors of Y (yellow), M (magenta), C (cyan), and K (black). These components have the same configuration except for the toner stored therein, and therefore, hereinafter, the symbol representing the color may be omitted. The image former 40 further includes an intermediate transfer unit 42 and a secondary transfer unit 43. These correspond to a transfer device.

**[0112]** The image forming unit 41 includes an exposure device 411, a developing device 412, an electrophotographic photoreceptor (image bearing member) 413, a charging device 414, and a drum cleaning device 415. The charging device 414 is, for example, a corona charger. The charging device 414 may be a contact charging device that charges the electrophotographic photoreceptor 413 by bringing a contact charging member such as a charging roller, a charging brush, or a charging blade into contact with the electrophotographic photoreceptor 413. The exposure device 411 includes, for example, a semiconductor laser as a light source, and a light deflection device (polygon motor) that irradiates the electrophotographic photoreceptor 413 with laser light corresponding to an image to be formed. The electrophotographic photoreceptor 413 is a negatively chargeable organic photosensitive member having photoconductivity. The electrophotographic photoreceptor 413 is charged by the charging device 414.

**[0113]** The developing device 412 is a developing device of a two component developing method. The developing device 412 includes, for example, a developing container that stores a two-component developer, a developing roller (magnetic roller) that is rotatably disposed at an opening portion of the developing container, and a partition wall that partitions the inside of the developing container such that the two-component developer can communicate with each

other. The developing device further includes a conveyance roller for conveying the two-component developer on an opening side in the developing container toward the developing roller, and a stirring roller for stirring the two-component developer in the developing container. The developing container stores, for example, a two-component developer.

**[0114]** The intermediate transfer unit 42 includes an intermediate transfer belt (intermediate transfer member) 421 and a primary transfer roller 422 that brings the intermediate transfer belt 421 into pressure-contact with the electrophotographic photoreceptor 413. The intermediate transfer unit 42 further includes a plurality of support rollers 423 including backup rollers 423A, and a belt cleaning device 426. The intermediate transfer belt 421 is stretched in a loop around the plurality of support rollers 423. The rotation of at least one drive roller of the plurality of support rollers 423 causes the intermediate transfer belt 421 to run in the arrow direction A at a constant speed.

**[0115]** The belt cleaning device 426 includes an elastic member 426a. The elastic member 426a comes into contact with the intermediate transfer belt 421 after the secondary transfer to remove the attached substance on the surface of the intermediate transfer belt 421. The elastic member 426a is formed of an elastic body, and includes a cleaning blade, a brush, or the like.

**[0116]** The secondary transfer unit 43 includes an endless secondary transfer belt 432 and a plurality of support rollers 431 including a secondary transfer roller 431A. The secondary transfer belt 432 is stretched in a loop around the secondary transfer roller 431A and the support rollers 431.

**[0117]** The fixing device 60 includes, for example, a fixing roller 62 and an endless heating belt 10 covering an outer circumferential surface of the fixing roller 62 and for heating and melting the toner constituting the toner image on a sheet S. The fixing device further includes a pressure roller 63 that presses the sheet S toward the fixing roller 62 and the heating belt 10. The sheet S corresponds to a recording medium.

**[0118]** The image forming apparatus 1 further includes an image reader 70, an image processor 30, and a sheet conveyor 50. The image reader 70 includes a sheet feed device 71 and a scanner 72. The sheet conveyor 50 includes sheet feeders 51, a sheet ejector 52, and a conveyance path 53. Sheets S, identified on the basis of a basis weight, a size, and the like, are stored according to preset paper types (a standard sheet or a special sheet) in the three respective sheet feed tray units 51a to 51c constituting the sheet feeder 51. The conveyance path 53 includes a plurality of conveyance roller pairs such as registration roller pairs 53a.

**[0119]** Formation of an image by the image forming apparatus 1 will be described.

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**[0120]** The scanner 72 optically scans and reads a document D on the exposure glass. Reflected light from the document D is read by a CCD sensor 72a and becomes input image data. The input image data undergoes predetermined image processing in the image processor 30 and is sent to the exposure device 411.

**[0121]** The electrophotographic photoreceptor 413 rotates at a constant circumferential speed. The charging device 414 uniformly and negatively charges the surface of the electrophotographic photoreceptor 413. In the exposure device 411, the polygon mirror of the polygon motor rotates at a high speed, and the laser light corresponding to the input image data of each color component spreads along the axial direction of the electrophotographic photoreceptor 413 and the outer circumferential surface of the electrophotographic photoreceptor 413 is irradiated with the light along the axial direction. Thus, an electrostatic latent image is formed on the surface of the electrophotographic photoreceptor 413.

**[0122]** In the developing device 412, the toner base particles are charged by stirring and conveying the two-component developer in the developing container, and the two-component developer is conveyed to the developing roller to form a magnetic brush on the surface of the developing roller. The charged toner base particles are electrostatically attached to a portion of the electrostatic latent image on the electrophotographic photoreceptor 413 from the magnetic brush. Thus, the electrostatic latent image on the surface of the electrophotographic photoreceptor 413 is visualized, and a toner image corresponding to the electrostatic latent image is formed on the surface of the electrophotographic photoreceptor 413. Note that the term "toner image" refers to a state in which toner is aggregated into an image shape.

**[0123]** The toner image on the surface of the electrophotographic photoreceptor 413 is transferred to the intermediate transfer belt 421 by the intermediate transfer unit 42. The transfer residual toner remaining on the surface of the electrophotographic photoreceptor 413 after transfer is removed by the drum cleaning device 415 including a drum cleaning blade that comes in sliding contact with the surface of the electrophotographic photoreceptor 413.

[0124] The intermediate transfer belt 421 is pressed against the electrophotographic photoreceptor 413 by the primary transfer roller 422, so that a primary transfer nip is formed for each electrophotographic photoreceptor by the electrophotographic photoreceptor 413 and the intermediate transfer belt 421. At the primary transfer nips, the toner images in a corresponding colors are sequentially transferred onto the intermediate transfer belt 421 in a superimposed manner. [0125] On the other hand, the secondary transfer roller 431A is pressed against the backup roller 423A via the intermediate transfer belt 421 and the secondary transfer belt 432. Thus, a secondary transfer nip is formed by the intermediate transfer belt 421 and the secondary transfer belt 432. The sheet S passes through the secondary transfer nip. The sheet S is conveyed to the secondary transfer nip (attacher) by the sheet conveyor 50. The correction of the inclination of the sheet S and the adjustment of the conveyance timing are performed by a registration roller portion in which a registration roller pair 53a is arranged.

[0126] When the sheet S is conveyed to the secondary transfer nip, a transfer bias is applied to the secondary transfer

roller 431A. By the application of the transfer bias, the toner image carried on the intermediate transfer belt 421 is transferred onto the sheet S (a step of attaching the electrostatic latent image developing toner to the recording medium). The sheet S on which the toner image has been transferred is conveyed toward the fixing device 60 by the secondary transfer belt 432.

[0127] Attached substances, such as transfer residual toner remaining on the surface of the intermediate transfer belt 421 after the secondary transfer, are removed by the belt cleaning device 426 having a cleaning blade to be brought into sliding contact with the surface of the intermediate transfer belt 421. At this time, since the above-described intermediate transfer member is used as the intermediate transfer belt, the dynamic frictional force can be reduced with time.

[0128] The fixing device 60 forms a fixing nip by sandwiching the heating belt 10 between the rotating fixing roller 62 and the pressure roller 63, and heats and pressurizes the conveyed sheet S at the fixing nip portion. Thus, the toner image is fixed to the sheet S (a step of fixing the electrostatic latent image developing toners to the recording medium). The sheet S carrying the fixed toner image is ejected to the outside of the apparatus by the sheet ejector 52 having a sheet ejection roller 52a.

**[0129]** In the present embodiment, the fixing of the toner image onto the sheet S may be performed in two stages. That is, the image forming apparatus 1 may include two different fixing devices 60, and fixing may be continuously performed by the two fixing devices 60. That is, before the toner image heated by the fixing device 60 in the first stage is completely cooled, heating and pressing by the fixing device 60 in the second stage may be performed. Thus, the toner image can be heated sufficiently and for a longer time to precipitate the C16-35 saturated compound from the toner base particles sufficiently, thereby further enhancing the application property of the varnish and releasability from the fixing device 60 in the second stage.

**[0130]** Note that the second stage fixing may be performed immediately after the fixing in the first stage, or for example, after the sheet S is reversed and another image is attached and fixed to the back surface, the sheet S may be reversed again and the fixing in the second stage may be performed on the front surface. At this time, it is preferable that the sheet S is further reversed and the fixing in the second stage is also performed on the back surface.

**[0131]** The third and subsequent stages of fixing may be performed.

**[0132]** Further, the fixing device may be configured to form a fixing nip by a non-rotating pressure pad.

**[0133]** Fig. 4 is a schematic diagram illustrating a schematic configuration of the fixing device 600 that forms a planar fixing nip by a non-rotating pressure pad. In the fixing device 600, a heating belt 650 which is a rotating endless belt stretched around a heating roller 630 and a steer roller 640 is sandwiched between a non-rotating pressure pad 610 and a pressure roller 620. Thus, the heating roller 630 contacts the inner circumferential surface of the heating belt 650. Thus, a fixing nip is formed, and a conveyed sheet S is heated and pressurized at the fixing nip portion. The pressure pad 610 is pressed against the heating belt by a pressing member 660 made of stainless steel, thereby pressing the heating belt 650 against the pressure pad 610 to form a fixing nip.

**[0134]** The pressure pad 610 is a substantially rectangular parallelepiped pad member formed of a liquid crystal polymer (LCP) or the like, and presses the heating belt 650 with one surface of the rectangular parallelepiped to form a planar fixing nip. A lubricating sheet (not shown) is interposed between the pressure pad 610 and the heating belt 650 to allow the heating belt 650 to rotate smoothly. The lubricating sheet may be, for example, a polyimide sheet coated with polytetrafluoroethylene (PTFE) having a thickness of 100  $\mu$ m. Further, the polyimide sheet may be formed with protrusions of 100  $\mu$ m at 1 mm intervals to reduce contact areas with the heating belt 650, thereby reducing sliding resistance. Furthermore, a lubricant such as silicone oil may be applied to a surface of the heating belt 650 that comes into contact with the lubricating sheet to enable the heating belt 650 to rotate smoothly.

**[0135]** By forming the planar nip portion with such a configuration, the fixing time can be further increased. Thus, the toner image can be heated sufficiently and for a longer time to precipitate the C16-35 saturated compound from the toner base particles sufficiently, thereby further enhancing the application property of the varnish and releasability from the fixing device 60 in the second stage.

**[0136]** When fixing is performed in two stages as described above, both of the two fixing devices may be fixing devices each having a pressure pad, or one of the two fixing devices (the first stage fixing device or the second stage fixing device) may be a fixing device having a pressure pad. As a matter of course, both of the two fixing devices may be a fixing device having a rotating fixing roller.

[0137] Note that the above-described apparatus configuration and image forming method are merely exemplary modes for carrying out the present invention, and the present invention is not limited thereto.

#### 3. Varnish Coat Formation

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[0138] Varnish may be applied to the image formed by the above-described image forming method to form a varnish coat.

**[0139]** When the varnish coat is formed, for example, a photocurable varnish containing a photopolymerizable compound is applied onto the image formed in the above-described image forming process, and is cured to form a varnish

layer. The photocurable varnish may be applied so as to cover the entire image, or may be applied so as to cover only a part of the image.

**[0140]** The method for applying the photocurable varnish onto the image is not particularly limited as long as the photocurable varnish can be uniformly applied. Examples of the coating apparatus include a varnish coater, a roll coater, a flexocoater, a rod coater, a blade, a wire bar, an air knife, a curtain coater, and a slide coater. Examples of the coating apparatus include a doctor knife, a screen coater, and a gravure coater (e.g., an offset gravure coater). Examples of coating apparatus includes liquid film coating devices including slot coaters and extrusion coaters, and the like. In addition, any one of those of well-known systems such as forward and reverse roll coating, offset gravure, curtain coating, lithographic coating, screen coating and gravure coating can be used.

**[0141]** Here, the photocurable varnish to be applied onto the image described above may contain a photopolymerizable compound (polymerizable monomer for varnish), but usually contains a polymerization initiator (sensitizer) together with the photopolymerizable compound.

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**[0142]** The photopolymerizable compound may be a monomer, an oligomer, or a polymer. Provided that it includes at least diol di(meth) acrylate having a linear hydrocarbon structure. When the photocurable varnish contains the diol di(meth) acrylate, the affinity with the crystalline polyester in the toner particles is increased, the wettability of the photocurable varnish with respect to an image is improved, and the adhesion between the varnish layer to be obtained and the image is increased.

**[0143]** Here, the diol di(meth) acrylate having a linear hydrocarbon structure is a monomer obtained by dehydration assembly of an aliphatic diol and two (meth) acrylic acids. Note that the hydrocarbon structure of the diol di(meth) acrylate may be partially branched. In this case, a hydrocarbon chain sandwiched between two oxygen atoms derived from the diol is specified as the linear hydrocarbon structure.

**[0144]** The number of carbon atoms of the linear hydrocarbon structure of the diol di(meth) acrylate is preferably 4 or more and 12 or less, more preferably 6 or more and 10 or less, and still more preferably 6 or more and 9 or less. When the number of carbon atoms of the linear hydrocarbon structure of the diol di(meth) acrylate is within the above range, the viscosity of the photocurable varnish is likely to be in an appropriate range and the application property is likely to be satisfactory. In addition, affinity for the crystalline polyester in the toner particles is also likely to be satisfactory.

**[0145]** Specific examples of the diol di(meth) acrylate include hexanediol diacrylate, nonanediol diacrylate, decanediol diacrylate, and the like, and among these, hexanediol diacrylate is particularly preferable.

**[0146]** The amount of the diol di(meth) acrylate having a linear hydrocarbon structure is preferably 10% by mass or more and 80% by mass or less, more preferably 20% by mass or more and 65% by mass or less, based on the total mass of the photopolymerizable compounds. When the amount of the diol di(meth) acrylate is within the above range, the adhesion between an image and the varnish layer becomes satisfactory.

**[0147]** Examples of the photopolymerizable compound other than diol di(meth) acrylate include polymerizable oligomers and polymerizable polymers such as acrylic resins, vinyl-acrylic resins, acrylic acid esters of polyhydric alcohols, epoxy acrylates, urethane acrylates, polyester acrylates, polyether acrylates, acrylate alkyds, and melamine acrylates. In addition, (meth) acrylate monomers such as trimethylolpropane (meth) acrylate and phenoxyethyl (meth) acrylate, tri (meth) acrylate monomers, and the like are also included. The amount and type of the photopolymerizable compound other than the diol di(meth) acrylate are appropriately selected in accordance with the curability, viscosity, surface tension, and the like of the photocurable varnish.

**[0148]** Examples of the polymerization initiator (sensitizer) include known anthraquinone-based initiators, benzophenone-based initiators, 2-ethylanthraquinone-based initiators, acylphosphine oxide-based initiators, and alkylphenone-based photopolymerization initiators. The amount of the polymerization initiator is preferably 5% by mass or more and 25% by mass or less based on the total mass of the photocurable varnish. When the amount of the polymerization initiator is within the above range, the curability of the photocurable varnish becomes satisfactory.

**[0149]** Furthermore, the photocurable varnish may contain a surfactant, and examples thereof include anionic surfactants, nonionic surfactants, silicone surfactants, and fluorosurfactants. Examples of the anionic surfactant include sulfosuccinates, disulfonates, phosphate esters, sulfates, and sulfonates. Examples of the nonionic surfactant include polyvinyl alcohol, polyacrylic acid, isopropyl alcohol, and acetylene-based diol. Also, ethoxylated octyl phenols, ethoxylated branched secondary alcohols, perfluorobutane sulfonates, alkoxylated alcohols and the like can be used. Examples of the silicone surfactant include polyether-modified polydimethylsiloxane. Examples of fluorosurfactants include ethoxylated nonylphenol and the like. When the photocurable varnish contains a surfactant, the adhesion between the image and the varnish layer may be improved. It is also possible to adjust the surface tension of the photocurable varnish to enhance the wettability of the photocurable varnish.

**[0150]** The surface tensions of the photocurable varnishes at 25°C are preferably 10 mN/m or more and 50 mN/m or less, more preferably 15 mN/m or more and 45 mN/m or less, still more preferably 20 mN/m or more and 40 mN/m or less. When the surface tension of the photocurable varnish is within the above range, the photocurable varnish easily wets and spreads on an image. The surface tensions of the photocurable varnish is measured by a plate method with KYOWA DY300 (manufactured by Kyowa Interface Science Co., Ltd).

**[0151]** On the other hand, the viscosity of the photocurable varnish at 25°C measured 30 seconds after a vibrator is immersed in the liquid is preferably 100 mPa·s or more and 800 mPa·s or less. The viscosity is more preferably 150 mPa·s or more and 700 mPa·s or less. The viscosity is more preferably 200 mPa·s or more and 600 mPa·s or less. When the viscosity of the photocurable varnish is within the above range, it becomes easy to apply the photocurable varnish by the above-described method.

**[0152]** After the application of the photocurable varnish, the photocurable varnish is cured by irradiation with light energy. The type of the light energy to be applied is appropriately selected depending on the type of the polymerization initiator or the like, but it can usually be ultraviolet light, visible light or the like. Examples of the light source of light energy include a low-pressure mercury lamp, a medium-pressure mercury lamp, a high-pressure mercury lamp, an ultrahigh-pressure mercury lamp, a xenon lamp, a carbon arc lamp, a metal halide lamp, a fluorescent lamp, a tungsten lamp, and an LED, and the amount of light, the irradiation time, and the like thereof are appropriately selected.

**[0153]** The varnish coat may be formed by a method of applying a solvent-based varnish and drying the solvent, other than the above-described photo-curable varnish.

15 Example

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[0154] Hereinafter, the present invention will be described in more detail with reference to Examples, but the present invention is not limited thereto.

**[0155]** In the following Examples, unless otherwise specified, the average particle diameter of each particle is a volume-based average particle diameter measured using Coulter Multisizer 3 manufactured by Beckman Coulter, Inc.

- 1. Material Preparation
- 1-1. Saturated Hydrocarbon Compound

**[0156]** Saturated hydrocarbons having 20 carbon atoms, 26 carbon atoms, 30 carbon atoms, and 34 carbon atoms (GL Sciences Inc) were fractionated at a mass ratio of 20:30:30:20, melted and mixed at 80°C, and then cooled and solidified to obtain saturated hydrocarbon compounds having 16 or more and 35 or less carbon atoms.

30 1-2. Release Agent

(Microcrystalline Wax)

[0157] A microcrystalline wax having a melting point of 84°C, which was obtained by solvent crystallization from a vacuum distillation residual oil and filtration, was prepared. The molecular distillation was repeated until the average number of carbon atoms became 43 and a component having 16 or more and 35 or less carbon atoms became undetectable, to obtain a microcrystalline wax as a release agent. The molecular distillation was carried out at a temperature of 240°C and a pressure of 0.2 Pa to remove low-molecular-weight components, and then at a temperature of 400°C and a pressure of 0.2 Pa to remove the other components. The number of carbon atoms was detected qualitatively by GC-MS and quantitatively by GC-FID. The melting point of the obtained microcrystalline wax was 78°C. Note that the melting point of the microcrystalline wax is defined as a temperature at which a peak having a half value width of an endothermic peak of 15°C or less is observed when measured at a temperature increase rate of 10°C/min in DSC.

(Behenic Acid Behenate)

[0158] Commercially available behenic acid behenate was used as the behenic acid behenate as the release agent.

1-3. Binder Resin

50 (Polyester Resin)

#### [0159]

- Terephthalic acid: 55.6 parts by mass
- Propylene oxide adduct of bisphenol A (BPA-PO): 28.8 parts by mass
  - Propanediol: 15.5 parts by mass
  - Tin 2-ethylhexanoate (esterification catalyst): 0.50 parts by mass

**[0160]** The above materials were charged into a reaction tank equipped with a cooling tube, a stirrer, a nitrogen introduction tube, and a thermocouple. Thereafter, the inside of the reaction vessel was replaced with nitrogen gas, the temperature was gradually raised while stirring, and the above materials were reacted over 3 hours while stirring at a temperature of 140°C.

**[0161]** Next, the temperature in the reactor was lowered to 8.3 kPa, and the temperature was raised to 200°C while stirring, followed by a reaction for 4 hours. Thereafter, the pressure in the reaction tank was reduced again to 5 kPa or less, and the contents were reacted at 200°C for 3 hours, to obtain a polyester resin as a binder resin.

(Styrene-acrylic Resin)

[0162]

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Styrene: 81.0 parts by mass
Butyl acrylate: 19.0 parts by mass

Di-tert-butyl peroxide (Perbutyl D available from NOF CORPORATION): 1.00 parts by mass

**[0163]** While replacing with nitrogen, 100 parts of propylene glycol monomethyl ether was heated and refluxed at a liquid temperature of 120°C or more, and the mixture of the above-described materials was added dropwise thereto over 3 hours.

**[0164]** After completion of the dropwise addition, the mixture was stirred for 3 hours, then distilled under atmospheric pressure while raising the liquid temperature to 170°C, and after the liquid temperature reached 170°C, distilled under reduced pressure in a 1 hPa for 1 hour to remove the solvent, thereby obtaining a resinous solid. The resin solid was dissolved in tetrahydrofuran, and the solution was reprecipitated with N-hexane. The precipitated solid was collected by filtration to obtain styrene-acrylic resin 1 as a binder resin.

1-4. Dispersion of Resin Particles

(Dispersion of Coloring Agent Particles)

**[0165]** An aqueous solution was prepared by adding 11.5 parts by mass of N-dodecyl sodium sulfate to 160 parts by mass of ion-exchanged water and stirring to dissolve N-dodecyl sodium sulfate, and 24.5 parts by mass of monoazo yellow (C. I. Pigment Yellow 74) was gradually added. Subsequently, a dispersion treatment was performed using a stirrer (CLEARMIX W Motion CLM-0.8, manufactured by M Technique Co., Ltd) to prepare a dispersion of colorant fine particles having a volume-based median size of 126 nm.

(Dispersion of Styrene-acrylic Resin Particles)

[0166]

Styrene: 584 parts by mass
 N-butyl acrylate: 160 parts by mass
 Methacrylic acid: 56 parts by mass

[0167] A monomer mixed liquid containing the above components was prepared.

**[0168]** A reaction vessel equipped with a stirrer, a temperature sensor, a cooling tube, and a nitrogen introduction device was charged with 4 parts by mass of sodium polyoxyethylene (2) dodecyl ether sulfate and 3000 parts by mass of ion-exchanged water. Under a nitrogen stream, the internal temperature was increased to 80°C while stirring at a stirring speed of 230 rpm. After the temperature increase, an aqueous solution prepared by dissolving 10 parts by mass of potassium persulfate in 200 parts by mass of ion exchanged water was added, the liquid temperature was set to 75°C, and the monomer mixture was added dropwise thereto over 1 hour. The mixture was further stirred while heating at 75°C for 2 hours to polymerize these monomers, thereby preparing a dispersion of resin fine particles.

**[0169]** Into a reaction vessel equipped with a stirrer, a temperature sensor, a cooling tube, and a nitrogen introducing device, an aqueous solution prepared by dissolving 2 parts by mass of sodium polyoxyethylene (2) dodecyl ether sulfate in 3000 parts by mass of ion-exchanged water was introduced. After heating to 80°C, 42 parts by mass (in terms of solid content) of the dispersion liquid of the resin fine particles [1] and a mixed liquid in which the following monomers and a chain transfer agent were dissolved at 85°C were added. Thereafter, a mixing and dispersing process was performed

for 1 hour using a mechanical disperser (CLEARMIX, manufactured by M Technique Co., Ltd) having a circulation path, to prepare a dispersion liquid containing emulsified particles (oil droplets).

Styrene: 239 parts by mass
N-butyl acrylate: 111 parts by mass
Methacrylic acid: 26 parts by mass
N-octyl mercaptan: 3 parts by mass
Methacrylic acid: 49 parts by mass
N-octyl mercaptan: 0.51 parts by mass

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**[0170]** Subsequently, an aqueous initiator solution in which 5 parts by mass of potassium persulfate was dissolved in 100 parts by mass of ion-exchanged water was added to the dispersion, and the system was heated and stirred at 80°C for 1 hour to polymerize the monomers, thereby preparing a dispersion of resin fine particles [2].

**[0171]** A solution in which 10 parts by mass of potassium persulfate was dissolved in 200 parts by mass of ion exchanged water was further added to the dispersion liquid of the resin fine particles [2] described above, and a mixed liquid of the following monomers was added dropwise over 1 hour under a temperature condition of 80°C.

Styrene 380 parts by mass
N-butyl acrylate: 132 parts by mass
Methacrylic acid: 39 parts by mass
N-octyl mercaptan: 6 parts by mass

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**[0172]** After the completion of the dropwise addition, the mixture was heated and stirred for 2 hours to polymerize the monomers, and the mixture was cooled to 28°C to obtain a dispersion of styrene-acrylic resin particles 2.

1-5. External Additives

30 (Strontium Titanate 1)

**[0173]** Metatitanic acid obtained by a sulfuric acid method is subjected to deironization bleaching treatment, and then, an aqueous sodium hydroxide solution was added to adjust the pH level to 9.0 for desulfurization, and the mixture was then neutralized with hydrogen chloride to pH5. 8, filtered, and washed with water. Water was added to the washed cake thus obtained to obtain a slurry having a concentration of 1.5 mol/L on the basis of TiOz, and then hydrochloric was added thereto to pH1.5, followed by a peptizing treatment.

[0174] The metatitanic acid slurry which had been desulfurized and dpeptized was collected and charged into a reaction vessel 3 L. An aqueous strontium chloride solution was added to the reactor in such an amount that the SrO/TiO<sub>2</sub> molar ratio was 1.18, and then the concentration was adjusted to 0.9 mol/L on the basis of TiO<sub>2</sub>. Next, the slurry was heated to 87°C under normal pressure while being stirred and mixed. An aqueous solution of 10 N sodium hydroxide from 444 mL was added over a period of 80 minutes while microbubbling nitrogen at 600 ml/min. Thereafter, the mixture was stirred at 92°C for 1 hour while nitrogen microbubbling was performed at 400 ml/min.

[0175] Thereafter, the slurry was stirred and rapidly cooled to 12°C while cooling water at 10°C was allowed to flow through the jacket of the reactor, and hydrochloride acid was added until the pH2.0 was attained, and the stirring was further continued for 1 hour. The thus-obtained precipitate was washed by decantation, and then, 6 N' s-hydrochloric acid was added to adjust to pH2.0, and 7.0 parts of isobutylethoxysilane with respect to 100 parts of the solids content was added and stirred for 18 hours. Finally, the mixture was neutralized with a 4 N sodium hydroxide aqueous solution, stirred for 2 hours, filtered and separated, and dried in the air at 120°C for 8 hours to obtain a powder of an external additive. When this powder was measured by powder X-ray diffraction, it showed a diffraction peak of strontium titanate. This powder was defined as strontium titanate 1. The average primary particle diameter of the strontium titanate 1 was 50 nm.

(Strontium Titanate 2 to Strontium Titanate 5)

[0176] Strontium titanate 2 to strontium titanate 5 were produced by performing the production and production processing of strontium titanate 1 except that the amount of the raw materials charged, the molar ratio of the raw materials, and the reaction temperature were changed.

- 2. Preparation of Toner Base Particles
- 2-1. Toner Base Particle 1

## <sup>5</sup> [0177]

- · Polyester resin: 100 parts by mass
- Microcrystalline wax (release agent): 5.00 parts by mass
- · Saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms: 0.06 parts by mass
- Monoazo Yellow (C. I. Pigment Yellow 74): 6.00 parts by mass

**[0178]** The above materials were charged into a Henschel mixer (FM-75 type, manufactured by Mitsui Mining Co., Ltd) and mixed under the conditions of rotational speeds of 20 s<sup>-1</sup> and a rotational time of 5 min. Thereafter, these were kneaded using a twin-screw kneader (PCM-30 type, manufactured by Ikegai Corporation) set to a temperature of 150°C. The obtained kneaded product was cooled and coarsely pulverized to 1 mm or less by a hammermill to obtain a coarsely pulverized product. The obtained coarsely pulverized product was finely pulverized with a mechanical pulverizer (T-250, manufactured by Turbo Kogyo Co., Ltd.) Furthermore, classification was performed by using a sphere classifier (Faculty).

- pulverized product. The obtained coarsely pulverized product was finely pulverized with a mechanical pulverizer (T-250, manufactured by Turbo Kogyo Co., Ltd). Furthermore, classification was performed by using a sphere classifier (Faculty F-300, manufactured by Hosokawa Micron Corporation) at classification rotor rotational speeds of 130 s<sup>-1</sup> and dispersion rotor rotational speeds of 120 s<sup>-1</sup>.
- [0179] The classified particles were heat-treated by the surface treatment apparatus illustrated in Fig. 1. At this time, the temperature of the heat treatment chamber was 200°C, and the heat treatment time was 30 second. Thus, toner base particles 1 having an average particle diameter of 6.50 μm and an average circularity of 0.96 were obtained.
  - 2-2. Toner Base Particles 2

**[0180]** Toner base particles 2 were obtained in the same manner as in the preparation of the toner base particles 1 except that the styrene-acrylic resin 1 was used instead of the polyester resin.

- 2-3. Toner Base Particles 3
- **[0181]** Toner base particles 3 were obtained bin the same manner as in the preparation of the toner base particles 1 except that behenic acid behenate was used instead of the microcrystalline wax.
- 2-4. Toner Base Particles 4
- **[0182]** Toner base particles 4 were in the same manner as in the preparation of the toner base particles 1 except that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.0002 parts by mass.
- 40 2-5. Toner Base Particles 5
  - **[0183]** Toner base particles 5 were obtained in the same manner as in the preparation of the toner base particles 1 except that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.12 parts by mass.
  - 2-6. Toner Base Particles 6

[0184] Into a reaction vessel equipped with a stirrer, a temperature sensor, a cooling tube, and a nitrogen introducing device, 946 parts by mass (in terms of solid content) of the dispersion of styrene-acrylic resin particles 2, 1100 parts by mass of ion exchanged water, and 54 parts by mass (in terms of solid content) of the dispersion of colorant particles were charged. The liquid temperature was adjusted to 30°C. The pH level was adjusted to 10 with 5 N of an aqueous sodium hydroxide solution. Next, an aqueous solution in which 60 parts by mass of magnesium chloride was dissolved in 60 parts by mass of ion-exchanged water was added under stirring at 30°C over 10 minutes. Thereafter, after being held for 3 minutes, the temperature elevation is started to elevate the temperature to 85°C over 60 minute, and while being held at 85°C, the aggregation and the particle growth reaction are allowed to continue. In this state, the particle diameter of the aggregated particles was measured, and when the volume-based median diameter reached 6.5  $\mu$ m, an aqueous solution prepared by dissolving 40 parts by mass of sodium chloride in 160 parts by mass of ion-exchanged water was added to stop the particle growth. Further, as an aging step, the mixture was heated and stirred at a liquid

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temperature of 80°C for 1 hour to promote fusion between particles, thereby preparing a dispersion of toner base particles 6 having an average circularity of 0.69.

[0185] The produced dispersion liquid of the toner base particles 6 was subjected to solid-liquid separation with a basket-type centrifugal separator (MARKIII Model No.  $60 \times 40$  + M, manufactured by Matsumoto Machine Co., Ltd) to form a wetcake of the toner base particles 6. The wet cake was washed with ion-exchanged water at 40°C by the basket type centrifugal separator until the electric conductivity of the filtrate became  $5\mu$  S/cm. Thereafter, the resultant was placed in a dryer (Flash Jet Dryer, product of Seishin Enterprise Co., Ltd) and dried until the water content became 0.5% by mass, to obtain toner base particles 6.

10 2-7. Toner Base Particles 7

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**[0186]** Toner base particles 7 were obtained in the same manner as in the preparation of the toner base particles 1 except that that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.008 parts by mass.

2-8. Toner Base Particles 8

**[0187]** Toner base particles 8 were obtained in the same manner as in the preparation of the toner base particles 1 except that that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.014 parts by mass.

2-9. Toner Base Particles 9

- **[0188]** Toner base particles 9 were obtained in the same manner as in the preparation of the toner base particles 1 except that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.113 parts by mass.
  - 2-10. Toner Base Particles 10
- [0189] Toner base particles 10 were obtained in the same manner as in the preparation of the toner base particles 1 except that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.105 parts by mass.
  - 2-11. Toner Base Particles 11

**[0190]** Toner base particles 11 were obtained in the same manner as in the preparation of the toner base particles 1 except that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.0001 parts by mass.

40 2-12. Toner Base Particles 12

**[0191]** Toner base particles 12 were obtained in the same manner as in the preparation of the toner base particles 1 except that the amount of the saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms added was changed to 0.125 parts by mass.

- 3. Preparation of Toner
- 3-1. Toner 1
- [0192] 100 parts by mass of the toner base particles 1, and 1.0 parts by mass of hydrophobic silica fine particles (BET specific surface area:200 m²/g) hydrophobized with hexamethyldisilazane), and 1.0 parts by mass of titanium dioxide fine particles surface-treated with isobutyltrimethoxysilane (BET specific surface:80 m²/g), and 0.5 parts by mass of strontium titanate 1 were mixed using a Henschel mixer (FM-75, manufactured by Mitsui Miike Machinery Co., Ltd) at a rotational speed of 30 s⁻¹ and a rotational time of 10 min to obtain a toner 1.
  - 3-2. Toner 2 to Toner 6, and Toner 12 to Toner 17

[0193] Toner 2 to toner 6 and toner 12 to toner 17 were obtained in the same manner as in the preparation of toner

- 1, except that the toner base particles were changed to toner base particles 2 to toner base particles 8, respectively.
- 3-3. Toner 7 to Toner 11
- <sup>5</sup> **[0194]** Toner 7 to toner 11 were obtained in the same manner as in the preparation of toner 1 except that strontium titanate 1 was changed to strontium titanate 2 to strontium titanate 5, respectively.
  - 4. Determination of the Amount of C16-35 Saturated Compounds
- [0195] Hydrocarbon compounds were extracted from each of the toners by solid-liquid extraction using N-hexane. At this time, cyclohexyl was added as an internal standard. Thereafter, epoxidation of the unsaturated hydrocarbon with metachloroperbenzoic acid (mCPBA) was performed by a conventional method. Saturated hydrocarbon compounds were purified and extracted by solid-phase extraction using silver-nitrate silica gel as a solid phase, and GC-FID was performed under the following conditions to quantify C16-35 saturated compounds.

(GC Condition)

#### [0196]

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Device used: Shimadzu GC-2010 Plus

Injection amount:  $1\mu L$ , saturated hydrocarbon concentration 500 to 1000mg/l

Guard column: Restek MXT Siltek (10m  $\times$  0.53 mm id) Column: Restek MTX-1 (15 m  $\times$  0.25 mm id  $\times$  0.1  $\mu$ m df)

<sup>25</sup> **[0197]** The elution time of n-alkanes (number of carbon atoms: 10, 16, 24, 35 and 50) was measured in advance under the same conditions. In addition, only N-hexane was preliminarily injected into the apparatus to prepare a blank chromatogram.

**[0198]** When the chromatogram of the blank was subtracted from the chromatogram obtained from each toner, a stable horizontal straight base line was able to be created before and after the peak derived from the saturated hydrocarbon compound. Perpendicular lines were drawn to C16 and C35, and the area of the part surrounded by these perpendicular lines in the chromatogram above the base line was determined. Note that peaks that were confirmed not to be saturated hydrocarbon compounds were excluded from the calculation. The mass of the saturated hydrocarbon compound having a carbon number of at least 16 and no greater than 35 was obtained from the ratio of this area and the area of bicyclohexyl added as the internal standard. This mass was divided by the mass of the toner to determine the amount of C16-35 saturated compound in the toner.

**[0199]** Table 1 shows the materials and production method of the toners 1 to 17, the particle diameter of strontium titanate, and the amount of saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms in the toner base particles. In the release agent column, "hydrocarbon" represents microcrystalline wax, and "ester" represents behenic acid behenate.

[Table 1]

				[			
	Toner Base particles No.	Release agent	Fixing resin		Srontium titanate		Amount of
Toner No.				Preparation method	No.	Average particle diameter (nm)	Amount of C16-35 saturated compounds (ppm)
1	1	Hydrocarbon	Polyester	Pulverization	1	50	501
2	2	Hydrocarbon	Styrene- acrylic	Pulverization	1	50	498
3	3	Ester	Polyester	Pulverization	1	50	505
4	4	Hydrocarbon	Polyester	Pulverization	1	50	1
5	5	Hydrocarbon	Polyester	Pulverization	1	50	1000
6	6	Hydrocarbon Styrene- acrylic		Polymerization	1	50	503

(continued)

	Toner Base particles No.	Release agent	Fixing resin	Preparation method	Sron	tium titanate	Amount of C16-35 saturated compounds (ppm)
Toner No.					No.	Average particle diameter (nm)	
7	1	Hydrocarbon	Polyester	Pulverization	None	-	501
8	1	Hydrocarbon	Polyester	Pulverization	2	20	501
9	1	Hydrocarbon	Polyester	Pulverization	3	200	501
10	1	Hydrocarbon	Polyester	Pulverization	4	30	501
11	1	Hydrocarbon	Polyester	Pulverization	5	150	501
12	7	Hydrocarbon	Polyester	Pulverization	1	50	51
13	8	Hydrocarbon	Polyester	Pulverization	1	50	105
14	9	Hydrocarbon	Polyester	Pulverization	1	50	955
15	10	Hydrocarbon	Polyester	Pulverization	1	50	898
16	11	Hydrocarbon	Polyester	Pulverization	1	50	0.7
17	12	Hydrocarbon	Polyester	Pulverization	1	50	1050
[0194] 5	. Evaluation						

(Creation of Image)

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**[0200]** Toner 1 to Toner 17 were sequentially loaded into the multifunction peripheral for Example 1 to Example 11, Example 14 to Example 17, and Comparative Example 1 and Comparative Example 2. The multifunction peripheral was from bizhub PRESS C1070 (manufactured by Konica Minolta Inc.), which was remodeled so that the toner adhesion amount could be freely set.

**[0201]** For Example 12, the same processes as in Examples 1 to 11 were performed using a multifunction peripheral (bizhub PRESS manufactured by Konica Minolta, Inc., C8000) that performs fixing of a toner image in two stages, and an image was output.

**[0202]** For Example 13, an unfixed image was collected using a modified machine of a multifunction peripheral (bizhub PRESS C1070, manufactured by Konica Minolta Inc.), which had been modified so that an image could be collected before fixing. The unfixed image was fixed by a fixing device from a multifunction peripheral (imagePRESS V1000, manufactured by CANON INC) whose fixing device (fixing device with a fixing nip formed by a non-rotating pressure pad) had been taken out and modified so as to be able to be driven alone.

#### 5-1. Varnish Application Property

(Creation of Image)

**[0203]** A solid image having an adhesion amount of 8.0 g/m was output on evaluation paper (POD-157 gloss coated paper manufactured by Oji Paper Co., Ltd) under normal fixing conditions.

(Application of Varnish)

[0204] A varnish (UV VECTA 3KW2 PC-COAT VARNISH, manufactured by T&K Co., Ltd) was applied to the produced image with a bar coater so as to have a thickness of 5  $\mu$ m. Thereafter, the varnish was cured by irradiation with ultraviolet rays from a high-pressure mercury lamp such that the integrated light amount on the image surface was 120 to 130 mJ/cm², thereby forming a varnish layer. Note that the varnish used was a varnish containing a polymerizable monomer for varnish having a polymerizable functional group containing an ethylenic double bond and a photopolymerization initiator (radical polymerization initiator).

(Evaluation of Application Property)

**[0205]** The surfaces of the varnish layers of the obtained images were visually observed to confirm whether the varnishes were clearly repelled, and in a case where the varnishes were not repelled, the number of pinholes in a range of  $10 \text{ cm} \times 10 \text{ cm}$  was counted. Based on these results, the varnish application property was evaluated according to the following evaluation criteria. A sample in which the varnish was not clearly repelled and the number of pinholes was 10 or less was determined to be as "pass."

- A: Zero or more and one or less pinholes were present in the range of the 10 cm imes 10 cm
- B: Two or more and four or less minute pinholes were present in the range of the 10 cm imes 10 cm
- C: Five or more and ten or less minute pinholes were present in the range of the 10 cm  $\times$  10 cm
- D: 11 or more pinholes or repelling occurs in the range of the 10 cm imes 10 cm

#### 5-2. Varnish Adhesion

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(Evaluation of Adhesion)

**[0206]** A photograph of the surface of the varnish layer of the solid image with varnish obtained in the "varnish application property" was taken at a magnification of 100 times using a microscope (manufactured by Keyence Corporation, digital microscope VHX-6000). The captured image was binarized using image processing software (LUSEX-AP, manufactured by Nireco Corporation).

**[0207]** Thereafter, a polyimide tape (manufactured by Sumitomo 3M Co., Ltd., Mending Tape No.810-3-12) was lightly pasted on the surface of the varnish layer, and the sample was rubbed back and forth 3.5 times on the applied tape with a 1 kPa. Thereafter, the tape was peeled off from the varnish layer with a 200 g force at an angle of 180°.

**[0208]** A photograph of the surface of the varnish layer after the tape was peeled off was taken at a magnification of 100 times using a microscope (digital microscope VHX-6000, manufactured by Keyence Corporation). The captured image was binarized using image processing software (LUSEX-AP, manufactured by Nireco Corporation). Then, the varnish peeling rate was calculated by the following formula.

**[0209]** Varnish peeling rate [%] =  $(1 - \text{area of concealing portion of varnish with respect to image region after tape peeling)/area of concealing portion of resin with respect to image region by powder before tape peeling) <math>\times$  100.

**[0210]** Based on the calculated varnish peeling rate, the varnish adhesion was evaluated according to the following evaluation criteria. When the peeling rate was less than 5%, the sample was determined to be as "pass."

- A: Varnish peeling rate was 0% or more and less than 1%
- B: Varnish peeling rate was 1% or more and less than 3%
- C: Varnish peeling rate was 3% or more and less than 5%
- D: Varnish peeling rate was 5% or more
- 5-3. Fixing Separability

(Creation of Image)

**[0211]** Coated A4 size paper (manufactured by Oji Paper Co., Ltd., OK Top Coat + (basis weight: 85.0 g/m²)) was used as evaluation paper. The temperature of the upper fixing belt is set to a temperature (U.O. avoidance temperature + 25°C) that is increased by 25°C based on the temperature at which under-offset does not occur (U.O. avoidance temperature), the temperature of the lower fixing roller was set to 90°C, and a solid image (adhesion amount: 8.0 g/m²) was produced. Note that image formation was performed under a normal temperature and normal humidity environment (NN environment: 25°C and 50% RH).

50 (Evaluation of Fixing Separability)

**[0212]** Images were sequentially formed while changing the amount of leading edge margin, and the amount of leading edge margin immediately before a sheet jam occurred was used as a measure of fixing separability.

**[0213]** In addition, the smaller the possible leading end margin, the more excellent the thin paper releasability. When the leading edge margin was less than 7 mm, the sample was determined to be as "pass." Note that for Example 12, the fixing separability was evaluated using the first stage fixing device.

**[0214]** Table 2 shows the evaluation results.

[Table 2]

5		Toner	Varnish application properties		Varnish adhesion		Fixing separability	
ŭ		No.	Evaluation	Pinhole number	Evaluation	Varnish removal rate (%)	Evaluation	Leading edge margin (mm)
10	Example 1	1	А	1	В	1.5	Pass	4
	Example 2	2	Α	1	В	2.8	Pass	4
	Example 3	3	С	5	В	1.0	Pass	6
15	Example 4	4	С	10	А	0.7	Pass	6
	Example 5	5	А	0	С	4.4	Pass	3
	Example 6	6	В	2	С	3.2	Pass	6
20	Example 7	7	С	5	В	1.1	Pass	6
	Example 8	8	В	3	В	1.3	Pass	5
	Example 9	9	В	3	О	3.3	Pass	2
	Example 10	10	В	2	В	1.4	Pass	2
	Example 11	11	В	2	В	2.5	Pass	3
25	Example 12	1	Α	0	В	1.6	Pass	3
	Example 13	1	В	0	В	1.7	Pass	3
30	Example 14	12	С	7	А	0.8	Pass	6
	Example 15	13	В	4	Α	0.9	Pass	5
	Example 16	14	В	0	С	3.6	Pass	3
	Example 17	15	В	0	В	2.9	Pass	3
	Comparative example 1	16	D	11	А	0.6	Failed	7
	Comparative example 2	17	А	0	D	5.1	Pass	3

[0215] As is clear from Table 2, when the content of the C16-35 saturated compound was 1 ppm or more and 1000 ppm or less based on the total mass of the toner (the mass including the toner base particles and the external additive), the varnish applicability and adhesion were satisfactory, and the fixing separability was also satisfactory.

#### **Industrial Applicability**

**[0216]** According to the present invention, when a varnish coat is applied to an image formed with a toner, the application property and adhesiveness of the varnish can be enhanced. Furthermore, since fixing separability of a toner image is also improved, the present invention is useful even when no varnish coat is applied.

#### Reference Signs List

# [0217]

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1 Image forming apparatus

10 Heating belt

30 Image processor

40 image former

41Y, 41M, 41C, 41K Image forming unit

	42 Intermediate transfer unit
	43 Secondary transfer unit
	50 Sheet conveyor
	51 Sheet feeder
5	51A, 51B, 51C Sheet feed tray unit
	52 Sheet ejector
	52A Sheet ejection roller
	53 Conveyance path
	53A Registration roller pair
10	60 Fixing device
	62 Fixing roller
	63 Pressure roller
	70 Image reader
	71 Sheet feed device
15	72 Scanner
	72A CCD Sensor
	100 Surface treatment apparatus
	110 Hopper
	120 Mixing chamber
20	130 Nozzle
	140 Dispersion airflow
	50 Diffuser
	160 Heat treatment chamber
	170 Hot-air swirling chamber
25	180 Cold air supplier
	190 Ejector
	200 surface treatment apparatus
	210 Heat treatment chamber
	220 Introduction tube
30	222 Protrusion-shaped member
	230 Supply tube
	240 Powder particle supply port
	250 Hot-air supplying means
	260 Hot-air introducing section
35	270 Swirling member
00	280 Distribution member
	290 Cold air introducing section
	411 Exposure device
40	412 Developing device 413 Electrophotographic photoreceptor
70	414 Charging device
	415 Drum cleaning device
	421 Intermediate transfer belt
	422 Primary transfer roller
45	-
40	423, 431 Support roller
	423A Backup roller
	426 Belt cleaning device 426A Elastic member
E0	431A Secondary transfer roller
50	432 Secondary transfer belt
	600 Fixing device
	610 Pressure Pad
	620 Pressure roller
	630 Heating roller
55	640 Steer roller
	650 Heating belt
	660 Pressing member
	D Document

S Sheet

**[0218]** Although embodiments of the present invention have been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and not limitation, the scope of the present invention should be interpreted by terms of the appended claims.

#### **Claims**

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- 1. An electrostatic latent image developing toner, comprising: a saturated hydrocarbon compound having 16 or more and 35 or less carbon atoms at a content of 1 ppm to 1000 ppm based on a total mass of the electrostatic latent image developing toner.
- 2. The electrostatic latent image developing toner according to claim 1, wherein the content of the saturated hydrocarbon compound is 100 ppm or more and 900 ppm or less based on the total mass of the electrostatic latent image developing toner.
  - **3.** The electrostatic latent image developing toner according to claim 1 or 2, further comprising: a hydrocarbon wax having 36 or more and 76 or less carbon atoms as a release agent.
  - **4.** The electrostatic latent image developing toner according to any one of claims 1 to 3, further comprising: a polyester resin as a binder resin.
- 5. The electrostatic latent image developing toner according to any one of claims 1 to 4, wherein the electrostatic latent image developing toner is a pulverized toner.
  - **6.** The electrostatic latent image developing toner according to any one of claims 1 to 5, further comprising: strontium titanate as an external additive.
- **7.** The electrostatic latent image developing toner according to claim 6, wherein the strontium titanate is in a form of a particle having a number-average primary particle diameter of 20 nm or more and 200 nm or less.
  - **8.** The electrostatic latent image developing toner according to claim 6 or 7, wherein the strontium titanate is in a form a particle having a number-average primary particle diameter of 30 nm or more and 150 nm or less.
  - **9.** An image forming method comprising:
    - attaching the electrostatic latent image developing toner according to any one of claims 1 to 8 to a recording medium; and
  - fixing the attached electrostatic latent image developing toner to the recording medium.
  - **10.** The image forming method according to claim 9, wherein the fixing includes fixing the electrostatic latent image developing toner to the recording medium in two stages.
- 45 **11.** The image forming method according to claim 9 or 10, wherein the fixing includes fixing the electrostatic latent image developing toner to the recording medium by causing the recording medium, to which the electrostatic latent image developing toner is attached, to pass through a planar nip portion formed by a non-rotating pad.
  - **12.** The image forming method according to claim 11, wherein:

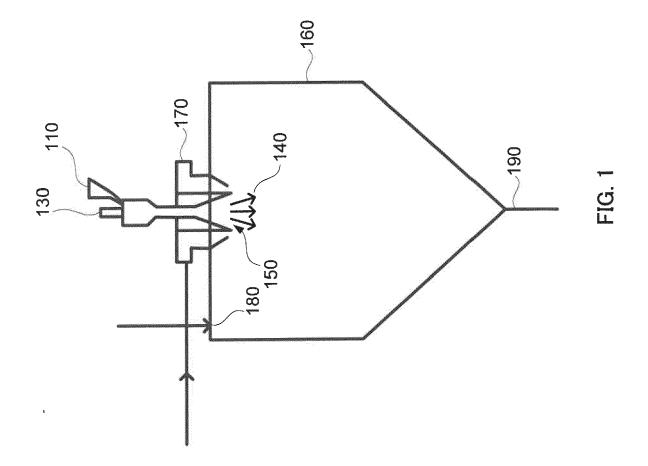
the nip portion is formed by the pad and a pressure roller pinching a rotating endless belt in between; and in the fixing, the endless belt is heated by a heating roller in contact with an inner peripheral surface of the endless belt.

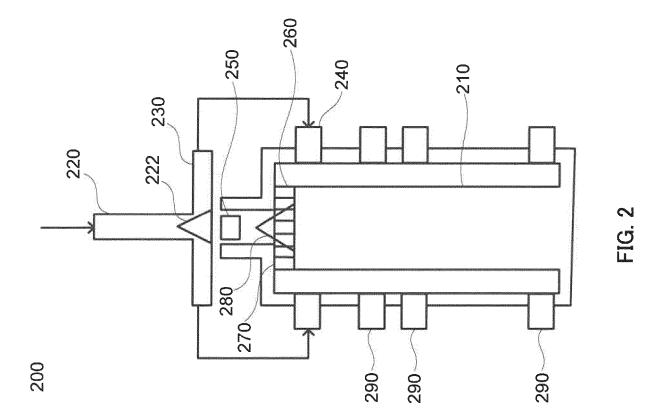
13. The image forming method according to any one of claims 9 to 12, further comprising: forming a varnish coat by applying a varnish to a surface of a toner image formed by fixing of the electrostatic latent image developing toner.

## **14.** An image forming apparatus comprising:

an attacher that attaches the electrostatic latent image developing toner according to any one of claims 1 to 8 to a recording medium; and

a fixer that fix the attached electrostatic latent image developing toner to the recording medium.





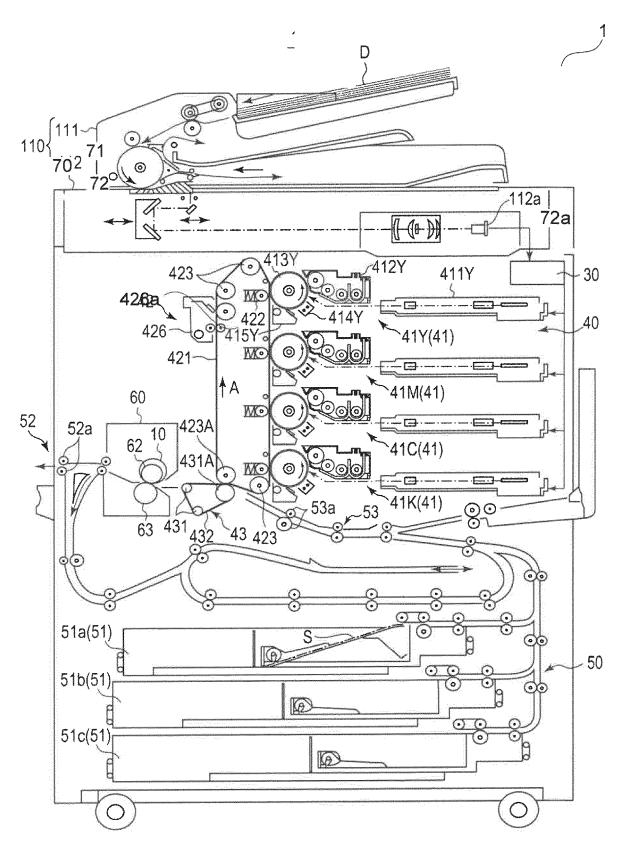


FIG. 3

620

FIG. 4

#### REFERENCES CITED IN THE DESCRIPTION

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