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TONER FOR DEVELOPING ELECTROSTATIC IMAGE,
IMAGE FORMING METHOD AND PROCESS CARTRIDGE

FIELD OF THE INVENTION AND RELATED ART

5 The present invention relates to a toner,
particularly a negatively chargeable toner, for
developing electrostatic images in image forming
methods, such as electrophotography, and electrostatic
printing. The present invention also relates to an
10 image forming method and a process cartridge using the
toner.

Hitherto, a large number of electro-
photographic processes have been known, as disclosed
in U.S. Patent Nos. 2,297,691; 3,666,363; 4,071,361
15 and others. In these processes, an electric latent
image is formed on a photosensitive member comprising
a photoconductive material by various means, then the
latent image is developed and visualized with a toner,
and the resultant toner image is, after transferred
20 onto a transfer-receiving material, such as paper, as
desired, fixed by heating, pressing, heating and
pressing, etc., to obtain a copy or a print. In the
case of including the step of transferring a toner
image, a step of removing a residual toner remaining
25 on the photosensitive member is ordinarily also
included.

Known developing methods for visualizing

electrical latent images with a toner may include, e.g., the magnetic brush method described in U.S. Patent No. 2,874,063, the cascade developing method disclosed in U.S. Patent No. 2,618,552, the powder
5 cloud method disclosed U.S. Patent No. 2,221,776, and a method using an electroconductive magnetic toner disclosed in U.S. Patent No. 3,909,258.

As for the step of fixing the toner image onto a sheet material such as paper which is the final
10 step in the above process, various methods and apparatus have been developed, of which the most popular one is a heating and pressing fixation system using hot rollers.

In the heating and pressing system, a sheet
15 carrying a toner image to be fixed (hereinafter called "fixation sheet") is passed through hot rollers, while a surface of a hot roller having a releasability with the toner is caused to contact the toner image surface of the fixation sheet under pressure, to fix the toner
20 image. In this method, as the hot roller surface and the toner image on the fixation sheet contact each other under a pressure, a very good heat efficiency is attained for melt-fixing the toner image onto the fixation sheet to afford quick fixation.

25 Recently, in place of hot rollers, there has been commercialized a fixing apparatus comprising a heating member and a pressing member which is disposed

opposite to the heating member and presses a recording medium (such as paper) to contact the heating member via a film.

On the other hand, in recent years, there
5 have been also desired high-quality copy or print images in accordance with the use of digitalized copying machines and fine toner particles.

More specifically, it has been desired to obtain a photographic image accompanied with
10 characters, so that the character images are clear while the photographic image is excellent in density gradation faithful to the original. Generally, in a copy of a photographic image accompanied with characters, if the line density is increased so as to
15 provide clear character images, not only the density gradation characteristic of the photograph image is impaired, but also the halftone part thereof are roughened.

Further, resolution failure (collapsion) of
20 line images and scattering are liable to be caused at the time of fixation as described above, so that the image qualities of the resultant copy images are rather liable to be deteriorated.

Further, in case where the line image density
25 is increased, because of an increased toner coverage, a thick toner image is pushed against a photosensitive member to be attached to the photosensitive member in

the toner transfer step, so that a so-called transfer failure (or a hollow image), i.e., a partial lack toner image (line images in this case), in the transferred image, is liable to be caused, thereby providing poor quality of copy images. On the other hand, in case where the gradation characteristic of a photographic image is intended to be improved, the density of characters or line images are liable to be lowered, thus providing unclear images.

In recent years, there has been obtained some improvement in density gradation characteristic by a system including image density readout and digital conversion. However, a further improvement has been desired.

Regarding density gradation characteristic, it is impossible to obtain a linear relationship between a developing potential (difference between a photosensitive member potential and a developer-carrying member potential) and a resultant (copy) image density. In a halftone region, a slight change in developing potential leads to a remarkable change in image density. This provides a complexity in obtaining a satisfactory density gradation characteristic.

Generally, copied images appear clearer because of an edge effect of attracting an increased amount of toner so that clear line images can be

retained in case where a maximum density of ca. 1.30 is attained at a solid image part which is less affected by the edge effect.

In case of a photographic image, however, the
5 maximum density of a photograph appears less at a glance because of its surface gloss but actually amounts to a very high level of 1.90 - 2.00. Accordingly, in a copy of a photographic image, even if the surface gloss is suppressed, a solid part image
10 density of ca. 1.4 - 1.5 is required since a density increase due to the edge effect cannot be excepted because of a large image area.

Accordingly, in providing a copy of a photographic image accompanied with characters, it
15 becomes very important to obtain a developing potential-image density relationship which is close to the first order (linear) one and also a maximum image density of 1.4 - 1.5.

Further, the density gradation
20 characteristic is liable to be remarkably affected by the saturation charge and the charging speed of a developer used. In case where the saturation charge is appropriate for the developing conditions, a developer showing a slow charging speed provides a low
25 maximum image density, thus generally thin and blurred images in the initial stage of copying. In this case, however, non-problematic images can be obtained if the

maximum image density is ca. 1.3, as described above, thus being able to obviate an adverse effect of the slow chargeability. Even in case of the slow charging speed, the initial copy image density is increased if
5 the saturation charge is increased. However, on continuation of copying, the charge of the developer is gradually increased to finally exceed an appropriate charge for development, thereby resulting in a lower copy image density. Also in this case, no
10 problem occurs in line images if the maximum image density is ca. 1.3

From the above, it is understood that a photographic image is more remarkably affected by the saturation charge and the charging speed of a
15 developer than a line image.

In case where a smaller particle size toner is used, the dispersion state of a charge control agent and a colorant remarkably affects the chargeability of the toner.

20 A toner for developing electrostatic images may generally contain a dye called a charge control agent for controlling the chargeability of the toner. In order to provide a toner with a negative chargeability, chromium complex compounds have been
25 principally used.

Japanese Laid-Open Patent Application (JP-A) 60-170864, describes that, among such chromium complex

compounds, those having a good mutual solubility with a binder resin show a uniform negative chargeability and provide clear copy images but are liable to be accompanied with difficulties, such as remaining of a toner residue on a photosensitive member due to cleaning failure and filming, and those being insoluble within a binder resin (particularly in a polyester resin) show good chargeability and also good anti-filming characteristic.

However, a metal complex salt compound insoluble or incompatible with a binder resin shows a poor dispersibility. Accordingly, when a toner containing such a metal complex salt compound is formulated into fine particles, the toner is liable to be charged excessively particularly in a low-humidity environment, thus leading to a density lowering. This is because a fine particle size fraction and a coarse particle size fraction formed through a pulverization step of toner production are caused to have remarkably different contents (weight ratios) of the charge control agent (i.e., so-called localization of a charge control agent), so that toner particles are caused to have different chargeabilities.

In case where a fine powder fraction and a coarse powder fraction recovered from the classifying step are re-utilized as a material for toner

production, the above-mentioned liability of localization of a charge control agent is further promoted to cause difficulties, such as a lowering in image density and fog due to a toner

5 electrification insufficiency under a low-humidity condition. For this reason, it has been hitherto difficult to reutilize both fine powder and coarse powder by-produced in the classification step for toner production, and coarse powder alone has been

10 reutilized as proposed in JP-A 3-209266. JP-A 61-155464 and JP-A 62-177561 have proposed an azo-type iron complex as a charge control agent showing good dispersibility within a binder resin. A toner

15 containing the azo-type iron complex is, however, accompanied with difficulties, such as a slow rate of electrification and a lowering in image density after a long period of standing or in a high humidity environment. In recent years, a smaller particle size

20 (at most 9 μm in terms of a weight-average particle size (diameter)) is recommended for providing high-quality images. A small particle size toner is liable to have a remarkably high charge under a low-humidity condition and cause difficulties, such as thinning of line images, a lowering in image density and

25 occurrence of reversal potential fog caused by a toner charged to an opposite polarity due to charging failure on a developer-carrying member, such as a

developing sleeve, due to the copresence of the excessively charged toner.

In order to improve the chargeability of a toner containing such an azo-type iron complex, JP-A 1-306862 has proposed a silicone resin-coated carrier which has a high chargeability-imparting effect, and JP-A 2-153362 has proposed a developing apparatus including an improved toner layer thickness-regulating member and an improved toner replenishment-assisting member. In these proposals, the developing performance of the toner is retained by charge-imparting or -assisting members and it is difficult to retain good image quality for a long period due to deterioration or soiling of the charge-imparting or -assisting member.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a toner for developing electrostatic images having solved the above-mentioned problems and capable of retaining a high-quality image forming performance for a long period.

An object of the present invention is to provide a toner having a good dispersibility of a charge control agent and a uniform chargeability, capable of retaining a high image density for a long period and capable of providing images free from fog

and with a high resolution.

Another object of the present invention is to provide a toner which can be quickly charged and can provide good toner images similarly as before standing
5 even after standing for a long period or in a high-humidity environment.

Another object of the present invention is to provide a toner which can provide high-quality images without using a charge-assisting member.

10 Another object of the present invention is to provide a fine particle size toner which can provide satisfactory developed images for a long period under various environmental conditions even in case of providing high-resolution developed images.

15 Another object of the present invention is to provide a toner which allows re-utilization of fine powder and coarse powder by-produced in the classification step in toner production.

Another object of the present invention is to
20 provide a toner highly suitably adapted to an electrophotographic process not adversely affecting a photosensitive member or a developer-carrying member.

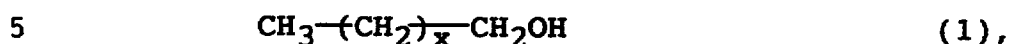
A further object of the present invention is to provide an image forming method and a process
25 cartridge using such a toner as described above.

According to the present invention, there is provided a toner for developing electrostatic images,

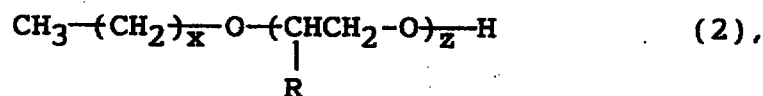
comprising:

(a) a binder resin,

(b) a long-chain alkyl compound represented by the following formula (1), (2) or (3):



wherein x denotes an average value in the range of 35 - 150,

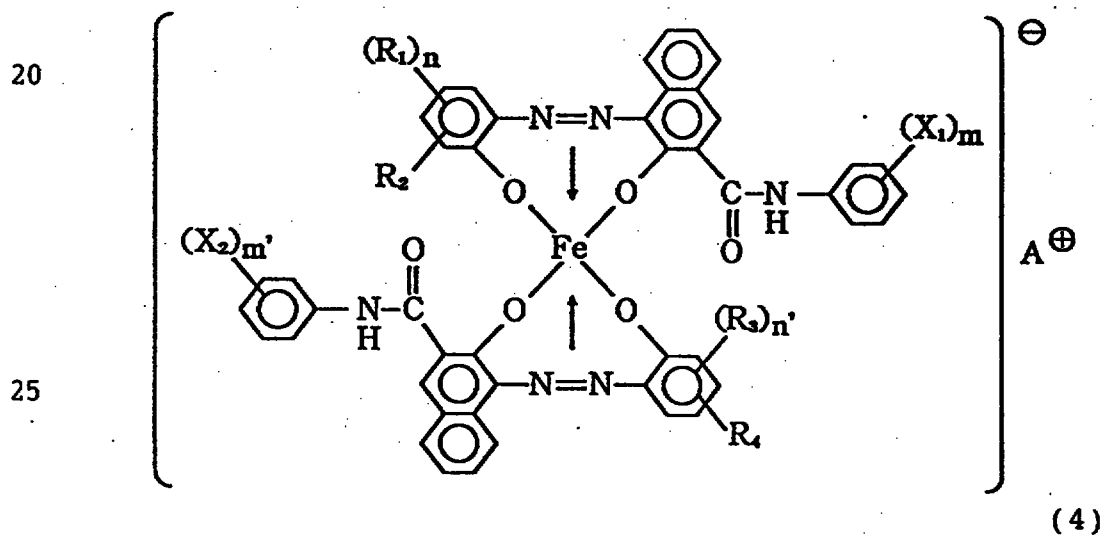


10 wherein x denotes an average value in the range of 35 - 150; z denotes an average value in the range of 1 - 5, and R denotes H or an alkyl group having 1 - 10 carbon atoms,



15 wherein y denotes an average value in the range of 35 - 150; and

(c) an azo-type iron complex compound represented by the following formula (4);



wherein X_1 and X_2 independently denote hydrogen atom,
lower alkyl group, lower alkoxy group, nitro group or
halogen atom; m and m' denote an integer of 1 - 3; R_1
and R_3 independently denote hydrogen atom, C_{1-18} alkyl
5 or alkenyl, sulfonamide, mesyl, sulfonic acid group,
carboxy ester group, hydroxy, C_{1-18} alkoxy,
acetylamino, benzoylamino or halogen atom; n and n'
denote an integer of 1 - 3; R_2 and R_4 denote hydrogen
atom or nitro group; and A^+ denotes a cation including
10 75 - 98 mol. % of ammonium ion and another ion
selected from the group consisting of hydrogen ion,
sodium ion, potassium ion and mixtures thereof.

According to another aspect of the present
invention, there is provided an image forming method,
15 comprising:

a charging step of supplying a voltage to a
charging means in contact with a member to be charged
to charge the member to be charged,

a step of forming an electrostatic image on
20 the charged member to be charged,

a developing step of developing the
electrostatic image with a toner as described above to
form a toner image on the member to be charged,

a transfer step of transferring the toner
25 image to a transfer-receiving material directly or via
an intermediate transfer member, and

a fixing step of fixing the toner image onto

the transfer-receiving material.

According to a further aspect of the present invention, there is provided a process-cartridge, comprising at least a developing means and a
5 photosensitive member,

the developing means and the photosensitive member being integrated into a cartridge which is detachably mountable to a main body of an image forming apparatus,

10 wherein the developing means contains a toner as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of an
15 image forming apparatus used in Examples of the present invention.

Figure 2 is an exploded perspective view of essential parts of a fixing apparatus used in Examples of the invention.

20 Figure 3 is an enlarged sectional view of a fixing apparatus including a film in a non-driven state used in Examples of the present invention.

Figure 4 is a partial illustration of a checker pattern for evaluating the developing
25 performance of a toner.

Figure 5 is a schematic illustration of an embodiment of the process-cartridge according to the

present invention.

DETAILED DESCRIPTION OF THE INVENTION

As a result of our study, it has been found
5 possible to provide a toner capable of forming stable
images while retaining a high development performance
and without being affected by an environmental change.

An azo-type iron complex, when used as a
charge control agent for an electrophotographic toner,
10 provides a toner which shows an insufficient charging
speed under a high-humidity condition and fails to
provide a sufficient image density at an initial stage
or a long period of standing under a high-humidity
condition. Under a low-humidity condition, in a long
15 period of continual use, the toner is liable to cause
an accumulation of an excessive triboelectric charge
(charge-up), thus resulting in images with a low image
density and noticeable fog.

In contrast thereto, a chromium or aluminum
20 complex compound insoluble in a binder resin
alleviates the above-mentioned problems and has been
therefore widely used. A toner using such a chromium
or aluminum complex compound is accompanied with a
problem that classified fine powder and classified
25 coarse powder thereof cannot be readily re-utilized.
This is because the chromium or aluminum complex
compound is contained in different weight ratios in

the classified fine powder, classified medium powder (used as a toner) and classified coarse powder, so that a toner produced by re-utilization of the classified fine powder and the classified coarse powder is liable to cause a lowering in image density and fog during a long period of continual use in a low-humidity environment.

We have noted in combination that an azo-type iron complex compound shows little localization in classified powders and that a binder containing an azo-type chromium complex compound insoluble in a binder resin shows a good developing performance, whereby we have succeeded in improving the charge controllability of an azo-type iron complex compound while retaining the non-localizability of the azo-type iron complex compound, by forming micro-domains (aggregations) of the azo-type iron complex compound in toner particles.

The formation of an azo-type iron complex compound is accomplished by the presence of a long-chain alkyl compound in toner particles. This is considered because the OH groups or carboxyl groups in the long-chain alkyl compound respectively form an associated state and, under the influence of the associations, the azo-type iron complex compound forms microdomain. As a result, the azo-type iron complex compound can be provided with an improved charge

controllability while maintaining the non-localizability.

The localization of an azo-type metal complex in classified fine powder, classified medium powder
5 (used as a toner) and classified coarse powder resultant after a classification step in a toner production process using the azo-type metal complex is evaluated in the following manner. Each powder fraction is weighed in a prescribed amount within a
10 range of 1.0 - 3.0 g and is dispersed in 200 ml of ethyl alcohol under stirring for 48 hours, followed by filtration to recover a filtrate. Then, the absorption spectrum in the visible range of the filtrate is obtained and a relative absorbance at a
15 wavelength showing an absorption, e.g., $\lambda = 480$ nm, attributable to the metal complex is measured. The localization characteristic of the metal complex is evaluated by factors (ratios):

$$OD_F/OD_M \text{ and } OD_C/OD_M,$$

20 wherein OD_F denotes an absorbance of a filtrate obtained from classified fine powder, OD_M denotes an absorbance of a filtrate obtained from classified medium powder and OD_C denotes an absorbance of a filtrate obtained from classified coarse powder.

25 An azo-type iron complex compound represented by the above-mentioned formula (4) wherein A^+ comprises 75 - 98 mol. % of ammonium ions, has been

found to exhibit a preferred performance in forming stable toner images. An azo-type iron complex compound having cations consisting solely of ammonium ions tends to provide a toner showing an image density
5 which slowly increases after standing in a high-humidity environment. On the other hand, an azo-type iron complex compound having cations consisting only of protons or alkali metal ions tends to provide a toner showing a low image density in a high-humidity
10 environment.

As a result of our study, the use of cations including both ammonium ions and alkali metal ions and/or protons provides a compound giving a toner showing a good performance after a long period of
15 standing. The inclusion of ammonium ions at 75 - 98 mol. % provides particularly good results regarding image density increasing speed and image density level after the increase.

When the ammonium ion content is below 75 %,
20 the image density is lowered and, above 98 %, the image density tends to increase slowly.

As a result of further study of ours, the azo-type iron complex compound used in the toner according to the present invention may preferably have
25 a solubility in methanol of 0.1 - 8 g/100 ml, more preferably 0.3 - 4 g/100 ml, further preferably 0.4 - 2 g/100 ml.

In case where the solubility is below 0.1 g/100 ml, the charge control agent (azo-type iron complex compound) shows a low dispersibility in the toner even if the long-chain alkyl compound is used in combination, thus providing a toner which has an unstable triboelectric chargeability and is liable to cause image fog and scattering.

On the other hand, in case where the solubility exceeds 8 g/100 ml, the toner performances are liable to be affected by the temperature and humidity during a long period of standing in a high temperature - high humidity environment, so that the toner chargeability is impaired and it becomes difficult to obtain a sufficient image density.

The charge control agent may preferably be used in a proportion of 0.2 - 5 wt. parts per 100 wt. parts of the binder resin.

The solubility of the charge control agent may be measured in the following manner.

<Solubility measurement of charge control agent>

2 g of a charge control agent is weighed and placed in a 300 ml Erlenmeyer flask to which 100 ml of methanol is added. The system is heated to 50 °C under stirring and the stirring is further continued for 1 hour (when all the charge control agent is dissolved, the charge control agent is further added successively at an increment of 2 g each under

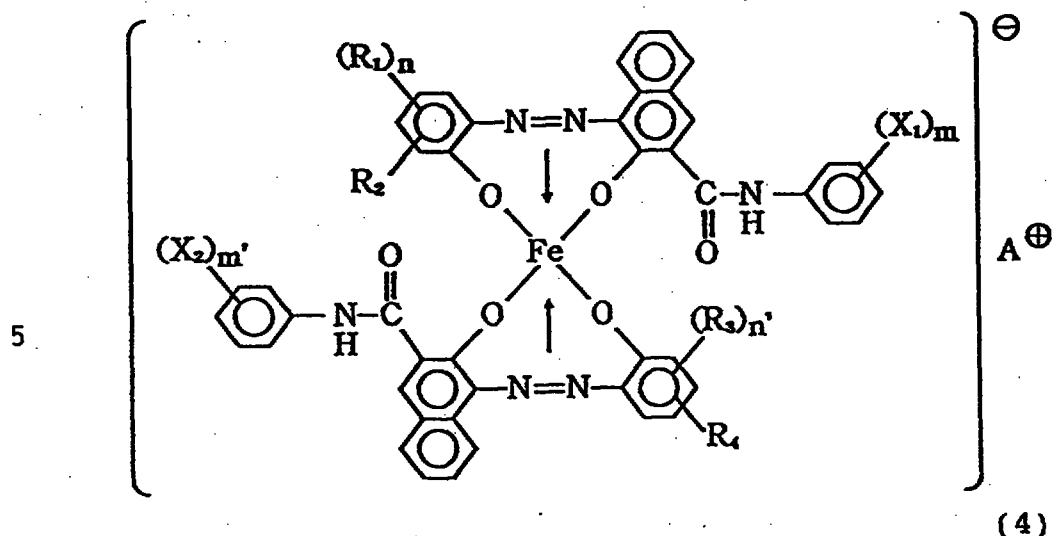
continued stirring). Then, the system is cooled to room temperature and the insoluble charge control agent is removed by a 0.1 μ m-filter to measure the absorbance (A) of the solution at a maximum absorption wavelength by using a spectrophotometer.

On the other hand, a standard solution of the charge control agent (at a concentration C_0 (= 0.02 g/l (= 20 ppm)) is prepared, and the absorbance (A_0) thereof is measured. From these data, the solubility of the charge control agent (C (g/l)) is calculated by $A/A_0 = C/C_0$, based on the Lambert-Beer's law represented by the following formula:

$$A = -\log_e (I_0/I) = \epsilon_0 C d,$$

wherein I denotes a transmitted light intensity through a solution, I_0 denotes a transmitted light intensity through a solvent (= methanol), ϵ_0 denotes an absorption coefficient, C denotes the concentration of the charge control agent, and d denotes the thickness of the solution for the absorbance measurement.

The azo-type iron complex compound used in the present invention has a structure represented by the following general formula (4):



wherein X_1 and X_2 independently denote hydrogen atom,
 10 lower alkyl group, lower alkoxy group, nitro group or
 halogen atom; m and m' denote an integer of 1 - 3; R_1
 and R_3 independently denote hydrogen atom, C_{1-18} alkyl
 or alkenyl, sulfonamide, mesyl, sulfonic acid group,
 carboxy ester group, hydroxy, C_{1-18} alkoxy,
 15 acetyl amino, benzoyl amino or halogen atom; n and n'
 denote an integer of 1 - 3; R_2 and R_4 denote hydrogen
 atom or nitro group; and A^+ denotes a cation including
 75 - 98 mol. % of ammonium ion and another ion
 selected from the group consisting of hydrogen ion,
 20 sodium ion, potassium ion and mixtures thereof.

The above azo-type iron complex which is
 suitably used as a negative charge control agent may
 be synthesized according to a known process.

The negative charge control agent may be used
 25 singly or in combination of two or more species or in
 combination with another negative charge control
 agent.

Representative examples of the azo-type iron complex represented by the above formula may include those having structures as shown below wherein $A^{\oplus}$ denotes the same meaning as defined above:

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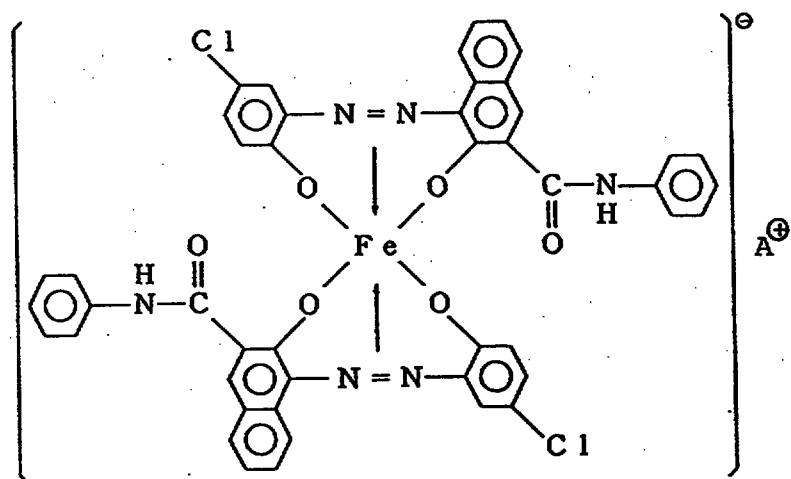
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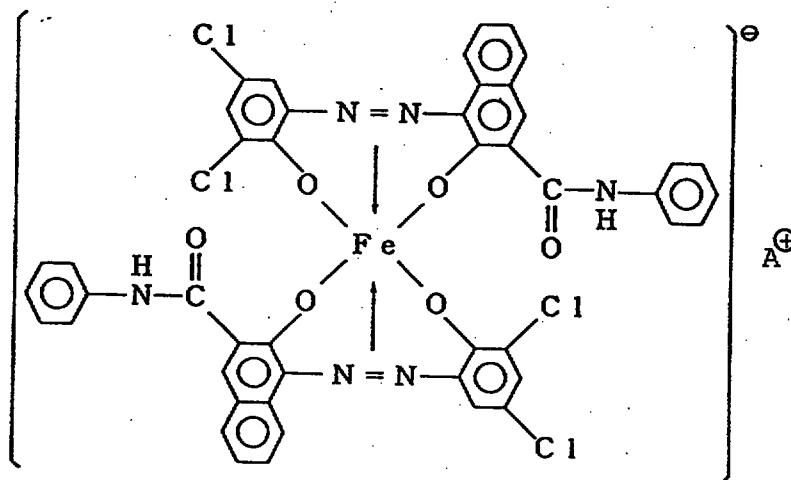
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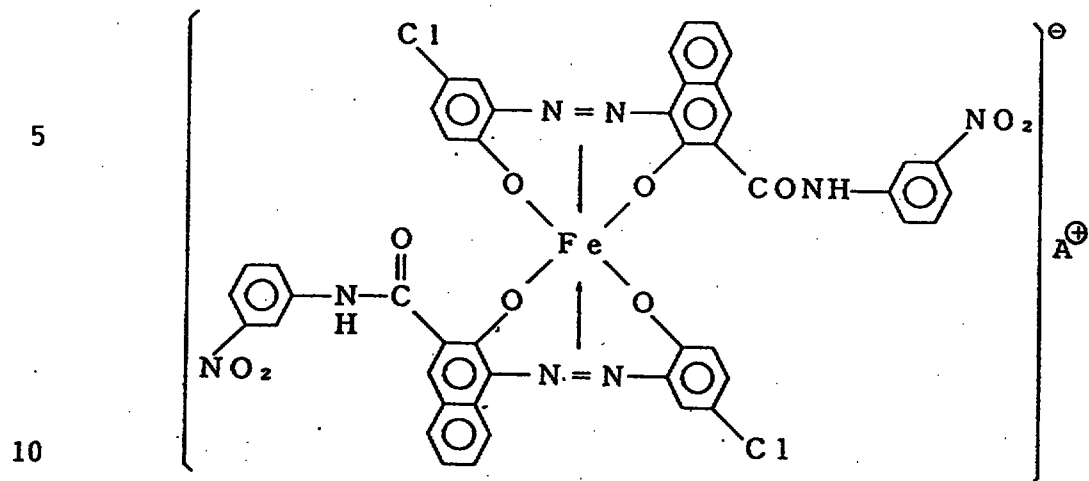
Iron Complex (1)



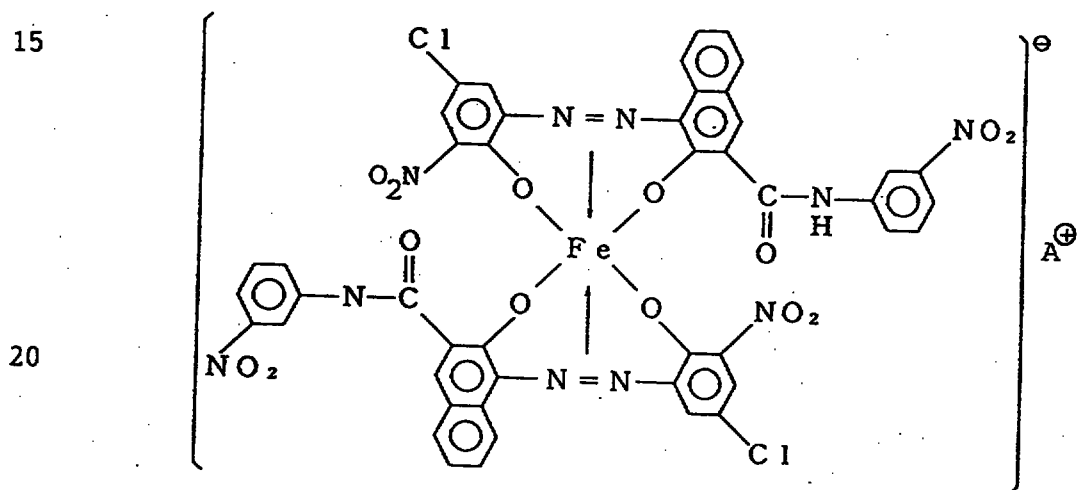
Iron Complex (2)



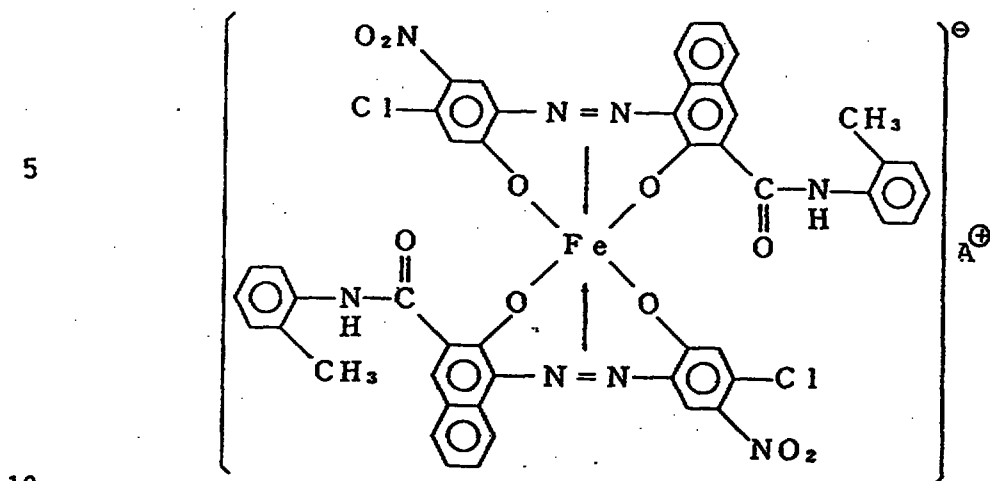
Iron Complex (3)



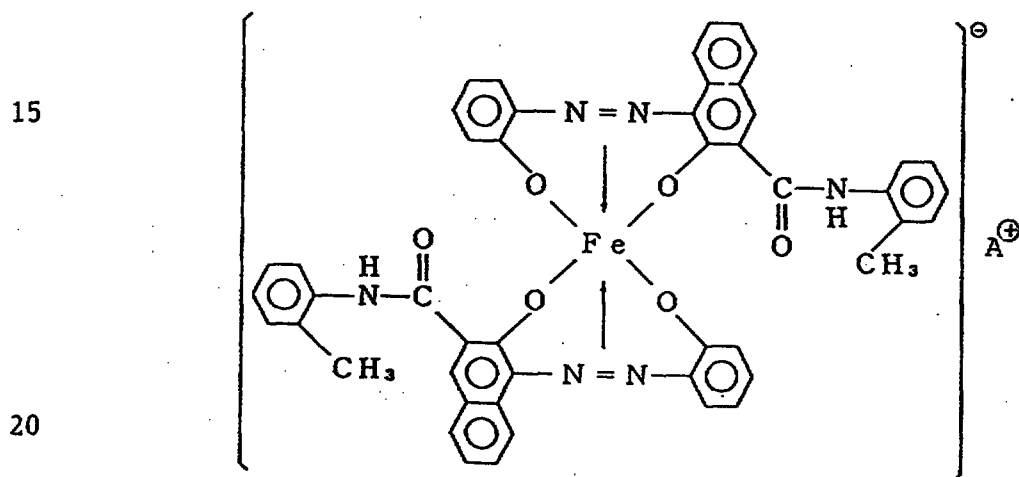
Iron Complex (4)



Iron Complex (5)

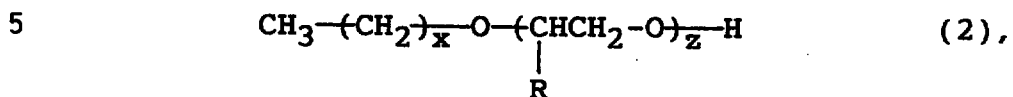


Iron Complex (6)



In the toner for developing the electrostatic images the azo-type ion complex may preferably be used in an amount of 0.1 - 10 wt. parts, more preferably 0.1 - 5 wt. parts, per 100 wt. parts of the binder resin.

The long-chain alkyl compound used in the present invention may be represented by the following formula (1), (2) or (3).



wherein x denotes an average value in the range of 35 - 150; z denotes an average value in the range of 1 - 5, and R denotes H or an alkyl group having 1 - 10 carbon atoms.

The long-chain alkyl compound of the above formulae may for example be produced as follows. Ethylene is polymerized in the presence of a Ziegler catalyst and, after the polymerization, oxidized to provide an alkoxide of the catalyst metal and polyethylene, which is then hydrolyzed to provide an objective long-chain alkyl compound of formula (1). By reacting the long-chain alkyl alcohol of formula (1) with an epoxy group-containing substance, it is possible to obtain a long-chain alkoxy alcohol of formula (2). The thus prepared long-chain alkyl alcohols have little branching and a sharp molecular weight distribution and are suitably used in the present invention.



wherein y denotes an integer of 35 - 150.

The long-chain alkyl compound of formula (3)

may be obtained by oxidizing the long-chain alkyl compound of formula (1).

For the compound represented by the above formula (1), (2) or (3), x and y may preferably be 35
5 - 150. If x and y are below 35, the resultant toner is liable to cause melt-sticking onto the photosensitive member or a lower storage stability. If x and y are larger than 150, the above-mentioned contribution to toner chargeability (i.e., promoting
10 the formation of microdomains of the azo-type iron complex) is lowered, thus being unsuitable for accomplishing the object of the present invention. z is preferably at most 5. If z is larger than 5, the resultant toner is liable to cause melt-sticking onto
15 the photosensitive member. For similar reasons, it is preferred that R is H or a C₁ - C₁₀ alkyl group.

The long-chain alkyl compound used in the present invention may suitably be a mixture of compounds having different molecular weights and can
20 further contain at most 30 wt. %, preferably at most 25 wt. % of hydrocarbon compounds free from functional groups such as hydroxyl and carboxyl group as by-produced through the above-mentioned production processes of the compounds of the formulae (1) - (3).
25 The long-chain alkyl compound may preferably have a number-average molecular weight (M_n) of 150 - 2500, a weight-average molecular weight (M_w) of 250 - 5000,

and an Mw/Mn ratio of at most 3.

In case where Mn is below 150 or Mw is below 250, the toner is liable to cause melt-sticking onto the photosensitive member or a lower storage stability. In case where Mn exceeds 2500 or Mw exceeds 5000, the contribution to toner chargeability is lowered, thus being liable to cause problems, such as fog.

The long-chain alkyl compound of formula (1) or (2) used in the present invention may preferably have an OH value of 2 - 150 mgKOH/g, more preferably 10 - 120 mgKOH/g. If the long-chain alkyl compound has an OH value below 2 mgKOH/g, the dispersibility thereof in the binder resin is lowered to result in ununiform toner chargeability leading to a density decrease, fog, and inferior image quality in copy images. In case where the long-chain alkyl compound has an OH value exceeding 150 mgKOH/g, the localization of the OH group charge density is increased to exceed the charge density localization of the OH groups in the binder resin, so that copy images in the initial state of image formation are liable to have a low density and a poor image quality. Alternatively, even if the initial density is high, the density is liable to be lowered gradually on continuation of copying. Further, in case where the OH value exceeds 150 mgKOH/g, the long-chain alkyl

compound is caused to contain a large amount of low-molecular weight molecules so that the resultant toner is liable to cause a melt-sticking onto the photosensitive member and lower the storage stability.

5 The long-chain alkyl compound of formula (3) used in the present invention may preferably have an acid value of 2 - 150 mgKOH/g, more preferably 5 - 120 mgKOH/g. If the long-chain alkyl compound has an acid value below 2 mgKOH/g, the dispersion thereof in the
10 binder resin becomes worse, thereby resulting in inferior image qualities of copy images. Further, as the carboxyl groups do not sufficiently associate each other, the environmental characteristic is liable to be impaired. Further, the resultant toner is liable
15 to show a low charging velocity, to result in a lower density at the initial stage of copying. In case where the acid value of the long-chain alkyl compound exceeds 150 mgKOH/g, it contains a large amount of low-molecular weight molecules, the resultant toner is
20 liable to cause melt-sticking onto the photosensitive member and lower the storage stability.

 The long-chain alkyl compounds, when used singly, may preferably be contained in an amount of 0.1 - 30 wt. parts, particularly 0.5 - 20 wt. parts,
25 per 100 wt. parts of the binder resin.

 In case where the long-chain alkyl compounds are used in combination, the total amount thereof may

preferably be 0.1 - 30 wt. parts, more preferably 0.5 - 20 wt. parts, per 100 wt. parts of the binder resin.

It is preferred for the toner according to the present invention to contain 3 - 90 % by number of toner particles having a particle size of 5 μ m or smaller. Hitherto, it has been considered difficult to control the charge imparted to toner particles of 5 μ m or smaller. Further, such fine toner particles are considered to impair the fluidity of the toner, soil the carrier and developing sleeve, cause cleaning failure and filming onto the drum and scatter to soil the interior of an image forming apparatus. Thus, it has been considered necessary to remove or decrease toner particles of 5 μ m or smaller.

As a result of our study, however, in case of a toner containing a specific long-chain alkyl compound and an azo-type iron complex of the above-mentioned formula, it has been found that toner particles of 5 μ m or smaller are very effective for providing images of a fine definition and a high resolution.

In the toner used in the present invention, it is also preferred that toner particles of 6.35 - 10.08 μ m constitute 1 - 80 % by number and the toner has a weight-average particle size of 4.0 - 10 μ m, more preferably 4.5 - 9.0 μ m.

Toner particles of 5 μ m or smaller are able

to strictly cover and faithfully reproduce an electrostatic image, but an electrostatic image per se has a higher electric field intensity at the peripheral edge than the middle or central portion.

5 As a result, toner particles are attached to the central portion in a smaller thickness than to the peripheral part, so that the inner part is liable to be thin in density. We have found that this problem can be solved to provide a clear image by using toner
10 particles of 6.35 - 10.08 μm in a proportion of 1 - 80 % by number. This may be attributable to a fact that toner particles of 6.35 - 10.08 μm are supplied to an inner part having a smaller intensity than the edge of a latent image presumably because they have a
15 moderately controlled charge relative to toner particles of 5 μm or smaller, thereby to compensate for the less coverage of toner particles and result in a uniform developed image. As a result, a sharp image having a high density and excellent in resolution and
20 gradation characteristic can be attained.

Further, it is most preferred that the contents of the toner particles of 5 μm or smaller in terms of % by number (N %) and % by volume (V %) satisfy the relationship of $N/V = -0.05N+k$, wherein 3
25 $\leq k \leq 12$, and $5 \leq N \leq 90$. The toner having a particle size distribution satisfying the relationship in combination with the other characteristic features

according to the present invention accomplishes a better developing performance with respect to a digital latent image composed of minute spots.

We have found a certain state of presence of fine powder accomplishing the intended performance satisfying the above formula during our study on the particle size distribution with respect to particles of 5 μm or smaller. For a certain value of N, a large N/V value is understood to mean that a large proportion of particles smaller than 5 μm are present with a broad particle size distribution, and a small N/V value is understood to mean that particles having a particle size in the neighborhood of 5 μm is present in a large proportion and particles smaller than that are present in a small proportion. A further better thin-line reproducibility and high resolution in a large quantity of copying or printing are accomplished when the N/V is in the range of 1.0 - 7.45, N is in the range of 5 - 90 and the above formula relationship is satisfied.

Toner particles of 12.7 μm or larger are suppressed to be not more than 2.0 % by volume. The fewer, the better.

The particle size distribution of the toner used in the present invention is described more specifically below.

Toner particles of 5 μm or smaller may be

contained in a proportion of 5 - 90 % by number,
further preferably 9 - 75 % by number, of the total
number of particles. If the content of the toner
particles of 5 μm or smaller is below 5 % by number, a
5 portion of the toner particles effective for providing
a high image quality is few and particularly, as the
toner is consumed during a continuation of copying or
printing-out, the effective component is
preferentially consumed to result in an awkward
10 particle size distribution of the toner and gradually
deteriorates the image quality. If the content is
above 90 % by number, mutual agglomeration of the
toner particles and charge-up are liable to occur,
thus leading to difficulties, such as cleaning
15 failure, a low image density, and a large difference
in density between the contour and interior of an
image to provide a somewhat hollow image.

It is preferred that the content of the
particles in the range of 6.35 - 10.08 μm is 1 - 80 %
20 by number, further preferably 5 - 70 % by number.
Above 80 % by number, the image quality becomes worse,
and excess of toner coverage is liable to occur, thus
resulting in a lower thin-line reproducibility and an
increased toner consumption. Below 5 % by number, it
25 becomes difficult to obtain a high image density in
some cases.

For similar reasons as N, V may preferably be

0.5 - 70 % by volume.

The k value may preferably be 3 - 12, more preferably 4 - 10.

If $k < 3.0$, toner particles of 5.0 μm or
5 below are insufficient, and the resultant image
density, resolution and sharpness decrease. When fine
toner particles in a toner, which have conventionally
been considered useless, are present in an appropriate
amount, they are effective for achieving closest
10 packing of toner in development and contribute to the
formation of a uniform image. Particularly, these
particles fill thin-line portions and contour portions
of an image, thereby to visually improve the sharpness
thereof. On the other hand, if $k > 12$, an excess of
15 fine powder is present, whereby the balance of
particle size distribution can be disturbed during
successive copying or print-out, thus leading to
difficulties such as a somewhat lower image density
and filming.

20 The amount of toner particles having a
particle size of 12.7 μm or larger should be 2.0 % by
volume or smaller, preferably 1.0 % by volume or
smaller, more preferably 0.5 % by volume or smaller.
If the above amount is larger than 2.0 % by volume,
25 these particles are liable to impair thin-line
reproducibility.

The toner used in the present invention may

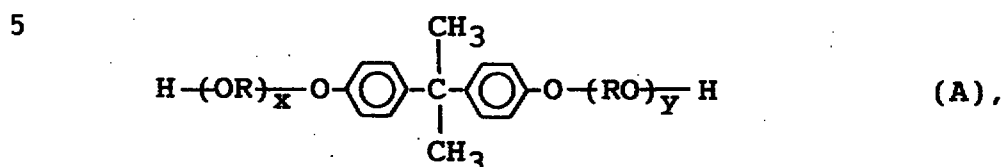
have a weight-average particle size of 4 - 10 μm , more preferably 4.5 - 9 μm . This value cannot be considered separately from the above-mentioned factors. If the weight-average particle size is below 5 4 μm , the toner is liable to cause soiling of the interior of an apparatus with scattered toner, a lowering in image density in a low-humidity environment and cleaning failure of the photosensitive member. If the weight-average particle size exceeds 9 10 μm , a minute spot of 100 μm or smaller cannot be developed with a sufficient resolution and noticeable scattering to non-image part is observed, thus being liable to provide inferior images.

Examples of the binder resin used in the 15 toner of the present invention may include polyester resins, vinyl resins and epoxy resins. Among these, polyester resins or vinyl resins may preferably be used in view of charging characteristic and fixing characteristic.

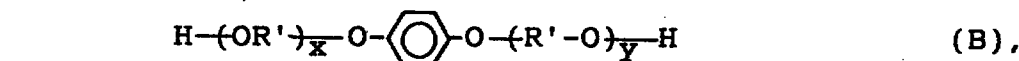
20 A polyester resin preferably used in the present invention may have a composition that it comprises 45 - 55 mol. % of alcohol component and 55 - 45 mol. % of acid component.

Examples of the alcohol component may 25 include: diols, such as ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, diethylene glycol, triethylene glycol,

1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 2-ethyl-1,3-hexanediol, hydrogenated bisphenol A, bisphenols and derivatives represented by the following formula (A):



wherein R denotes an ethylene or propylene group, x and y are independently a positive integer of at least 1 with the proviso that the average of x+y is in the range of 2 - 10; diols represented by the following formula (B):



15 wherein R' denotes $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-$ or $-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\underset{|}{\text{C}}}}-$,

x' and y' are a positive integer of at least 1 with the proviso that the average of x'+y' is in the range of 1 - 10.

20 Examples of the dibasic acid constituting at least 50 mol. % of the total acid may include benzenedicarboxylic acids, such as phthalic acid, terephthalic acid and isophthalic acid, and their anhydrides; alkyldicarboxylic acids, such as succinic acid, adipic acid, sebacic acid and azelaic acid, and their anhydrides; C₆ - C₁₈ alkyl or alkenyl-

substituted succinic acids, and their anhydrides; and unsaturated dicarboxylic acids, such as fumaric acid, maleic acid, citraconic acid and itaconic acid, and their anhydrides.

5 An especially preferred class of alcohol components constituting the polyester resin is a bisphenol derivative represented by the above formula (A), and preferred examples of acid components may include dicarboxylic acids inclusive of phthalic acid,
10 terephthalic acid, isophthalic acid and their anhydrides; succinic acid, n-dodecenylsuccinic acid, and their anhydrides, fumaric acid, maleic acid, and maleic anhydride.

 The polyester resin may preferably have a
15 glass transition temperature of 40 - 90 °C, particularly 45 - 85 °C, a number-average molecular weight (Mn) of 1,000 - 50,000, particularly 1,500 - 20,000, and a weight-average molecular weight (Mw) of 3×10^3 - 5×10^6 , particularly 4×10^3 - 1.5×10^6 .

20 Examples of a vinyl monomer for providing the vinyl resin may include: styrene; styrene derivatives, such as o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxystyrene, p-phenylstyrene, p-chlorostyrene, 3,4-dichlorostyrene, p-ethylstyrene,
25 2,4-dimethylstyrene, p-n-butylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, and p-n-

dodecylstyrene; ethylenically unsaturated monoolefins, such as ethylene, propylene, butylene, and isobutylene; unsaturated polyenes, such as butadiene; halogenated vinyls, such as vinyl chloride, vinylidene chloride, vinyl bromide, and vinyl fluoride; vinyl esters, such as vinyl acetate, vinyl propionate, and vinyl benzoate; methacrylates, such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-octyl methacrylate, dodecyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl methacrylate; acrylates, such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, propyl acrylate, n-octyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, 2-chloroethyl acrylate, and phenyl acrylate, vinyl ethers, such as vinyl methyl ether, vinyl ethyl ether, and vinyl isobutyl ether; vinyl ketones, such as vinyl methyl ketone, vinyl hexyl ketone, and methyl isopropenyl ketone; N-vinyl compounds, such as N-vinylpyrrole, N-vinylcarbazole, N-vinylindole, and N-vinyl pyrrolidone; vinylnaphthalenes; acrylic acid derivatives or methacrylic acid derivatives, such as acrylonitrile, methacrylonitrile, and acrylamide; the esters of the above-mentioned α,β -unsaturated acids and the diesters of the above-mentioned dibasic acids.

Examples of a carboxy group-containing vinyl monomer may include: unsaturated dibasic acids, such as maleic acid, citraconic acid, itaconic acid, alkenylsuccinic acid, fumaric acid, and mesaconic acid; unsaturated dibasic acid anhydrides, such as maleic anhydride, citraconic anhydride, itaconic anhydride, and alkenylsuccinic anhydride; unsaturated dibasic acid half esters, such as mono-methyl maleate, mono-ethyl maleate, mono-butyl maleate, mono-methyl citraconate, mono-ethyl citraconate, mono-butyl citraconate, mono-methyl itaconate, mono-methyl alkenylsuccinate, monomethyl fumarate, and mono-methyl mesaconate; unsaturated dibasic acid esters, such as dimethyl maleate and dimethyl fumarate; α,β -unsaturated acids, such as acrylic acid, methacrylic acid, crotonic acid, and cinnamic acid; α,β -unsaturated acid anhydrides, such as crotonic anhydride, and cinnamic anhydride; anhydrides between such an α,β -unsaturated acid and a lower aliphatic acid; alkenylmalonic acid, alkenylglutaric acid, alkenyladipic acid, and anhydrides and monoesters of these acids.

It is also possible to use a hydroxyl group-containing vinyl monomer: inclusive of acrylic or methacrylic acid esters, such as 2-hydroxyethyl acrylate, and 2-hydroxyethyl methacrylate; 4-(1-hydroxy-1-methylbutyl)styrene, and 4-(1-hydroxy-1-

methylhexyl)styrene.

The vinyl resin may have a glass transition point of 45 - 80 °C, preferably 55 - 70 °C, a number-average molecular weight (M_n) of 2.5×10^3 - 5×10^4 , and
5 a weight-average molecular weight (M_w) of 1×10^4 - 1.5×10^6 .

In the present invention, it is also possible to use a mixture binder resin including a vinyl homopolymer or copolymer, a polyester, polyester,
10 epoxy resin, polyvinyl butyral, rosin, modified rosin, terpene resin, phenolic resin, aliphatic or alicyclic-hydrocarbon resin or aromatic petroleum resin, in addition to the above-mentioned binder resin.

In case of using a mixture binder resin
15 including two or more resins of the same or different types, the two or more resins may preferably have different molecular weights and may be mixed with each other in appropriate ratios.

The toner according to the present invention
20 may be either a magnetic toner or a non-magnetic toner. In order to constitute a magnetic toner, it is preferred to use a magnetic material as described below.

Examples of the magnetic material contained
25 in the insulating magnetic toner used in the present invention may include: iron oxides, such as magnetite, hematite, and ferrite; iron oxides containing another

metal oxide; metals, such as Fe, Co and Ni, and alloys of these metals with other metals, such as Al, Co, Cu, Pb, Mg, Ni, Sn, Zn, Sb, Be, Bi, Cd, Ca, Mn, Se, Ti, W and V; and mixtures of the above.

5 Specific examples of the magnetic material may include: triiron tetroxide (Fe_3O_4), diiron trioxide ($\gamma\text{-Fe}_2\text{O}_3$), zinc iron oxide (ZnFe_2O_4), yttrium iron oxide ($\text{Y}_3\text{Fe}_5\text{O}_{12}$), cadmium iron oxide (CdFe_2O_4), gadolinium iron oxide ($\text{Gd}_3\text{Fe}_5\text{O}_{12}$), copper iron oxide
10 (CuFe_2O_4), lead iron oxide ($\text{PbFe}_{12}\text{O}_{19}$), nickel iron oxide (NiFe_2O_4), neodymium iron oxide (NdFe_2O_3), barium iron oxide ($\text{BaFe}_{12}\text{O}_{19}$), magnesium iron oxide (MgFe_2O_4), manganese iron oxide (MnFe_2O_4), lanthanum iron oxide (LaFeO_3), powdery iron (Fe), powdery cobalt
15 (Co), and powdery nickel (Ni). The above magnetic materials may be used singly or in mixture of two or more species. Particularly suitable magnetic material for the present invention is fine powder of triiron tetroxide or γ -diiron trioxide.

20 The magnetic material may have an average particle size (Dav.) of 0.1 - 2 μm , preferably 0.1 - 0.3 μm . The magnetic material may preferably show magnetic properties when measured by application of 10 kilo-Oersted, inclusive of: a coercive force (H_c) of
25 20 - 150 Oersted, a saturation magnetization (σ_s) of 50 - 200 emu/g, particularly 50 - 100 emu/g, and a residual magnetization (σ_r) of 2 - 20 emu/g.

The magnetic material may be contained in the toner in a proportion of 10 - 200 wt. parts, preferably 20 - 150 wt. parts, per 100 wt. parts of the binder resin.

5 The toner according to the present invention may optionally contain a colorant, inclusive of arbitrary pigments or dyes.

 Examples of the pigment may include: carbon black, aniline black, acetylene black, Naphthol
10 Yellow, Hansa Yellow, Rhodamine Lake, Alizarine Lake, red iron oxide, Phthalocyanine Blue, and Indanthrene Blue. It is preferred to use 0.1 - 20 wt. parts, particularly 1 - 10 wt. parts, of a pigment per 100 wt. parts of the binder resin. For similar purpose,
15 there may also be used dyes, such as azo dyes, anthraquinone dyes, xanthene dyes, and methine dyes, which may preferably be used in an amount of 0.1 - 20 wt. parts, particularly 0.3 - 10 wt. parts, per 100 wt. parts of the resin.

20 In the present invention, it is also possible to incorporate one or two or more species of release agent, as desired, within a toner.

 Examples of the release agent may include: aliphatic hydrocarbon waxes, such as low-molecular
25 weight polyethylene, low-molecular weight polypropylene, microcrystalline wax, and paraffin wax, oxidation products of aliphatic hydrocarbon waxes,

such as oxidized polyethylene wax, and block copolymers of these; waxes containing aliphatic esters as principal constituents, such as carnauba wax, montanic acid ester wax, and partially or totally

5 deacidified aliphatic esters, such as deacidified carnauba wax. Further examples of the release agent may include: saturated linear aliphatic acids, such as palmitic acid, stearic acid, and montanic acid; unsaturated aliphatic acids, such as brassidic acid,

10 eleostearic acid and parinaric acid; saturated alcohols, such as stearyl alcohol, behenyl alcohol, ceryl alcohol, and melissyl alcohol; polyhydric alcohols, such as sorbitol; aliphatic acid amides, such as linoleylamide, oleylamide, and laurylamide;

15 saturated aliphatic acid bisamides, methylene-bisstearylamine, ethylene-biscaprylamide, and ethylene-biscaprylamide; unsaturated aliphatic acid amides, such as ethylene-bisoleylamide, hexamethylene-bisoleylamide, N,N'-dioleyladipoylamide,

20 and N,N'-dioleylsebacoylamide, aromatic bisamides, such as m-xylene-bisstearoylamide, and N,N'-distearylisophthaloylamide; aliphatic acid metal salts (generally called metallic soap), such as calcium stearate, calcium laurate, zinc stearate, and

25 magnesium stearate; grafted waxes obtained by grafting aliphatic hydrocarbon waxes with vinyl monomers, such as styrene and acrylic acid; partially esterified

products between aliphatic acids and polyhydric alcohols, such as behenic acid monoglyceride; and methyl ester compounds having hydroxyl group as obtained by hydrogenating vegetable fat and oil.

5 The particularly preferred class of release agent in the present invention may include aliphatic hydrocarbon waxes because of good dispersibility within the binder resin (preferably one having an acid value of 5 - 50), thus providing not only a good
10 fixability of the resultant toner but also a minimum abrasion of an organic photoconductor when used in combination with the toner according to the present invention.

 Specific examples of the release agent
15 preferably used in the present invention may include e.g., a low-molecular weight alkylene polymer obtained through polymerization of an alkylene by radical polymerization under a high pressure or in the presence of a Ziegler catalyst under a low pressure;
20 an alkylene polymer obtained by thermal decomposition of an alkylene polymer of a high molecular weight; and a hydrocarbon wax obtained by subjecting a mixture gas containing carbon monoxide and hydrogen to the Arge process to form a hydrocarbon mixture and distilling
25 the hydrocarbon mixture to recover a residue.

Fractionation of wax may preferably be performed by the press sweating method, the solvent method, vacuum

distillation or fractionating crystallization. As the source of the hydrocarbon wax, it is preferred to use hydrocarbons having up to several hundred carbon atoms as obtained through synthesis from a mixture of carbon monoxide and hydrogen in the presence of a metal oxide catalyst (generally a composite of two or more species), e.g., by the Synthol process, the Hydrocol process (using a fluidized catalyst bed), and the Arge process (using a fixed catalyst bed) providing a product rich in waxy hydrocarbon, and hydrocarbons obtained by polymerizing an alkylene, such as ethylene, in the presence of a Ziegler catalyst, as they are rich in saturated long-chain linear hydrocarbons and accompanied with few branches. It is further preferred to use hydrocarbon waxes synthesized without polymerization because of their structure and molecular weight distribution suitable for easy fractionation.

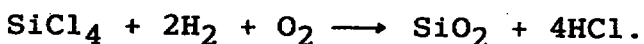
As for the molecular weight distribution of the wax, it is preferred that the wax shows a peak in a molecular weight region of 400 - 2400, further 450 - 2000, particularly 500 - 1600. By satisfying such molecular weight distribution, the resultant toner is provided with preferable thermal characteristics.

The release agent may preferably be used in an amount of 0.1 - 20 wt. parts, particularly 0.5 - 10 wt. parts, per 100 wt. parts of the binder resin.

The release agent may be uniformly dispersed in the binder resin by a method of mixing the release agent in a solution of the resin at an elevated temperature under stirring or melt-kneading the binder resin together with the release agent.

A flowability-improving agent may be optionally blended with the toner to improve the flowability of the toner. Examples thereof may include: powder of fluorine-containing resin, such as polyvinylidene fluoride fine powder and polytetrafluoroethylene fine powder; titanium oxide fine powder, hydrophobic titanium oxide fine powder; fine powdery silica such as wet-process silica and dry-process silica, and treated silica obtained by surface-treating such fine powdery silica with silane coupling agent, titanium coupling agent, silicone oil, etc.

A preferred class of the flowability-improving agent includes dry process silica or fumed silica obtained by vapor-phase oxidation of a silicon halide. For example, silica powder can be produced according to the method utilizing pyrolytic oxidation of gaseous silicon tetrachloride in oxygen-hydrogen flame, and the basic reaction scheme may be represented as follows:



In the above preparation step, it is also

possible to obtain complex fine powder of silica and other metal oxides by using other metal halide compounds such as aluminum chloride or titanium chloride together with silicon halide compounds. Such
5 is also included in the fine silica powder to be used in the present invention.

It is preferred to use fine silica powder having an average primary particle size of 0.001 - 2 μm , particularly 0.002 - 0.2 μm .

10 Commercially available fine silica powder formed by vapor phase oxidation of a silicon halide to be used in the present invention include those sold under the trade names as shown below.

	AEROSIL	130
15	(Nippon Aerosil Co.)	200
		300
		380
		TT 600
		MOX 170
20		MOX 80
		COK 84
	Cab-O-Sil	M-5
	(Cabot Co.)	MS-7
		MS-75
25		HS-5
		EH-5
	Wacker HDK	N 20

(WACKER-CHEMIE GMBH) V 15
N 20E
T 30
T 40

5 D-C Fine Silica
(Dow Corning Co.)
Fransol
(Fransil Co.)

It is further preferred to use treated silica
10 fine powder obtained by subjecting the silica fine
powder formed by vapor-phase oxidation of a silicon
halide to a hydrophobicity-imparting treatment. It is
particularly preferred to use treated silica fine
powder having a hydrophobicity of 30 - 80 as measured
15 by the methanol titration test.

Silica fine powder may be imparted with a
hydrophobicity by chemically treating the powder with
an organosilicone compound, etc., reactive with or
physically adsorbed by the silica fine powder.

20 Example of such an organosilicone compound
may include: hexamethyldisilazane, trimethylsilane,
trimethylchlorosilane, trimethylethoxysilane,
dimethyldichlorosilane, methyltrichlorosilane,
allyldimethylchlorosilane, allylphenyldichlorosilane,
25 benzyldimethylchlorosilane, bromomethyl-
dimethylchlorosilane, α -chloroethyltrichlorosilane,
 β -chloroethyltrichlorosilane, chloromethyldimethyl-

chlorosilane, triorganosilylmercaptans such as trimethylsilylmercaptan, triorganosilyl acrylates, vinyl dimethylacetoxysilane, dimethylethoxysilane, dimethyldimethoxysilane, diphenyldiethoxysilane, 5 hexamethyldisiloxane, 1,3-divinyldimethyltetramethyldisiloxane, 1,3-diphenyldimethyltetramethyldisiloxane, and dimethylpolysiloxane having 2 to 12 siloxane units per molecule and containing each one hydroxyl group bonded to Si at the terminal units. These may be used alone 10 or as a mixture of two or more compounds.

The flowability-improving agent used in the present invention may have a specific surface area of at least 30 m²/g, preferably 50 m²/g, as measured by the BET method according to nitrogen adsorption. The 15 flowability-improving agent may be used in an amount of 0.01 - 8 wt. parts, preferably 0.1 - 4 wt. parts, per 100 wt. parts of the toner.

In case where the toner according to the present invention is used for constituting a two- 20 component type developer, the toner is blended with a carrier. Examples of the carrier used in the present invention may include: surface-oxidized or -unoxidized powder of metals, such as iron, nickel, copper, zinc, cobalt, manganese, chromium and rare earth metals, 25 particles of alloys of these metal, oxide particles, and ferrite particles.

A coated carrier obtained by coating the

above carrier particles with a resin may preferably be used particularly in a developing method wherein a developing bias is supplied with an AC bias voltage. The coating may be performed according to known
5 methods inclusive of a method applying a coating liquid obtained by dissolving or suspending a coating material such as a resin into a solvent onto the surface of carrier core particles, and a method of powder blending carrier core particles and a coating
10 material.

Examples of the coating material firmly applied onto the core particles may include: polytetrafluoroethylene, monochlorotrifluoroethylene polymer, polyvinylidene fluoride, silicone resin,
15 polyester resin, styrene resin, acrylic resin, polyamide, polyvinyl butyral, aminoacrylate resin, basic dyes and lakes thereof, silica fine powder and alumina fine powder. These coating materials may be used singly or in combination of plural species.

20 The coating material may be applied onto the core particles in a proportion of 0.1 - 30 wt. %, preferably 0.5 - 20 wt. %, based on the carrier core particles. The carrier may preferably have an average particle size of 10 - 100 μm , more preferably
25 20 - 70 μm .

A particularly preferred type of carrier may comprise particles of a magnetic ferrite such as Cu-

Zn-Fe ternary ferrite surface-coated with a fluorine-containing resin or a styrene-based resin. Preferred coating materials may include mixtures of a fluorine containing resin and a styrene copolymer, such as a
5 mixture of polyvinylidene fluoride and styrene-methyl methacrylate resin, and a mixture of polytetrafluoroethylene and styrene-methyl methacrylate resin. The fluorine-containing resin may also be a copolymer, such as vinylidene
10 fluoride/tetrafluoroethylene (10/90 - 90/10) copolymer. Other examples of the styrene-based resin may include styrene/2-ethylhexyl acrylate (20/80 - 80/20) copolymer and styrene/2-ethylhexyl acrylate/methyl methacrylate (20 - 60/5 - 30/10 - 50)
15 copolymer. The fluorine-containing resin and the styrene-based resin may be blended in a weight ratio of 90:10 - 20:80, preferably 70:30 - 30:70. The coating amount may be 0.01 - 5 wt. %, preferably 0.1 - 1 wt. % of the carrier core.

20 The coated magnetic ferrite carrier may preferably include at least 70 wt. % of particles of 250 mesh-pass and 400 mesh-on, and have an average particle size of 10 - 100 μm , more preferably 20 - 70 μm . A sharp particle size distribution is
25 preferred.

The characteristic values of a binder resin and a long-chain alkyl compound and the particle size

distribution of a toner referred to herein may be measured according to the following methods.

(1) Glass transition temperature T_g

Measurement may be performed in the following manner by using a differential scanning calorimeter ("DSC-7", available from Perkin-Elmer Corp.).

A sample in an amount of 5 - 20 mg, preferably about 10 mg, is accurately weighed.

The sample is placed on an aluminum pan and subjected to measurement in a temperature range of 30 - 200 °C at a temperature-raising rate of 10 °C/min in a normal temperature - normal humidity environment in parallel with a blank aluminum pan as a reference.

In the course of temperature increase, a main absorption peak appears in the temperature region of 40 - 100 °C.

In this instance, the glass transition temperature is determined as a temperature of an intersection between a DSC curve and an intermediate line pressing between the base lines obtained before and after the appearance of the absorption peak.

(2) Molecular weight distribution (for binder resin)

The molecular weight (distribution) of a binder resin may be measured based on a chromatogram obtained by GPC (gel permeation chromatography).

In the GPC apparatus, a column is stabilized in a heat chamber at 40 °C, tetrahydrofuran (THF)

solvent is caused to flow through the column at that temperature at a rate of 1 ml/min., and 50 - 200 μ l of a GPC sample solution adjusted at a concentration of 0.05 - 0.6 wt. % is injected. The identification of sample molecular weight and its molecular weight distribution is performed based on a calibration curve obtained by using several monodisperse polystyrene samples and having a logarithmic scale of molecular weight versus count number. The standard polystyrene samples for preparation of a calibration curve may be available from, e.g., Pressure Chemical Co. or Toso K.K. It is appropriate to use at least 10 standard polystyrene samples inclusive of those having molecular weights of, e.g., 6×10^2 , 2.1×10^3 , 4×10^3 , 1.75×10^4 , 5.1×10^4 , 1.1×10^5 , 3.9×10^5 , 8.6×10^5 , 2×10^6 and 4.48×10^6 . The detector may be an RI (refractive index) detector. For accurate measurement, it is appropriate to constitute the column as a combination of several commercially available polystyrene gel columns in order to effect accurate measurement in the molecular weight range of 10^3 - 2×10^6 . A preferred example thereof may be a combination of μ -styrigel 500, 10^3 , 10^4 and 10^5 available from Waters Co.; a combination of Shodex KF-801, 802, 803, 804, 805, 806 and 807 available from Showa Denko K.K.

(3) Molecular weight distribution (for long-chain alkyl compound)

The molecular weight (distribution) of a long-chain alkyl compound may be measured by GPC under the following conditions:

Apparatus: "GPC-150C" (available from Waters Co.)

5 Column: "GMH-HT" 30 cm-binary (available from Toso K.K.)

Temperature: 135 °C

Solvent: o-dichlorobenzene containing 0.1 % of ionol.

10 Flow rate: 1.0 ml/min.

Sample: 0.4 ml of a 0.15 %-sample.

Based on the above GPC measurement, the molecular weight distribution of a sample is obtained once based on a calibration curve prepared by
15 monodisperse polystyrene standard samples, and recalculated into a distribution corresponding to that of polyethylene using a conversion formula based on the Mark-Houwink viscosity formula.

(4) Measurement of acid values and OH values

20 1) re: Acid value

A sample material is accurately weighed and dissolved in a mixture solvent, and water is added thereto. The resultant liquid is titrated with 0.1N-NaOH by potentiometric titration using glass
25 electrodes (according to JIS K1557-1970).

2) re: Hydroxyl value (OH value)

A sample is accurately weighed into a 100 ml-

volumetric flask, and 5 ml of an acetylating agent is accurately added thereto. Then, the system is heated by dipping into a bath of $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$. After 1 - 2 hours, the flask is taken out of the bath and allowed
5 to cool by standing, and water is added thereto, followed by shaking to decompose acetic anhydride. In order to complete the decomposition, the flask is again heated for more than 10 min. by dipping into the bath. After cooling, the flask wall is sufficiently
10 washed with an organic solvent. The resultant liquid is titrated with a N/2-potassium hydroxide solution in ethyl alcohol by potentiometric titration using glass electrodes (according to JIS K0070-1966).

(5) Particle size distribution measurement

15 Coulter Multisizer II (available from Coulter Electronics Inc.) is used as an instrument for measurement, to which an interface (available from Nikkaki K.K.) for providing a number-basis distribution, and a volume-basis distribution and a
20 personal computer PC 9801 (available from NEC K.K.) are connected.

For measurement, a 1 %-NaCl aqueous solution as an electrolytic solution is prepared by using a reagent-grade sodium chloride. Into 100 to 150 ml of
25 the electrolytic solution, 0.1 to 5 ml of a surfactant (preferably an alkylbenzenesulfonic acid salt) is added as a dispersant, and 2 to 20 mg of a

sample is added thereto. The resultant dispersion of the sample in the electrolytic liquid is subjected to a dispersion treatment for about 1 - 3 minutes by means of an ultrasonic disperser, and then subjected
5 to measurement of particle size distribution in the range of 2 - 40 μm by using the above-mentioned Coulter Multisizer II with a 100 micron-aperture to obtain a volume-basis distribution and a number-basis distribution. Form the results of the volume-basis
10 distribution and number-basis distribution in the range of 2 - 40 μm , a weight-average particle size (D4) is calculated with a central value of each channel taken as a representative value of the channel.

15 Next, an embodiment of the image forming method according to the present invention will be described with reference to Figures 1 - 3. Figure 1 shows an electrophotographic apparatus usable as an example of a copying machine or a printer for
20 practicing the image forming method according to the present invention. The apparatus includes a developing means 1 containing a toner 13 according to the present invention. The toner may be a magnetic toner or a non-magnetic toner. In an image forming
25 apparatus other than the one shown in Figure 1, it is possible to use a developing means including a two-component type developer comprising a toner and a

carrier.

Referring again to Figure 1, the surface of a photosensitive member 3 (e.g., an OPC photosensitive drum, an amorphous silicon photosensitive drum or a polysilicon photosensitive drum) is charged by a charging means 11 (e.g., a contact charging means such as a charging roller as shown, a charging brush or a charging blade) supplied with a voltage from a bias voltage application means 34. Then, the charged surface of the photosensitive member 3 is irradiated with light 5 (e.g., laser light or light from a halogen lamp) carrying image data to form an electrostatic image on the photosensitive member. The electrostatic image is developed with a magnetic toner 13 (in this embodiment) on a developing sleeve 6 enclosing a magnetic field generating means 15 (e.g., a magnet) of the developing means 1 also equipped with a toner applicator blade 8 (e.g., an elastic blade or a magnetic blade) for applying the toner 13 onto the developing sleeve 6. The development is performed by either the normal development scheme or the reversal development scheme to form a toner image on the photosensitive member 3. At the developing station, the developing sleeve may be supplied, as desired, with an alternating, a pulse, and/or a DC bias voltage from a bias voltage application means 12. When the toner image on the photosensitive member 3 arrives at

a transfer station to which also a transfer material is conveyed, the back side (side opposite the photosensitive member 3) of the transfer member P is pressed and charged by a transfer means 4 (e.g., a transfer roller as shown or a transfer belt) to which a voltage is applied from a bias application means 33, to electrostatically transfer the toner image on the photosensitive member 3 onto the transfer material P. As the case may be, the toner image on the photosensitive member 3 can be transferred onto an intermediate transfer member (not shown, such as an intermediate transfer drum or an intermediate transfer belt) and then to the transfer material P.

The toner image on the transfer material P separated from the photosensitive member 3 may be fixed onto the transfer material P by a heat-and-pressure application means 35 (e.g., a fixing means as shown wherein a pressure roller 23 is pressed against a fixed heat-generating member 21 via a heat-resistant sheet 22; or a heat-pressure roller fixing means). A portion, if any, of the toner remaining on the photosensitive member 3 after the transfer step may be removed, as desired, from the surface of the photosensitive member 3 by a cleaning means 7 (e.g., a cleaning blade as shown, a cleaning roller or a cleaning brush). The photosensitive member 3 after the cleaning is again subjected to an image forming

cycle as described above starting from the charging step by the charging means 11.

The photosensitive member 3 as a member to be charged and also an electrostatic image-bearing member generally comprises a photosensitive layer and an electroconductive substrate and is rotated in the direction of an arrow as indicated. The developing sleeve 6 comprising a non-magnetic cylinder as a toner carrying member is rotated in the same direction as the photosensitive member 3 at the developing station. Inside the developing sleeve 6, a multi-polar permanent magnet (magnet roll) 15 as a magnetic field-generating means is fixedly disposed. The magnetic toner 13 contained inside the developing means 1 is applied by the applicator blade 8 onto the surface of the developing sleeve, and the toner particles constituting the toner are triboelectrically charged by friction with the applicator blade 8 and/or the developing sleeve 6. The toner may be uniformly applied by the applicator blade 8 in a layer of e.g., 10 - 300 μm on the surface of the developing sleeve 6. At the developing station, the developing sleeve 6 may be supplied with an AC bias voltage of $f = 200 - 4000$ Hz and $V_{pp} = 500 - 3000$ V.

At the developing station, toner particles are transferred onto the electrostatic image on the photosensitive member due to the electrostatic force

of the photosensitive member surface and the action of an AC or pulse bias voltage.

Incidentally, in Examples described hereinafter, an image forming apparatus having
5 structure as shown in Figures 1 to 3 was used, of which the included members are denoted by reference numerals as shown below.

That is, reference numeral 3 denotes an electrostatic image-bearing member (photosensitive
10 drum); 11, a charger (charging roller); 2, a process-cartridge; 7, a cleaning means; 5, an exposure means; 15, a developer container; 6, a developer-carrying member (developing sleeve); 15, a magnetic field generating means; 8, a layer thickness-regulating
15 elastic member; 4, a transfer means (transfer roller); 20, a stay; 21, a heating member; 21a, a heater substrate; 21b, a heat-generating member; 21c, a surface protective layer; 21d, a temperature-detecting element; 22, a fixing film; 23, a pressing roller; 24,
20 a coil spring; 25, a film edge-regulating member; 26, an electricity-supplying connector; 27, an electricity interrupting member; 28, an inlet guide; and 29, an outlet guide (separation guide).

Further, Figure 5 is a schematic sectional
25 view of a process-cartridge detached from a main body of an image forming apparatus as described above. The process-cartridge at least includes a developing means

and an electrostatic image-bearing member which are integrated into a cartridge, so as to be detachably mountable to a main body of an image forming apparatus, such as a copying machine or a laser beam
5 printer.

In this embodiment shown in Figure 5, the process-cartridge integrally includes a developing means 1, a drum-shaped electrostatic image bearing member (photosensitive drum) 3, a cleaner including a
10 cleaning blade 7, and a primary charger (charging roller) 11.

In this embodiment, the developing means 1 includes a toner layer thickness-regulating member 8 and a toner vessel containing a magnetic toner 13. At
15 the time of development, a prescribed bias electric field is applied between the photosensitive drum 3 and the developing sleeve 6 carrying the magnetic toner 13 to effect a development of an electrostatic image formed on the photosensitive drum 3.

20 Hereinbelow, the present invention will be described based on specific Examples.

Resin Production Example 1

	Terephthalic acid	12 mol. %
	Fumaric acid	18 mol. %
25	Adipic acid	10 mol. %
	Trimellitic anhydride	12 mol. %
	Bisphenol derivatives of the above-	

described formula (A)

(R = propylene, $x + y = 2.2$) 15 mol. %

(R = ethylene, $x + y = 2.2$) 33 mol. %

The above ingredients were subjected to poly-
5 condensation to obtain a polyester (called "Resin A")
having $M_n = 5,000$, $M_w = 57,000$, $T_g = 60^\circ\text{C}$, acid
value = 20, OH value = 20.

Resin Production Example 2

	Styrene	87 wt.parts
10	Butyl acrylate	13 "
	Di-tert-butyl peroxide	3 "

The above ingredients were added dropwise in
4 hours to 200 wt. parts of xylene heated to the
reflux temperature. Further, the polymerization was
15 completed under xylene reflux ($138 - 144^\circ\text{C}$), followed
by heating to 200°C under a reduced pressure to
remove the xylene. The thus-obtained resin is called
"Resin B".

	Styrene	75 wt.part (s)
20	Butyl acrylate	25 "
	2,2-Bis(4,4-di-tert-butyl- peroxycyclohexyl)propane	0.1 "
	Benzoyl peroxide	0.1 "

To a mixture liquid comprising the above
25 ingredients, 170 wt. parts of water containing 0.12
wt. part of partially saponified polyvinyl alcohol was
added, and the system as vigorously stirred to form a

suspension liquid. The suspension liquid was added to a reaction vessel containing 50 wt. parts of water and aerated with nitrogen, and was subjected to suspension polymerization at 80 °C for 8 hours. After the

5 reaction, the product was washed to obtain Resin C.

The above Resin B and Resin C at a weight ratio of 70:30 were dissolved in xylene and uniformly mixed, followed by removal of xylene to obtain Resin D, which showed a molecular weight distribution
10 providing peaks at molecular weights of 1.2×10^4 and 8×10^5 , M_n (number-average molecular weight) = 0.7×10^4 and M_w (weight-average molecular weight) = 2.5×10^5 , and $T_g = 61$ °C.

Resin Production Example 3

15	Styrene	80.0 wt.parts
	Butyl acrylate	10.0 "
	Monobutyl maleate	10.0 "
	Di-tert-butyl peroxide	6.0 "

Resin E was prepared from the above
20 ingredients otherwise in the same manner as in production of Resin B in Resin Production Example 2 above.

	Resin E	40.0 wt.part(s)
	Styrene	45.0 "
25	Butyl acrylate	15.0 "
	Divinylbenzene	0.5 "
	Benzoyl peroxide	0.5 "

A mixture liquid comprising the above ingredients was subjected to suspension polymerization in the same manner as in production of Resin C in Resin Production Example 2 to obtain Resin F, which showed $T_g = 60^\circ\text{C}$, $M_n = 1 \times 10^4$ and $M_w = 1 \times 10^5$.

Example 1

Resin A 100 wt.parts

Magnetic iron oxide 90 wt.parts

(average particle size ($D_{av.}$) = $0.15 \mu\text{m}$,

10 $H_c = 115$ oersted, $\sigma_s = 80$ emu/g,

$\sigma_r = 11$ emu/g)

Long-chain alkyl alcohol of

Formula (1) 3 wt.parts

($x = 48$ as an average value, $M_n = 440$,

15 $M_w = 870$, $M_w/M_n = 1.98$, OH value = 66)

Azo-type iron complex (1) 2 wt.%

($A^+ = 90\%:\text{NH}_4$, $10\%:\text{Na}^+$ and H^+

mixture; S_{MeOH} (solubility in methanol)

= $0.87 \text{ g}/100 \text{ ml}$)

20 The above ingredients were pre-mixed by a Henschel mixer and melt-kneaded through a twin screw extruder at 130°C . After cooling, the melt-kneaded product was coarsely crushed by a cutter mill, pulverized by a jet stream pulverizer, and classified
25 by a pneumatic classifier to obtain a magnetic toner (1) having a weight-average particle size (D_4) of $6.6 \mu\text{m}$, content of $\leq 5 \mu\text{m}$ particles: 49.3% (N, % by

number), 9.6 % (V, % by volume). The characterizing data of the toner are summarized in Table 1.

The localization factors of the azo-type iron complex in the fine and coarse power fractions were

5 $OD_F/OD_M = 1.012$ and $OD_G/OD_M = 0.998$.

100 wt. parts of the magnetic toner (1) and 1.0 wt. part of hydrophobic silica surface-treated with hexamethyldisilazane were blended in a Henschel mixer to obtain Developer No. 1.

10 The thus-obtained Developer No. 1 was charged in a commercially available digital copying machine ("GP-55", available from Canon K.K.) and subjected to image formation of 5×10^4 sheets under normal temperature/low humidity (N/L = 23.5 °C/5 %RH)
15 conditions and further 3×10^4 sheets under high temperature/high humidity (H/H = 32.5 °C/80 %RH) conditions. Further, Developer No. 1 was also charged in a commercially available analog copying machine ("NP-9800", available from Canon K.K.) and subjected
20 to image formation of 2×10^5 sheets under the normal temperature/low humidity (N/L) conditions and further 1×10^5 sheets under the high temperature/ high humidity (H/H) conditions. The results of the image formation tests are shown in Tables 3 and 4.

25 In Tables 3 and 4, the evaluation results are indicated by symbols respectively indicating the following performances.

- ⊙: Very good
- o: Good
- oΔ: Practically of no problem
- Δ: Slightly problematic
- 5 x: Practically unacceptable

Further, a commercially available laser beam printer ("LBP-SX", available from Canon K.K.) was remodeled as shown in Figure 1 (schematic view). More specifically, the process cartridge 2 was equipped with a urethane rubber-made electric blade 8 and a charging roller 9. Further, the main body was equipped with a charging roller 4 and the heat-fixing apparatus was remodeled into an apparatus 35 shown in Figure 1, Figure 2 (exploded perspective view) and Figure 3 (sectional view). Image formation was performed by using Developer No. 1 under the following conditions.

An OPC photosensitive member 3 was primarily charged at a potential of -600 volts and exposed to form an electrostatic latent image thereon having a light part potential V_L of -150 volts. At the developing station, the photosensitive drum 3 and the developing sleeve 6 (enclosing a magnet 15) were disposed with a gap of 300 μm so that the developer layer on the sleeve 6 did not contact the photosensitive member 3, and an AC bias ($f = 1800 \text{ Hz}$, $V_{pp} = 1500 \text{ V}$ and a DC bias ($V_D = -400 \text{ V}$) were applied

in superposition from a bias application means 12 to the developing sleeve 6, thereby developing the electrostatic latent image by a reversal development scheme to form a toner image on the OPC photosensitive member 3. The thus-formed toner image was transferred onto plain paper by applying a positive transfer potential and the plain paper carrying the toner image was applied through the heat fixing apparatus 35 to fix the toner image onto the plain paper. In the heat-fixing apparatus, the surface temperature detected by a sensor element 21d of a heating member 21 was set to 130 °C, and a total pressure of 6 kg was applied between the heating member 21 and a pressing roller 23 with a nip of 3 mm between the pressing roller 23 and a fixing film 22. The fixing film 22 comprised a 50 µm-thick heat-resistant polyimide film coated, on its side contacting the transfer material P, with a low-resistivity release layer comprising polytetrafluoroethylene with an electroconductive substance dispersed therein.

Under the above set conditions, an image formation test (a printing test) was performed continuously for 7000 A4-sheets at a rate of 8 A4-sheets/min. while replenishing the developer as required under normal temperature/normal humidity (N/N = 25 °C/60 %RH) conditions.

Similar image formation tests were performed

under high temperature/high humidity (H/H = 32.5 °C/90 %RH) conditions and low temperature/low humidity (L/L = 10 °C/15 %RH) conditions. In the high temperature - high humidity environment, after a 6500 sheets image formation test, the apparatus and developer were left standing for 5 days in the same environment and then further subjected to a 500 sheet image formation test.

The results are shown in Tables 5 and 6.

Examples 2 - 21 and Comparative Examples 1 - 8

10 Toners having particle size distributions respectively shown in Table 1 were prepared in the same manner as in Example 1 except that prescriptions also shown in Table 1 were used. (In Table 1, values x, y and z are average values.) The localization factors of the metal complex compounds (inclusive of 15 azo-type iron complex compound used in Examples) for the respective toners are shown in Table 2. From these toners, Developers Nos. 2 - 21 and Comparative Developers Nos. 1 - 8 were prepared in the same manner as in Example 1. 20

The resultant developers were respectively evaluated by the same image formation as in Example 1. The results are summarized in Tables 3 - 6.

25 The evaluation items listed in Tables 3 - 6 are supplemented hereinbelow.

<Evaluation by Digital copier GP-55 and Analog copier NP-9800 (Tables 3 and 4)>

The image resolution was evaluated as follows. An original image was prepared so as to comprise 12 types of resolution images including different number of thin lines per mm, i.e., 2.8, 3.2, 3.6, 4.0, 4.5, 5.0, 5.6, 6.3, 7.1, 8.0, 9.0 and 10.0 lines/mm, respectively, each type including 5 thin lines spaced regularly so as to have a line width and a spacing which were equal to each other. A copy image was prepared by reproducing the original image under the respective image forming conditions and observed through a magnifying glass, whereby the largest number of lines/mm at which the adjacent lines could be observed clearly separately was taken as a resolution.

Higher number means a higher resolution.
<Evaluation by Laser beam printer LBP-SX (Tables 5 and 6)>

The evaluation was performed in the following manners for the respective items.

(1) Image density

The density of an image formed on an ordinary plain paper for copying machine (75 g/m²) after printing 7000 sheets was evaluated by a MacBeth Reflection Densitometer (available from MacBeth Co.) as a relative density against a density of 0.00 allotted to a printed white background portion.

(2) Fog

Image fog (%) was evaluated as a difference between the whiteness of a white background portion of a printed image and the whiteness of an original transfer paper by measurement with "Reflectometer" (available from Tokyo Denshoku K.K.). A fog value exceeding 4 % is practically problematic.

(3) Image quality

A checker pattern shown in Figure 4 was printed out and the dot reproducibility was evaluated by counting the number of lacked dots. The results were evaluated according to the following standards:

- (very good): lack of 2 dots or less/100 dots
- o (good): lack of 3 - 5 dots/100 dots
- △ (fair): lack of 6 - 10 dots/100 dots
- x (poor): lack of 11 dots or more/100 dots

(4) Fixability

A fixed image was rubbed with a soft tissue paper under a load of 50 g/cm², and the fixability was evaluated by a lowering (%) in image density after the rubbing. The results were evaluated according to the following standards.

- (excellent): 5 % or below
- o (good): at least 5 % and below 10 %
- △ (fair): at least 10 % and below 20 %
- x (poor): at least 20 %

(5) Anti-offset characteristic

A sample image having an image percentage

of about 5 % was printed out, and the anti-offset characteristic was evaluated by the degree of s soiling on the image after printing of 3000 sheets. The results were evaluated by the following standards.

- ⊙: Very good (non-observable)
- o: Good (substantially non-observable)
- Δ: Fair
- x: Poor

10 (6) Sleeve soiling

After the printing test, the state of residual toner sticking onto the developing sleeve surface and the influence thereof on the printed images were evaluated by observation with eyes. The results were evaluated according to the following standards.

- ⊙: Very good (not observable)
- o: Good (substantially non-observable)
- Δ: Fair (sticking was observed but did not affect the images)
- x: Poor (much sticking was observed and resultant in image irregularity)

20 (7) Film soiling

After the printing test, the state of residual toner sticking onto the surface of the fixing film was evaluated by observation with eyes. The results are evaluated according to the following

standards.

- ⊙: Very good (not observable)
- o: Good (substantially non-observable)
- Δ: Fair
- x: Poor

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Table 1: Toner Description and Particle Size

Ex. or Comp.Ex.	Internal prescription					Particle size			
	Resin	Magnetic iron oxide	Long-chain alkyl compound (or related compound)	Release agent	Azo-type iron complex (or related metal complex)	D ₄ (μ m)	N (%) $\leq 5\mu$ m	V (%) $\leq 5\mu$ m	N/V
Ex. 1	A : 100 wt.parts	Dav = 0.15 μ m Hc = 115 Oe σ_s = 80 emu/g σ_r = 11 emu/g 90 wt.parts	Formula (1) (alcohol) x = 48, Mn = 440, Mw = 870, Mw/Mn = 1.98, OH value = 66 3 wt.parts	None	Complex (1) (NH ₄ ⁺ : 90 %, Na ⁺ , H ⁺ : 10 %, S _{MeOH} = 0.87 g/100 ml) 2 wt.parts	6.6	49.3	19.6	2.5
Ex. 2	ditto	ditto	ditto	None	Complex (1) (NH ₄ ⁺ : 80 %, Na ⁺ , H ⁺ , K ⁺ : 20 %, S _{MeOH} = 0.87 g/100 ml) 2 wt.parts	6.0	57.8	28.2	2.0
Ex. 3	ditto	ditto	ditto	None	Complex (2) (NH ₄ ⁺ : 76 %, Na ⁺ , H ⁺ : 24 %, S _{MeOH} = 0.75 g/100 ml) 2 wt.parts	7.2	28.2	8.1	3.5
Ex. 4	ditto	ditto	ditto	None	Complex (3) (NH ₄ ⁺ : 90 %, H ⁺ , K ⁺ : 10 %, S _{MeOH} = 0.71 g/100 ml) 2 wt.parts	7.0	36.5	11.5	3.2

...cont.

Table 1 (continued)

Ex. 5	ditto	ditto	ditto	None	Complex (4) (NH ₄ ⁺ : 98 %, Na ⁺ , H ⁺ : 2 %, S _{MeOH} = 0.65 g/100 ml) 2 wt.parts	7.2	28.7	8.5	3.4
Ex. 6	ditto	ditto	ditto	None	Complex (5) (NH ₄ ⁺ : 90 %, Na ⁺ , H ⁺ : 10 %, S _{MeOH} = 0.65 g/100 ml) 2 wt.parts	7.0	36.1	11.6	3.1
Ex. 7	ditto	ditto	ditto	None	Complex (6) (NH ₄ ⁺ : 90 %, Na ⁺ , H ⁺ : 10 %, S _{MeOH} = 0.76 g/100 ml) 2 wt.parts	7.4	40.4	10.9	3.7
Ex. 8	ditto	ditto	Formula (1) (alcohol) x = 40, Mn = 350, Mw = 710, Mw/Mn = 2.0, OH value = 80 3 wt.parts	None	Same as in Ex. 1	6.7	52.0	21.0	2.5
Ex. 9	ditto	ditto	Formula (1) (alcohol) x = 35, Mn = 290, Mw = 600, Mw/Mn = 2.07 OH value = 89 3 wt.parts	None	ditto	7.2	26.7	7.7	3.5

...cont.

Table 1 (continued)

Ex. 10	ditto	ditto	Formula (1) (alcohol) $x = 140$, $M_n = 1100$, $M_w = 3000$, $M_w/M_n = 2.73$, OH value = 18 3 wt.parts	None	ditto	6.9	32.0	13.5	2.4
Ex. 11	ditto	ditto	Formula (1) (alcohol) $x = 48$, $M_n = 340$, $M_w = 1400$, $M_w/M_n = 4.1$, OH value = 65 3 wt.parts	None	ditto	7.0	38.0	14.2	2.7
Ex. 12	ditto	ditto	Same as in Ex. 1	H.C. wax *1 1 wt.part	ditto	6.8	40.0	12.5	3.2
Ex. 13	ditto	ditto	Formula (2) (alcohol) $x = 55$, $z = 2$, $R = H$, $M_n = 690$, $M_w = 1500$, $M_w/M_n = 2.17$, OH value = 50 3 wt.parts	None	ditto	7.5	35.0	11.7	3.1
Ex. 14	ditto	ditto	Formula (3) (acid) $x = 50$, $M_n = 350$, $M_w = 950$, $M_w/M_n = 2.71$, Acid value = 60 3 wt.parts	None	ditto	6.5	40.3	16.8	2.4

*1: Hydrocarbon wax (peak molecular weight = 600)

...cont.

Table 1 (continued)

Ex. 15	D: 100 wt.parts	ditto	ditto	None	ditto	5.8	59.3	31.5	1.9
Ex. 16	F: 100 wt.parts	ditto	ditto	None	ditto	7.3	30.0	11.1	2.7
Ex. 17	A: 100 wt.parts	ditto	ditto	None	ditto	9.2	9.2	0.8	11.5
Ex. 18	ditto	ditto	ditto	None	ditto	6.5	30.5	14.1	2.2
Ex. 19	A: 100 wt.parts *2 F.P. from Ex. 15 100 wt.parts	ditto	ditto	None	ditto	7.0	35.0	13.5	2.6
Ex. 20	D: 100 wt.parts *2 F.P. from Ex. 15 100 wt.parts	ditto	ditto	None	ditto	6.7	38.0	16.0	2.4
Ex. 21	F: 100 wt.parts *2 F.P. from Ex. 16 100 wt.parts	ditto	ditto	None	ditto	7.2	28.5	9.5	3.0

...cont.

*2: Classified fine powder recovered as a by-product after a classification step in a particular Example indicated.

Table 1 (continued)

Comp.Ex. 1	F: 100 parts F.P. from Ex.16 ^{*2} 100 wt.parts	ditto	LMW polyethylene ^{*3} 3 wt.parts	H.C. wax ^{*1} 1 wt.part	ditto	7.1	30.0	11.2	2.7
Comp.Ex. 2	ditto	ditto	Same as in Ex.1	None	Aluminum complex ^{*4} 2 wt.parts	6.5	33.0	12.8	2.6
Comp.Ex. 3	A: 100 wt.parts	ditto	None	None	Chromium complex ^{*5} 2 wt.parts	6.2	43.0	20.5	2.1
Comp.Ex. 4	ditto	ditto	Formula (1) x = 300, Mn = 2500, Mw = 6100, Mw/Mn = 2.44 OH value = 1.5 3 wt.parts	None	Same as in Ex. 1	7.8	25.7	9.3	2.8
Comp.Ex. 5	A: 100 wt.parts F.P. from ^{*2} Comp.Ex. 2 100 wt.parts	ditto	Same as in Ex. 1	None	ditto	6.6	40.0	18.7	2.1
Comp.Ex. 6	A: 100 wt.parts F.P. from ^{*2} Comp.Ex. 3 100 wt.parts	ditto	None	None	Same as in Comp.Ex.3	6.4	45.3	22.0	2.1

...cont.

*3: Low molecular weight polyethylene (peak molecular weight = 600) produced as an intermediate product for synthesizing a long-chain alkyl alcohol.

*4: 3,5-Di-tert-butylsalicylic acid aluminum complex ($S_{MeOH} = 0.03$ g/100 ml).

*5: Azo-type chromium complex ("Spiron Black TRH", available from Hodogaya Kagaku K.K.; $S_{MeOH} = 0.03$ g/100 ml).

Table 1 (continued)

Comp.Ex. 7	A: 100 wt.parts F.P. from *2 Comp.Ex. 1 100 wt.parts	ditto	LMW polyethylene *3 3 wt.parts (Same as in Comp. Ex.1)	H.C.*1 wax. 1 wt.part	Same as in Ex. 1	6.8	36.0	14.0	2.6
Comp.Ex. 8	A: 100 wt.parts	ditto	None	None	ditto	7.3	31.4	11.0	2.9

Table 2
Localization factors of azo-type iron
complex compounds (and related compounds)

5	Ex. or Comp. Ex.	To classified fine powder OD_F/OD_M	To classified coarse powder OD_G/OD_M
	Ex. 1	1.012	0.998
10	2	1.015	0.990
	3	1.014	0.991
	4	1.014	0.992
	5	1.016	0.988
	6	1.020	0.982
	7	1.013	0.995
	8	1.010	0.998
15	9	1.009	0.997
	10	1.025	0.980
	11	1.015	0.990
	12	1.010	0.997
	13	1.014	0.992
20	14	1.023	0.981
	15	1.020	0.980
	16	1.010	0.997
	17	1.025	0.998
	18	1.013	0.988
25	19	1.010	0.998

...cont.

Table 2 (continued)

	20	1.018	0.997
	21	1.013	0.998
5	Comp. Ex. 1	1.013	0.997
	2*	1.120	0.870
	3*	1.085	0.902
	4	1.012	0.996
	5*	1.210	0.860
10	6*	1.113	0.885
	7	1.019	0.996
	8	1.012	0.998

15 * The contents of aluminum or chromium in
classified fine powder, coarse powder and medium
powder (toner) were respectively measured by the
atomic absorption spectrometry and the ratios among
these values were obtained.

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Table 3: Evaluation by Digital Copier GP-55

Ex. or Comp.Ex	N/L (23.5°C, 5 %RH)								H/H (32.5°C, 80 %RH)				Sticking ^{*5}
	Initial				After 5x10 ⁴ sheets				After 8x10 ⁴ sheets ^{*4}				
	*1 I.D.	Fog	*2 Grad- ation	*3 Res. (lines/mm) L/T	I.D.	Fog	Grad- ation	Res. (lines/mm) L/T	I.D.	Fog	Grad- ation	Res. (lines/mm) L/T	
Ex. 1	1.52	⊙	⊙	10.0/10.0	1.52	⊙	⊙	10.0/10.0	1.48	⊙	⊙	10.0/9.0	○
2	1.50	⊙	⊙	10.0/10.0	1.50	⊙	⊙	10.0/10.0	1.46	⊙	⊙	10.0/9.0	○
3	1.48	○	⊙	9.0/9.0	1.48	○	○	9.0/8.0	1.40	○	○	8.0/8.0	○
4	1.47	○	⊙	9.0/9.0	1.47	○	○	9.0/8.0	1.41	○	○	8.0/8.0	○
5	1.48	○	⊙	9.0/9.0	1.48	○	○	9.0/8.0	1.40	○	○	8.0/8.0	○
6	1.48	○	⊙	9.0/9.0	1.48	○	○	9.0/8.0	1.40	○	○	8.0/8.0	○
7	1.49	○	⊙	9.0/9.0	1.48	○	○	9.0/8.0	1.42	○	○	8.0/8.0	○
8	1.50	⊙	⊙	10.0/10.0	1.50	⊙	⊙	10.0/9.0	1.48	○	⊙	9.0/9.0	○
9	1.50	○	⊙	9.0/9.0	1.48	⊙	⊙	9.0/8.0	1.46	⊙	⊙	8.0/7.1	○
10	1.50	○	○	9.0/9.0	1.50	○	○	9.0/9.0	1.42	○	○	9.0/8.0	○

Notes to Table 3

...cont.

- *1: Image density, *2: Density gradation reproduction,
 *3: Resolution (lines/mm) (longitudinal/transverse),
 *4: Cumulative member (after 3x10⁴ sheets in high temperature/high humidity),
 *5: Melt-sticking of toner onto photosensitive member.

Table 3 (continued)

Ex. 11	1.50	○	○	10.0/10.0	1.50	○△	○△	9.0/9.0	1.39	○	○△	8.0/8.0	○
12	1.52	⊙	⊙	10.0/10.0	1.52	⊙	⊙	10.0/10.0	1.47	⊙	⊙	10.0/9.0	○
13	1.48	⊙	⊙	9.0/9.0	1.48	○	○	9.0/8.0	1.40	○	○	8.0/7.1	○
14	1.48	○	○	9.0/9.0	1.48	○△	○△	8.0/7.1	1.40	○△	○△	8.0/7.1	○
15	1.50	⊙	⊙	10.0/9.0	1.50	○	○	9.0/9.0	1.46	○	○	9.0/8.0	○
16	1.52	⊙	⊙	10.0/10.0	1.52	⊙	⊙	10.0/9.0	1.48	○	○	9.0/9.0	○
17	1.52	⊙	⊙	10.0/10.0	1.42	○△	○△	9.0/8.0	1.40	○	○	9.0/9.0	○
18	1.52	⊙	⊙	10.0/10.0	1.42	⊙	⊙	9.0/8.0	1.46	⊙	⊙	8.0/7.1	○
19*	1.52	⊙	⊙	10.0/10.0	1.52	⊙	⊙	10.0/9.0	1.46	⊙	⊙	9.0/9.0	○
20*	1.50	⊙	⊙	10.0/9.0	1.47	○	○	9.0/8.0	1.42	○	○	8.0/8.0	○
21*	1.52	⊙	⊙	10.0/10.0	1.50	⊙	⊙	9.0/9.0	1.44	○	○	9.0/8.0	○
Comp. Ex. 1	1.30	○	x	7.1/7.1	1.20	△	x	6.3/5.6	1.04	△	x	5.6/5.6	○
2	1.35	○	x	7.1/7.1	1.30	△	x	6.3/5.6	1.02	x	x	3.6/3.6	○
3	1.40	○	△	9.0/8.0	1.30	△	x	8.0/8.0	1.10	△	x	6.3/5.6	○
4	1.40	○	○	8.0/8.0	1.35	○△	△	6.3/5.6	1.30	△	△	5.6/5.6	○
5*	1.30	△	x	7.1/6.3	1.27	△	x	5.6/5.6	0.95	x	x	Failed	○
6*	1.33	△	x	7.1/6.3	1.10	△	x	6.3/6.3	1.00	x	x	Failed	○
7*	1.28	○	x	5.6/5.6	1.20	△	x	5.6/5.6	1.02	x	x	2.8/2.8	○
8	1.30	△	x	7.1/6.3	1.15	x	x	6.3/5.6	1.00	△	x	3.6/3.6	△

*: Recovered fine powder re-utilized.

Table 4: Evaluation by Analog Copier NP-9800

Ex. or Comp.Ex.	N/L (23.5°C, 5 %RH)						H/H (32.5°C, 80 %RH)					*6 Storage	*5 Sticking
	Initial			After 2x10 ⁵ sheets			After 3x10 ⁵ sheets ^{*7}			After 1 M in H/H ^{*8}			
	*1 I.D.	Fog	*3 Res. (lines/mm) L/T	I.D.	Fog	Res. (lines/mm) L/T	I.D.	Fog	Res. (lines/mm) L/T	I.D.	Fog		
Ex. 1	1.45	⊙	10.0/10.0	1.45	⊙	10.0/10.0	1.45	⊙	9.0/9.0	1.42	⊙	○	○
2	1.43	⊙	10.0/10.0	1.43	⊙	10.0/10.0	1.42	⊙	9.0/9.0	1.40	⊙	○	○
3	1.40	⊙	9.0/9.0	1.40	⊙	9.0/8.0	1.39	○	8.0/8.0	1.36	○	○	○
4	1.42	⊙	9.0/9.0	1.40	⊙	9.0/8.0	1.40	○	8.0/8.0	1.37	○	○	○
5	1.41	⊙	9.0/9.0	1.40	⊙	8.0/8.0	1.39	○	8.0/7.1	1.36	○	○	○
6	1.44	⊙	8.0/8.0	1.42	⊙	8.0/8.0	1.40	○	8.0/7.1	1.37	○	○	○
7	1.42	⊙	9.0/8.0	1.41	⊙	8.0/8.0	1.40	○	8.0/7.1	1.37	○	○	○
8	1.44	⊙	10.0/10.0	1.44	⊙	10.0/9.0	1.42	○	9.0/8.0	1.40	○	○	○
9	1.42	⊙	10.0/10.0	1.43	⊙	9.0/9.0	1.43	⊙	8.0/7.1	1.41	○	○	○
10	1.45	⊙	10.0/10.0	1.43	⊙	9.0/9.0	1.42	○	9.0/9.0	1.38	○	○	○
11	1.42	⊙	10.0/10.0	1.40	○	10.0/9.0	1.38	○	8.0/7.1	1.35	⊙Δ	⊙Δ	○

...cont.

Notes to Table 4

*1, *3, *4, *5: Same as in Table 3

*6: Storage stability, *7: Cumulative (after 1x10⁵ sheets in H/H),

*8: After standing for 1 month in the H/H environment.

Table 4 (continued)

Ex. 12	1.45	⊙	10.0/10.0	1.45	⊙	10.0/10.0	1.44	⊙	9.0/8.0	1.42	⊙	○	○
13	1.41	⊙	9.0/9.0	1.40	⊙	9.0/8.0	1.38	⊙	8.0/8.0	1.35	⊙	○	○
14	1.43	○	9.0/9.0	1.40	⊙Δ	9.0/8.0	1.38	⊙Δ	8.0/8.0	1.36	⊙Δ	○	○
15	1.45	⊙	10.0/10.0	1.44	⊙	10.0/9.0	1.41	⊙	9.0/8.0	1.40	○	○	○
16	1.44	⊙	10.0/10.0	1.43	⊙	10.0/10.0	1.42	⊙	9.0/8.0	1.40	⊙	○	○
17	1.44	○	9.0/9.0	1.37	⊙Δ	8.0/7.1	1.40	⊙Δ	8.0/7.1	1.35	⊙Δ	○	○
18	1.42	⊙	10.0/10.0	1.40	⊙	10.0/10.0	1.45	⊙	9.0/9.0	1.43	⊙	○	○
19*	1.45	⊙	10.0/10.0	1.44	⊙	10.0/10.0	1.44	⊙	9.0/8.0	1.42	⊙	○	○
20*	1.44	⊙	10.0/10.0	1.44	⊙	9.0/9.0	1.44	⊙	8.0/8.0	1.40	⊙	○	○
21*	1.43	⊙	10.0/10.0	1.43	⊙	10.0/9.0	1.43	⊙	9.0/8.0	1.40	⊙	○	○
Comp. Ex. 1	1.30	○	7.1/7.1	1.12	Δ	5.6/5.6	1.22	Δ	5.0/4.0	1.00	x	○	○
2	1.37	○	7.1/7.1	1.0	Δ	7.1/6.3	1.00	x	**	0.80	x	○	○
3	1.40	○	9.0/8.0	1.35	Δ	7.1/7.1	1.30	⊙Δ	6.3/6.3	1.25	Δ	○	○
4	1.37	○	8.0/8.0	1.25	Δ	6.3/5.6	1.15	Δ	3.6/3.6	1.10	Δ	○	○
5*	1.20	○	6.3/5.6	1.10	Δ	5.6/3.6	0.95	x	**	0.70	x	○	○
6*	1.30	○	6.3/6.3	1.15	Δ	5.6/3.6	0.97	x	**	0.90	x	○	○
7*	1.30	Δ	6.3/6.3	1.10	x	3.6/3.6	1.17	x	**	0.97	x	○	○
8	1.28	Δ	6.3/5.6	1.12	x	3.2/3.2	1.10	x	**	0.95	x	○	Δ

*: Recovered fine powder re-utilized.

**: Resolution failed.

Table 5: Evaluation by LBP-SX

Ex. or Comp.Ex.	Image density						Fog (both sides)	Image quality
	N/N		L/L	H/H			L/L	H/H
	Initial	Final stage	Final stage	Initial	Final stage standing	Final stage	After 5000 sheets	After 6000 sheets
Ex. 1	1.47	1.46	1.47	1.45	1.42	1.45	1.8	⊙
2	1.46	1.45	1.47	1.44	1.43	1.45	1.8	⊙
3	1.45	1.45	1.46	1.45	1.42	1.43	1.9	○
4	1.46	1.45	1.46	1.44	1.43	1.44	2.1	○
5	1.45	1.45	1.46	1.45	1.43	1.44	2.2	○
6	1.45	1.45	1.45	1.44	1.42	1.43	2.3	○
7	1.46	1.45	1.45	1.44	1.42	1.43	1.9	○
8	1.45	1.44	1.46	1.44	1.43	1.44	1.9	⊙
9	1.46	1.45	1.45	1.44	1.43	1.44	2.0	○
10	1.45	1.44	1.45	1.43	1.42	1.43	2.1	○
11	1.45	1.44	1.45	1.40	1.38	1.39	3.1	△
12	1.45	1.44	1.44	1.43	1.42	1.42	2.5	○
13	1.46	1.45	1.45	1.44	1.42	1.43	2.0	○
14	1.44	1.43	1.44	1.41	1.37	1.39	3.3	△
15	1.46	1.46	1.47	1.46	1.43	1.44	1.8	⊙
16	1.46	1.47	1.46	1.45	1.42	1.45	1.8	⊙
17	1.46	1.46	1.46	1.45	1.42	1.44	1.8	△

...cont.

Table 5 (continued)

Ex. 18	1.46	1.46	1.47	1.45	1.44	1.45	1.7	⊙
19	1.47	1.46	1.47	1.45	1.42	1.45	1.8	⊙
20	1.46	1.45	1.47	1.44	1.42	1.43	1.8	⊙
21	1.46	1.45	1.46	1.44	1.42	1.43	1.8	⊙
Comp.								
Ex. 1	1.35	1.33	1.31	1.28	1.25	1.27	3.0	x
2	1.32	1.30	1.30	1.25	1.21	2.21	4.7	x
3	1.33	1.31	1.30	1.28	1.27	1.28	2.3	Δ
4	1.35	1.33	1.32	1.30	1.28	1.28	4.6	x
5	1.35	1.34	1.33	1.25	1.24	1.23	4.8	x
6	1.33	1.32	1.31	1.26	1.22	1.21	4.9	x
7	1.35	1.32	1.30	1.26	1.24	1.25	3.3	x
8	1.32	1.29	1.28	1.24	1.21	1.22	5.0	x

Table 6
Evaluation of LBP-SX

	Fixability	Anti- offset	Sleeve soil	Film soil
5				
	Ex. 1	⊙	⊙	⊙
	Ex. 2	⊙	⊙	⊙
	Ex. 3	⊙	○	⊙
	Ex. 4	⊙	○	⊙
10	Ex. 5	⊙	○	⊙
	Ex. 6	⊙	○	⊙
	Ex. 7	⊙	○	⊙
	Ex. 8	⊙	⊙	⊙
	Ex. 9	⊙	○	⊙
15	Ex. 10	○	⊙	⊙
	Ex. 11	⊙	Δ	○
	Ex. 12	⊙	○	⊙
	Ex. 13	○	⊙	⊙
	Ex. 14	⊙	Δ	○
20	Ex. 15	⊙	⊙	⊙
	Ex. 16	⊙	⊙	⊙
	Ex. 17	Δ	○	⊙
	Ex. 18	⊙	⊙	⊙
	Ex. 19	⊙	⊙	⊙
25	Ex. 20	⊙	○	⊙

...cont.

Table 6 (continued)

	Ex. 21	○	○	○	○
5	Comp. Ex. 1	○	○	x	△
	Comp. Ex. 2	○	△	△	△
	Comp. Ex. 3	△	x	x	△
10	Comp. Ex. 4	x	△	○	○
	Comp. Ex. 5	○	△	△	△
	Comp. Ex. 6	△	x	x	△
	Comp. Ex. 7	○	△	x	△
15	Comp. Ex. 8	△	x	x	△

20

25

* C L M S *

(a) a binder resin,

$$\text{CH}_3-(\text{CH}_2)_{\overline{x}}-\text{CH}_2\text{OH} \quad (1),$$
$$\text{CH}_3-(\text{CH}_2)_x-\text{O}-\underset{\text{R}}{\underset{|}{\text{CH}}}\text{CH}_2-\text{O})_z-\text{H} \quad (2),$$
$$\text{CH}_3-(\text{CH}_2)_{\text{y}}-\text{CH}_2\text{COOH} \quad (3),$$

(c) an azo-type iron complex compound

(4)



wherein X_1 and X_2 independently denote hydrogen atom,
lower alkyl group, lower alkoxy group, nitro group or
halogen atom; m and m' denote an integer of 1 - 3; R_1
and R_3 independently denote hydrogen atom, C_{1-18} alkyl
5 or alkenyl, sulfonamide, mesyl, sulfonic acid group,
carboxy ester group, hydroxy, C_{1-18} alkoxy,
acetylamino, benzoylamino or halogen atom; n and n'
denote an integer of 1 - 3; R_2 and R_4 denote hydrogen
atom or nitro group; and A^+ denotes a cation including
10 75 - 98 mol. % of ammonium ion and another ion
selected from the group consisting of hydrogen ion,
sodium ion, potassium ion and mixtures thereof.

2. The toner according to Claim 1, wherein said
15 long-chain alkyl compound comprises a long-chain alkyl
alcohol represented by the formula (1).

3. The toner according to Claim 1, wherein said
long-chain alkyl compound comprises a long-chain alkyl
20 alkoxyalcohol represented by the formula (2).

4. The toner according to Claim 1, wherein said
azo-type iron complex compound has a solubility in
methanol of 0.1 - 8 g/100 ml.

25

5. The toner according to Claim 4, wherein said
azo-type iron complex compound has a solubility in

methanol of 0.3 - 4 g/100 ml.



6. The toner according to Claim 5, wherein said
azo-type iron complex compound has a solubility in
5 methanol of 0.4 - 2 g/100 ml.

7. The toner according to Claim 1, wherein said
long-chain alkyl compound has a number-average
molecular weight Mn of 200 - 2500, a weight-average
10 molecular weight Mw of 400 - 5000, and a ratio
therebetween Mw/Mn of at most 3.

8. The toner according to Claim 2, wherein said
long-chain alkyl compound has an OH value of 2 - 150
15 mgKOH/g.

9. The toner according to Claim 8, wherein said
long-chain alkyl compound has an OH value of 10 - 120
mgKOH/g.

20

10. The toner according to Claim 1, wherein said
long-chain alkyl compound has an acid value of 2 - 150
mgKOH/g.

25 11. The toner according to Claim 10, wherein said
long-chain alkyl compound has an acid value of 5 - 120
mgKOH/g.



12. The toner according to Claim 1, wherein said toner has a weight-average particle size of 4.0 - 10 μm and contain toner particles of 5 μm or smaller in terms of % by number (N %) and % by volume (V %)

5 satisfying $N/V = -0.05N + k$, wherein k is a number of 3 - 12.

13. The toner according to Claim 12, wherein said toner has a weight-average particle size of 4.5 - 9 μm
10 and contain toner particles of 5 μm or smaller in terms of % by number (N %) and % by volume (V %) satisfying $N/V = -0.05N + k$, wherein k is a number of 4 - 10.

14. The toner according to Claim 1, having a
15 negative triboelectric chargeability.

15. An image forming method, comprising:
a charging step of supplying a voltage to a
20 charging means in contact with a member to be charged to charge the member to be charged,
a step of forming an electrostatic image on the charged member to be charged,
a developing step of developing the
25 electrostatic image with a toner to form a toner image on the member to be charged,
a transfer step of transferring the toner



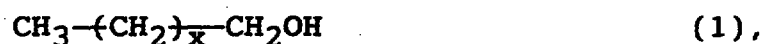
image to a transfer-receiving material directly or via an intermediate transfer member, and

a fixing step of fixing the toner image onto the transfer-receiving material,

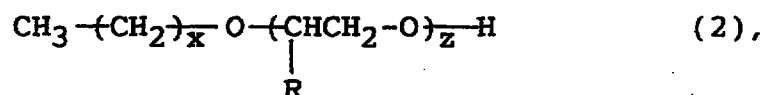
5 wherein said toner comprises:

(a) a binder resin,

(b) a long-chain alkyl compound represented by the following formula (1), (2) or (3):



10 wherein x denotes an average value in the range of 35 - 150,

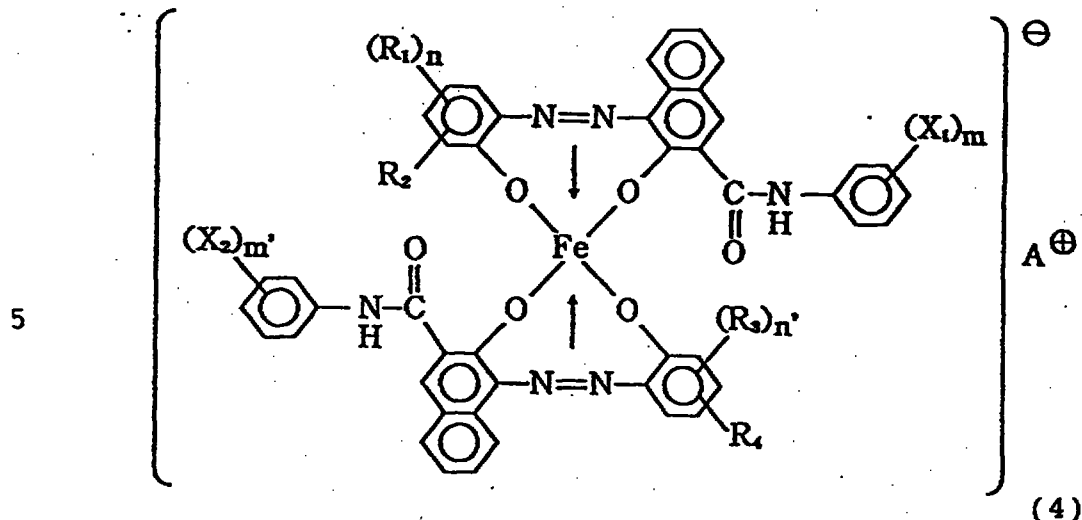


wherein x denotes an average value in the range of 35
15 - 150; z denotes an average value in the range of 1 - 5, and R denotes H or an alkyl group having 1 - 10 carbon atoms,



wherein y denotes an average value in the range of 35
20 - 150; and

(c) an azo-type iron complex compound represented by the following formula (4),



wherein X_1 and X_2 independently denote hydrogen atom,
 10 lower alkyl group, lower alkoxy group, nitro group or
 halogen atom; m and m' denote an integer of 1 - 3; R_1
 and R_3 independently denote hydrogen atom, C_{1-18} alkyl
 or alkenyl, sulfonamide, mesyl, sulfonic acid group,
 carboxy ester group, hydroxy, C_{1-18} alkoxy,
 15 acetyl amino, benzoyl amino or halogen atom; n and n'
 denote an integer of 1 - 3; R_2 and R_4 denote hydrogen
 atom or nitro group; and A^+ denotes a cation including
 75 - 98 mol. % of ammonium ion and another ion
 selected from the group consisting of hydrogen ion,
 20 sodium ion, potassium ion and mixtures thereof.

16. The image forming method according to Claim
 15, wherein said charging means comprises a charging
 roller means supplied with a voltage.

25

17. The image forming method according to Claim
 15, wherein said charging means comprises a charging



brush means supplied with a voltage.

18. The image forming method according to Claim
15, wherein said charging means comprises a charging
5 blade means supplied with a voltage.

19. The image forming method according to Claim
15, wherein the toner image on the member to be
charged is transferred to the transfer-receiving
10 material by a transfer roller means supplied with a
voltage.

20. The image forming method according to Claim
15, wherein the toner image on the member to be
15 charged is transferred to the transfer-receiving
material by a transfer belt means supplied with a
voltage.

21. The image forming method according to Claim
20 15, wherein the toner image on the member to be
charged is transferred to the intermediate transfer
member, and the toner image on the intermediate
transfer member is transferred to the transfer-
receiving material by a transfer roller means supplied
25 with a voltage.

22. The image forming method according to Claim



15, wherein the toner image on the member to be
charged is transferred to the intermediate transfer
member, and the toner image on the intermediate
transfer member is transferred to the transfer-
5 receiving material by a transfer belt means supplied
with a voltage.

23. The image forming method according to Claim
15, wherein said long-chain alkyl compound comprises a
10 long-chain alkyl alcohol represented by the formula
(1).

24. The image forming method according to Claim
15, wherein said long-chain alkyl compound comprises a
15 long-chain alkyl alkoxyalcohol represented by the
formula (2).

25. The image forming method according to Claim
15, wherein said azo-type iron complex compound has a
20 solubility in methanol of 0.1 - 8 g/100 ml.

26. The image forming method according to Claim
25, wherein said azo-type iron complex compound has a
solubility in methanol of 0.3 - 4 g/100 ml.

25

27. The image forming method according to Claim
26, wherein said azo-type iron complex compound has a



solubility in methanol of 0.4 - 2 g/100 ml.

28. The image forming method according to Claim 15, wherein said long-chain alkyl compound has a
5 number-average molecular weight M_n of 200 - 2500, a weight-average molecular weight M_w of 400 - 5000, and a ratio therebetween M_w/M_n of at most 3.

29. The image forming method according to Claim
10 23, wherein said long-chain alkyl compound has an OH value of 2 - 150 mgKOH/g.

30. The image forming method according to Claim 29, wherein said long-chain alkyl compound has an OH
15 value of 10 - 120 mgKOH/g.

31. The image forming method according to Claim 15, wherein said long-chain alkyl compound has an acid
20 value of 2 - 150 mgKOH/g.

32. The image forming method according to Claim 31, wherein said long-chain alkyl compound has an acid
value of 5 - 120 mgKOH/g.

25 33. The image forming method according to Claim 15, wherein said toner has a weight-average particle size of 4.0 - 10 μm and contain toner particles of 5



μm or smaller in terms of % by number (N %) and % by volume (V %) satisfying $N/V = -0.05N + k$, wherein k is a number of 3 - 12.

5 34. The image forming method according to Claim 33, wherein said toner has a weight-average particle size of 4.5 - 9 μm and contain toner particles of 5 μm or smaller in terms of % by number (N %) and % by volume (V %) satisfying $N/V = -0.05N + k$, wherein k is
10 a number of 4 - 10.

35. The image forming method according to Claim 15, wherein said toner has a negative triboelectric chargeability.

15

36. A process-cartridge, comprising at least a developing means and a photosensitive member,
the developing means and the photosensitive member being integrated into a cartridge which is
20 detachably mountable to a main body of an image forming apparatus,

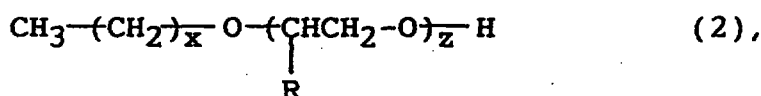
wherein the developing means contains a toner, and the toner comprises:

(a) a binder resin,
25 (b) a long-chain alkyl compound represented by the following formula (1), (2) or (3):

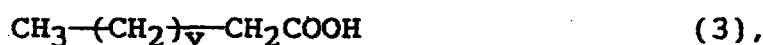




wherein x denotes an average value in the range of 35 - 150,

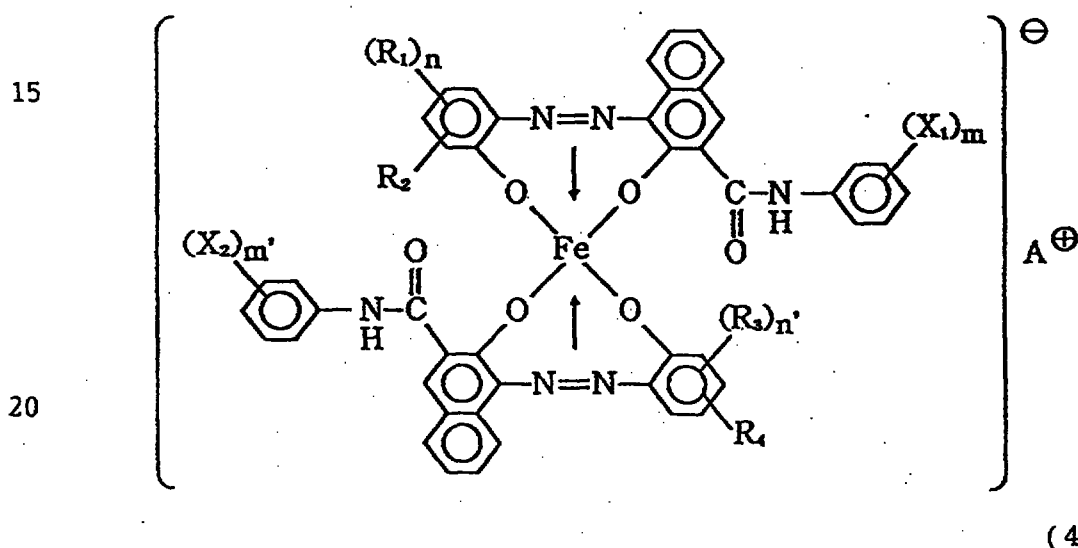


5 wherein x denotes an average value in the range of 35 - 150; z denotes an average value in the range of 1 - 5, and R denotes H or an alkyl group having 1 - 10 carbon atoms,



10 wherein y denotes an average value in the range of 35 - 150; and

(c) an azo-type iron complex compound represented by the following formula (4);



wherein X_1 and X_2 independently denote hydrogen atom, lower alkyl group, lower alkoxy group, nitro group or
25 halogen atom; m and m' denote an integer of 1 - 3; R_1 and R_3 independently denote hydrogen atom, C_{1-18} alkyl or alkenyl, sulfonamide, mesyl, sulfonic acid group,



carboxy ester group, hydroxy, C₁₋₁₈ alkoxy,
acetylamino, benzoylamino or halogen atom; n and n'
denote an integer of 1 - 3; R₂ and R₄ denote hydrogen
atom or nitro group; and A⁺ denotes a cation including
5 75 - 98 mol. % of ammonium ion and another ion
selected from the group consisting of hydrogen ion,
sodium ion, potassium iron and mixtures thereof.

37. The process cartridge according to Claim 36,
10 wherein said photosensitive member comprises a
photosensitive drum.

38. The process cartridge according to Claim 36,
wherein a contact charging means is disposed in
15 contact with the photosensitive drum.

39. The process cartridge according to Claim 38,
wherein the contact charging means comprises a
charging roller.
20

40. The process cartridge according to Claim 38,
wherein the contact charging means comprises a
charging brush.

25 41. The process cartridge according to Claim 38,
wherein the contact charging means comprises a
charging blade.



42. The process cartridge according to Claim 36,
wherein a cleaning means is disposed in contact with
the photosensitive member.

5 43. The process cartridge according to Claim 42,
wherein said cleaning means comprises a cleaning
blade.

44. The process cartridge according to Claim 36,
10 wherein said long-chain alkyl compound comprises a
long-chain alkyl alcohol represented by the formula
(1).

45. The process cartridge according to Claim 36,
15 wherein said long-chain alkyl compound comprises a
long-chain alkyl alkoxyalcohol represented by the
formula (2).

46. The process cartridge according to Claim 36,
20 wherein said azo-type iron complex compound has a
solubility in methanol of 0.1 - 8 g/100 ml.

47. The process cartridge according to Claim 46,
wherein said azo-type iron complex compound has a
25 solubility in methanol of 0.3 - 4 g/100 ml.

48. The process cartridge according to Claim 47,



wherein said azo-type iron complex compound has a solubility in methanol of 0.4 - 2 g/100 ml.

49. The process cartridge according to Claim 36,
5 wherein said long-chain alkyl compound has a number-average molecular weight M_n of 200 - 2500, a weight-average molecular weight M_w of 400 - 5000, and a ratio therebetween M_w/M_n of at most 3.

10 50. The process cartridge according to Claim 44, wherein said long-chain alkyl compound has an OH value of 2 - 150 mgKOH/g.

51. The process cartridge according to Claim 50,
15 wherein said long-chain alkyl compound has an OH value of 10 - 120 mgKOH/g.

52. The process cartridge according to Claim 36,
wherein said long-chain alkyl compound has an acid
20 value of 2 - 150 mgKOH/g.

53. The process cartridge according to Claim 52,
wherein said long-chain alkyl compound has an acid
value of 5 - 120 mgKOH/g.

25

54. The process cartridge according to Claim 36,
wherein said toner has a weight-average particle size



of 4.0 - 10 μm and contain toner particles of 5 μm or smaller in terms of % by number (N %) and % by volume (V %) satisfying $N/V = -0.05N + k$, wherein k is a number of 3 - 12.

5

55. The process cartridge according to Claim 54, wherein said toner has a weight-average particle size of 4.5 - 9 μm and contain toner particles of 5 μm or smaller in terms of % by number (N %) and % by volume
10 (V %) satisfying $N/V = -0.05N + k$, wherein k is a number of 4 - 10.

56. The process cartridge according to Claim 36, wherein said toner has a negative triboelectric
15 chargeability.

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