

1 Magnetic Toner for Developing
 Electrostatic Image

BACKGROUND OF THE INVENTION

5 Field of the invention

This invention relates to a magnetic toner for developing an electrostatic image, used in image forming processes such as electrophotography and electrostatic recording, to render electrostatic latent images visible.

Related Background Art

As electrophotography, various methods are disclosed in U.S. Patent No. 2,297,691, Japanese Patent Publication No. 42-23910 and Japanese Patent Publication No. 43-24748 and so forth.

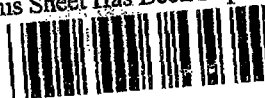
Developing systems applied in such electrophotography are roughly grouped into a dry developing method and a wet developing method. The former is further grouped into a method making use of one-component developers and a method making use of two-component developers. The developing method making use of one-component developer has a feature that developing apparatus can be made small-sized. This method, however, has difficulty in imparting sufficient triboelectricity to the toner and hence it has a problem that the allowable scope of the designing of toners and developing systems is narrow.



1 On the other hand, the developing method making use of
the two-component developer can impart sufficient
charges to toners and hence has the advantage that it
has wider tolerance for designing, but has a problem
5 that it requires a means for uniformly controlling the
mixing ratio of the toner and the carrier, making its
apparatus complicated.

As toners used in these developing methods,
fine powders comprising a colorant such as a dye or
10 pigment dispersed in a natural or synthetic resin are
hitherto used. For example, toner particles are
prepared by pulverizing a dispersion of a colorant in
a binder resin such as polystyrene to a size of about
1 to 30 μm . As a magnetic toner, toner particles
15 containing magnetic material particles such as
magnetite are used.

Toners have positive charges or negative
charges depending on the polarity of electrostatic
latent images to be developed. In order to charge
20 toners, it is possible to utilize triboelectric
chargeability of resins that compose toners. In such
a method, however, the chargeability of the toner is
so small that toner images obtained by development
tend to be foggy and unclear. In order to impart a
25 desired triboelectric chargeability to toners, a dye
or pigment capable of controlling chargeability and
also a charge control agent are commonly added.



1 However, toners containing such charge control
agents tend to contaminate the toner carrying members
such as the developing sleeve, and hence such toners
tend to cause a decrease in quantity of
5 triboelectricity as the number of copies taken
increases, resulting in a decrease in image density.
Charge control agents of a certain type have a small
quantity of triboelectricity to tend to be affected by
temperature and humidity, and hence may cause
10 variations of image density in accordance with
environmental changes. Certain charge control agents
have a poor dispersibility in resins, and hence toners
making use of such charge control agents tend to have
uneven triboelectricity between toner particles,
15 tending to cause fogging. Certain charge control
agents have poor storage stability so that toners may
undergo a decrease in triboelectric performance during
a long-term storage.

 As a means for solving these problems,
20 Japanese Patent Publication Nos. 43-17955, 55-42752
and 63-1994 propose various kinds of metal complexes
as charge control agents. These charge control agents
certainly have a good negative triboelectric
chargeability. Most of them, however, are chromium
25 compounds, and more improvement has been sought from
the viewpoint of environmental safety.

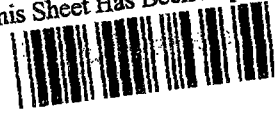
Japanese Patent Application Laid-open Nos. 61-



- 1 155464, 61-101558 and 61-155463 propose iron complexes.

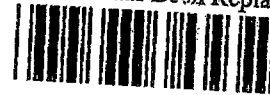
These publications disclose that the iron complexes have a negative triboelectric chargeability and have a very good compatibility with resins. However, studies made by the present inventors have revealed that only some of them can provide magnetic toners providing a more stable image quality in the one-component development system as described later.

- 10 In order to maintain the high image quality obtained at the initial stage, without regard to the number of copies taken, it is insufficient to only maintain the quantity of triboelectricity, but the particle size distribution of the toner at the initial stage must be kept constant. In particular, it is important for the toner particles of relatively large particle size (coarse powder) to be used in development in a good efficiency to prevent their accumulation. For such purpose, the magnetic properties and quantity of triboelectricity of magnetic toners must be adjusted to proper values. Taking these points into account, the present inventors have studied charge control agents to find that quantity of negative triboelectricity becomes smaller when organic ammonium ions are used as counter ions. The reason is unclear, but is presumed to be due to a positive triboelectric chargeability inherent



1 in organic ammonium ions as usually known in the art.
Japanese Patent Application Laid-open No. 61-101558
discloses that organic ammonium ions are effective to
improve the dispersibility of metal complexes in
5 resins. According to the studies made by the present
inventors, however, in the case of one-component
developers making use of magnetic toners, the organic
ammonium ions exert greater influence on a decrease in
triboelectric chargeability than on the improvement of
10 dispersibility, so that the coarse powder in the toner
accumulates as developing is repeated many times, to
cause a slight lowering of image quality.

Polyvalent inorganic ions disclosed in
Japanese Patent Application Laid-open No. 63-267793
15 also have caused accumulation of the coarse powder in
toners. Negative charge control agents disclosed in
Japanese Patent Application Laid-open No. 63-267793
have polyvalent ions as counter ions to make the
molecular structure larger, so that they show improved
20 dispersibility in resins than the negative charge
control agent disclosed in Japanese Patent Application
Laid-open No. 61-155464 does. As a result, the
carrier contamination due to the toner can be
repressed prolonging the life time of the developer
25 from 50,000 to 100,000 sheet copying to 200,000 sheet
or more as so disclosed therein. According to the
studies made by the present inventors, however, in

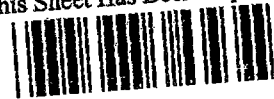


1 order to maintain the good image quality at the
initial stage using a magnetic toner in one-component
development, it is necessary not only to keep the
quantity of triboelectricity constant, but as
5 previously stated, also to maintain a high quantity of
triboelectricity, so that the coarse powder in the
toner can also participate in the development. From
such viewpoints, the iron complexes of polyvalent ions
as disclosed in Japanese Patent Application Laid-open
10 No. 63-267793 are not suited for magnetic toners. The
coarse powder tend to accumulate also in the case of
the iron complexes having a substituent such as a
nitro group as shown in Japanese Patent Application
Laid-open No. 61-155463, or those having a sulfonamide
15 group, in Japanese Patent Application Laid-open No. 61-
155464.

Meanwhile, with regard to magnetic properties
of magnetic toners, proposals are made as follows:

Japanese Patent Application Laid-open Nos. 58-
20 95748, 58-98744 and 3-95578 report the magnetic
properties of magnetic toners.

According to Japanese Patent Application Laid-
open No. 58-95748, saturation magnetization has an
influence on transport performance of magnetic toner
25 particles. Those with a saturation magnetization less
than 23 emu/g weaken magnetic transport power to tend
to cause uneven development. Those with a saturation



1 magnetization more than 50 emu/g come to have a large
quantity of magnetic powder in magnetic toners to make
fixing performance low or developing performance poor.
Toner particles with a coercive force less than 150
5 oersted extremely lower the developing performance,
and those with a coercive force more than 350 oertsted
strengthen agglomeration force of toner particles to
cause a problem in toner transport performance.

Japanese Patent Application Laid-open No. 58-
10 98744 discloses that coercive force of 150 oersted or
more is required in order to obtain fog-free images in
reversal development.

Japanese Patent Application Laid-open No. 3-
95578 discloses to reduce the quantity of a magnetic
15 material so that a color toner with less turbidity can
be obtained. For this reason, the magnetic toner is
made to have a saturation magnetization of 40 emu/g or
less, and a magnetic roller (a developing sleeve) is
designed so as to compensate any lowering of the
20 transport power of the magnetic toner. In any cases,
the saturation magnetization is controlled taking
account of the transport performance of magnetic
toners and the coercive force is controlled for
developing performance. Although the image quality at
25 the initial stage can be improved by controlling
magnetic properties of the magnetic toner, it is
difficult to control image deterioration due to



1 changes in toner particle size that may occur as
developing is repeated many times. In order to
prevent the magnetic toner from the change in particle
size, both the quantity of triboelectricity of the
5 magnetic toner and the magnetic properties thereof
must be taken into account.

SUMMARY OF THE INVENTION

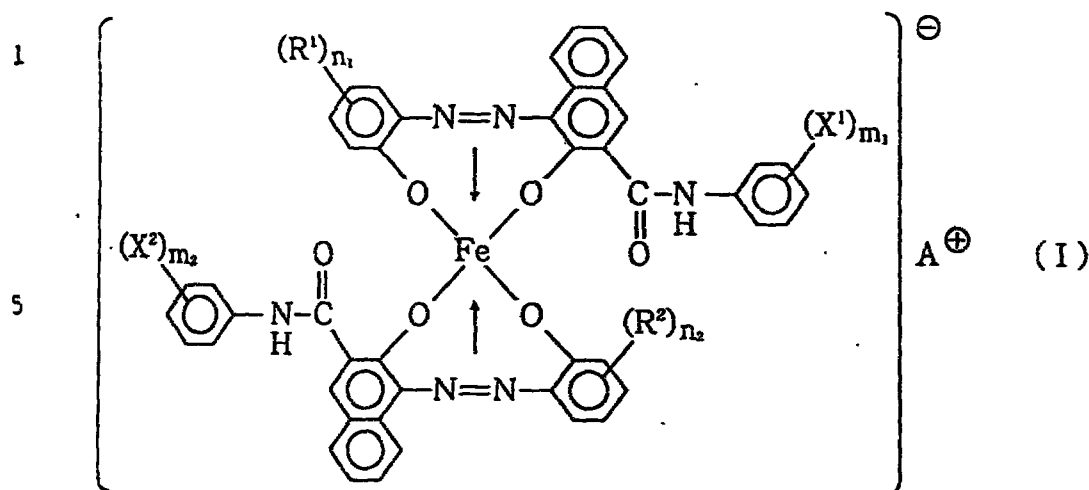
10 An object of the present invention is to
provide a magnetic toner for developing an
electrostatic image, having solved the problems
discussed above.

Another object of the present invention is to
provide a toner for developing an electrostatic image,
15 causing less image deterioration during the
development of a large number of copying sheets.

Still another object of the present invention
is to provide a magnetic toner having a superior
environmental stability.

20 A further object of the present invention is
to provide a magnetic toner having a superior
stability when left to stand.

This invention provides a magnetic toner for
developing an electrostatic image, comprising a binder
25 resin, a magnetic material and an iron compound
represented by the following formula (I):



wherein R^1 and R^2 each represent a hydrogen atom, a sulfonic acid group, a carboxylic acid group, a carboxylate group, a hydroxyl group or a halogen atom, and may be the same or different; n_1 and n_2 each represent an integer of 1 to 4; X^1 and X^2 each represent a hydrogen atom or a halogen atom; m_1 and m_2 each represent an integer of 1 to 3; and $A^\oplus$ represents a hydrogen ion, an alkali metal ion or an ammonium ion;

said magnetic toner having a saturation magnetization of from $20 \text{ Am}^2/\text{kg}$ to $50 \text{ Am}^2/\text{kg}$ and a coercive force of from 40 oersted to 200 oersted.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an example of a developing assembly in which the magnetic toner of the present invention can be applied.

Fig. 2 schematically illustrates a measuring device for measuring quantity of triboelectricity of



1 magnetic toners.

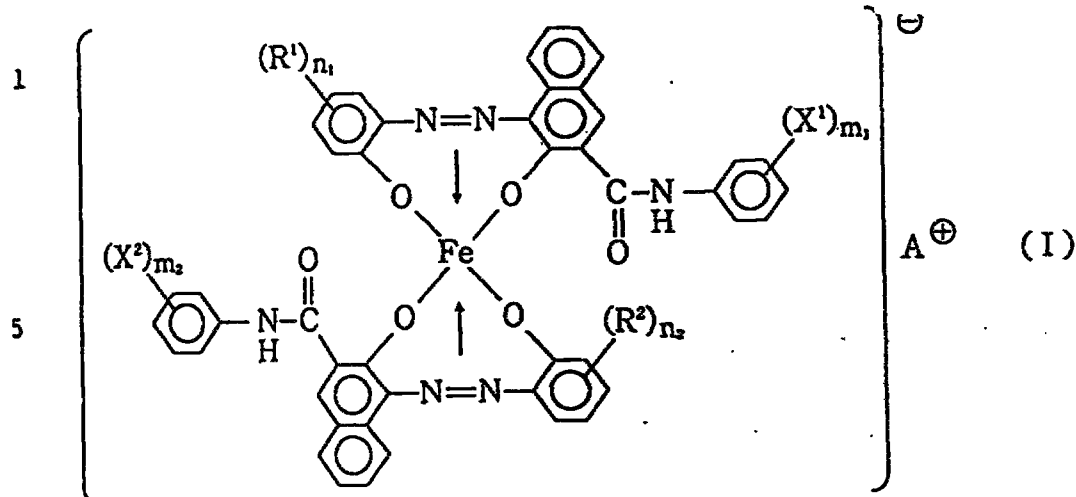
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the studies made by the present
5 inventors, it is important to properly balance the
quantity of triboelectricity and magnetic properties
of a magnetic toner in order to maintain the initial
good image quality when the magnetic toner is used in
one-component developing system. Based on such a
10 finding, the present inventors studied various types
of charge control agents in magnetic toner of various
magnetic properties. As a result, they discovered
that changes in particle size of magnetic materials
that may occur as developing is repeated many times
15 can be inhibited and the initial good image quality
can be maintained when a specific iron compound is
used in a toner for developing electrostatic images,
where the toner has a saturation magnetization of from
20 to 50 Am²/kg and a coercive force of from 40 to 200
20 oersted. They have thus accomplished the present
invention.

The iron compound used in the present
invention is represented by the following formula (I).

Formula (I)

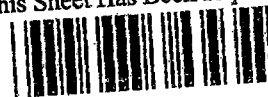
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wherein R^1 and R^2 each represent a hydrogen atom, a sulfonic acid group, a carboxylic acid group, a carboxylate group, a hydroxyl group or a halogen atom, and may be the same or different; n_1 and n_2 each represent an integer of 1 to 4; X^1 and X^2 each represent a hydrogen atom or a halogen atom; m_1 and m_2 each represent an integer of 1 to 3; and A^+ represents a hydrogen ion, an alkali metal ion or an ammonium ion;

A^+ may preferably be an ammonium ion or be mainly composed of an ammonium ion (70 mol% or more). A^+ may more preferably be a mixture of an ammonium ion and an alkali metal ion and/or a hydrogen ion, and be mainly composed of an ammonium ion. Still more preferably, in the above mixture, the ammonium ion may be in a content of from 80 to 98 mol%, and more preferably from 85 to 95 mol%.

According to the studies made by the present inventors, when the compound has ammonium ions and



1 alkali metal ions or hydrogen ions in combination, the
quantity of triboelectricity of the magnetic toner
having been left to stand in an environment of high
humidity can be restored to the original (i.e., before
5 leaving to stand) quantity of triboelectricity, and
also can be recovered more quickly with a stable image
quality. On the other hand, when the compound has
only protons or alkali metal ions as cations, the
magnetic toner having been left in an environment of
10 high humidity can be triboelectrically charged
quickly, but the quantity of triboelectricity can not
be well restored to the original quantity of
triboelectricity, tending to cause a decrease in image
density.

15 According to the studies made by the present
inventors, a good compound that shows less
deterioration even when left to stand over a long
period of time can be obtained when ammonium ions and
alkali metal ions or hydrogen ions are present
20 together in the compound.

In particular, the rate and the level of
restoration can be well maintained when ammonium ions
are in a content of from 80 mol% to 98 mol%. If
ammonium ions are in a content of less than 80 mol%,
25 the restored level of triboelectricity may become a
little lower than the original quantity of
triboelectricity. On the other hand, if they are in a



1 content more than 98 mol%, the rate of restoration may
become lower. When the ammonium ions are in a content
of from 85 mol% to 95 mol%, the rate of restoration
preferably become higher. In addition, better results
5 can be obtained also on restoration performance in an
environment of high humidity.

The reason therefor is, according to the
mechanism of ion conduction proposed as one of the
mechanisms of triboelectric charging, presumed as
10 follows:

It is presumed that when water content is
relatively large as in the environment of high
humidity, monovalent cations with small ion radii have
high mobility so that charges once having leaked when
15 the toner is left to stand can be quickly restored.

For that purpose, it is preferable for the
alkali metal ions or hydrogen ions as the monovalent
cations to be in a uniform content of at least 2
mol%, and more preferably at least 5 mol%.

20 In the present invention, the performance of
restoration of the quantity of triboelectricity is
expressed by a proportion of the restored charge to
the original charge when a triboelectrically charged
magnetic toner in an environment of high humidity is
25 left to stand for a long period of time and thereafter
shaked together with an iron powder carrier.

Stated specifically, 2.5 g of a magnetic toner



1 and 47.5 g of an iron powder carrier are collected in a
50 cm³ polyethylene container, and left to stand for 2
days in an environment of a temperature of 30°C and a
relative humidity of 80%RH in an uncovered state.
5 These are then shaken in a tumbling mixer for 240
seconds, and thereafter an about 0.5 g portion of the
powdery mixture is collected to measure the quantity
of triboelectricity of the magnetic toner by blowing-
off. The measurement thus obtained is regarded as the
10 original quantity of triboelectricity. After the
powdery mixture is further left to stand for 4 days in
an uncovered state, followed by shaking in the
tumbling mixer for 0, 60 or 240 seconds to measure the
corresponding quantities of triboelectricity of the
15 magnetic toner, and its percentage to the quantity of
triboelectricity of the original magnetic toner is
calculated.

Fig. 2 illustrates an apparatus for measuring
the quantity of triboelectricity. In a measuring
20 container 2 made of a metal at the bottom of which is
provided an electroconductive screen 3 of 500 meshes
(appropriately changeable to the size the screen may
not pass the carrier particles), the sample is put and
the container is covered with a plate 4 made of a
25 metal. Next, in a suction device 1 (made of an
insulating material at least at the part coming into
contact with the measuring container 2), air is sucked



1 from a suction opening 7 and an air-flow control valve
6 is operated to control the pressure indicated by a
vacuum indicator 5 to be 250 mmHg. In this state,
suction is sufficiently carried out (for about 1
5 minute). The potential indicated by a potentiometer
at this time is expressed by V (volt). Reference
numeral 8 denotes a capacitor, whose capacitance is
expressed by C (μ F). The charges obtained therefrom
is divided by the weight (g) of the magnetic toner
10 removed by suction to obtain a value which is the
quantity of triboelectricity (mC/Kg).

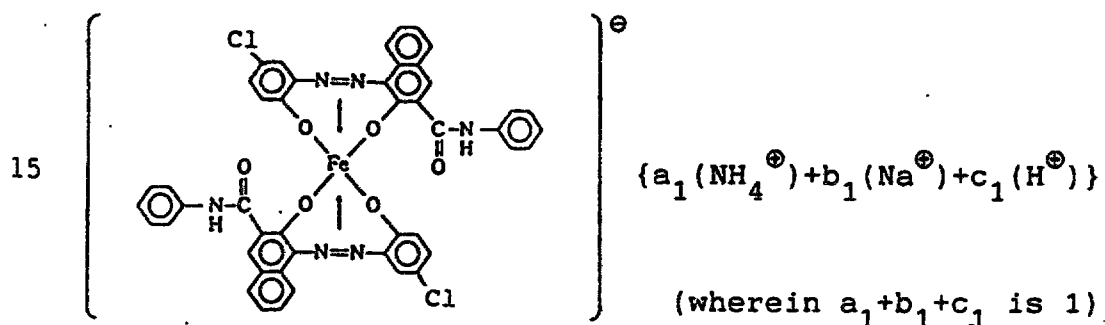
The magnetic toner of the present invention
can also well prevent photosensitive members from
being scraped. It can be presumed that, because of a
15 good transfer rate of the magnetic toner of the
present invention, the amount of the magnetic toner
remaining on a photosensitive member after the step of
transfer is so small resulting in a small load in the
step of cleaning. As can be also considered, the iron
20 compound used in the present invention acts on the
surface of the magnetic material to improve its state
of dispersion in a resin, so that the magnetic
material present on the surfaces of the magnetic toner
particles has decreased.

25 In the present invention, complexes
represented by formula (I) may be mixed to obtain the
iron compound having the mixture of cations. A better

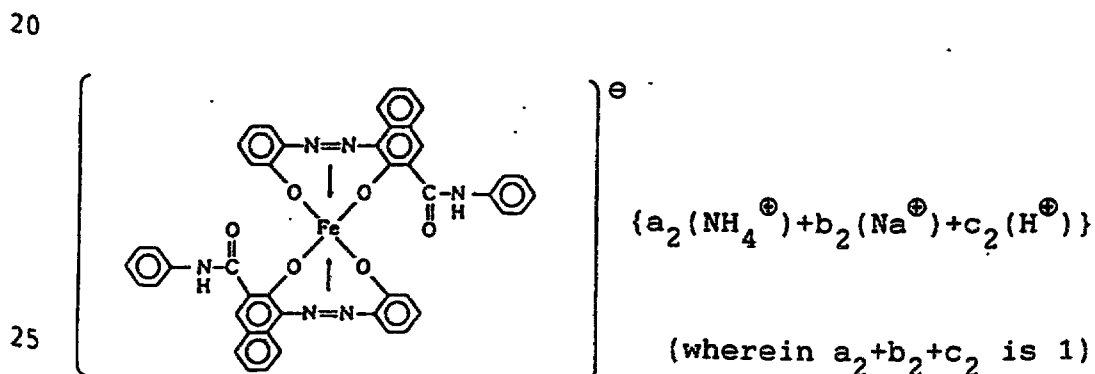
- 1 shelf stability can be obtained when the iron compound
is synthesized at one time while changing the
percentage or pH of cationic components during its
synthesis. This is presumably because the respective
5 cations can be more uniformly dispersed and at the
same time different cationic complexes can preferably
interact, when the compound is synthesized at one
time.

Examples of the iron compound represented by
10 formula (I) are shown below.

Iron compound (1)



Iron compound (2)

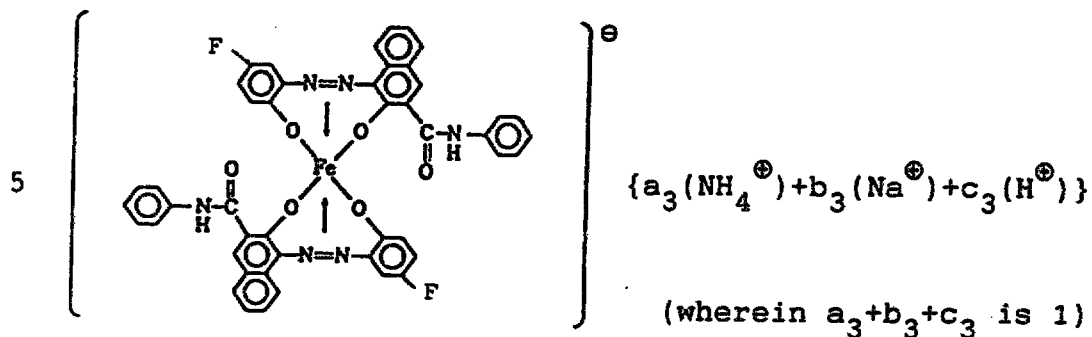


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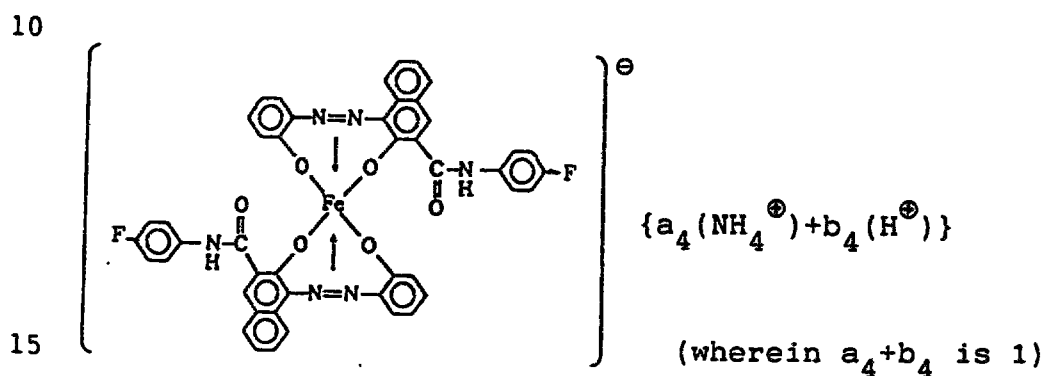


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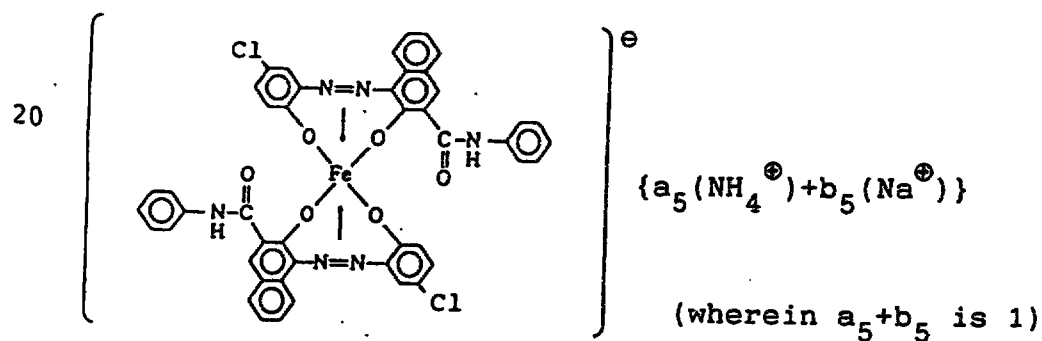
1 Iron compound (3)



Iron compound (4)



Iron compound (5)



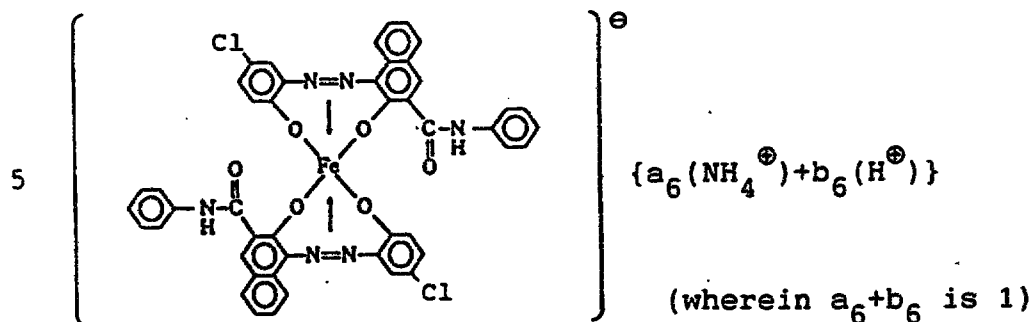
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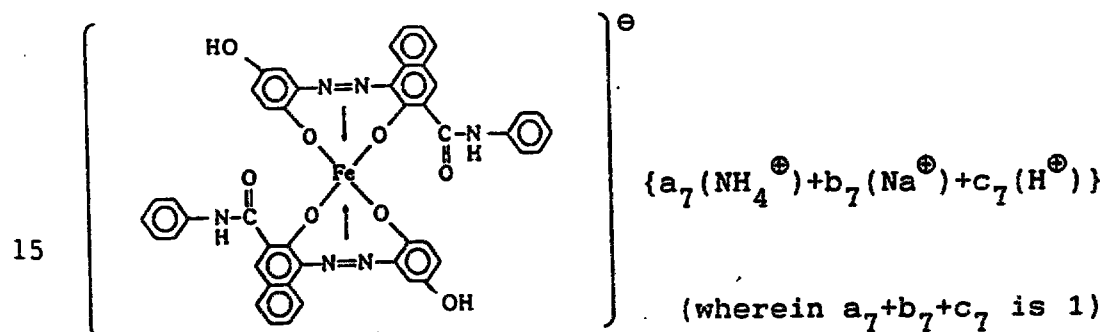


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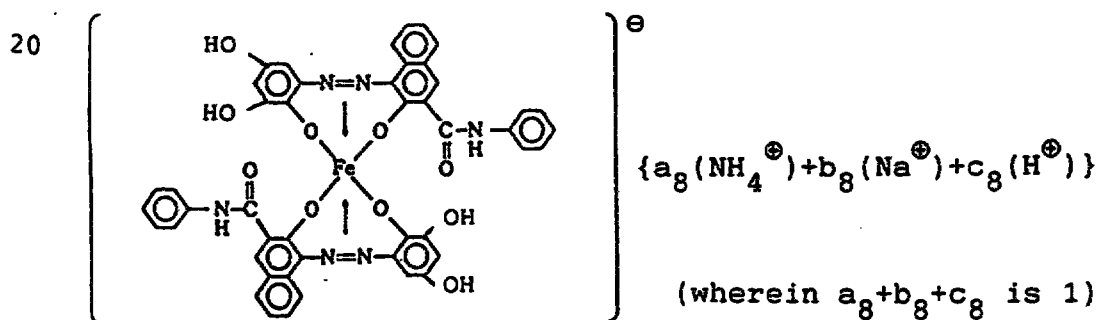
1 Iron compound (6)



10 Iron compound (7)



Iron compound (8)

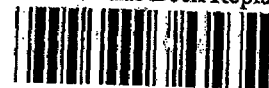


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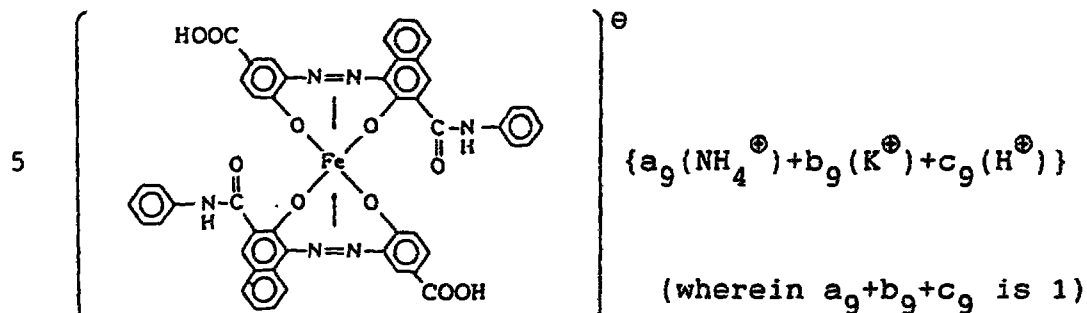


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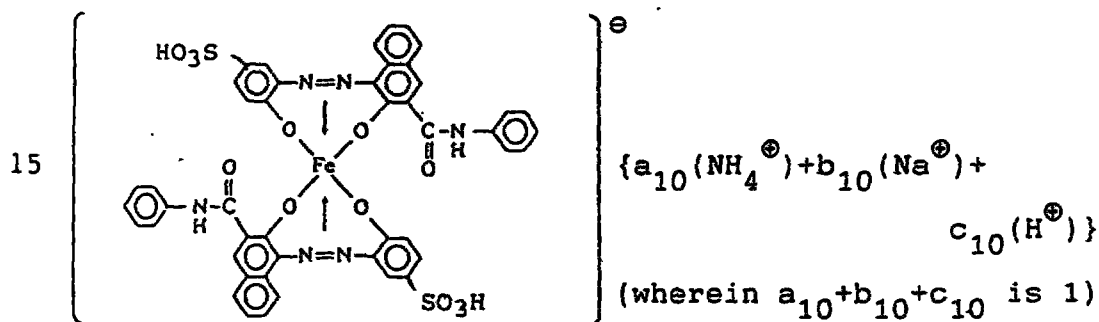


1 Iron compound (9)



10

Iron compound (10)



20 In the above exemplary iron compounds (1) to (10), a_1 through a_{10} may preferably be 0.80 to 0.98; b_1 through b_{10} , 0.01 to 0.20; and c_1 through c_{10} , the balance. More preferably, a_1 through a_{10} may be 0.85 to 0.95; b_1 through b_{10} , 0.01 to 0.05; and c_1 through c_{10} , the balance.

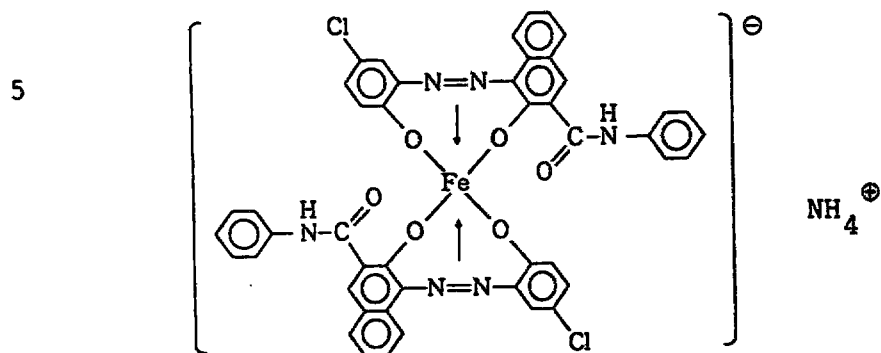
25 In the above iron compound (1), a_1 may preferably be 0.80 to 0.98; b_1 , 0.01 to 0.19; and c_1 , 0.01 to 0.19. More preferably, a_1 may be 0.85 to

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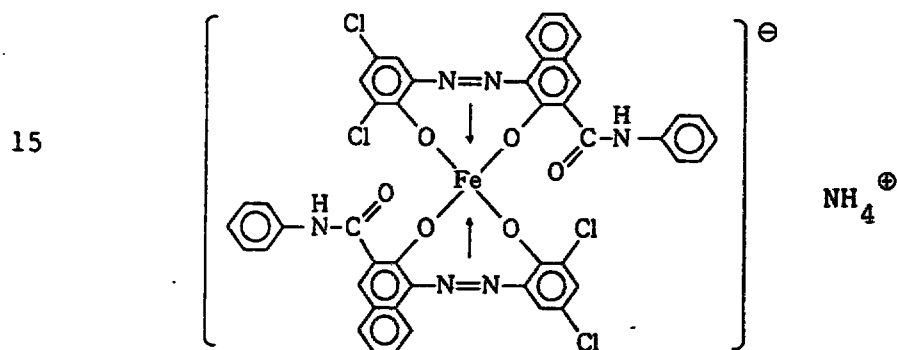
1 0.95; b_1 , 0.01 to 0.14; and c_1 , 0.01 to 0.14.

Iron compound (11)

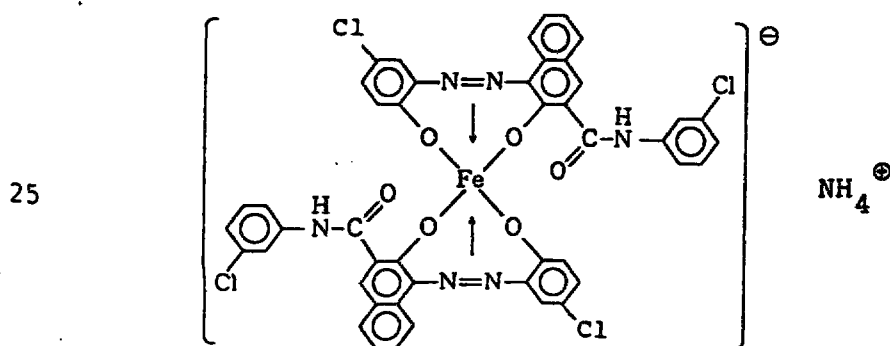


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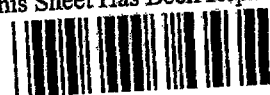
Iron compound (12)



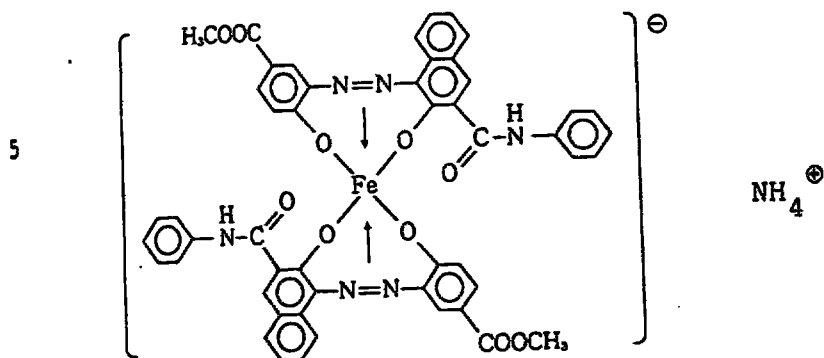
20 Iron compound (13)



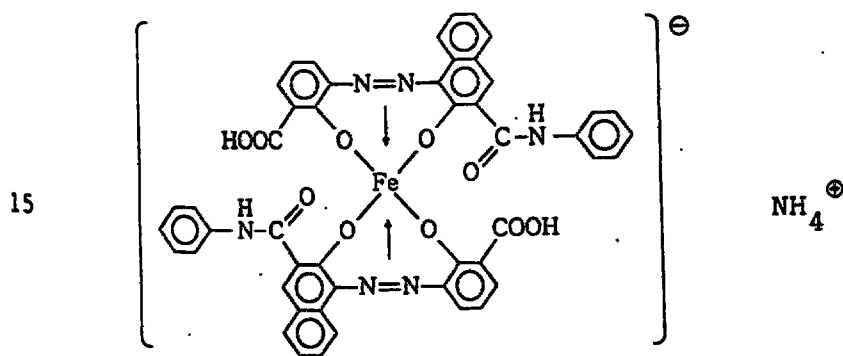
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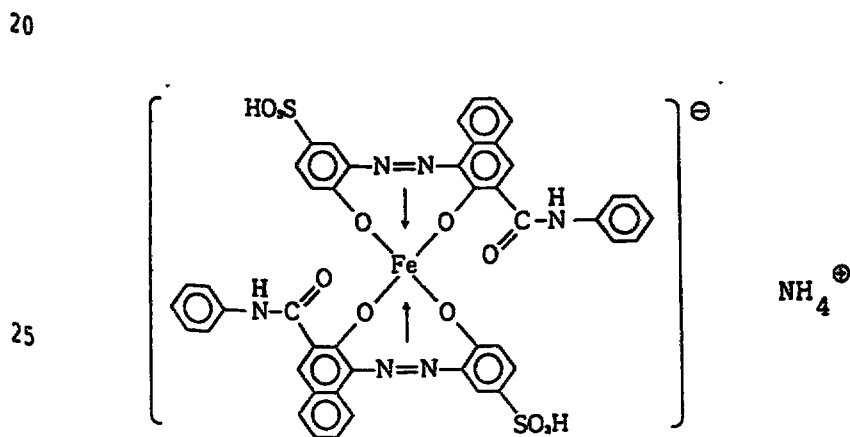
1 Iron compound (14)



10 Iron compound (15)



Iron compound (16)



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1 The iron compound can be incorporated into the
toner by a method in which it is internally added to
the inside of magnetic toner particles or externally
added to the particles. The iron compound may
5 preferably be used in an amount ranging from 0.1 part
to 10 parts by weight, and more preferably from 0.1
part to 5 parts by weight, based on 100 parts by
weight of the binder resin. When it is externally
added, it may preferably be in an amount of from 0.01
10 part to 10 parts by weight, and more preferably from
0.01 part to 3 parts by weight, based on 100 parts by
weight of the binder resin. In particular, it is
preferred for iron compound particles to be
mechanochemically fixed on the surfaces of the
15 magnetic toner particles.

The iron compound used in the present
invention may be used in combination with any
conventionally known charge control agents so long as
the effect of the iron compound is not damaged.

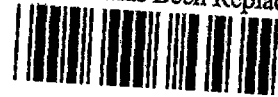
20 According to the studies made by the present
inventors, in order to prevent the changes in particle
size of magnetic toners that may occur during repeated
developing, for the purpose of maintaining the initial
high image quality, it is important to use the iron
25 compound of the present invention and also make the 20
to 50 Am²/kg and a coercive force of from 40 to 200
oersteds. In particular, it is preferable for the



1 magnetic toner to have a saturation magnetization of
from 25 to 40 Am²/kg and a coercive force of from 50
to 150 oersted.

5 As conventionally pointed out, magnetic toners
come to have a low transport performance if their
saturation magnetization is less than 20 Am²/kg. In
particular, the transport performance of coarse powder
in a magnetic toner to a developing zone may become
poor, tending to cause the coarse powder in the
10 magnetic toner to accumulate in a developing assembly
as developing is repeated many times. If the
saturation magnetization is more than 50 Am²/kg, the
magnetic binding force on a developing sleeve
increases, resulting, in particular, in a lowering of
15 developing performance of the coarse powder. The
cause thereof is not necessarily clear, but it is
presumed as follows: The quantity of triboelectricity
of a magnetic toner is considered proportional to the
square of a particle diameter of the magnetic toner,
20 and on the other hand the saturation magnetization is
proportional to the cube of the same. Hence,
particularly in the coarse powder of the magnetic
toner, the magnetic binding force on the developing
sleeve becomes larger than the quantity of
25 triboelectricity, to cause a lowering of developing
performance and cause the coarse powder to accumulate.

As for the coercive force of the magnetic



1 toner, the coarse powder tends to accumulate when it
is more than 200 oersted.

For the measurement of magnetizing force,
values at a magnetic field of 1 k oersted are measured
5 using, e.g., VSM, manufactured by Toei Kogyo K.K..

The magnetic material contained in the
magnetic toner of the present invention may include
iron oxides such as magnetite, γ -iron oxide, ferrite
and iron-excess ferrite; metals such as iron, cobalt
10 and nickel, or alloys of any of these with a metal
such as aluminum, cobalt, copper, lead, magnesium,
tin, zinc, antimony, beryllium, bismuth, cadmium,
calcium, manganese, selenium, titanium, tungsten or
vanadium, and mixtures of any of these.

15 These magnetic materials may preferably be
those having an average particle diameter of from 0.1
to 1 μm , and preferably from 0.1 to 0.5 μm .

The magnetic material may preferably be
contained in the magnetic toner in an amount that may
20 satisfy the following expression.

$$MT = -(10/3) \times d + (70 \pm 15)$$

wherein MT represents a content (% by weight) of the
magnetic material, and d represents a weight average
particle diameter (μm) of the magnetic toner, provided
25 that d is not more than 9 μm .

Use of the magnetic material in an amount less
than the above limit may generally result in a low



1 saturation magnetization of the magnetic toner,
tending to cause lowering of the transport performance
of the magnetic toner. As a result, the magnetic
toner can not be fed to the developing zone in a
5 sufficient quantity and hence only toner images with a
low density can be obtained. On the other hand, if a
magnetic material with a higher saturation
magnetization is used in an amount less than the above
limit to obtain a magnetic toner with a good
10 transport performance, the toner has a high
electrical resistivity because of the decrease of the
magnetic material. As a result, when the iron
compound of formula (I) is used, the quantity of
triboelectricity becomes higher than the proper value
15 tending to cause lowering of developing performance.

On the other hand, the use of the magnetic
material in an amount more than the foregoing limit
makes the saturation magnetization or coercive force
of the magnetic toner excessively large, so that the
20 fluidity of the magnetic toner may decrease or the
magnetic binding force on the developing sleeve may
increase. As a result, the developing performance of
the magnetic toner may be lowered or the coarse powder
of the magnetic toner may accumulate as developing is
25 repeated many times, tending to cause lowering of
image quality. An increase in the quantity of the
magnetic material also result in a decrease in the



1 quantity of triboelectricity of the magnetic material.
Hence, this also can be the cause of a lowering of the
developing performance of the magnetic toner.

Thus, in order to prevent the accumulation of
5 the coarse powder as developing is repeated many times
and to maintain the initial high image quality, it is
important to control both the magnetic properties and
the quantity of triboelectricity of the magnetic toner
as described above. For that purpose, the quantity of
10 triboelectricity of the magnetic toner must be
controlled using the specific iron compound of formula
(I) as a charge control agent, and on that occasion
the amount of the magnetic material may preferably be
within the range set out above.

15 In the magnetic toner of the present
invention, the magnetic toner may preferably have a
weight average particle diameter of from 3 to 9 μm .
In particular, a magnetic toner having a weight
average particle diameter of from 5 to 9 μm is
20 preferred.

The particle size distribution of the magnetic
toner can be measured by various methods. In the
present invention, it is suitable to measure it using
a Coulter counter.

25 A Coulter counter Type TA-II (manufactured by
Coulter Electronics, Inc.) is used as a measuring
device. The volume distribution and number

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1 distribution of particles of 2 μm to 40 μm are
calculated by measuring the volume and number
distribution of the toner particles, using an aperture
of 100 μm as its aperture. Then the weight-based,
5 weight average particle diameter D_4 is calculated from
the volume distribution of the present invention
(representative value of each channel is the median of
each channel) and the weight-based, coarse-powder
content is calculated from the volume distribution.

10 In the magnetic toner of the present
invention, it is preferable to use a fine inorganic
oxide powder by its external addition.

As the fine inorganic oxide powder, various
materials can be used, as exemplified by silica,
15 titanium oxide, aluminum oxide, cerium oxide and
strontium titanate. In particular, those having metal
ions with an electronegativity of from 10 to 15 are
preferred in view of charging rate and environmental
stability.

20 For the purpose such as imparting fluidity to
the magnetic toner of the present invention, it is
very preferable to externally add fine silica powder
or fine titanium oxide powder.

The fine silica powder may include anhydrous
25 silicon dioxide (silica), as well as silicates such as
aluminum silicate, sodium silicate, potassium
silicate, manganese silicate and zinc silicate, any of



1 which can be used.

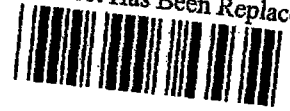
Of the above fine silica powders, those having a specific surface area, as measured by the BET method using nitrogen absorption, of not less than $30 \text{ m}^2/\text{g}$,

5 and particularly from 50 to $400 \text{ m}^2/\text{g}$, are preferred as base material silica.

Any of these fine silica powder, or those treated as described below, may preferably be used in an amount of from 0.01 part to 20% by weight, and
10 particularly preferably from 0.03 part to 5% by weight, based on the weight of the magnetic toner.

The fine silica powder may be optionally treated with a treatment agent such as a silane coupling agent or an organic silicon compound, or with
15 silicone oil or the like.

Such a treatment agent can be exemplified by hexamethyldisilazane, trimethylsilane, trimethylchlorosilane, trimethylethoxysilane, dimethyldichlorosilane, methyltrichlorosilane,
20 allyldimethylchlorosilane, allylphenyldichlorosilane, benzyldimethylchlorosilane, bromomethyldimethylchlorosilane, α -chloroethyltrichlorosilane, β -chloroethyltrichlorosilane, chloromethyldimethylchlorosilane, triorganosilyl mercaptan, trimethylsilyl
25 mercaptan, triorganosilyl acrylate, vinyl dimethylacetoxysilane, dimethylethoxysilane, dimethyldimethoxysilane, diphenyldiethoxysilane,



1 hexamethyldisiloxane, 1,3-divinyltetramethyldi-
siloxane, 1,3-diphenyltetramethyldisiloxane, and a
dimethylpolysiloxane having 2 to 12 siloxane units in
its molecule and containing a hydroxyl group bonded to
5 each Si in its units positioned at the terminals. Any
of these may be used alone or in the form of a mixture
of two or more kinds.

When the treated fine silica powder has been
made hydrophobic to such degree that it shows a
10 hydrophobicity of a value ranging from 30 to 80 as
measured by methanol titration, a magnetic toner
containing such a fine silica powder is preferred
since its quantity of triboelectricity comes to show a
sharp and uniform positive chargeability. Here, the
15 methanol titration is a test method to determine the
hydrophobicity of fine silica powder whose surfaces
have been made hydrophobic.

In order to evaluate the hydrophobicity of the
treated fine silica powder, the "methanol titration"
20 as defined in the present specification is carried out
in the following way: 0.2 g of fine silica powder is
added to 50 ml of water contained in a 250 ml
Erlenmeyer flask. Methanol is dropwise added from a
buret until the whole fine silica powder has been
25 wetted. Here, the solution inside the flask is
continually stirred using a magnetic stirrer. The end
point can be observed upon suspension of the whole



- 1 fine silica powder in the solution. The hydrophobicity is expressed as the percentage of the methanol present in the liquid mixture of methanol and water when the reaction has reached the end point.
- 5 The binder resin used in the present invention may include polystyrene; homopolymers of styrene derivatives such as poly-p-chlorostyrene and polyvinyltoluene; styrene copolymers such as a styrene/p-chlorostyrene copolymer, a
- 10 styrene/vinyltoluene copolymer, a styrene/vinylnaphthalene copolymer, a styrene/acrylate copolymer, a styrene/methacrylate copolymer, a styrene/methyl α -chloromethacrylate copolymer, a styrene/acrylonitrile copolymer, a styrene/methyl
- 15 vinyl ether copolymer, a styrene/ethyl vinyl ether copolymer, a styrene/methyl vinyl ketone copolymer, a styrene/butadiene copolymer, a styrene/isoprene copolymer and a styrene/acrylonitrile/indene copolymer; polyvinyl chloride, phenol resins, natural
- 20 resin modified phenol resins, natural resin modified maleic acid resins, acrylic resins, methacrylic resins, polyvinyl acetate, silicone resins, polyester resins, polyurethane resins, polyamide resins, furan resins, epoxy resins, xylene resins, polyvinyl
- 25 butyral, terpene resins, cumarone indene resins, and petroleum resins.

Cross-linked styrene copolymers are also



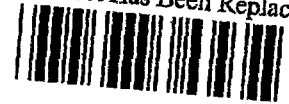
1 preferable binder resins.

Comonomers copolymerizable with styrene monomers in styrene copolymers may include monocarboxylic acids having a double bond and derivatives thereof such as acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, dodecyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, phenyl acrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 10 octyl methacrylate, acrylonitrile, methacrylonitrile and acrylamide; dicarboxylic acids having a double bond and derivatives thereof such as maleic acid, butyl maleate, methyl maleate and dimethyl maleate; vinyl esters such as vinyl acetate and vinyl benzoate; 15 olefins such as ethylene, propylene and butylene; vinyl ketones such as methyl vinyl ketone and hexyl vinyl ketone; and vinyl ethers such as methyl vinyl ether, ethyl vinyl ether and isobutyl vinyl ether. Any of these vinyl monomers may be used alone or in 20 combination of two or more.

As a cross-linking agent, compounds having at least two polymerizable double bonds are mainly used, which include, for example, aromatic divinyl compounds such as divinyl benzene and divinyl naphthalene; 25 carboxylic acid esters having two double bonds such as ethylene glycol diacrylate, ethylene glycol dimethacrylate and 1,3-butanediol dimethacrylate;



- 1 divinyl compounds such as divinyl aniline, divinyl
ether, divinyl sulfide and divinyl sulfone; and
compounds having at least three vinyl groups. Any of
these may be used alone or in the form of a mixture.
- 5 In particular, styrene copolymers having at least one
peak of molecular weight distribution in the region of
from 3×10^3 to 5×10^4 and at least one peak or
shoulder in the region of 10^5 or more as measured by
gel permeation chromatography (GPC) are preferred.
- 10 The molecular weight distribution is measured
by GPC under the following conditions.
- Columns are stabilized in a heat chamber of
40°C. To the columns kept at this temperature, THF as
a solvent is flowed at a flow rate of 1 ml per minute,
15 and 100 μ l of THF sample solution is injected
thereinto to make measurement. In measuring the
molecular weight of the sample, the molecular weight
distribution of the sample is calculated from the
relationship between the logarithmic value of the
20 molecular weight and the count number of the eluate (a
calibration curve) prepared using several kinds of
monodisperse polystyrene standard samples. As the
standard polystyrene samples used for the preparation
of the calibration curve, it is suitable to use
25 samples with molecular weights of from 10^2 to 10^7 ,
which are available from Toso Co., Ltd. or Showa Denko
KK., and to use at least about 10 standard polystyrene



1 samples. An RI (refractive index) detector is used as
a detector. Columns should be used in combination of
a plurality of commercially available polystyrene gel
columns. For example, they may preferably comprise a
5 combination of Shodex GPC KF-801, KF-802, KF-803, KF-
804, KF-805, KF-806, KF-807 and KF-800P, available
from Showa Denko K.K.; or a combination of TSKgel
G1000H(H_{XL}), G2000H(H_{XL}), G3000H(H_{XL}), G4000H(H_{XL}),
G5000H(H_{XL}), G6000H(H_{XL}), G7000H(H_{XL}) and TSK guard
10 column, available from Toso Co., Ltd.

The sample is prepared in the following way:

The binder resin or the magnetic toner is put
in THF, and is left to stand for several hours,
followed by thorough shaking so as to be well mixed
15 with the THF until coalescent matters of the sample
has disappeared, which is further left to stand for at
least 12 hours. At this time, the sample is so left
as to stand in THF for at least 24 hours. Thereafter,
the solution having been passed through a sample-
20 treating filter (pore size: 0.45 to 0.5 μ m; for
example, MAISHORI DISK-25-5, available from Toso Co.,
Ltd. or EKICHO DISK 25CR, available from German
Science Japan, Ltd., can be utilized) is used as
the sample for GPC. The sample is so adjusted to have
25 resin components in a concentration of from 0.5 to 5
mg/ml.

When a pressure fixing system is employed, a



1 pressure-fixable resin can be used. It may include,
for example, polyethylenes, polypropylene,
polymethylene, polyurethane elastomers, an
ethylene/ethyl acrylate copolymer, an ethylene/vinyl
5 acetate copolymer, ionomer resins, a styrene/butadiene
copolymer, a styrene/isoprene copolymer, linear
saturated polyesters, and paraffin.

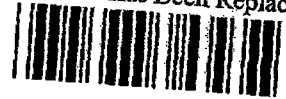
The magnetic toner of the present invention
may be optionally mixed with additives. The additives
10 may include, for example, lubricants such as zinc
stearate, abrasives such as cerium oxide and silicon
carbide, fluidity-providing agents such as aluminum
oxide, anti-caking agents, and conductivity-providing
agents such as carbon black and tin oxide.

15 Fine fluorine-containing polymer powders such
as fine polyvinylidene fluoride powder are also
preferable additives in view of fluidity, abrasion and
static charging stability.

For the purpose of improving releasability at
20 the time of heat-roll fixing, it is one of preferred
embodiments of the present invention to add to the
toner a waxy material such as a low-molecular weight
polyethylene, a low-molecular weight polypropylene,
microcrystalline wax, carnauba wax, sasol wax and
25 paraffin wax in an amount of from 0.5 to 5% by weight.
In particular, sasol wax is one of preferred release
agents.

1 The magnetic toner of the present invention
may preferably be produced by a process comprising the
steps of thoroughly mixing the magnetic toner
component materials in a mixing machine such as a ball
5 mill, well mixing the mixture by means of a heat
kneading machine such as a heat roll kneader and an
extruder, cooling the kneaded product to solidify,
thereafter mechanically pulverizing the solidified
product, and classifying the pulverized product to
10 obtain a magnetic toner. Alternatively, the magnetic
toner can also be produced by a method in which the
component materials are dispersed in a binder resin
solution, followed by spray drying to obtain a toner;
a method in which given materials are mixed in
15 monomers that constitute a binder resin to make up an
emulsion dispersion, followed by polymerization to
obtain a toner; and a method in which, in a . . .
microcapsule toner comprised of a core material and a
shell material, given materials are incorporated into
20 the core material or the shell material or into both
of them. The magnetic toner can also be produced by a
method in which desired additives and the magnetic
toner are optionally further thoroughly blended by
means of a mixing machine such as a Henschel mixer to
25 obtain a magnetic toner.

 The magnetic toner of the present invention
can be well used to for development, to convert



1 electrostatic images into visible images in
electrophotography, electrostatic recording,
electrostatic printing and so forth.

Fig. 1 shows an embodiment of a developing
5 assembly in which the magnetic toner of the present
invention can be applied.

An electrostatic image bearing member 1 is
rotated in the direction of an arrow. A non-magnetic
cylinder (a developing sleeve) 4 serving as a toner
10 carrier member is rotated in the same direction as the
electrostatic image bearing member 1 at a developing
zone. The developing sleeve 4 is provided in its
inside with a multi-polar permanent magnet 9. A
magnetic toner 11 delivered from a toner container 12
15 is spread on the developing sleeve 4, and a magnetic
blade 10 control the magnetic toner layer in a small
and uniform thickness. In the developing zone, a DC
bias voltage is applied to the developing sleeve 4
through a bias applying means 13. At this time, an AC
20 bias may also be applied simultaneously. The AC bias
when applied may preferably have a frequency of from
200 to 4,000 Hz and a potential difference between
peaks, of from 3,000 to 5,000 V. In Fig. 1, the
magnetic blade 10 is not in touch with the developing
25 sleeve 4, but a blade made of an elastic material such
as plastic or rubber may be in touch with it so that
the magnetic toner layer thickness can be controlled.



1

EXAMPLES

The present invention will be described below in greater detail by giving Examples. These by no means limit the present invention. In the following
5 formulation, "part(s)" refers to "part(s) by weight" in all occurrences.

Example 1

Styrene/butyl methacrylate copolymer 100 parts
(weight average molecular weight: 250,000;
10 first peak (peak 1): molecular weight 10,000;
second peak (peak 2): molecular weight 70,000)
Magnetic material 80 parts
(average particle diameter: 0.2 μ m; coercive
force: 90 oersted)
15 Sasol wax 3 parts
Iron compound (1) 2 parts
(molar ratio of NH_4^+ to Na^+ to H^+ :
0.9:0.05:0.05)

The above materials were thoroughly premixed
20 using a blender, and then kneaded using a twin-screw
kneading extruder set to 130°C. The resulting kneaded
product was cooled, and then crushed. Thereafter, the
crushed product was finely pulverized using a fine
grinding mill utilizing a jet stream. The resulting
25 finely pulverized product was further put in a multi-
division classifier utilizing the Coanda effect (Elbow
Jet Classifier, manufactured by Nittetsu Kogyo Co.) to



1 strictly classify and remove ultrafine powder and
coarse powder at the same time. Thus, a black fine
powder (a negatively chargeable magnetic toner) with
a weight average particle diameter of 8.5 μm was
5 obtained.

Then, 100 parts of the negatively chargeable
magnetic toner thus obtained, 0.6 part of hydrophobic
fine silica powder (average particle diameter: 15 nm)
and 0.3 part of fine strontium titanate powder
10 (average particle diameter: 1 μm) were mixed using a
Henschel mixer to obtain a one-component magnetic
toner. This magnetic toner had a saturation
magnetization of 28 Am^2/kg and a coercive force of 90
oersted.

15 The one-component magnetic toner obtained was
applied in a commercially available
electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and latent images
were formed, followed by developing, transferring and
20 fixing to make copying tests.

Copies were taken on 20,000 copy sheets in an
environment of normal temperature and normal humidity,
a temperature of 23°C and a humidity of 60%RH. As a
result, sharpe images with an image density of 1.40
25 ± 0.03 were obtained at the initial and following
stages. With regard to resolution of images also, a
resolution of 6.3 lines/mm at the initial stage was



1 maintained.

Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a
5 result, good images with an image density of 1.40 ± 0.03 were obtained at the initial and following stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of
10 80%RH, a 10,000 sheet copying test was also made. As a result, good images with an image density of 1.35 ± 0.03 were obtained at the initial and following stages. After the toner in the copying machine was left to stand for 4 days in the environment of high
15 temperature and high humidity, copies were taken on 10,000 copy sheets. Good images with a density of 1.35 ± 0.03 were obtained on the first and following copy sheets after copying was again started.

Restoration performance of the quantity of
20 triboelectricity of the magnetic toner in the environment of high humidity is shown in Table 1.

Example 2

Styrene/butyl methacrylate copolymer 100 parts
(weight average molecular weight: 250,000;
25 first peak: molecular weight 10,000; second peak: molecular weight 70,000)
Magnetic material 80 parts



- 1 (average particle diameter: 0.2 μm ; coercive
force: 90 oersted)

Sasol wax 3 parts

Iron compound (1) 2 parts

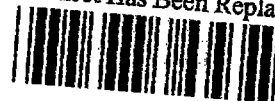
- 5 (molar ratio of NH_4^+ to Na^+ to H^+ :
0.98:0.01:0.01)

A one-component magnetic toner was obtained in
the same manner as in Example 1 except that the above
materials were used. This magnetic toner had a
10 saturation magnetization of 28 Am^2/kg and a coercive
force of 90 oersted.

The one-component magnetic toner obtained was
applied in a commercially available
electrophotographic copying machine NP-6060 (trade
15 name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

Copies were taken on 20,000 copy sheets in an
environment of a temperature of 23°C and a humidity of
60%RH. As a result, sharpe images with an image
20 density of 1.40 $\pm$ 0.03 were obtained at the initial and
following stages. With regard to resolution of images
also, a resolution of 6.3 lines/mm at the initial
stage was maintained.

Next, in an environment of low temperature and
25 low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.40



- 1 ± 0.03 were obtained at the initial and following stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of 80%RH, a 10,000 sheet copying test was also made. As a result, good images with an image density of 1.35 ± 0.03 were obtained at the initial and following stages. After the toner in the copying machine was left to stand for 4 days in the environment of high temperature and high humidity, copies were taken on 10,000 copy sheets. On the first sheet after copying was again started, images had an image density of 1.30 which was a little lower than that obtained before the toner had been left, but good images with a density of 1.35 ± 0.03 were obtained on the 10th and following copy sheets.

Restoration performance of the quantity of triboelectricity of the magnetic toner in the environment of high humidity is shown in Table 1.

20 Example 3

Styrene/butyl methacrylate copolymer 100 parts
(weight average molecular weight: 250,000;
first peak: molecular weight 10,000; second
peak: molecular weight 70,000)

25 Magnetic material 80 parts
(average particle diameter: 0.2 μ m; coercive
force: 90 oersted)



- 1 Sasol wax 3 parts
Iron compound (1) 2 parts

(molar ratio of NH_4^+ to Na^+ to H^+ :
0.8:0.15:0.05)

- 5 A one-component magnetic toner was obtained in the same manner as in Example 1 except that the above materials were used. This magnetic toner had a saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90 oersted.

- 10 The one-component magnetic toner obtained was applied in a commercially available electrophotographic copying machine NP-6060 (trade name; manufactured by Canon Inc.), and copying tests were made in the same manner as in Example 1.

- 15 Copies were taken on 20,000 copy sheets in an environment of a temperature of 23°C and a humidity of 60%RH. As a result, sharpe images with an image density of 1.40 ± 0.03 were obtained at the initial and following stages. With regard to resolution of images
20 also, a resolution of 6.3 lines/mm at the initial stage was maintained.

- Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a
25 result, good images with an image density of 1.40 ± 0.03 were obtained at the initial and following stages.

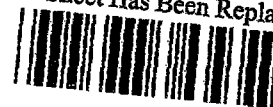


1 In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.35
5 ± 0.03 were obtained at the initial and following
stages. After the toner in the copying machine was
left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. On the first sheet after copying
10 was again started, images had an image density of 1.28
which was a little lower than that obtained before the
toner had been left, but good images with a density of
1.35 ± 0.03 were obtained on the 30th and following
copy sheets.

15 Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Example 4

Styrene/butyl methacrylate copolymer	100 parts
20 (weight average molecular weight: 250,000; first peak: molecular weight 10,000; second peak: molecular weight 70,000)	
Magnetic material	80 parts
25 (average particle diameter: 0.2 μ m; coercive force: 90 oersted)	
Sasol wax	3 parts
Iron compound (1)	2 parts



1 (molar ratio of $\text{NH}_4^{\oplus}$ to $\text{Na}^{\oplus}$ to $\text{H}^{\oplus}$:
0.5:0.2:0.3)

A one-component magnetic toner was obtained in the same manner as in Example 1 except that the above
5 materials were used. This magnetic toner had a saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90 oersted.

The one-component magnetic toner obtained was applied in a commercially available
10 electrophotographic copying machine NP-6060 (trade name; manufactured by Canon Inc.), and copying tests were made in the same manner as in Example 1.

Copies were taken on 20,000 copy sheets in an environment of a temperature of 23°C and a humidity of
15 60%RH. As a result, sharpe images with an image density of 1.40 ± 0.03 were obtained at the initial and following stages. With regard to resolution of images also, a resolution of 6.3 lines/mm at the initial stage was maintained.

20 Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a result, good images with an image density of 1.40 ± 0.03 were obtained at the initial and following
25 stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of



1 80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.35
±0.03 were obtained at the initial and following
stages. After the toner in the copying machine was
5 left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. On the first sheet after copying
was again started, images had an image density of 1.25
which was a little lower than that obtained before the
10 toner had been left, but good images with a density of
1.30 ±0.03 were obtained on the 30th and following
copy sheets.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
15 environment of high humidity is shown in Table 1.

Example 5

A one-component magnetic toner was obtained in
the same manner as in Example 1 except that the amount
of the magnetic material was changed to 120 parts.
20 This magnetic toner had a saturation magnetization of
42 Am²/kg and a coercive force of 90 oersted.

The one-component magnetic toner obtained was
applied in a commercially available
electrophotographic copying machine NP-6060 (trade
25 name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

Copies were taken on 20,000 copy sheets in an



1 environment of a temperature of 23°C and a humidity of
60%RH. As a result, sharpe images with an image
density of 1.35 ± 0.03 were obtained at the initial and
following stages. With regard to resolution of images
5 also, a resolution of 6.3 lines/mm at the initial
stage was maintained.

Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
10 result, good images with an image density of 1.40
 ± 0.03 were obtained at the initial and following
stages.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
15 80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.30
 ± 0.03 were obtained at the initial and following
stages. After the toner in the copying machine was
left to stand for 4 days in the environment of high
20 temperature and high humidity, copies were taken on
10,000 copy sheets. Good images with a density of
 1.30 ± 0.03 were obtained on the first and following
copy sheets after copying was again started.

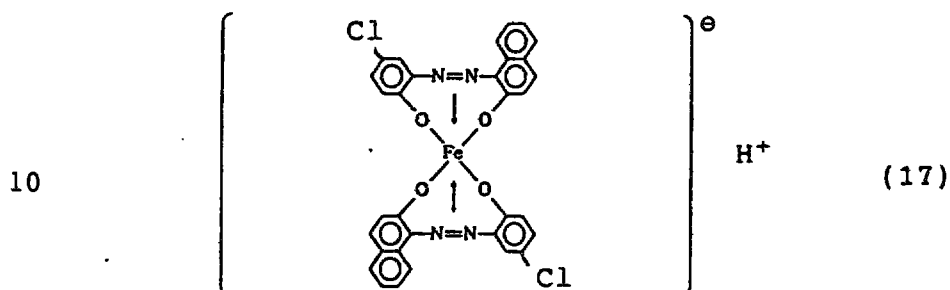
Restoration performance of the quantity of
25 triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Example 6

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- 1 A one-component magnetic toner was obtained in the same manner as in Example 1 except that the iron compound (1) was replaced with 3 parts of an iron compound represented by formula (17) shown below.
- 5 This magnetic toner had a saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90 oersted.



- The one-component magnetic toner obtained was applied in a commercially available
- 15 electrophotographic copying machine NP-6060 (trade name; manufactured by Canon Inc.), and copying tests were made in the same manner as in Example 1.

- Copies were taken on 20,000 copy sheets in an environment of a temperature of 23°C and a humidity of
- 20 60%RH. As a result, sharpe images with an image density of 1.35 ± 0.05 were obtained at the initial and following stages. With regard to resolution of images also, a resolution of 6.3 lines/mm at the initial stage was maintained.

- 25 Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a



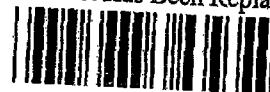
1 result, good images with an image density of 1.40
±0.05 were obtained at the initial and following
stages.

5 In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.25
±0.05 were obtained at the initial and following
stages. After the toner in the copying machine was
10 left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. However, on the first sheet after
copying was again started, images had an image density
of 1.05 which was lower than that obtained before the
15 toner had been left. Also after copying on the 100th
sheet, images had an image density of 1.20 ±0.05,
which was inferior to the images obtained before the
toner had been left.

Restoration performance of the quantity of
20 triboelectricity of the magnetic toner in the
environment of high temperature and high humidity is
shown in Table 1.

Example 7

A one-component magnetic toner was obtained in
25 the same manner as in Example 1 except that the
styrene/butyl methacrylate copolymer was replaced with
polyester resin (weight average molecular weight:



1 20,000) was used. This magnetic toner had a
saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive
force of 90 oersted.

5 The one-component magnetic toner obtained was
applied in a commercially available
electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

10 Copies were taken on 20,000 copy sheets in an
environment of a temperature of 23°C and a humidity of
60%RH. As a result, sharpe images with an image
density of 1.40 ± 0.03 were obtained at the initial and
following stages. With regard to resolution of images
also, a resolution of 6.3 lines/mm at the initial
15 stage was maintained.

Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.40
20 ± 0.03 were obtained at the initial and following
stages.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
25 a result, good images with an image density of 1.35
 ± 0.03 were obtained at the initial and following
stages. After the toner in the copying machine was



1 left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. Good images with a density of
1.35 $\pm$ 0.03 were obtained on the first and following
5 copy sheets after copying was again started.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high temperature and high humidity is
shown in Table 1.

10 Example 8

Styrene/butyl methacrylate copolymer 100 parts

(weight average molecular weight: 300,000;

first peak: molecular weight 6,000; second

peak: molecular weight 100,000)

15 Magnetic material 100 parts

(average particle diameter: 0.2 μ m; coercive
force: 90 oersted)

Low-molecular weight polypropylene wax 3 parts

Iron compound (1) 2 parts

20 (molar ratio of NH_4^+ to Na^+ to H^+ :

0.92:0.04:0.04)

The above materials were thoroughly premixed
using a blender, and then kneaded using a twin-screw
kneading extruder set to 130°C. The resulting kneaded
25 product was cooled, and then crushed. Thereafter, the
crushed product was finely pulverized using a fine
grinding mill utilizing a jet stream. The resulting



1 finely pulverized product was further put in a multi-
division classifier utilizing the Coanda effect (Elbow
Jet Classifier, manufactured by Nittetsu Kogyo Co.) to
strictly classify and remove ultrafine powder and
5 coarse powder at the same time. Thus, a black fine
powder (a negatively chargeable magnetic toner) with
a weight average particle diameter of $6.5 \mu\text{m}$ was
obtained. This magnetic toner had a saturation
magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90
10 oersted.

Then, 100 parts of the magnetic toner thus
obtained and 1 part of hydrophobic fine silica powder
(average particle diameter: 15 nm) were mixed using a
Henschel mixer to obtain a one-component magnetic
15 toner.

The one-component magnetic toner obtained was
applied in a commercially available laser beam printer
LBP-KT (trade name; manufactured by Canon Inc.) to
make printing tests.

20 Prints were obtained on 6,000 copy sheets in
an environment of a temperature of 23°C and a humidity
of 60%RH. As a result, sharp images with an image
density of 1.40 ± 0.03 were obtained at the initial and
following stages.

25 Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 6,000 sheet printing test was made. As a



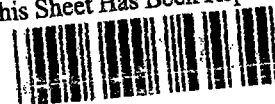
1 result, good images with an image density of 1.40
±0.03 were obtained at the initial and following
stages.

In an environment of high temperature and high
5 humidity, a temperature of 30°C and a humidity of
80%RH, a 3,000 sheet printing test was also made. As
a result, good images with an image density of 1.35
±0.03 were obtained at the initial and following
stages. After the toner in the printer was left to
10 stand for 4 days in the environment of high
temperature and high humidity, prints were obtained on
3,000 copy sheets. Good images with a density of 1.35
±0.03 were obtained on the first and following copy
sheets after printing was again started, where no
15 decrease in image density due to the toner having been
left to stand was seen.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high temperature and high humidity is
20 shown in Table 1.

Example 9

A one-component magnetic toner was obtained in
the same manner as in Example 8 except that the iron
compound (1) was replaced with 1 part of the iron
25 compound (2) (molar ratio of NH_4^+ to Na^+ to H^+ :
0.93:0.04:0.03). This magnetic toner had a saturation
magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90



1 oersted.

The one-component magnetic toner obtained was applied in a commercially available laser beam printer LBP-KT (trade name; manufactured by Canon Inc.) to
5 make printing tests.

Prints were obtained on 6,000 copy sheets in an environment of a temperature of 23°C and a humidity of 60%RH. As a result, sharpe images with an image density of 1.40 ± 0.05 were obtained at the initial and
10 following stages.

Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 6,000 sheet printing test was made. As a result, good images with an image density of 1.40 ± 0.05 were obtained at the initial and following
15 stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of 80%RH, a 3,000 sheet printing test was also made. As
20 a result, good images with an image density of 1.35 ± 0.05 were obtained at the initial and following stages. After the toner in the printer was left to stand for 4 days in the environment of high temperature and high humidity, prints were obtained on
25 3,000 copy sheets. Good images with a density of 1.35 ± 0.05 were obtained on the first and following copy sheets after printing was again started, where no



- 1 decrease in image density due to the toner having been
left to stand was seen.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
5 environment of high temperature and high humidity is
shown in Table 1.

Example 10

- | | | |
|----|---|-----------|
| | Styrene/butyl methacrylate copolymer | 100 parts |
| | (weight average molecular weight: 250,000; | |
| 10 | first peak: molecular weight 10,000; second | |
| | peak: molecular weight 70,000) | |
| | Magnetic material | 80 parts |
| | (average particle diameter: 0.2 μ m; coercive | |
| | force: 140 oersted) | |
| 15 | Sasol wax | 3 parts |
| | Iron compound (11) | 2 parts |

- The above materials were thoroughly premixed
using a blender, and then kneaded using a twin-screw
kneading extruder set to 130°C. The resulting kneaded
20 product was cooled, and then crushed. Thereafter, the
crushed product was finely pulverized using a fine
grinding mill utilizing a jet stream. The resulting
finely pulverized product was further put in a multi-
division classifier utilizing the Coanda effect (Elbow
25 Jet Classifier, manufactured by Nittetsu Kogyo Co.) to
strictly classify and remove ultrafine powder and
coarse powder at the same time. Thus, a black fine



1 powder (a negatively chargeable magnetic toner) with
a weight average particle diameter of $8.5 \mu\text{m}$ was
obtained.

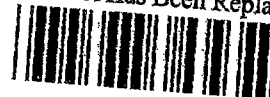
This magnetic toner had a saturation
5 magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 140
oersted.

Then, 100 parts of the magnetic toner thus
obtained and 0.6 part of hydrophobic fine silica
powder (BET specific surface area: $200 \text{ m}^2/\text{g}$) were
10 mixed using a Henschel mixer to obtain a one-component
magnetic toner with an average particle diameter of
 $8.5 \mu\text{m}$, having the hydrophobic fine silica powder.

The one-component magnetic toner obtained was
applied in a commercially available
15 electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and a 20,000 sheet
copying test was made in an environment of normal
temperature and normal humidity.

Sharpe images with an image density of 1.40
20 were obtained at the initial and following stages.
Images after 20,000 sheet copying also had sharp
images with a density of 1.39. With regard to
resolution of images also, a resolution of 6.3
lines/mm at the initial stage was maintained.

25 The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-10.8 \mu\text{c/g}$. The coarse powder



1 with a particle diameter larger than $10.8 \mu\text{m}$ was in a
quantity of 25% by weight before copying, and 28% by
weight after the copying, between which there was
little change.

5 Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.38
 ± 0.03 were obtained at the initial and following
10 stages.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.32
15 ± 0.03 were obtained at the initial and following
stages. Subsequently, after the toner in the copying
machine was left to stand for 4 days in the
environment of high temperature and high humidity,
copies were taken on 10,000 copy sheets. Good images
20 with a density of 1.32 ± 0.03 were obtained on the
first and following copy sheets after copying was
again started.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
25 environment of high humidity is shown in Table 1.

Example 11

Example 1 was repeated to obtain a magnetic



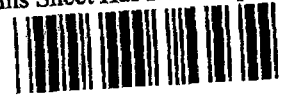
1 toner with a weight average particle diameter of 8.5
μm, except that a magnetic material (average particle
diameter: 0.2 μm; coercive force: 180 oersted) with
a higher coercive force than that in Example 10 was
5 used. The magnetic toner obtained had a saturation
magnetization of 33 Am²/kg and a coercive force of 180
oersted.

On the magnetic toner thus obtained, copying
tests were made in the same manner as in Example 10.

10 As a result, sharpe images with an image
density of 1.41 were obtained at the initial and
following stages. Images after 20,000 sheet copying
also had sharp images with a density of 1.37. With
regard to resolution of images, however, it was 6.3
15 lines/mm at the initial stage, but lowered to 5.6
lines/mm after 20,000 sheet copying.

The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was -11.3 μc/g. The coarse powder
20 with a particle diameter larger than 10.8 μm was in a
quantity of 23% by weight before copying, and 30% by
weight after 20,000 sheet copying, between which there
was a little increase.

Next, in an environment of low temperature and
25 low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.35



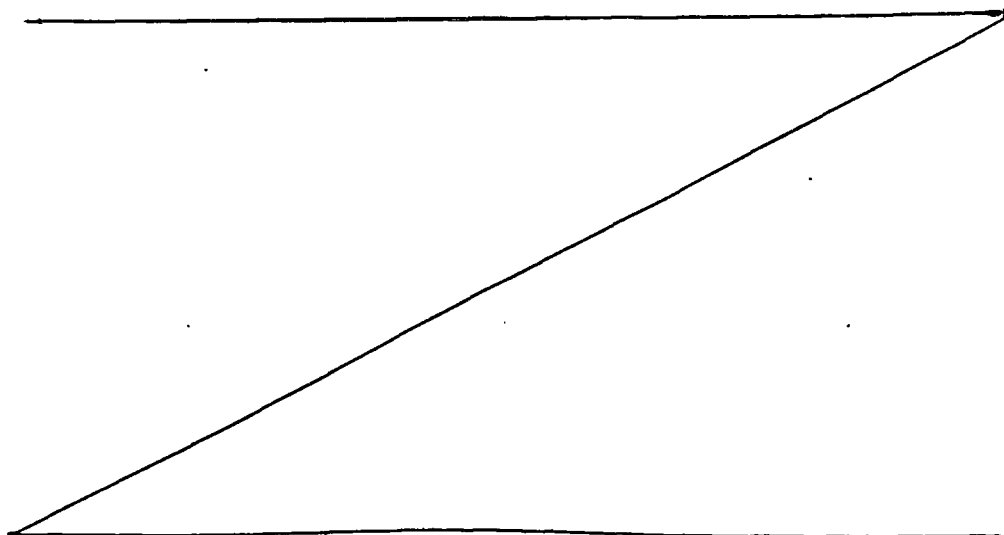
1 ± 0.03 were obtained at the initial and following stages.

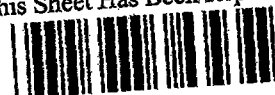
In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of 5 80%RH, a 10,000 sheet copying test was also made. As a result, good images with an image density of 1.31 ± 0.03 were obtained at the initial and following stages. Subsequently, after the toner in the copying machine was left to stand for 4 days in the 10 environment of high temperature and high humidity, copies were taken on 10,000 copy sheets. Good images with a density of 1.31 ± 0.03 were obtained on the first and following copy sheets after copying was again started.

15 Restoration performance of the quantity of triboelectricity of the magnetic toner in the environment of high humidity is shown in Table 1.

20

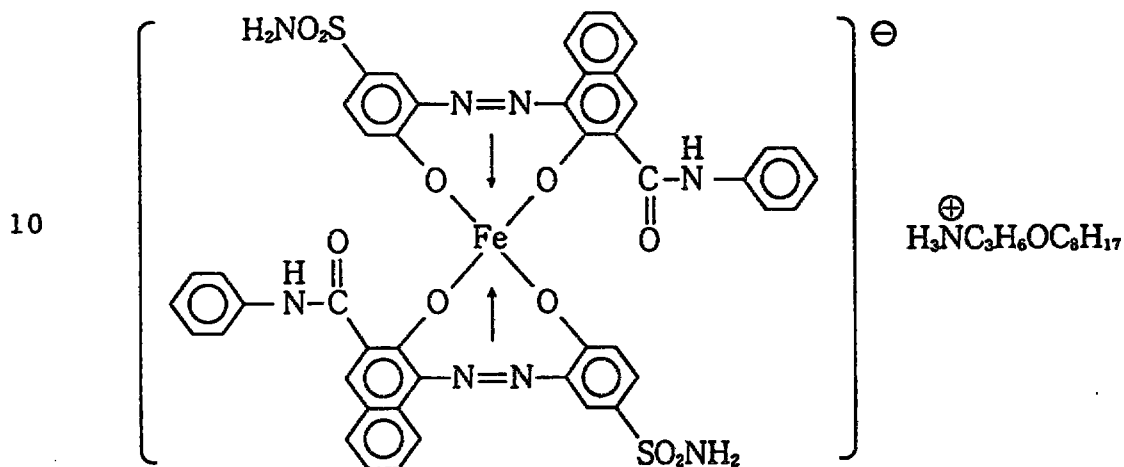
25





1 Comparative Example 1

A one-component magnetic toner was obtained in the same manner as in Example 10 except that the iron compound (11) was replaced with the iron compound (18) of the formula:



15 This one-component magnetic toner had a saturation magnetization of 28 Am²/kg and a coercive force of 140 oersted.

The obtained magnetic toner was used to conduct a copying test in the same manner as in Example 11.

Sharpe images with an image density of 1.37 were obtained at the initial stage of copying, but images after 20,000 sheet copying had a lowered image density of 1.25. With regard to resolution of images also, it was 6.3 lines/mm at the initial stage, but it was lowered to 4.5 lines/mm after 20,000 sheet



1 copying. The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-9.3 \mu\text{c/g}$. The coarse powder
with a particle diameter larger than $10.8 \mu\text{m}$ was in a
5 quantity of 25% by weight before copying, and it
increased to 39% by weight after 20,000 sheet copying.

Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
10 result, an initial image density of 1.35 decreased to
1.21.

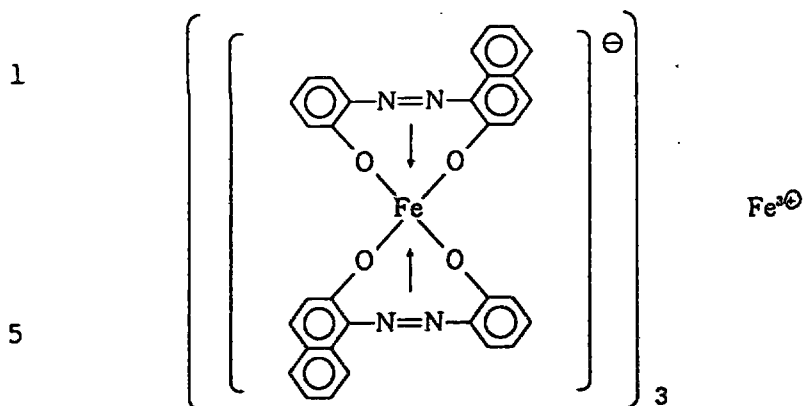
In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
15 a result, an initial image density of 1.25 lowered to
1.1. Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Comparative Example 2

20 A one-component magnetic toner was obtained in
the same manner as in Example 10 except that the iron
compound (11) was replaced with the iron compound (19)
of the formula:

25

This Sheet Has Been Replaced



This magnetic toner had a saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 140 oersteds.

10 The obtained magnetic toner was used to conduct a copying test in the same manner as in Example 10.

Sharpe images with an image density of 1.35 were obtained at the initial stage of copying, but after 20,000 sheet copying, the image density lowered to 1.21. With regard to resolution of images also, it was 6.3 lines/mm at the initial stage, but it was lowered to 4.0 lines/mm after 20,000 sheet copying. The quantity of triboelectricity of the magnetic toner was measured by blowing-off to ascertain that it was $-8.8 \mu\text{c/g}$. The coarse powder with a particle diameter larger than $10.8 \mu\text{m}$ was in a quantity of 27% by weight before copying, and it increased to 43% by weight after 20,000 sheet copying.

25 Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a

THIS SHEET HAS BEEN
REPLACED

This Sheet Has Been Replaced

1 result, an initial image density of 1.35 decreased to
1.23.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
5 80%RH, a 10,000 sheet copying test was also made. As
a result, an initial image density of 1.15 lowered to
1.00. Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

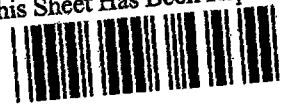
10 Comparative Example 3

A one-component magnetic toner was obtained in
the same manner as in Example 10 except that a
magnetic material having a coercive force (300
oersted) higher than in Example 11. The one-component
15 magnetic toner had a saturation magnetization of 31
 Am^2/kg and a coercive force of 300 oersted.

The obtained one-component magnetic toner was
used to conduct a copying test in the same manner as
in Example 10.

20 Sharpe images with an image density of 1.39
were obtained at the initial stage of copying, but
after 20,000 sheet copying, the image density lowered
to 1.22. With regard to resolution of images, it was
6.3 lines/mm at the initial stage, but it was lowered
25 to 4.5 lines/mm after 20,000 sheet copying. The
quantity of triboelectricity of the magnetic toner was
measured by blowing-off to ascertain that it was -10.1

THIS SHEET HAS BEEN
REPLACED



1 $\mu\text{c/g}$. The coarse powder with a particle diameter
larger than $10.8 \mu\text{m}$ was in a quantity of 26% by weight
before copying, and it increased to 44% by weight
5 after 20,000 sheet copying.

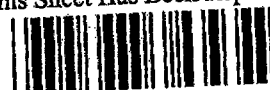
Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, an initial image density of 1.39 decreased to
10 1.25.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, an initial image density of 1.35 lowered to
15 1.21. Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Comparative Example 4

A one-component magnetic toner was obtained in
the same manner as in Example 10 except that a
20 magnetic material was used which had an average
particle diameter of $0.2 \mu\text{m}$, a saturation
magnetization of $30 \text{ Am}^2/\text{kg}$ and a coercive force of 140
oersted, and the amount of the magnetic material was
changed to 150 parts. This one-component magnetic
25 toner had a saturation magnetization of $18 \text{ Am}^2/\text{kg}$ and
a coercive force of 140 oersted.

The obtained one-component magnetic toner was



1 used to conduct a copying test in the same manner as
in Example 10.

The initial image density was 1.12, and the
density after 20,000 sheet copying further decreased
5 to 0.91. The images were not sharp with much fog.
With regard to the resolution of the images, the
initial one was 4.5 lines/mm, and after 20,000 sheet
copying, it was further lowered to 3.2 lines/mm.

The quantity of triboelectricity of the
10 magnetic toner was measured by blowing-off to
ascertain that it was $-5.4 \mu\text{c/g}$. The coarse powder
with a particle diameter larger than $10.8 \mu\text{m}$ was in a
quantity of 25% by weight before copying, and it
increased to 48% by weight after 20,000 sheet copying.

15 Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Example 12

Styrene/butyl methacrylate copolymer	100 parts
(weight average molecular weight: 250,000)	
20 Magnetic material	100 parts
(average particle diameter: $0.2 \mu\text{m}$; coercive force: 120 oersted)	
Low-molecular weight polypropylene wax	3 parts
25 Iron compound (12)	1 part

A black fine powder (magnetic toner) with a
weight average particle diameter of $6.5 \mu\text{m}$ was



1 obtained by using the above materials in the same
manner as in Example 10.

The magnetic toner had a saturation
magnetization of $32 \text{ Am}^2/\text{kg}$ and a coercive force of 120
5 oersted.

100 Parts of the obtained magnetic toner and
1.0 part of hydrophobic silica (BET specific surface
area: $200 \text{ m}^2/\text{g}$) were mixed using a Henschel mixer to
obtain a one-component magnetic toner.

10 The one-component magnetic toner obtained was
applied to a commercially available laser beam printer
LBP-KT (trade name; manufactured by Canon Inc.) to
make 6,000 sheet printing test.

Sharp images with an image density of 1.42
15 were obtained from the initial stage of printing.
Even images after 6,000 sheet printing were sharp with
a density of 1.45. With regard to the resolution of
the images also, an initial value of 7.1 lines/mm was
maintained.

20 The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-16.3 \text{ } \mu\text{c/g}$. The coarse powder
with a particle diameter larger than $8.0 \text{ } \mu\text{m}$ was in a
quantity of 10% by weight before printing, and 12% by
25 weight after 6,000 sheet printing so that there was
little change. Restoration performance of the
quantity of triboelectricity of the magnetic toner in



1 the environment of high humidity is shown in Table 1.

Example 13

A one-component magnetic toner was obtained in the same manner as in Example 12 except that the
5 amount of the magnetic material was changed to 150 parts. This one-component magnetic toner had a saturation magnetization of $42 \text{ Am}^2/\text{kg}$ and a coercive force of 120 oersted.

The obtained one-component magnetic toner was
10 used to conduct a printing test in the same manner as in Example 12.

As a result, sharpe images with an image density of 1.34 were obtained from the initial stage of printing. Images after 6,000 sheet printing were
15 sharp with a density of 1.32. On the other hand, as to the resolution of the images, it was 7.1 lines/mm at the initial stage, but it lowered to 5.6 lines/mm after 6,000 sheet printing.

The quantity of triboelectricity of the
20 magnetic toner was measured by blowing-off to ascertain that it was $-12.1 \text{ } \mu\text{C/g}$. The coarse powder with a particle diameter larger than $8.0 \text{ } \mu\text{m}$ was in a quantity of 12% by weight before printing, and it increased to 17% by weight after 6,000 sheet printing,
25 between which there was a little increase.

Restoration performance of the quantity of triboelectricity of the magnetic toner in the



1 environment of high humidity is shown in Table 1.

Example 14

Styrene/butyl methacrylate copolymer 100 parts

(weight average molecular weight: 350,000)

5 (peak 1: molecular weight 8,000; peak 2:

molecular weight 150,000)

Magnetic material 80 parts

(average particle diameter: 0.2 μm ; coercive

force: 110 oersted)

10 Sasol wax 3 parts

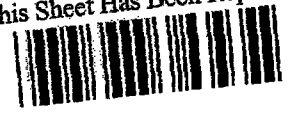
Iron compound (13) 3 parts

A black fine powder (negatively chargeable
magnetic toner) with a weight average particle
diameter of 7.5 μm was obtained by using the above
15 materials in the same manner as in Example 10.

The magnetic toner had a saturation
magnetization of 30 Am^2/kg and a coercive force of 110
oersted.

100 Parts of the obtained magnetic toner and
20 0.8 part of hydrophobic silica (BET specific surface
area: 200 m^2/g) were mixed using a Henschel mixer to
obtain a one-component magnetic toner.

The one-component magnetic toner obtained was
applied to a commercially available
25 electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.) to make 20,000 sheet
copying test.



1 As a result, sharp images with an image
density of 1.38 were obtained from the initial stage.
Images after 20,000 sheet copying were also sharp with
a density of 1.40. With regard to the resolution of
5 the images also, an initial value of 6.3 lines/mm was
maintained.

 The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-11.2 \mu\text{C/g}$. The coarse powder
10 with a particle diameter larger than $10.8 \mu\text{m}$ was in a
quantity of 33% by weight before printing, and 35% by
weight after 20,000 sheet copying, so that there was
little change. Restoration performance of the
quantity of triboelectricity of the magnetic toner in
15 the environment of high humidity is shown in Table 1.

20

25



Table 1

	Tribo- elec. 1)	Triboelectricity 2)					
		Shaken for 0 sec.		Shaken for 60 sec.		Shaken for 240 sec.	
		mC/kg	mC/kg %	mC/kg	%	mC/kg	%
Example 1	-11.0	- 9.9	90	-11.0	100	-11.0	100
2	-10.2	- 9.2	90	-10.0	98	-10.2	100
3	-10.4	- 9.4	90	-10.2	98	-10.4	98
4	-10.3	- 8.8	85	- 9.6	93	- 9.9	96
5	- 9.4	- 7.8	83	- 9.4	100	- 9.4	100
6	- 9.2	- 7.5	81	- 8.2	90	- 8.6	93
7	- 9.6	- 8.6	90	- 9.6	100	- 9.6	100
8	-12.5	-11.4	91	-12.5	100	-12.5	100
9	-11.2	-10.2	91	-11.2	100	-11.2	100
10	-10.0	- 8.3	83	- 9.2	92	- 9.5	95
11	-10.2	- 8.5	83	- 9.4	92	- 9.7	95
12	-13.0	-10.4	80	-11.3	87	-12.0	92
13	- 9.6	- 7.5	78	- 8.2	85	- 8.8	92
14	- 8.9	- 7.2	81	- 7.8	88	- 8.3	93
Comparative Example 1	- 6.8	- 5.1	75	- 5.6	82	- 6.1	89
2	- 6.2	- 4.3	70	- 4.7	75	- 5.1	82
3	- 8.5	- 7.0	82	- 7.7	90	- 7.9	93
4	- 4.2	- 3.3	78	- 3.7	88	- 3.9	92

Triboelectricity 1) : Quantity of triboelectricity of magnetic toner which was allowed to stand for 2 days at high temperature and high humidity in an uncovered polyethylene container and thereafter shaken in a tumbling mixer for 240 seconds.

Triboelectricity 2) : Quantity of triboelectricity of magnetic toner which was further allowed to stand for 4 days at high temperature and high humidity and thereafter shaken in a tumbling mixer.

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A magnetic toner for developing an electrostatic image is disclosed which has a binder resin, a magnetic material and an iron compound of the formula (I). The magnetic toner has a saturation magnetization of 20 to 50 Am²/kg and a coercive force of 40 to 200 oersted.

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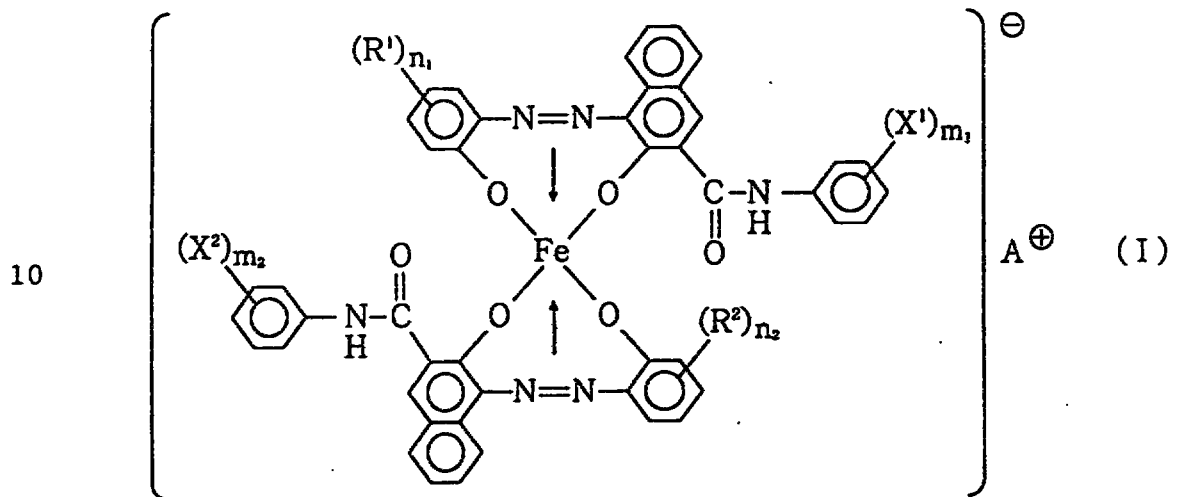
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1 WHAT IS CLAIMED IS:

1. A magnetic toner for developing an electrostatic image, comprising a binder resin, a magnetic material and a compound represented by the following formula (I):



- 15 wherein R¹ and R² each represent a hydrogen atom, a sulfonic acid group, a carboxylic acid group, a carboxylate group, a hydroxyl group or a halogen atom, and may be the same or different; n₁ and n₂ each represent an integer of 1 to 4; X¹ and X² each
- 20 represent a hydrogen atom or a halogen atom; m₁ and m₂ each represent an integer of 1 to 3; and A[⊕] represents a hydrogen ion, an alkali metal ion or an ammonium ion;

- said magnetic toner having a saturation
- 25 magnetization of from 20 Am²/kg to 50 Am²/kg and a coercive force of from 40 oersted to 200 oersted.

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- 1 2. The magnetic toner according to claim 1,
wherein the alkali metal ion is selected from the
group consisting of sodium ion and potassium ion.
- 5 3. The magnetic toner according to claim 1,
wherein the magnetic material is contained in an
amount satisfying the following expression:
$$MT = -(10/3) \times d + (70 \pm 15)$$

wherein MT represents a content (% by weight) of the
10 magnetic material, and d represents a weight average
particle diameter (μm) of the magnetic toner, provided
that d is not more than 9 μm .
- 15 4. The magnetic toner according to claim 1,
wherein $A^{\oplus}$ comprises an ammonium ion and an alkali
metal ion.
- 20 5. The magnetic toner according to claim 4,
wherein $A^{\oplus}$ has 80 to 98 mol% of ammonium ion.
- 25 6. The magnetic toner according to claim 5,
wherein $A^{\oplus}$ has 85 to 95 mol% of ammonium ion.
7. The magnetic toner according to claim 1,
25 wherein $A^{\oplus}$ comprises an ammonium ion and an hydrogen
ion.

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1 8. The magnetic toner according to claim 7,
wherein $A^{\oplus}$ has 80 to 98 mol% of ammonium ion.

5 9. The magnetic toner according to claim 8,
wherein $A^{\oplus}$ has 85 to 95 mol% of ammonium ion.

10 10. The magnetic toner according to claim 1,
wherein $A^{\oplus}$ comprises an ammonium ion, an alkali metal
ion and an hydrogen ion.

11. The magnetic toner according to claim 10,
wherein $A^{\oplus}$ has 80 to 98 mol% of ammonium ion.

15 12. The magnetic toner according to claim 11,
wherein $A^{\oplus}$ has 85 to 95 mol% of ammonium ion.

13. The magnetic toner according to claim 1,
which has negative triboelectricity.

20 14. The magnetic toner according to claim 1,
wherein the iron compound is contained in an amount of
0.1 to 10 parts by weight based on 100 parts by weight
of the binder resin.

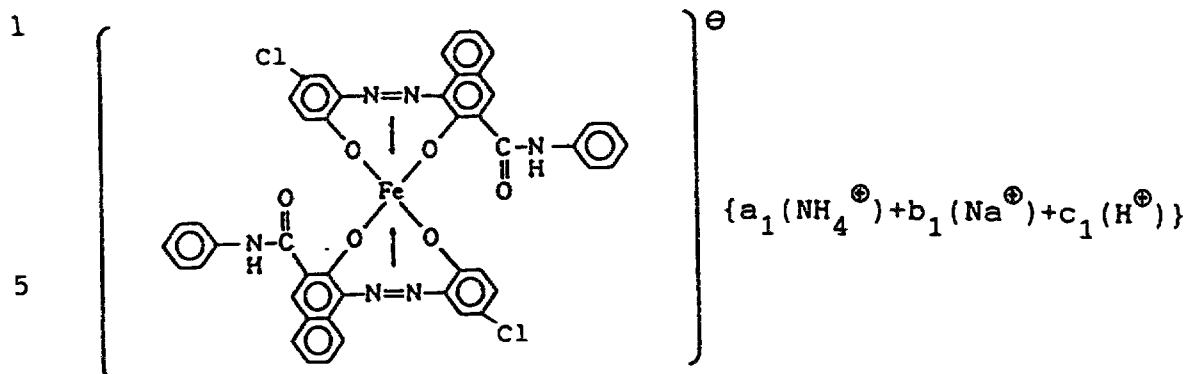
25 15. The magnetic toner according to claim 1,
wherein the iron compound is represented by the
following formula:



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wherein $a_1 + b_1 + c_1$ is 1.

16. The magnetic toner according to claim 15,
wherein a_1 is 0.8 to 0.98; b_1 is 0.01 to 0.19; and c_1
is 0.01 to 0.19.

17. The magnetic toner according to claim 16,
wherein a_1 is 0.85 to 0.95; b_1 is 0.01 to 0.14; and c_1
is 0.01 to 0.14.

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ABSTRACT OF THE DISCLOSURE

A magnetic toner for developing an electrostatic image is disclosed which has a binder resin, a magnetic material and an iron compound of the formula (I). The magnetic toner has a saturation magnetization of 20 to 50 Am²/kg and a coercive force of 40 to 200 oersted.

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FIG. 1

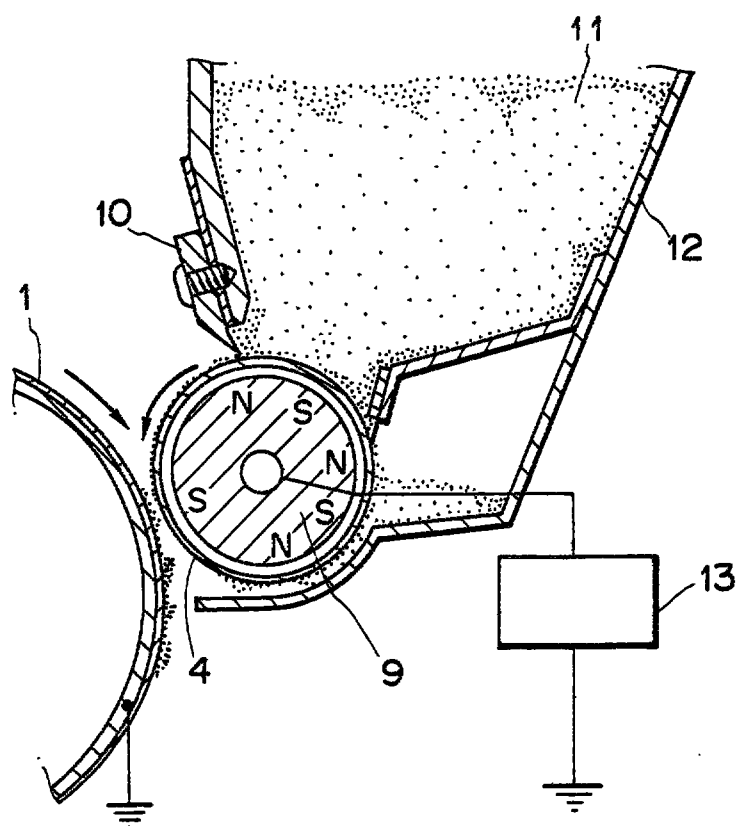
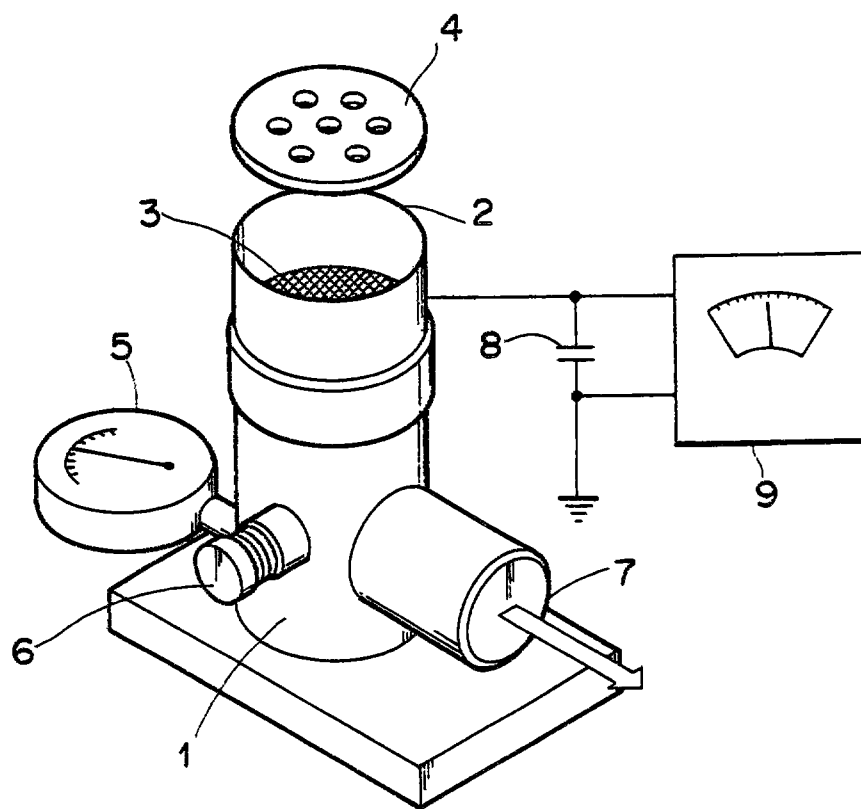
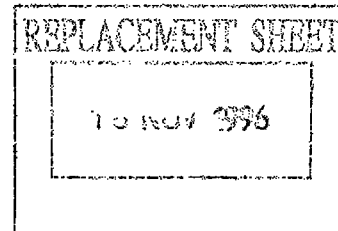


FIG. 2



- 1 -



1 Magnetic Toner for Developing
 Electrostatic Image

BACKGROUND OF THE INVENTION

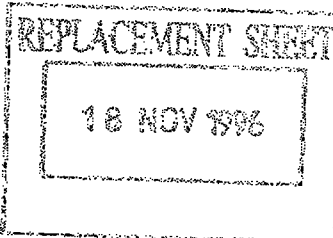
5 Field of the invention

 This invention relates to a magnetic toner for
developing an electrostatic image, used in image
forming processes such as electrophotography and
electrostatic recording, to render electrostatic
10 latent images visible.

Related Background Art

 As electrophotography, various methods are
disclosed in U.S. Patent No. 2,297,691, Japanese
Patent Publication No. 42-23910 and Japanese Patent
15 Publication No. 43-24748 and so forth.

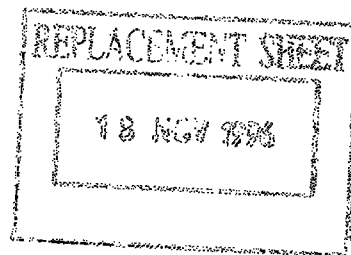
 Developing systems applied in such
electrophotography are roughly grouped into a dry
developing method and a wet developing method. The
former is further grouped into a method making use of
20 one-component developers and a method making use of
two-component developers. The developing method
making use of one-component developer has a feature
that developing apparatus can be made small-sized.
This method, however, has difficulty in imparting
25 sufficient triboelectricity to the toner and hence it
has a problem that the allowable scope of the
designing of toners and developing systems is narrow.



1 On the other hand, the developing method making use of
the two-component developer can impart sufficient
charges to toners and hence has the advantage that it
has wider tolerance for designing, but has a problem
5 that it requires a means for uniformly controlling the
mixing ratio of the toner and the carrier, making its
apparatus complicated.

As toners used in these developing methods,
fine powders comprising a colorant such as a dye or
10 pigment dispersed in a natural or synthetic resin are
hitherto used. For example, toner particles are
prepared by pulverizing a dispersion of a colorant in
a binder resin such as polystyrene to a size of about
1 to 30 μm . As a magnetic toner, toner particles
15 containing magnetic material particles such as
magnetite are used.

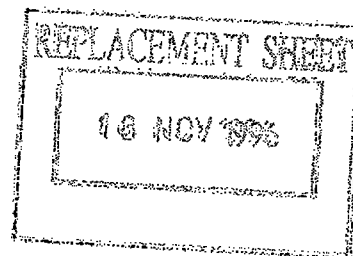
Toners have positive charges or negative
charges depending on the polarity of electrostatic
latent images to be developed. In order to charge
20 toners, it is possible to utilize triboelectric
chargeability of resins that compose toners. In such
a method, however, the chargeability of the toner is
so small that toner images obtained by development
tend to be foggy and unclear. In order to impart a
25 desired triboelectric chargeability to toners, a dye
or pigment capable of controlling chargeability and
also a charge control agent are commonly added.



1 However, toners containing such charge control
agents tend to contaminate the toner carrying members
such as the developing sleeve, and hence such toners
tend to cause a decrease in quantity of
5 triboelectricity as the number of copies taken
increases, resulting in a decrease in image density.
Charge control agents of a certain type have a small
quantity of triboelectricity to tend to be affected by
temperature and humidity, and hence may cause
10 variations of image density in accordance with
environmental changes. Certain charge control agents
have a poor dispersibility in resins, and hence toners
making use of such charge control agents tend to have
uneven triboelectricity between toner particles,
15 tending to cause fogging. Certain charge control
agents have poor storage stability so that toners may
undergo a decrease in triboelectric performance during
a long-term storage.

 As a means for solving these problems, .
20 Japanese Patent Publication Nos. 43-17955, 55-42752
and 63-1994 propose various kinds of metal complexes
as charge control agents. These charge control agents
certainly have a good negative triboelectric
chargeability. Most of them, however, are chromium
25 compounds, and more improvement has been sought from
the viewpoint of environmental safety.

 Japanese Patent Application Laid-open Nos. 61-



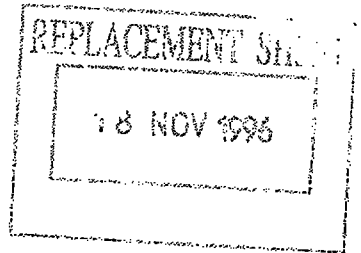
1 155464, 61-101558 and 61-155463 propose iron
complexes.

These publications disclose that the iron
complexes have a negative triboelectric chargeability
5 and have a very good compatibility with resins.
However, studies made by the present inventors have
revealed that only some of them can provide magnetic
toners providing a more stable image quality in the
one-component development system as described later.

10 In order to maintain the high image quality
obtained at the initial stage, without regard to the
number of copies taken, it is insufficient to only
maintain the quantity of triboelectricity, but the
particle size distribution of the toner at the initial
15 stage must be kept constant. In particular, it is
important for the toner particles of relatively large
particle size (coarse powder) to be used in
development in a good efficiency to prevent their
accumulation. For such purpose, the magnetic
20 properties and quantity of triboelectricity of
magnetic toners must be adjusted to proper values.
Taking these points into account, the present
inventors have studied charge control agents to find
that quantity of negative triboelectricity becomes
25 smaller when organic ammonium ions are used as counter
ions. The reason is unclear, but is presumed to be
due to a positive triboelectric chargeability inherent

1 in organic ammonium ions as usually known in the art.
Japanese Patent Application Laid-open No. 61-101558
discloses that organic ammonium ions are effective to
improve the dispersibility of metal complexes in
5 resins. According to the studies made by the present
inventors, however, in the case of one-component
developers making use of magnetic toners, the organic
ammonium ions exert greater influence on a decrease in
triboelectric chargeability than on the improvement of
10 dispersibility, so that the coarse powder in the toner
accumulates as developing is repeated many times, to
cause a slight lowering of image quality.

Polyvalent inorganic ions disclosed in
Japanese Patent Application Laid-open No. 63-267793
15 also have caused accumulation of the coarse powder in
toners. Negative charge control agents disclosed in
Japanese Patent Application Laid-open No. 63-267793
have polyvalent ions as counter ions to make the
molecular structure larger, so that they show improved
20 dispersibility in resins than the negative charge
control agent disclosed in Japanese Patent Application
Laid-open No. 61-155464 does. As a result, the
carrier contamination due to the toner can be
repressed prolonging the life time of the developer
25 from 50,000 to 100,000 sheet copying to 200,000 sheet
or more as so disclosed therein. According to the
studies made by the present inventors, however, in

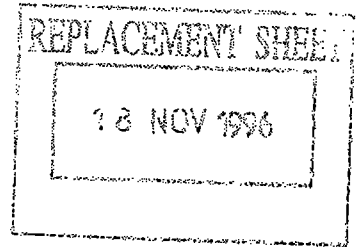


1 order to maintain the good image quality at the
initial stage using a magnetic toner in one-component
development, it is necessary not only to keep the
quantity of triboelectricity constant, but as
5 previously stated, also to maintain a high quantity of
triboelectricity, so that the coarse powder in the
toner can also participate in the development. From
such viewpoints, the iron complexes of polyvalent ions
as disclosed in Japanese Patent Application Laid-open
10 No. 63-267793 are not suited for magnetic toners. The
coarse powder tend to accumulate also in the case of
the iron complexes having a substituent such as a
nitro group as shown in Japanese Patent Application
Laid-open No. 61-155463, or those having a sulfonamide
15 group, in Japanese Patent Application Laid-open No. 61-
155464.

Meanwhile, with regard to magnetic properties
of magnetic toners, proposals are made as follows:

Japanese Patent Application Laid-open Nos. 58-
20 95748, 58-98744 and 3-95578 report the magnetic
properties of magnetic toners.

According to Japanese Patent Application Laid-
open No. 58-95748, saturation magnetization has an
influence on transport performance of magnetic toner
25 particles. Those with a saturation magnetization less
than 23 emu/g weaken magnetic transport power to tend
to cause uneven development. Those with a saturation

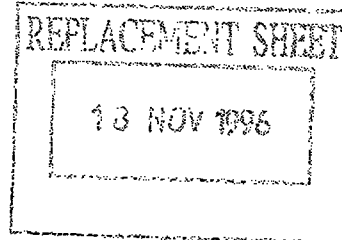


- 7 -

1 magnetization more than 50 emu/g come to have a large
quantity of magnetic powder in magnetic toners to make
fixing performance low or developing performance poor.
Toner particles with a coercive force less than 150
5 oersted extremely lower the developing performance,
and those with a coercive force more than 350 oersted
strengthen agglomeration force of toner particles to
cause a problem in toner transport performance.

Japanese Patent Application Laid-open No. 58-
10 98744 discloses that coercive force of 150 oersted or
more is required in order to obtain fog-free images in
reversal development.

Japanese Patent Application Laid-open No. 3-
95578 discloses to reduce the quantity of a magnetic
15 material so that a color toner with less turbidity can
be obtained. For this reason, the magnetic toner is
made to have a saturation magnetization of 40 emu/g or
less, and a magnetic roller (a developing sleeve) is
designed so as to compensate any lowering of the
20 transport power of the magnetic toner. In any cases,
the saturation magnetization is controlled taking
account of the transport performance of magnetic
toners and the coercive force is controlled for
developing performance. Although the image quality at
25 the initial stage can be improved by controlling
magnetic properties of the magnetic toner, it is
difficult to control image deterioration due to



1 changes in toner particle size that may occur as
developing is repeated many times. In order to
prevent the magnetic toner from the change in particle
size, both the quantity of triboelectricity of the
5 magnetic toner and the magnetic properties thereof
must be taken into account.

SUMMARY OF THE INVENTION

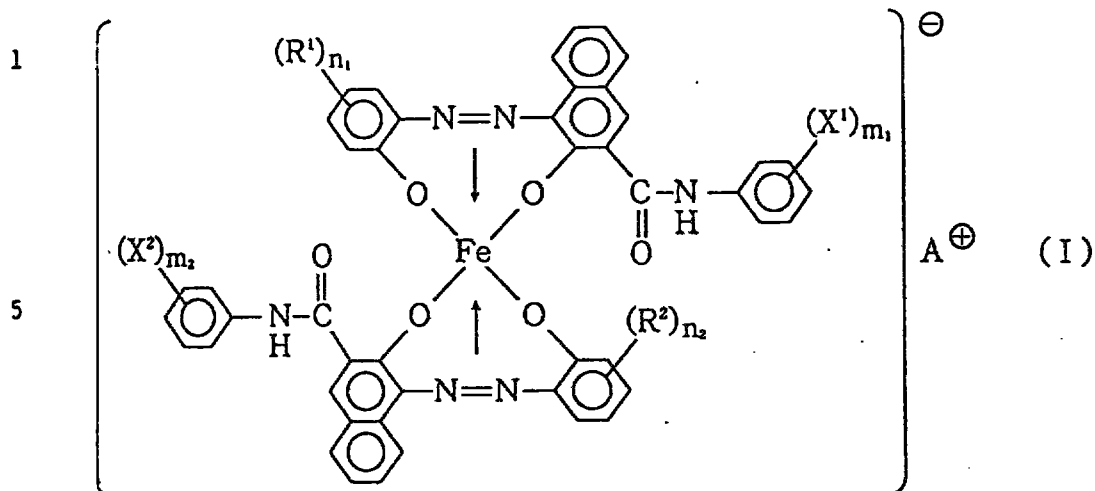
An object of the present invention is to
10 provide a magnetic toner for developing an
electrostatic image, having solved the problems
discussed above.

Another object of the present invention is to
provide a toner for developing an electrostatic image,
15 causing less image deterioration during the
development of a large number of copying sheets.

Still another object of the present invention
is to provide a magnetic toner having a superior
environmental stability.

20 A further object of the present invention is
to provide a magnetic toner having a superior
stability when left to stand.

This invention provides a magnetic toner for
developing an electrostatic image, comprising a binder
25 resin, a magnetic material and an iron compound
represented by the following formula (I):



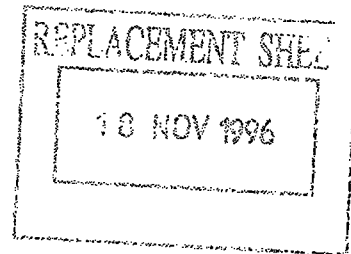
wherein R^1 and R^2 each represent a hydrogen atom, a
 10 sulfonic acid group, a carboxylic acid group, a
 carboxylate group, a hydroxyl group or a halogen atom,
 and may be the same or different; n_1 and n_2 each
 represent an integer of 1 to 4; X^1 and X^2 each
 represent a hydrogen atom or a halogen atom; m_1 and m_2
 15 each represent an integer of 1 to 3; and $A^\oplus$ represents
 a hydrogen ion, an alkali metal ion or an ammonium
 ion;

said magnetic toner having a saturation
 magnetization of from $20 \text{ Am}^2/\text{kg}$ to $50 \text{ Am}^2/\text{kg}$ and a
 20 coercive force of from 40 oersted to 200 oersted.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an example of a developing
 assembly in which the magnetic toner of the present
 25 invention can be applied.

Fig. 2 schematically illustrates a measuring
 device for measuring quantity of triboelectricity of



- 10 -

1 magnetic toners.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

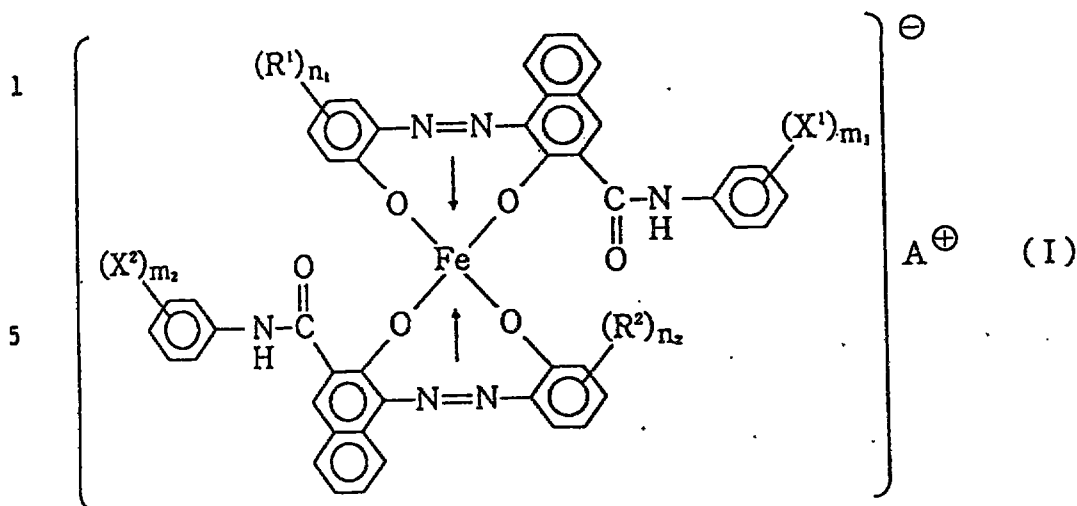
According to the studies made by the present
5 inventors, it is important to properly balance the
quantity of triboelectricity and magnetic properties
of a magnetic toner in order to maintain the initial
good image quality when the magnetic toner is used in
one-component developing system. Based on such a
10 finding, the present inventors studied various types
of charge control agents in magnetic toner of various
magnetic properties. As a result, they discovered
that changes in particle size of magnetic materials
that may occur as developing is repeated many times
15 can be inhibited and the initial good image quality
can be maintained when a specific iron compound is
used in a toner for developing electrostatic images,
where the toner has a saturation magnetization of from
20 to 50 Am²/kg and a coercive force of from 40 to 200
20 oersteds. They have thus accomplished the present
invention.

The iron compound used in the present
invention is represented by the following formula (I).
Formula (I)

25

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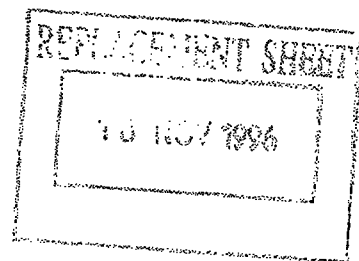
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wherein R^1 and R^2 each represent a hydrogen atom, a
 10 sulfonic acid group, a carboxylic acid group, a
 carboxylate group, a hydroxyl group or a halogen atom,
 and may be the same or different; n_1 and n_2 each
 represent an integer of 1 to 4; X^1 and X^2 each
 represent a hydrogen atom or a halogen atom; m_1 and m_2
 15 each represent an integer of 1 to 3; and $A^{\oplus}$ represents
 a hydrogen ion, an alkali metal ion or an ammonium
 ion;

$A^{\oplus}$ may preferably be an ammonium ion or be
 mainly composed of an ammonium ion (70 mol% or more).
 20 $A^{\oplus}$ may more preferably be a mixture of an ammonium ion
 and an alkali metal ion and/or a hydrogen ion, and be
 mainly composed of an ammonium ion. Still more
 preferably, in the above mixture, the ammonium ion may
 be in a content of from 80 to 98 mol%, and more
 25 preferably from 85 to 95 mol%.

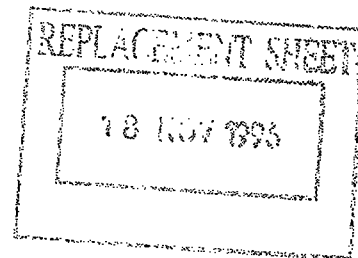
According to the studies made by the present
 inventors, when the compound has ammonium ions and



1 alkali metal ions or hydrogen ions in combination, the
quantity of triboelectricity of the magnetic toner
having been left to stand in an environment of high
humidity can be restored to the original (i.e., before
5 leaving to stand) quantity of triboelectricity, and
also can be recovered more quickly with a stable image
quality. On the other hand, when the compound has
only protons or alkali metal ions as cations, the
magnetic toner having been left in an environment of
10 high humidity can be triboelectrically charged
quickly, but the quantity of triboelectricity can not
be well restored to the original quantity of
triboelectricity, tending to cause a decrease in image
density.

15 According to the studies made by the present
inventors, a good compound that shows less
deterioration even when left to stand over a long
period of time can be obtained when ammonium ions and
alkali metal ions or hydrogen ions are present
20 together in the compound.

In particular, the rate and the level of
restoration can be well maintained when ammonium ions
are in a content of from 80 mol% to 98 mol%. If
ammonium ions are in a content of less than 80 mol%,
25 the restored level of triboelectricity may become a
little lower than the original quantity of
triboelectricity. On the other hand, if they are in a



1 content more than 98 mol%, the rate of restoration may
become lower. When the ammonium ions are in a content
of from 85 mol% to 95 mol%, the rate of restoration
preferably become higher. In addition, better results
5 can be obtained also on restoration performance in an
environment of high humidity.

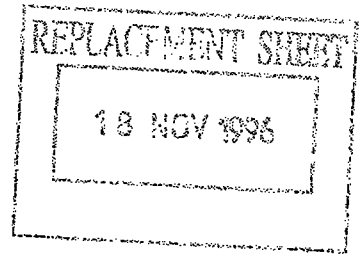
The reason therefor is, according to the
mechanism of ion conduction proposed as one of the
mechanisms of triboelectric charging, presumed as
10 follows:

It is presumed that when water content is
relatively large as in the environment of high
humidity, monovalent cations with small ion radii have
high mobility so that charges once having leaked when
15 the toner is left to stand can be quickly restored.

For that purpose, it is preferable for the
alkali metal ions or hydrogen ions as the monovalent
cations to be in a uniform content of at least 2
mol%, and more preferably at least 5 mol%.

20 In the present invention, the performance of
restoration of the quantity of triboelectricity is
expressed by a proportion of the restored charge to
the original charge when a triboelectrically charged
magnetic toner in an environment of high humidity is
25 left to stand for a long period of time and thereafter
shaked together with an iron powder carrier.

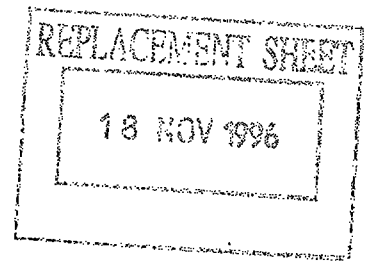
Stated specifically, 2.5 g of a magnetic toner



1 and 47.5 g of an iron powder carrier are collected in a
50 cm³ polyethylene container, and left to stand for 2
days in an environment of a temperature of 30°C and a
relative humidity of 80%RH in an uncovered state.

5 These are then shaken in a tumbling mixer for 240
seconds, and thereafter an about 0.5 g portion of the
powdery mixture is collected to measure the quantity
of triboelectricity of the magnetic toner by blowing-
off. The measurement thus obtained is regarded as the
10 original quantity of triboelectricity. After the
powdery mixture is further left to stand for 4 days in
an uncovered state, followed by shaking in the
tumbling mixer for 0, 60 or 240 seconds to measure the
corresponding quantities of triboelectricity of the
15 magnetic toner, and its percentage to the quantity of
triboelectricity of the original magnetic toner is
calculated.

Fig. 2 illustrates an apparatus for measuring
the quantity of triboelectricity. In a measuring
20 container 2 made of a metal at the bottom of which is
provided an electroconductive screen 3 of 500 meshes
(appropriately changeable to the size the screen may
not pass the carrier particles), the sample is put and
the container is covered with a plate 4 made of a
25 metal. Next, in a suction device 1 (made of an
insulating material at least at the part coming into
contact with the measuring container 2), air is sucked



1 from a suction opening 7 and an air-flow control valve
6 is operated to control the pressure indicated by a
vacuum indicator 5 to be 250 mmHg. In this state,
suction is sufficiently carried out (for about 1
5 minute). The potential indicated by a potentiometer
at this time is expressed by V (volt). Reference
numeral 8 denotes a capacitor, whose capacitance is
expressed by C (μ F). The charges obtained therefrom
is divided by the weight (g) of the magnetic toner
10 removed by suction to obtain a value which is the
quantity of triboelectricity (mC/Kg).

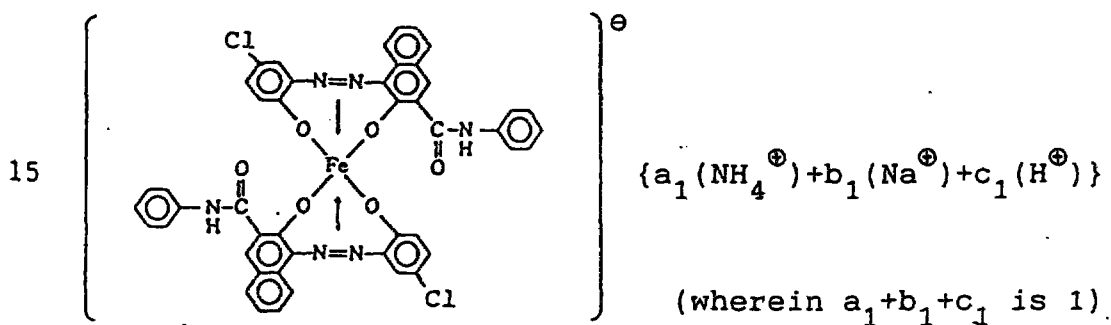
The magnetic toner of the present invention
can also well prevent photosensitive members from
being scraped. It can be presumed that, because of a
15 good transfer rate of the magnetic toner of the
present invention, the amount of the magnetic toner
remaining on a photosensitive member after the step of
transfer is so small resulting in a small load in the
step of cleaning. As can be also considered, the iron
20 compound used in the present invention acts on the
surface of the magnetic material to improve its state
of dispersion in a resin, so that the magnetic
material present on the surfaces of the magnetic toner
particles has decreased.

25 In the present invention, complexes
represented by formula (I) may be mixed to obtain the
iron compound having the mixture of cations. A better

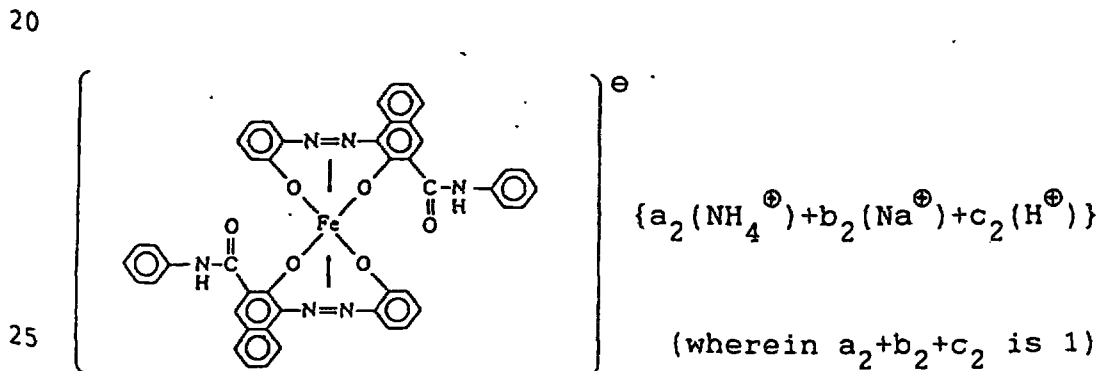
1 shelf stability can be obtained when the iron compound
is synthesized at one time while changing the
percentage or pH of cationic components during its
synthesis. This is presumably because the respective
5 cations can be more uniformly dispersed and at the
same time different cationic complexes can preferably
interact, when the compound is synthesized at one
time.

Examples of the iron compound represented by
10 formula (I) are shown below.

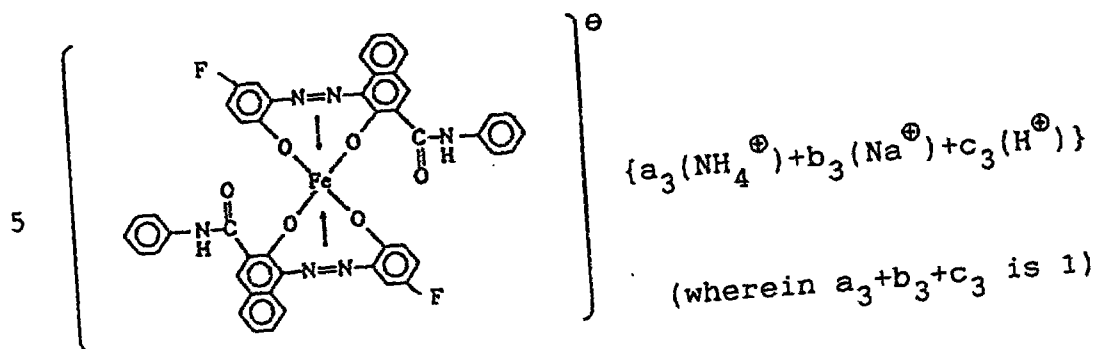
Iron compound (1)



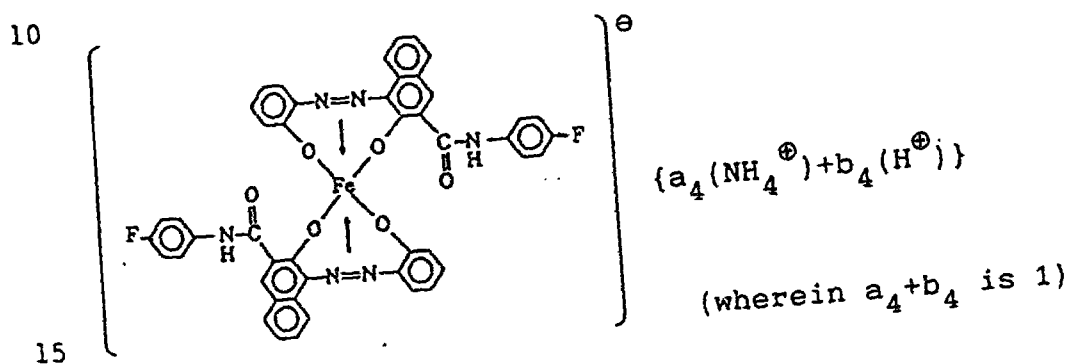
Iron compound (2)



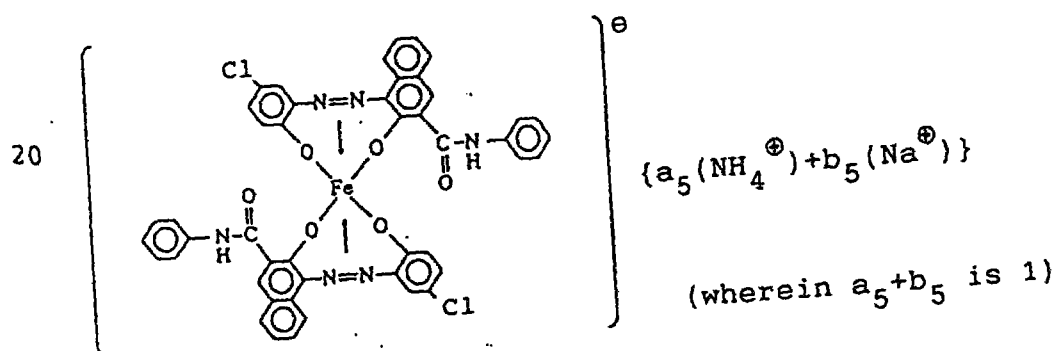
1 Iron compound (3)



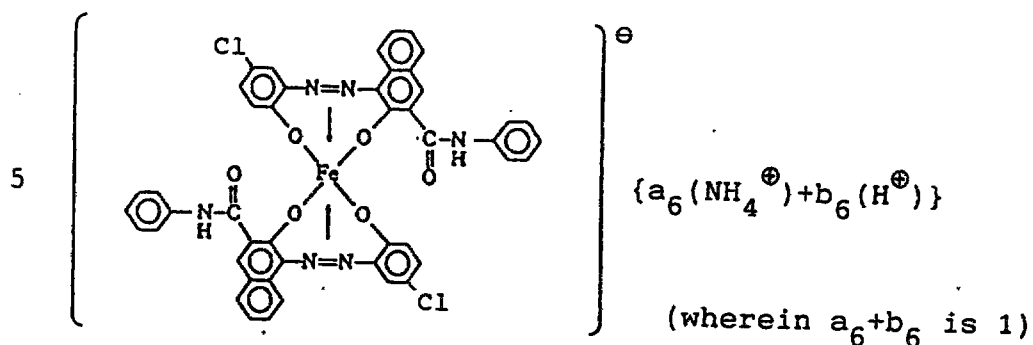
Iron compound (4)



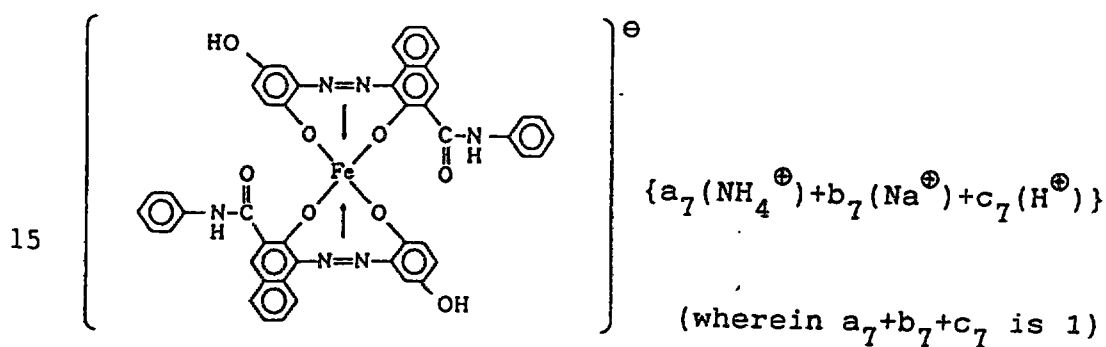
Iron compound (5)



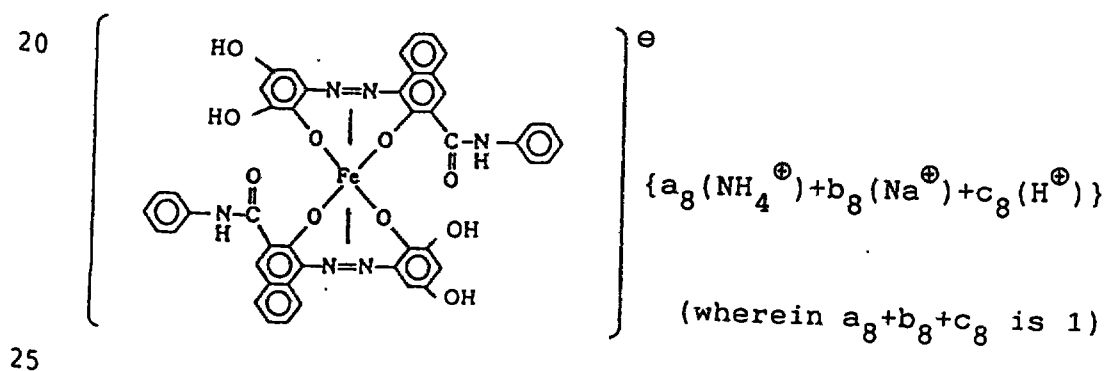
1 Iron compound (6)



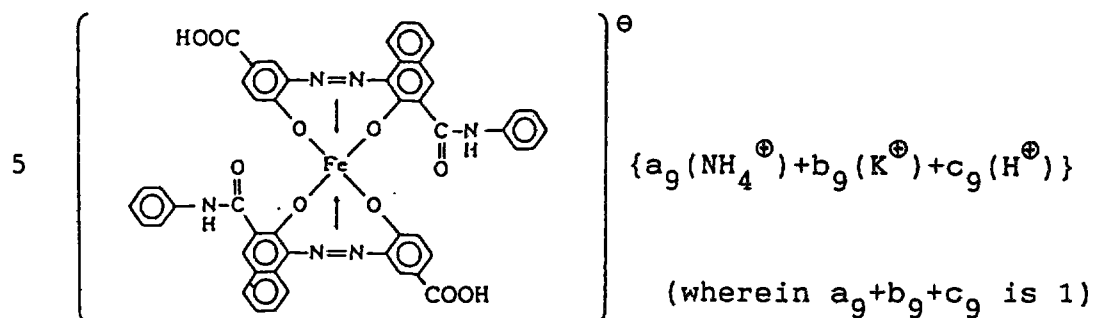
10 Iron compound (7)



Iron compound (8)

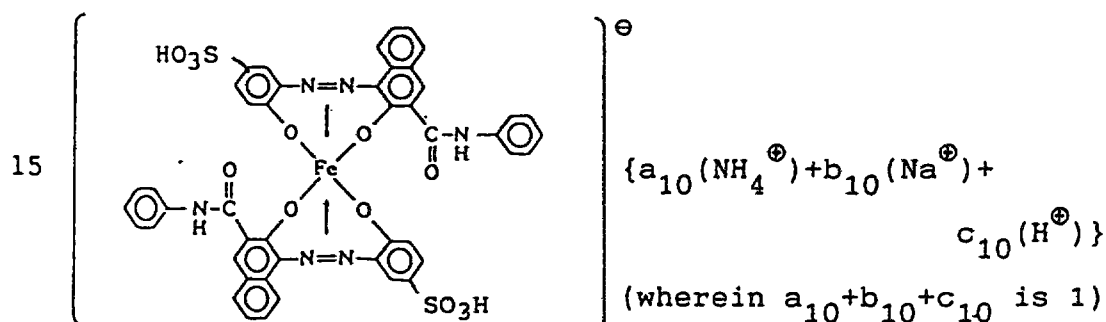


1 Iron compound (9)



10

Iron compound (10)



In the above exemplary iron compounds (1) to (10), a_1 through a_{10} may preferably be 0.80 to 0.98; b_1 through b_{10} , 0.01 to 0.20; and c_1 through c_{10} , the balance. More preferably, a_1 through a_{10} may be 0.85 to 0.95; b_1 through b_{10} , 0.01 to 0.05; and c_1 through c_{10} , the balance.

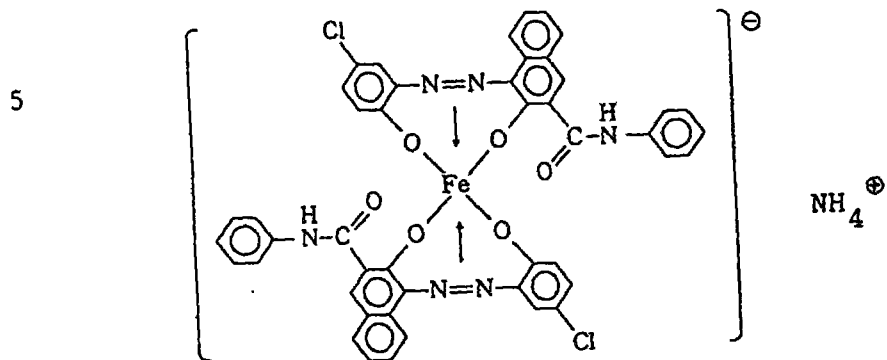
25 In the above iron compound (1), a_1 may preferably be 0.80 to 0.98; b_1 , 0.01 to 0.19; and c_1 , 0.01 to 0.19. More preferably, a_1 may be 0.85 to

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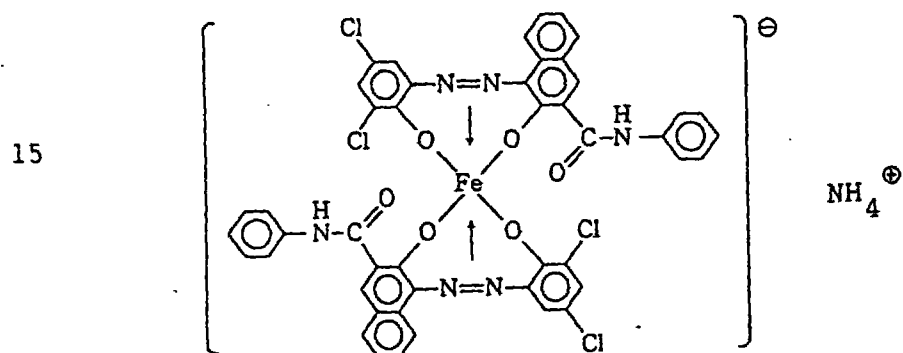
1 0.95; b_1 , 0.01 to 0.14; and c_1 , 0.01 to 0.14.

Iron compound (11)

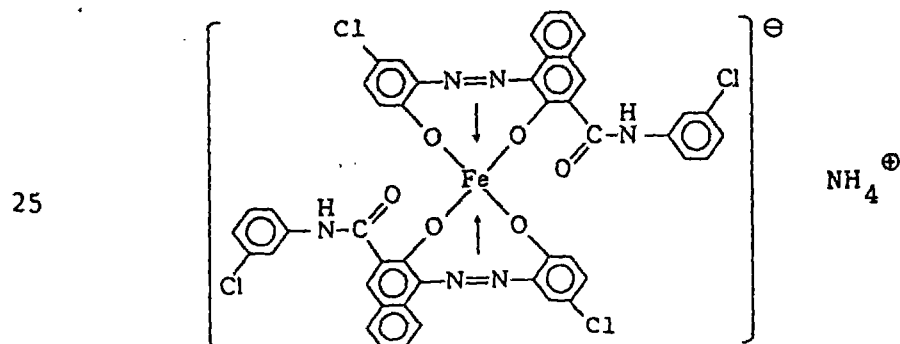


10

Iron compound (12)



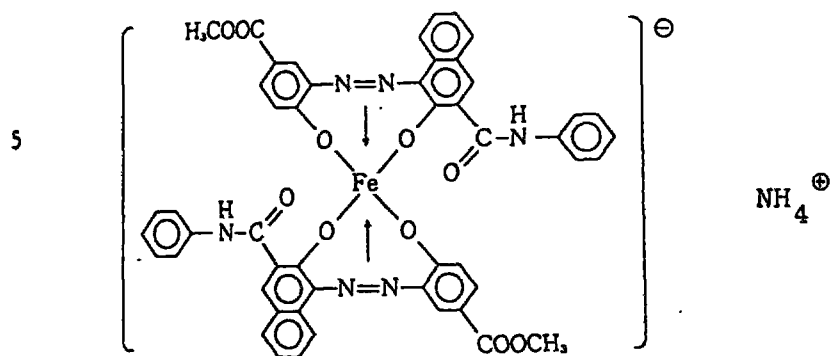
20 Iron compound (13)



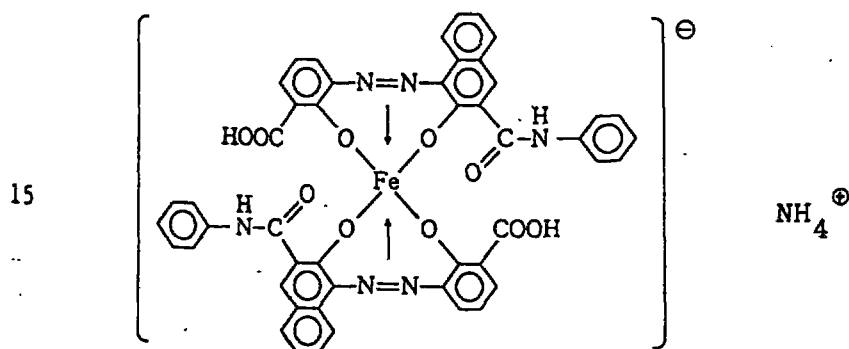
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1 Iron compound (14)

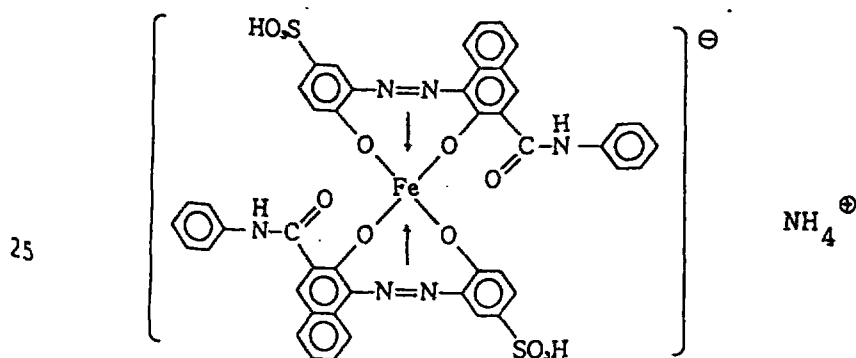


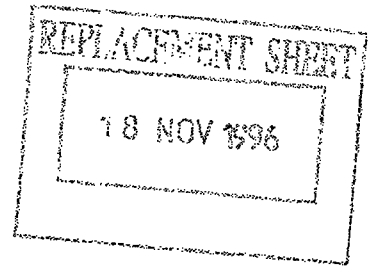
10 Iron compound (15)



Iron compound (16)

20





1 The iron compound can be incorporated into the
toner by a method in which it is internally added to
the inside of magnetic toner particles or externally
added to the particles. The iron compound may
5 preferably be used in an amount ranging from 0.1 part
to 10 parts by weight, and more preferably from 0.1
part to 5 parts by weight, based on 100 parts by
weight of the binder resin. When it is externally
added, it may preferably be in an amount of from 0.01
10 part to 10 parts by weight, and more preferably from
0.01 part to 3 parts by weight, based on 100 parts by
weight of the binder resin. In particular, it is
preferred for iron compound particles to be
mechanochemically fixed on the surfaces of the
15 magnetic toner particles.

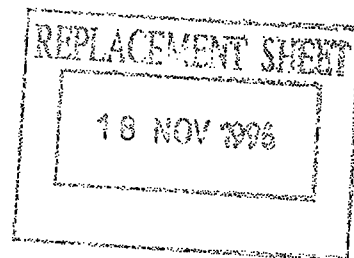
The iron compound used in the present
invention may be used in combination with any
conventionally known charge control agents so long as
the effect of the iron compound is not damaged.

20 According to the studies made by the present
inventors, in order to prevent the changes in particle
size of magnetic toners that may occur during repeated
developing, for the purpose of maintaining the initial
high image quality, it is important to use the iron
25 compound of the present invention and also make the 20
to 50 Am²/kg and a coercive force of from 40 to 200
oersted. In particular, it is preferable for the

1 magnetic toner to have a saturation magnetization of
from 25 to 40 Am^2/kg and a coercive force of from 50
to 150 oersted.

As conventionally pointed out, magnetic toners
5 come to have a low transport performance if their
saturation magnetization is less than 20 Am^2/kg . In
particular, the transport performance of coarse powder
in a magnetic toner to a developing zone may become
poor, tending to cause the coarse powder in the
10 magnetic toner to accumulate in a developing assembly
as developing is repeated many times. If the
saturation magnetization is more than 50 Am^2/kg , the
magnetic binding force on a developing sleeve
increases, resulting, in particular, in a lowering of
15 developing performance of the coarse powder. The
cause thereof is not necessarily clear, but it is
presumed as follows: The quantity of triboelectricity
of a magnetic toner is considered proportional to the
square of a particle diameter of the magnetic toner,
20 and on the other hand the saturation magnetization is
proportional to the cube of the same. Hence,
particularly in the coarse powder of the magnetic
toner, the magnetic binding force on the developing
sleeve becomes larger than the quantity of
25 triboelectricity, to cause a lowering of developing
performance and cause the coarse powder to accumulate.

As for the coercive force of the magnetic



1 toner, the coarse powder tends to accumulate when it
is more than 200 oersted.

For the measurement of magnetizing force,
values at a magnetic field of 1 k oested are measured
5 using, e.g., VSM, manufactured by Toei Kogyo K.K..

The magnetic material contained in the
magnetic toner of the present invention may include
iron oxides such as magnetite, γ -iron oxide, ferrite
and iron-excess ferrite; metals such as iron, cobalt
10 and nickel, or alloys of any of these with a metal
such as aluminum, cobalt, copper, lead, magnesium,
tin, zinc, antimony, beryllium, bismuth, cadmium,
calcium, manganese, selenium, titanium, tungsten or
banadium, and mixtures of any of these.

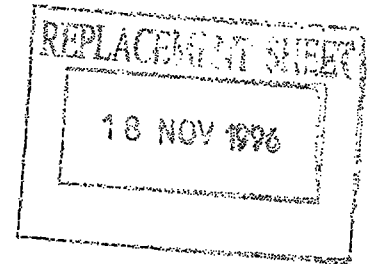
15 These magnetic materials may preferably be
those having an average particle diameter of from 0.1
to 1 μm , and preferably from 0.1 to 0.5 μm .

The magnetic material may preferably be
contained in the magnetic toner in an amount that may
20 satisfy the following expression.

$$MT = -(10/3) \times d + (70 \pm 15)$$

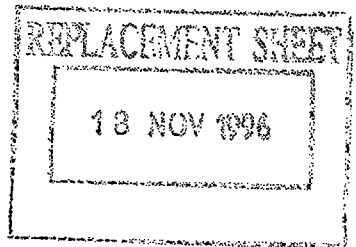
wherein MT represents a content (% by weight) of the
magnetic material, and d represents a weight average
particle diameter (μm) of the magnetic toner, provided
25 that d is not more than 9 μm .

Use of the magnetic material in an amount less
than the above limit may generally result in a low



1 saturation magnetization of the magnetic toner,
tending to cause lowering of the transport performance
of the magnetic toner. As a result, the magnetic
toner can not be fed to the developing zone in a
5 sufficient quantity and hence only toner images with a
low density can be obtained. On the other hand, if a
magnetic material with a higher saturation
magnetization is used in an amount less than the above
limit to obtain a magnetic toner with a good
10 transport performance, the toner has a high
electrical resistivity because of the decrease of the
magnetic material. As a result, when the iron
compound of formula (I) is used, the quantity of
triboelectricity becomes higher than the proper value
15 tending to cause lowering of developing performance.

On the other hand, the use of the magnetic
material in an amount more than the foregoing limit
makes the saturation magnetization or coercive force
of the magnetic toner excessively large, so that the
20 fluidity of the magnetic toner may decrease or the
magnetic binding force on the developing sleeve may
increase. As a result, the developing performance of
the magnetic toner may be lowered or the coarse powder
of the magnetic toner may accumulate as developing is
25 repeated many times, tending to cause lowering of
image quality. An increase in the quantity of the
magnetic material also result in a decrease in the



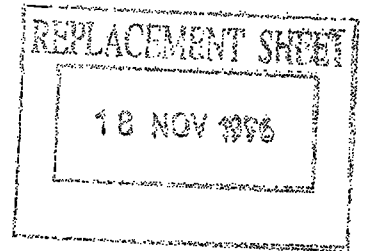
1 quantity of triboelectricity of the magnetic material.
Hence, this also can be the cause of a lowering of the
developing performance of the magnetic toner.

Thus, in order to prevent the accumulation of
5 the coarse powder as developing is repeated many times
and to maintain the initial high image quality, it is
important to control both the magnetic properties and
the quantity of triboelectricity of the magnetic toner
as described above. For that purpose, the quantity of
10 triboelectricity of the magnetic toner must be
controlled using the specific iron compound of formula
(I) as a charge control agent, and on that occasion
the amount of the magnetic material may preferably be
within the range set out above.

15 In the magnetic toner of the present
invention, the magnetic toner may preferably have a
weight average particle diameter of from 3 to 9 μm .
In particular, a magnetic toner having a weight
average particle diameter of from 5 to 9 μm is
20 preferred.

The particle size distribution of the magnetic
toner can be measured by various methods. In the
present invention, it is suitable to measure it using
a Coulter counter.

25 A Coulter counter Type TA-II (manufactured by
Coulter Electronics, Inc.) is used as a measuring
device. The volume distribution and number



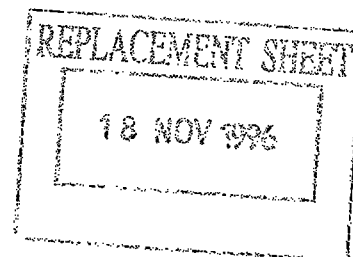
1 distribution of particles of 2 μm to 40 μm are
calculated by measuring the volume and number
distribution of the toner particles, using an aperture
of 100 μm as its aperture. Then the weight-based,
5 weight average particle diameter D_4 is calculated from
the volume distribution of the present invention
(representative value of each channel is the median of
each channel) and the weight-based, coarse-powder
content is calculated from the volume distribution.

10 In the magnetic toner of the present
invention, it is preferable to use a fine inorganic
oxide powder by its external addition.

As the fine inorganic oxide powder, various
materials can be used, as exemplified by silica,
15 titanium oxide, aluminum oxide, cerium oxide and
strontium titanate. In particular, those having metal
ions with an electronegativity of from 10 to 15 are
preferred in view of charging rate and environmental
stability.

20 For the purpose such as imparting fluidity to
the magnetic toner of the present invention, it is
very preferable to externally add fine silica powder
or fine titanium oxide powder.

The fine silica powder may include anhydrous
25 silicon dioxide (silica), as well as silicates such as
aluminum silicate, sodium silicate, potassium
silicate, magnesium silicate and zinc silicate, any of



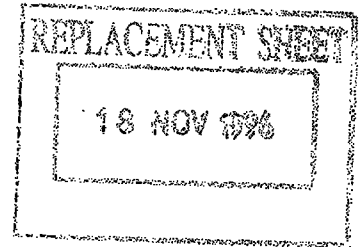
1 which can be used.

Of the above fine silica powders, those having a specific surface area, as measured by the BET method using nitrogen absorption, of not less than $30 \text{ m}^2/\text{g}$,
5 and particularly from 50 to $400 \text{ m}^2/\text{g}$, are preferred as base material silica.

Any of these fine silica powder, or those treated as described below, may preferably be used in an amount of from 0.01 part to 20% by weight, and
10 particularly preferably from 0.03 part to 5% by weight, based on the weight of the magnetic toner.

The fine silica powder may be optionally treated with a treatment agent such as a silane coupling agent or an organic silicon compound, or with
15 silicone oil or the like.

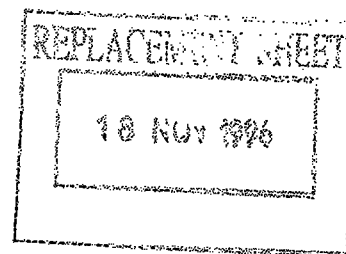
Such a treatment agent can be exemplified by hexamethyldisilazane, trimethylsilane, trimethylchlorosilane, trimethylethoxysilane, dimethyldichlorosilane, methyltrichlorosilane,
20 allyldimethylchlorosilane, allylphenyldichlorosilane, benzyldimethylchlorosilane, bromomethyldimethylchlorosilane, α -chloroethyltrichlorosilane, β -chloroethyltrichlorosilane, chloromethyldimethylchlorosilane, triorganosilyl mercaptan, trimethylsilyl
25 mercaptan, triorganosilyl acrylate, vinyl dimethylacetoxysilane, dimethylethoxysilane, dimethyldimethoxysilane, diphenyldiethoxysilane,



1 hexamethyldisiloxane, 1,3-divinyldtetramethyldi-
siloxane, 1,3-diphenyldtetramethyldisiloxane, and a
dimethylpolysiloxane having 2 to 12 siloxane units in
its molecule and containing a hydroxyl group bonded to
5 each Si in its units positioned at the terminals. Any
of these may be used alone or in the form of a mixture
of two or more kinds.

When the treated fine silica powder has been
made hydrophobic to such degree that it shows a
10 hydrophobicity of a value ranging from 30 to 80 as
measured by methanol titration, a magnetic toner
containing such a fine silica powder is preferred
since its quantity of triboelectricity comes to show a
sharp and uniform positive chargeability. Here, the
15 methanol titration is a test method to determine the
hydrophobicity of fine silica powder whose surfaces
have been made hydrophobic.

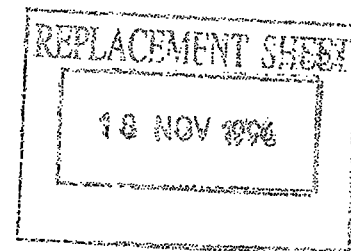
In order to evaluate the hydrophobicity of the
treated fine silica powder, the "methanol titration"
20 as defined in the present specification is carried out
in the following way: 0.2 g of fine silica powder is
added to 50 ml of water contained in a 250 ml
Erlenmeyer flask. Methanol is dropwise added from a
buret until the whole fine silica powder has been
25 wetted. Here, the solution inside the flask is
continually stirred using a magnetic stirrer. The end
point can be observed upon suspension of the whole



1 fine silica powder in the solution. The
hydrophobicity is expressed as the percentage of the
methanol present in the liquid mixture of methanol and
water when the reaction has reached the end point.

5 The binder resin used in the present invention
may include polystyrene; homopolymers of styrene
derivatives such as poly-p-chlorostyrene and
polyvinyltoluene; styrene copolymers such as a
styrene/p-chlorostyrene copolymer, a
10 styrene/vinyltoluene copolymer, a
styrene/vinylnaphthalene copolymer, a styrene/acrylate
copolymer, a styrene/methacrylate copolymer, a
styrene/methyl α -chloromethacrylate copolymer, a
styrene/acrylonitrile copolymer, a styrene/methyl
15 vinyl ether copolymer, a styrene/ethyl vinyl ether
copolymer, a styrene/methyl vinyl ketone copolymer, a
styrene/butadiene copolymer, a styrene/isoprene
copolymer and a styrene/acrylonitrile/indene
copolymer; polyvinyl chloride, phenol resins, natural
20 resin modified phenol resins, natural resin modified
maleic acid resins, acrylic resins, methacrylic
resins, polyvinyl acetate, silicone resins, polyester
resins, polyurethane resins, polyamide resins, furan
resins, epoxy resins, xylene resins, polyvinyl
25 butyral, terpene resins, cumarone indene resins, and
petroleum resins.

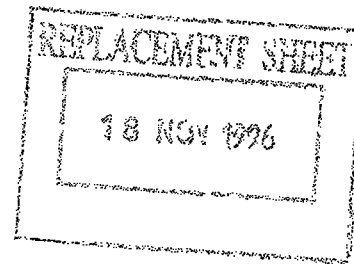
Cross-linked styrene copolymers are also



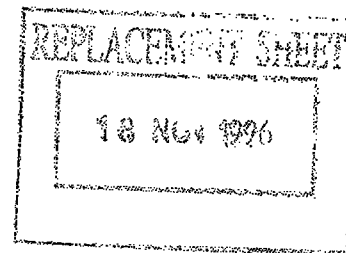
1 preferable binder resins.

Comonomers copolymerizable with styrene monomers in styrene copolymers may include monocarboxylic acids having a double bond and derivatives thereof such as acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, dodecyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, phenyl acrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 10 octyl methacrylate, acrylonitrile, methacrylonitrile and acrylamide; dicarboxylic acids having a double bond and derivatives thereof such as maleic acid, butyl maleate, methyl maleate and dimethyl maleate; vinyl esters such as vinyl acetate and vinyl benzoate; 15 olefins such as ethylene, propylene and butylene; vinyl ketones such as methyl vinyl ketone and hexyl vinyl ketone; and vinyl ethers such as methyl vinyl ether, ethyl vinyl ether and isobutyl vinyl ether. Any of these vinyl monomers may be used alone or in 20 combination of two or more.

As a cross-linking agent, compounds having at least two polymerizable double bonds are mainly used, which include, for example, aromatic divinyl compounds such as divinyl benzene and divinyl naphthalene; 25 carboxylic acid esters having two double bonds such as ethylene glycol diacrylate, ethylene glycol dimethacrylate and 1,3-butanediol dimethacrylate;



- 1 divinyl compounds such as divinyl aniline, divinyl
ether, divinyl sulfide and divinyl sulfone; and
compounds having at least three vinyl groups. Any of
these may be used alone or in the form of a mixture.
- 5 In particular, styrene copolymers having at least one
peak of molecular weight distribution in the region of
from 3×10^3 to 5×10^4 and at least one peak or
shoulder in the region of 10^5 or more as measured by
gel permeation chromatography (GPC) are preferred.
- 10 The molecular weight distribution is measured
by GPC under the following conditions.
- Columns are stabilized in a heat chamber of
40°C. To the columns kept at this temperature, THF as
a solvent is flowed at a flow rate of 1 ml per minute,
15 and 100 μ l of THF sample solution is injected
thereinto to make measurement. In measuring the
molecular weight of the sample, the molecular weight
distribution of the sample is calculated from the
relationship between the logarithmic value of the
20 molecular weight and the count number of the eluate (a
calibration curve) prepared using several kinds of
monodisperse polystyrene standard samples. As the
standard polystyrene samples used for the preparation
of the calibration curve, it is suitable to use
25 samples with molecular weights of from 10^2 to 10^7 ,
which are available from Toso Co., Ltd. or Showa Denko
KK., and to use at least about 10 standard polystyrene

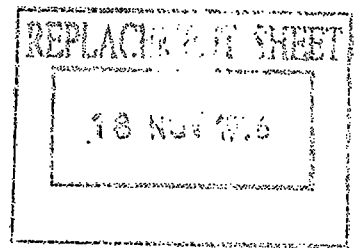


1 samples. An RI (refractive index) detector is used as
a detector. Columns should be used in combination of
a plurality of commercially available polystyrene gel
columns. For example, they may preferably comprise a
5 combination of Shodex GPC KF-801, KF-802, KF-803, KF-
804, KF-805, KF-806, KF-807 and KF-800P, available
from Showa Denko K.K.; or a combination of TSKgel
G1000H(H_{XL}), G2000H(H_{XL}), G3000H(H_{XL}), G4000H(H_{XL}),
G5000H(H_{XL}), G6000H(H_{XL}), G7000H(H_{XL}) and TSK guard
10 column, available from Toso Co., Ltd.

The sample is prepared in the following way:

The binder resin or the magnetic toner is put
in THF, and is left to stand for several hours,
followed by thorough shaking so as to be well mixed
15 with the THF until coalescent matters of the sample
has disappeared, which is further left to stand for at
least 12 hours. At this time, the sample is so left
as to stand in THF for at least 24 hours. Thereafter,
the solution having been passed through a sample-
20 treating filter (pore size: 0.45 to 0.5 μ m; for
example, MAISHORI DISK-25-5, available from Toso Co.,
Ltd. or EKICHO DISK 25CR, available from German
Science Japan, Ltd., can be utilized) is used as
the sample for GPC. The sample is so adjusted to have
25 resin components in a concentration of from 0.5 to 5
mg/ml.

When a pressure fixing system is employed, a

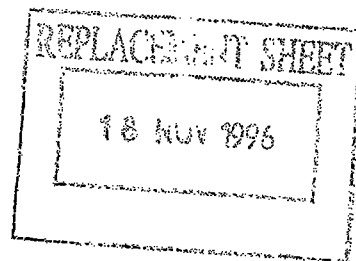


1 pressure-fixable resin can be used. It may include,
for example, polyethylenes, polypropylene,
polymethylene, polyurethane elastomers, an
ethylene/ethyl acrylate copolymer, an ethylene/vinyl
5 acetate copolymer, ionomer resins, a styrene/butadiene
copolymer, a styrene/isoprene copolymer, linear
saturated polyesters, and paraffin.

The magnetic toner of the present invention
may be optionally mixed with additives. The additives
10 may include, for example, lubricants such as zinc
stearate, abrasives such as cerium oxide and silicon
carbide, fluidity-providing agents such as aluminum
oxide, anti-caking agents, and conductivity-providing
agents such as carbon black and tin oxide.

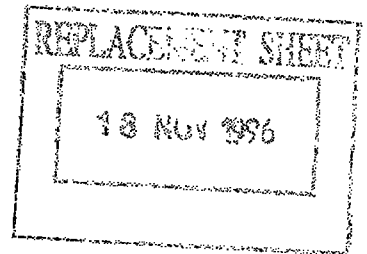
15 Fine fluorine-containing polymer powders such
as fine polyvinylidene fluoride powder are also
preferable additives in view of fluidity, abrasion and
static charging stability.

For the purpose of improving releasability at
20 the time of heat-roll fixing, it is one of preferred
embodiments of the present invention to add to the
toner a waxy material such as a low-molecular weight
polyethylene, a low-molecular weight polypropylene,
microcrysalline wax, carnauba wax, sasol wax and
25 paraffin wax in an amount of from 0.5 to 5% by weight.
In particular, sasol wax is one of preferred release
agents.



1 The magnetic toner of the present invention
may preferably be produced by a process comprising the
steps of thoroughly mixing the magnetic toner
component materials in a mixing machine such as a ball
5 mill, well mixing the mixture by means of a heat
kneading machine such as a heat roll kneader and an
extruder, cooling the kneaded product to solidify,
thereafter mechanically pulverizing the solidified
product, and classifying the pulverized product to
10 obtain a magnetic toner. Alternatively, the magnetic
toner can also be produced by a method in which the
component materials are dispersed in a binder resin
solution, followed by spray drying to obtain a toner;
a method in which given materials are mixed in
15 monomers that constitute a binder resin to make up an
emulsion dispersion, followed by polymerization to
obtain a toner; and a method in which, in a . .
microcapsule toner comprised of a core material and a
shell material, given materials are incorporated into
20 the core material or the shell material or into both
of them. The magnetic toner can also be produced by a
method in which desired additives and the magnetic
toner are optionally further thoroughly blended by
means of a mixing machine such as a Henschel mixer to
25 obtain a magnetic toner.

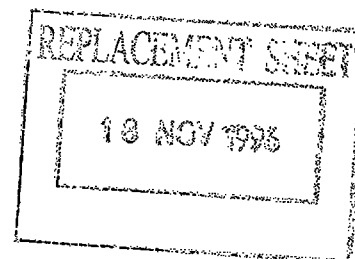
 The magnetic toner of the present invention
can be well used to for development, to convert



1 electrostatic images into visible images in
electrophotography, electrostatic recording,
electrostatic printing and so forth.

Fig. 1 shows an embodiment of a developing
5 assembly in which the magnetic toner of the present
invention can be applied.

An electrostatic image bearing member 1 is
rotated in the direction of an arrow. A non-magnetic
cylinder (a developing sleeve) 4 serving as a toner
10 carrier member is rotated in the same direction as the
electrostatic image bearing member 1 at a developing
zone. The developing sleeve 4 is provided in its
inside with a multi-polar permanent magnet 9. A
magnetic toner 11 delivered from a toner container 12
15 is spread on the developing sleeve 4, and a magnetic
blade 10 control the magnetic toner layer in a small
and uniform thickness. In the developing zone, a DC
bias voltage is applied to the developing sleeve 4
through a bias applying means 13. At this time, an AC
20 bias may also be applied simultaneously. The AC bias
when applied may preferably have a frequency of from
200 to 4,000 Hz and a potential difference between
peaks, of from 3,000 to 5,000 V. In Fig. 1, the
magnetic blade 10 is not in touch with the developing
25 sleeve 4, but a blade made of an elastic material such
as plastic or rubber may be in touch with it so that
the magnetic toner layer thickness can be controlled.



1

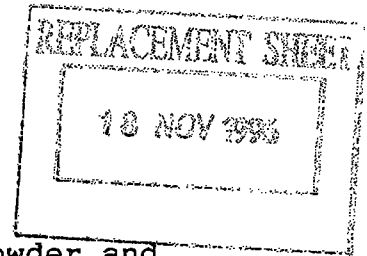
EXAMPLES

The present invention will be described below in greater detail by giving Examples. These by no means limit the present invention. In the following formulation, "part(s)" refers to "part(s) by weight" in all occurrences.

Example 1

Styrene/butyl methacrylate copolymer	100 parts
(weight average molecular weight: 250,000;	
first peak (peak 1): molecular weight 10,000;	
second peak (peak 2): molecular weight 70,000)	
Magnetic material	80 parts
(average particle diameter: 0.2 μ m; coercive	
force: 90 oersted)	
Sasol wax	3 parts
Iron compound (1)	2 parts
(molar ratio of NH_4^+ to Na^+ to H^+ :	
0.9:0.05:0.05)	

The above materials were thoroughly premixed using a blender, and then kneaded using a twin-screw kneading extruder set to 130°C. The resulting kneaded product was cooled, and then crushed. Thereafter, the crushed product was finely pulverized using a fine grinding mill utilizing a jet stream. The resulting finely pulverized product was further put in a multi-division classifier utilizing the Coanda effect (Elbow Jet Classifier, manufactured by Nittetsu Kogyo Co.) to

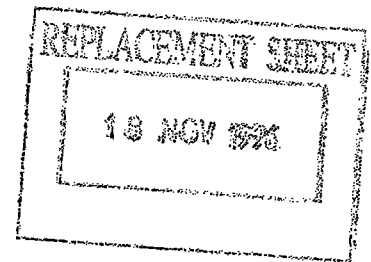


1 strictly classify and remove ultrafine powder and
coarse powder at the same time. Thus, a black fine
powder (a negatively chargeable magnetic toner) with
a weight average particle diameter of 8.5 μm was
5 obtained.

Then, 100 parts of the negatively chargeable
magnetic toner thus obtained, 0.6 part of hydrophobic
fine silica powder (average particle diameter: 15 nm)
and 0.3 part of fine strontium titanate powder
10 (average particle diameter: 1 μm) were mixed using a
Henschel mixer to obtain a one-component magnetic
toner. This magnetic toner had a saturation
magnetization of 28 Am^2/kg and a coercive force of 90
oersted.

15 The one-component magnetic toner obtained was
applied in a commercially available
electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and latent images
were formed, followed by developing, transferring and
20 fixing to make copying tests.

Copies were taken on 20,000 copy sheets in an
environment of normal temperature and normal humidity,
a temperature of 23°C and a humidity of 60%RH. As a
result, sharpe images with an image density of 1.40
25 ± 0.03 were obtained at the initial and following
stages. With regard to resolution of images also, a
resolution of 6.3 lines/mm at the initial stage was



1 maintained.

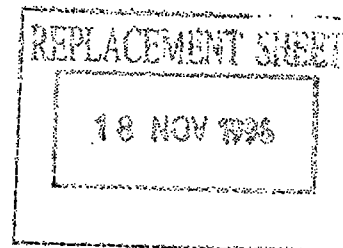
Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a
5 result, good images with an image density of 1.40 ± 0.03 were obtained at the initial and following stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of
10 80%RH, a 10,000 sheet copying test was also made. As a result, good images with an image density of 1.35 ± 0.03 were obtained at the initial and following stages. After the toner in the copying machine was left to stand for 4 days in the environment of high
15 temperature and high humidity, copies were taken on 10,000 copy sheets. Good images with a density of 1.35 ± 0.03 were obtained on the first and following copy sheets after copying was again started.

Restoration performance of the quantity of
20 triboelectricity of the magnetic toner in the environment of high humidity is shown in Table 1.

Example 2

	Styrene/butyl methacrylate copolymer	100 parts
	(weight average molecular weight: 250,000;	
25	first peak: molecular weight 10,000; second	
	peak: molecular weight 70,000)	
	Magnetic material	80 parts



1 (average particle diameter: 0.2 μm ; coercive
force: 90 oersted)

Sasol wax 3 parts

Iron compound (1) 2 parts

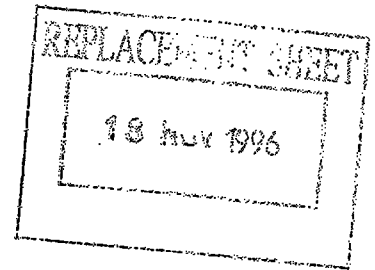
5 (molar ratio of NH_4^+ to Na^+ to H^+ :
0.98:0.01:0.01)

A one-component magnetic toner was obtained in
the same manner as in Example 1 except that the above
materials were used. This magnetic toner had a
10 saturation magnetization of 28 Am^2/kg and a coercive
force of 90 oersted.

The one-component magnetic toner obtained was
applied in a commercially available
electrophotographic copying machine NP-6060 (trade
15 name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

Copies were taken on 20,000 copy sheets in an
environment of a temperature of 23°C and a humidity of
60%RH. As a result, sharpe images with an image
20 density of 1.40 $\pm$ 0.03 were obtained at the initial and
following stages. With regard to resolution of images
also, a resolution of 6.3 lines/mm at the initial
stage was maintained.

Next, in an environment of low temperature and
25 low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.40



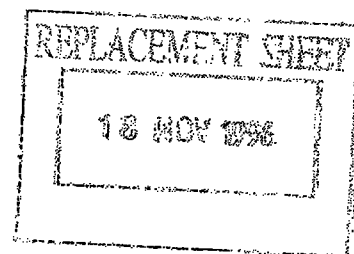
1 ± 0.03 were obtained at the initial and following stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of 5 80%RH, a 10,000 sheet copying test was also made. As a result, good images with an image density of 1.35 ± 0.03 were obtained at the initial and following stages. After the toner in the copying machine was left to stand for 4 days in the environment of high 10 temperature and high humidity, copies were taken on 10,000 copy sheets. On the first sheet after copying was again started, images had an image density of 1.30 which was a little lower than that obtained before the toner had been left, but good images with a density of 15 1.35 ± 0.03 were obtained on the 10th and following copy sheets.

Restoration performance of the quantity of triboelectricity of the magnetic toner in the environment of high humidity is shown in Table 1.

20 Example 3

Styrene/butyl methacrylate copolymer	100 parts
(weight average molecular weight: 250,000; first peak: molecular weight 10,000; second peak: molecular weight 70,000)	
25 Magnetic material	80 parts
(average particle diameter: 0.2 μm ; coercive force: 90 oersted)	



- 1 Sasol wax 3 parts
Iron compound (1) 2 parts

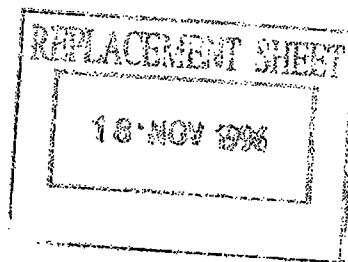
(molar ratio of NH_4^+ to Na^+ to H^+ :
0.8:0.15:0.05)

- 5 A one-component magnetic toner was obtained in the same manner as in Example 1 except that the above materials were used. This magnetic toner had a saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90 oersted.

- 10 The one-component magnetic toner obtained was applied in a commercially available electrophotographic copying machine NP-6060 (trade name; manufactured by Canon Inc.), and copying tests were made in the same manner as in Example 1.

- 15 Copies were taken on 20,000 copy sheets in an environment of a temperature of 23°C and a humidity of 60%RH. As a result, sharpe images with an image density of 1.40 ± 0.03 were obtained at the initial and following stages. With regard to resolution of images
20 also, a resolution of 6.3 lines/mm at the initial stage was maintained.

- Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a
25 result, good images with an image density of 1.40 ± 0.03 were obtained at the initial and following stages.

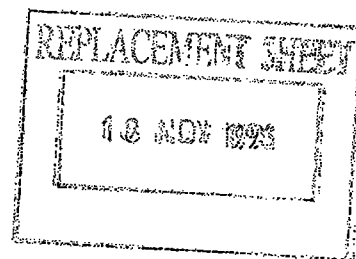


1 In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.35
5 ±0.03 were obtained at the initial and following
stages. After the toner in the copying machine was
left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. On the first sheet after copying
10 was again started, images had an image density of 1.28
which was a little lower than that obtained before the
toner had been left, but good images with a density of
1.35 ±0.03 were obtained on the 30th and following
copy sheets.

15 Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Example 4

	Styrene/butyl methacrylate copolymer	100 parts
20	(weight average molecular weight: 250,000; first peak: molecular weight 10,000; second peak: molecular weight 70,000)	
	Magnetic material	80 parts
	(average particle diameter: 0.2 μm; coercive 25 force: 90 oersted)	
	Sasol wax	3 parts
	Iron compound (1)	2 parts



1 (molar ratio of NH_4^+ to Na^+ to H^+ :
0.5:0.2:0.3)

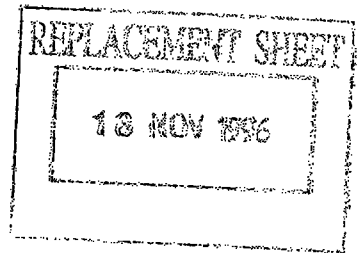
A one-component magnetic toner was obtained in
the same manner as in Example 1 except that the above
5 materials were used. This magnetic toner had a
saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive
force of 90 oersted.

The one-component magnetic toner obtained was
applied in a commercially available
10 electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

Copies were taken on 20,000 copy sheets in an
environment of a temperature of 23°C and a humidity of
15 60%RH. As a result, sharpe images with an image
density of 1.40 ± 0.03 were obtained at the initial and
following stages. With regard to resolution of images
also, a resolution of 6.3 lines/mm at the initial
stage was maintained.

20 Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.40
 ± 0.03 were obtained at the initial and following
25 stages.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of



1 80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.35
 ± 0.03 were obtained at the initial and following
stages. After the toner in the copying machine was
5 left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. On the first sheet after copying
was again started, images had an image density of 1.25
which was a little lower than that obtained before the
10 toner had been left, but good images with a density of
 1.30 ± 0.03 were obtained on the 30th and following
copy sheets.

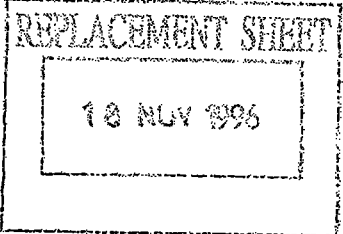
Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
15 environment of high humidity is shown in Table 1.

Example 5

A one-component magnetic toner was obtained in
the same manner as in Example 1 except that the amount
of the magnetic material was changed to 120 parts.
20 This magnetic toner had a saturation magnetization of
 $42 \text{ Am}^2/\text{kg}$ and a coercive force of 90 oersted.

The one-component magnetic toner obtained was
applied in a commercially available
electrophotographic copying machine NP-6060 (trade
25 name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

Copies were taken on 20,000 copy sheets in an



1 environment of a temperature of 23°C and a humidity of
60%RH. As a result, sharpe images with an image
density of 1.35 ± 0.03 were obtained at the initial and
following stages. With regard to resolution of images
5 also, a resolution of 6.3 lines/mm at the initial
stage was maintained.

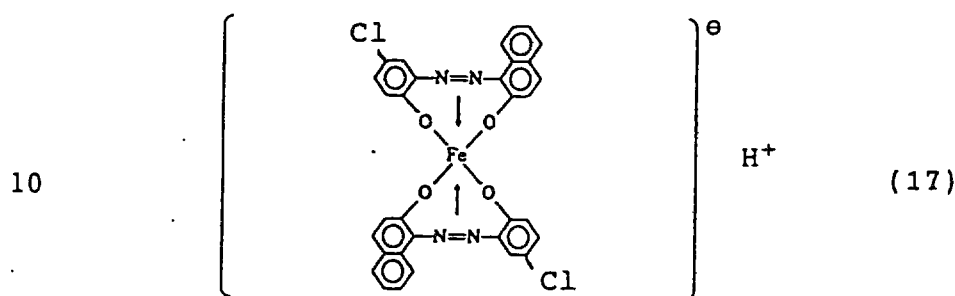
Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
10 result, good images with an image density of 1.40
 ± 0.03 were obtained at the initial and following
stages.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
15 80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.30
 ± 0.03 were obtained at the initial and following
stages. After the toner in the copying machine was
left to stand for 4 days in the environment of high
20 temperature and high humidity, copies were taken on
10,000 copy sheets. Good images with a density of
 1.30 ± 0.03 were obtained on the first and following
copy sheets after copying was again started.

Restoration performance of the quantity of
25 triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Example 6

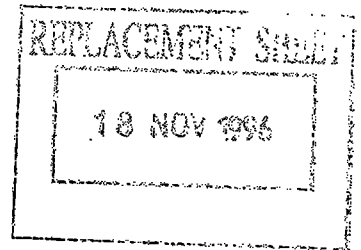
- 1 A one-component magnetic toner was obtained in
the same manner as in Example 1 except that the iron
compound (1) was replaced with 3 parts of an iron
compound represented by formula (17) shown below.
5 This magnetic toner had a saturation magnetization of
28 Am²/kg and a coercive force of 90 oersted.



- The one-component magnetic toner obtained was
applied in a commercially available
15 electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

- Copies were taken on 20,000 copy sheets in an
environment of a temperature of 23°C and a humidity of
20 60%RH. As a result, sharpe images with an image
density of 1.35 ± 0.05 were obtained at the initial and
following stages. With regard to resolution of images
also, a resolution of 6.3 lines/mm at the initial
stage was maintained.

- 25 Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a



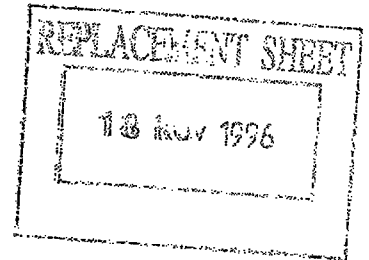
1 result, good images with an image density of 1.40
±0.05 were obtained at the initial and following
stages.

In an environment of high temperature and high
5 humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.25
±0.05 were obtained at the initial and following
stages. After the toner in the copying machine was
10 left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. However, on the first sheet after
copying was again started, images had an image density
of 1.05 which was lower than that obtained before the
15 toner had been left. Also after cpying on the 100th
sheet, images had an image density of 1.20 ±0.05,
which was inferior to the images obtained before the
toner had been left.

Restoration performance of the quantity of
20 triboelectricity of the magnetic toner in the
environment of high temperature and high humidity is
shown in Table 1.

Example 7

A one-component magnetic toner was obtained in
25 the same manner as in Example 1 except that the
styrene/butyl methacrylate copolymer was replaced with
polyester resin (weight average molecular weight:



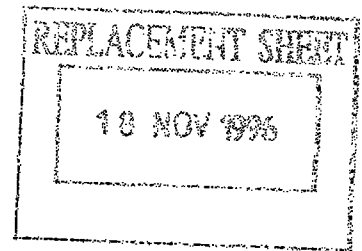
1 20,000) was used. This magnetic toner had a
saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive
force of 90 oersted.

The one-component magnetic toner obtained was
5 applied in a commercially available
electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and copying tests
were made in the same manner as in Example 1.

Copies were taken on 20,000 copy sheets in an
10 environment of a temperature of 23°C and a humidity of
60%RH. As a result, sharpe images with an image
density of 1.40 ± 0.03 were obtained at the initial and
following stages. With regard to resolution of images
also, a resolution of 6.3 lines/mm at the initial
15 stage was maintained.

Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.40
20 ± 0.03 were obtained at the initial and following
stages.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
25 a result, good images with an image density of 1.35
 ± 0.03 were obtained at the initial and following
stages. After the toner in the copying machine was



1 left to stand for 4 days in the environment of high
temperature and high humidity, copies were taken on
10,000 copy sheets. Good images with a density of
1.35 $\pm$ 0.03 were obtained on the first and following
5 copy sheets after copying was again started.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high temperature and high humidity is
shown in Table 1.

10 Example 8

Styrene/butyl methacrylate copolymer 100 parts
(weight average molecular weight: 300,000;
first peak: molecular weight 6,000; second
peak: molecular weight 100,000)

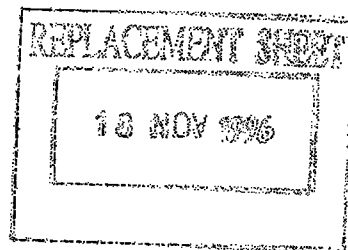
15 Magnetic material 100 parts
(average particle diameter: 0.2 μ m; coercive
force: 90 oersted)

Low-molecular weight polypropylene wax 3 parts

Iron compound (1) 2 parts

20 (molar ratio of NH_4^+ to Na^+ to H^+ :
0.92:0.04:0.04)

The above materials were thoroughly premixed
using a blender, and then kneaded using a twin-screw
kneading extruder set to 130°C. The resulting kneaded
25 product was cooled, and then crushed. Thereafter, the
crushed product was finely pulverized using a fine
grinding mill utilizing a jet stream. The resulting



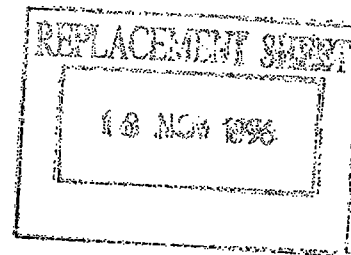
1 finely pulverized product was further put in a multi-
division classifier utilizing the Coanda effect (Elbow
Jet Classifier, manufactured by Nittetsu Kogyo Co.) to
strictly classify and remove ultrafine powder and
5 coarse powder at the same time. Thus, a black fine
powder (a negatively chargeable magnetic toner) with
a weight average particle diameter of $6.5 \mu\text{m}$ was
obtained. This magnetic toner had a saturation
magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90
10 oersted.

Then, 100 parts of the magnetic toner thus
obtained and 1 part of hydrophobic fine silica powder
(average particle diameter: 15 nm) were mixed using a
Henschel mixer to obtain a one-component magnetic
15 toner.

The one-component magnetic toner obtained was
applied in a commercially available laser beam printer
LBP-KT (trade name; manufactured by Canon Inc.) to
make printing tests.

20 Prints were obtained on 6,000 copy sheets in
an environment of a temperature of 23°C and a humidity
of 60%RH. As a result, sharpe images with an image
density of 1.40 ± 0.03 were obtained at the initial and
following stages.

25 Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 6,000 sheet printing test was made. As a



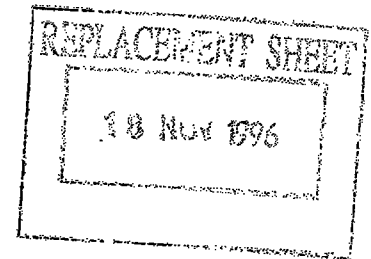
1 result, good images with an image density of 1.40
±0.03 were obtained at the initial and following
stages.

In an environment of high temperature and high
5 humidity, a temperature of 30°C and a humidity of
80%RH, a 3,000 sheet printing test was also made. As
a result, good images with an image density of 1.35
±0.03 were obtained at the initial and following
stages. After the toner in the printer was left to
10 stand for 4 days in the environment of high
temperature and high humidity, prints were obtained on
3,000 copy sheets. Good images with a density of 1.35
±0.03 were obtained on the first and following copy
sheets after printing was again started, where no
15 decrease in image density due to the toner having been
left to stand was seen.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high temperature and high humidity is
20 shown in Table 1.

Example 9

A one-component magnetic toner was obtained in
the same manner as in Example 8 except that the iron
compound (1) was replaced with 1 part of the iron
25 compound (2) (molar ratio of NH_4^+ to Na^+ to H^+ :
0.93:0.04:0.03). This magnetic toner had a saturation
magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 90



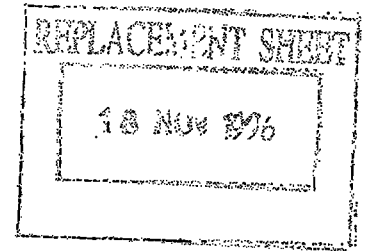
1 oersted.

The one-component magnetic toner obtained was applied in a commercially available laser beam printer LBP-KT (trade name; manufactured by Canon Inc.) to
5 make printing tests.

Prints were obtained on 6,000 copy sheets in an environment of a temperature of 23°C and a humidity of 60%RH. As a result, sharpe images with an image density of 1.40 ± 0.05 were obtained at the initial and
10 following stages.

Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 6,000 sheet printing test was made. As a result, good images with an image density of 1.40 ± 0.05 were obtained at the initial and following
15 stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of 80%RH, a 3,000 sheet printing test was also made. As
20 a result, good images with an image density of 1.35 ± 0.05 were obtained at the initial and following stages. After the toner in the printer was left to stand for 4 days in the environment of high temperature and high humidity, prints were obtained on
25 3,000 copy sheets. Good images with a density of 1.35 ± 0.05 were obtained on the first and following copy sheets after printing was again started, where no



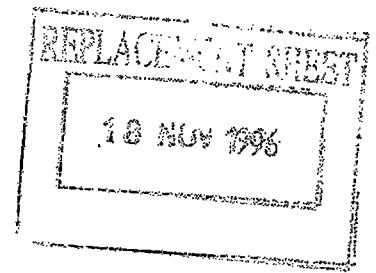
1 decrease in image density due to the toner having been
left to stand was seen.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
5 environment of high temperature and high humidity is
shown in Table 1.

Example 10

	Styrene/butyl methacrylate copolymer	100 parts
	(weight average molecular weight: 250,000; 10 first peak: molecular weight 10,000; second peak: molecular weight 70,000)	
	Magnetic material	80 parts
	(average particle diameter: 0.2 μ m; coercive force: 140 oersted)	
15	Sasol wax	3 parts
	Iron compound (11)	2 parts

The above materials were thoroughly premixed
using a blender, and then kneaded using a twin-screw
kneading extruder set to 130°C. The resulting kneaded
20 product was cooled, and then crushed. Thereafter, the
crushed product was finely pulverized using a fine
grinding mill utilizing a jet stream. The resulting
finely pulverized product was further put in a multi-
division classifier utilizing the Coanda effect (Elbow
25 Jet Classifier, manufactured by Nittetsu Kogyo Co.) to
strictly classify and remove ultrafine powder and
coarse powder at the same time. Thus, a black fine



1 powder (a negatively chargeable magnetic toner) with
a weight average particle diameter of $8.5 \mu\text{m}$ was
obtained.

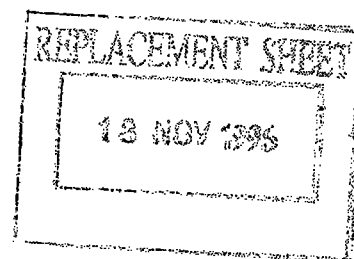
This magnetic toner had a saturation
5 magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive force of 140
oersted.

Then, 100 parts of the magnetic toner thus
obtained and 0.6 part of hydrophobic fine silica
powder (BET specific surface area: $200 \text{ m}^2/\text{g}$) were
10 mixed using a Henschel mixer to obtain a one-component
magnetic toner with an average particle diameter of
 $8.5 \mu\text{m}$, having the hydrophobic fine silica powder.

The one-component magnetic toner obtained was
applied in a commercially available
15 electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.), and a 20,000 sheet
copying test was made in an environment of normal
temperature and normal humidity.

Sharpe images with an image density of 1.40
20 were obtained at the initial and following stages.
Images after 20,000 sheet copying also had sharp
images with a density of 1.39. With regard to
resolution of images also, a resolution of 6.3
lines/mm at the initial stage was maintained.

25 The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-10.8 \mu\text{c/g}$. The coarse powder



1 with a particle diameter larger than $10.8 \mu\text{m}$ was in a
quantity of 25% by weight before copying, and 28% by
weight after the copying, between which there was
little change.

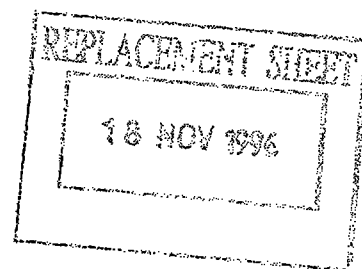
5 Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.38
 ± 0.03 were obtained at the initial and following
10 stages.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, good images with an image density of 1.32
15 ± 0.03 were obtained at the initial and following
stages. Subsequently, after the toner in the copying
machine was left to stand for 4 days in the
environment of high temperature and high humidity,
copies were taken on 10,000 copy sheets. Good images
20 with a density of 1.32 ± 0.03 were obtained on the
first and following copy sheets after copying was
again started.

Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
25 environment of high humidity is shown in Table 1.

Example 11

Example 1 was repeated to obtain a magnetic



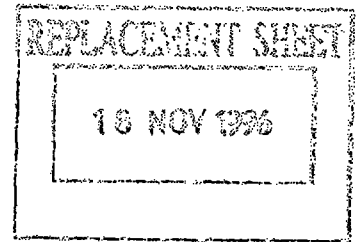
1 toner with a weight average particle diameter of 8.5
µm, except that a magnetic material (average particle
diameter: 0.2 µm; coercive force: 180 oersted) with
a higher coercive force than that in Example 10 was
5 used. The magnetic toner obtained had a saturation
magnetization of 33 Am²/kg and a coercive force of 180
oersted.

On the magnetic toner thus obtained, copying
tests were made in the same manner as in Example 10.

10 As a result, sharpe images with an image
density of 1.41 were obtained at the initial and
following stages. Images after 20,000 sheet copying
also had sharp images with a density of 1.37. With
regard to resolution of images, however, it was 6.3
15 lines/mm at the initial stage, but lowered to 5.6
lines/mm after 20,000 sheet copying.

The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was ~11.3 µc/g. The coarse powder
20 with a particle diameter larger than 10.8 µm was in a
quantity of 23% by weight before copying, and 30% by
weight after 20,000 sheet copying, between which there
was a little increase.

Next, in an environment of low temperature and
25 low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, good images with an image density of 1.35

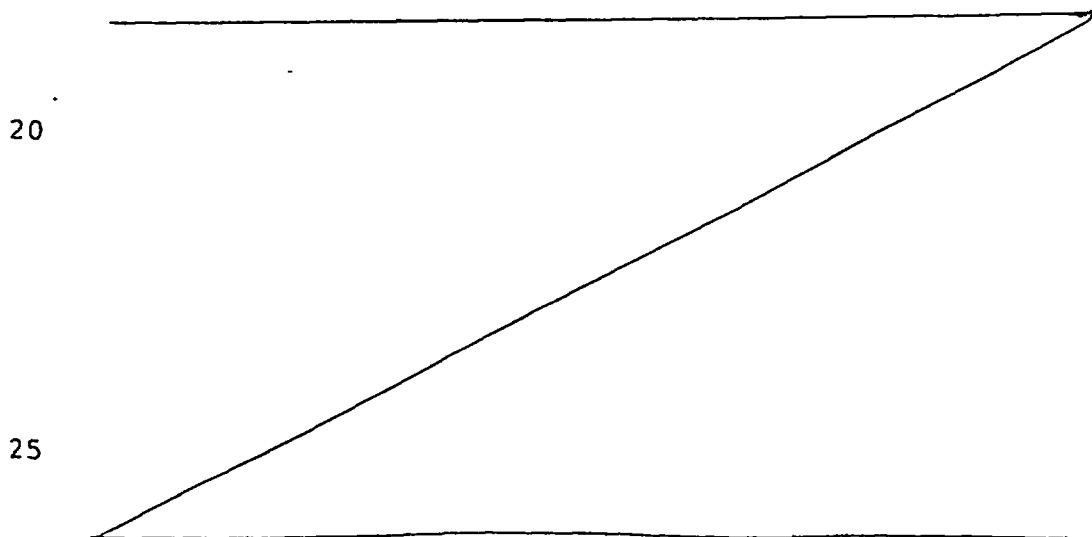


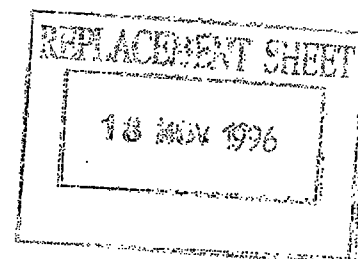
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1 ± 0.03 were obtained at the initial and following stages.

In an environment of high temperature and high humidity, a temperature of 30°C and a humidity of 80%RH, a 10,000 sheet copying test was also made. As a result, good images with an image density of 1.31 ± 0.03 were obtained at the initial and following stages. Subsequently, after the toner in the copying machine was left to stand for 4 days in the environment of high temperature and high humidity, copies were taken on 10,000 copy sheets. Good images with a density of 1.31 ± 0.03 were obtained on the first and following copy sheets after copying was again started.

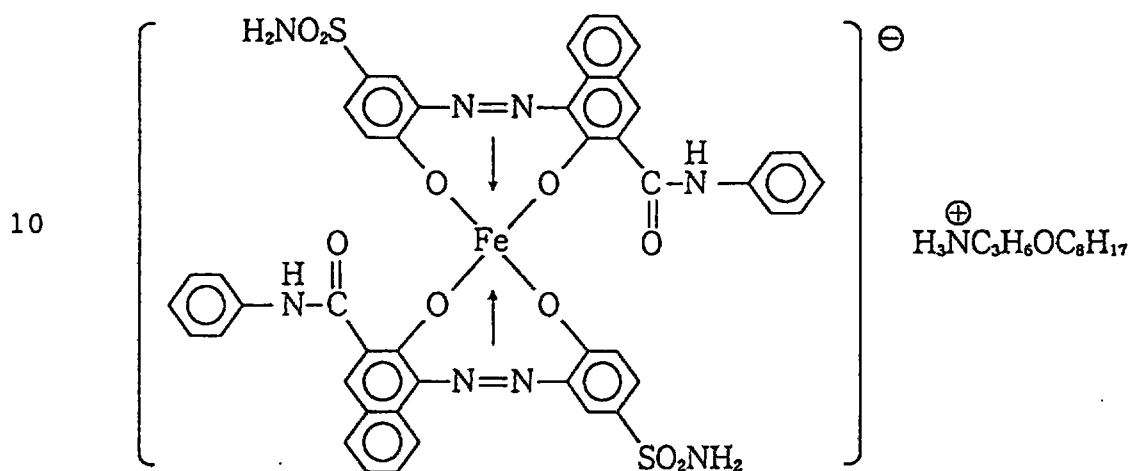
15 Restoration performance of the quantity of triboelectricity of the magnetic toner in the environment of high humidity is shown in Table 1.





1 Comparative Example 1

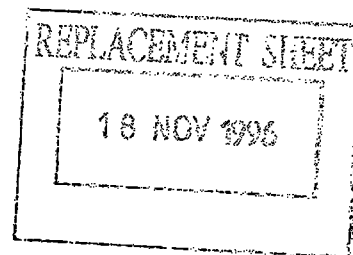
 A one-component magnetic toner was obtained in
the same manner as in Example 10 except that the iron
compound (11) was replaced with the iron compound (18)
5 of the formula:



 This one-component magnetic toner had a
saturation magnetization of $28 \text{ Am}^2/\text{kg}$ and a coercive
force of 140 oersted.

 The obtained magnetic toner was used to
20 conduct a copying test in the same manner as in
Example 11.

 Sharpe images with an image density of 1.37
were obtained at the initial stage of copying, but
images after 20,000 sheet copying had a lowered image
25 density of 1.25. With regard to resolution of images
also, it was 6.3 lines/mm at the initial stage, but it
was lowered to 4.5 lines/mm after 20,000 sheet



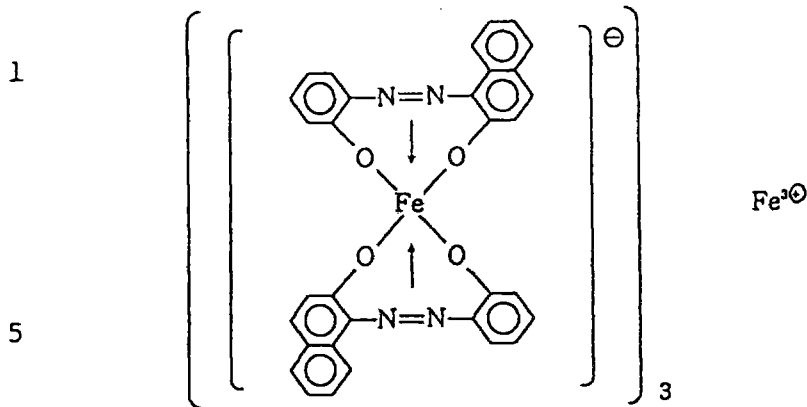
1 copying. The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-9.3 \mu\text{c/g}$. The coarse powder
with a particle diameter larger than $10.8 \mu\text{m}$ was in a
5 quantity of 25% by weight before copying, and it
increased to 39% by weight after 20,000 sheet copying.

Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
10 result, an initial image density of 1.35 decreased to
1.21.

In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
15 a result, an initial image density of 1.25 lowered to
1.1. Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Comparative Example 2

20 A one-component magnetic toner was obtained in
the same manner as in Example 10 except that the iron
compound (11) was replaced with the iron compound (19)
of the formula:

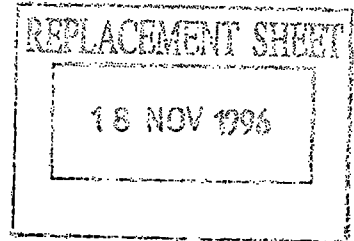


This magnetic toner had a saturation magnetization of 28 Am²/kg and a coercive force of 140 oersteds.

10 The obtained magnetic toner was used to conduct a copying test in the same manner as in Example 10.

Sharpe images with an image density of 1.35 were obtained at the initial stage of copying, but after 20,000 sheet copying, the image density lowered to 1.21. With regard to resolution of images also, it was 6.3 lines/mm at the initial stage, but it was lowered to 4.0 lines/mm after 20,000 sheet copying. The quantity of triboelectricity of the magnetic toner was measured by blowing-off to ascertain that it was -8.8 µc/g. The coarse powder with a particle diameter larger than 10.8 µm was in a quantity of 27% by weight before copying, and it increased to 43% by weight after 20,000 sheet copying.

25 Next, in an environment of low temperature and low humidity, a temperature of 15°C and a humidity of 10%RH, a 20,000 sheet copying test was made. As a



1 result, an initial image density of 1.35 decreased to
1.23.

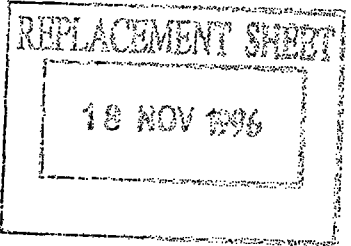
In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
5 80%RH, a 10,000 sheet copying test was also made. As
a result, an initial image density of 1.15 lowered to
1.00. Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

10 Comparative Example 3

A one-component magnetic toner was obtained in
the same manner as in Example 10 except that a
magnetic material having a coercive force (300
orested) higher than in Example 11. The one-component
15 magnetic toner had a saturation magnetization of 31
 Am^2/kg and a coercive force of 300 oersted.

The obtained one-component magnetic toner was
used to conduct a copying test in the same manner as
in Example 10.

20 Sharpe images with an image density of 1.39
were obtained at the initial stage of copying, but
after 20,000 sheet copying, the image density lowered
to 1.22. With regard to resolution of images, it was
6.3 lines/mm at the initial stage, but it was lowered
25 to 4.5 lines/mm after 20,000 sheet copying. The
quantity of triboelectricity of the magnetic toner was
measured by blowing-off to ascertain that it was -10.1



1 $\mu\text{c/g}$. The coarse powder with a particle diameter
larger than $10.8 \mu\text{m}$ was in a quantity of 26% by weight
before copying, and it increased to 44% by weight
after 20,000 sheet copying.

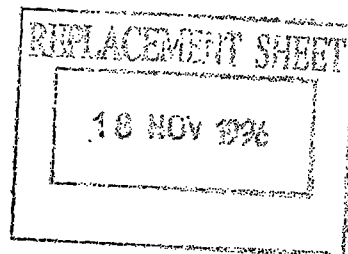
5 Next, in an environment of low temperature and
low humidity, a temperature of 15°C and a humidity of
10%RH, a 20,000 sheet copying test was made. As a
result, an initial image density of 1.39 decreased to
1.25.

10 In an environment of high temperature and high
humidity, a temperature of 30°C and a humidity of
80%RH, a 10,000 sheet copying test was also made. As
a result, an initial image density of 1.35 lowered to
1.21. Restoration performance of the quantity of
15 triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Comparative Example 4

20 A one-component magnetic toner was obtained in
the same manner as in Example 10 except that a
magnetic material was used which had an average
particle diameter of $0.2 \mu\text{m}$, a saturation
magnetization of $30 \text{ Am}^2/\text{kg}$ and a coercive force of 140
oersted, and the amount of the magnetic material was
changed to 150 parts. This one-component magnetic
25 toner had a saturation magnetization of $18 \text{ Am}^2/\text{kg}$ and
a coercive force of 140 oersted.

 The obtained one-component magnetic toner was



1 used to conduct a copying test in the same manner as
in Example 10.

The initial image density was 1.12, and the
density after 20,000 sheet copying further decreased
5 to 0.91. The images were not sharp with much fog.
With regard to the resolution of the images, the
initial one was 4.5 lines/mm, and after 20,000 sheet
copying, it was further lowered to 3.2 lines/mm.

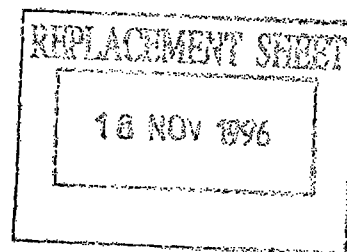
The quantity of triboelectricity of the
10 magnetic toner was measured by blowing-off to
ascertain that it was $-5.4 \mu\text{c/g}$. The coarse powder
with a particle diameter larger than $10.8 \mu\text{m}$ was in a
quantity of 25% by weight before copying, and it
increased to 48% by weight after 20,000 sheet copying.

15 Restoration performance of the quantity of
triboelectricity of the magnetic toner in the
environment of high humidity is shown in Table 1.

Example 12

20	Styrene/butyl methacrylate copolymer	100 parts
	(weight average molecular weight: 250,000)	
	Magnetic material	100 parts
	(average particle diameter: $0.2 \mu\text{m}$; coercive force: 120 oersted)	
	Low-molecular weight polypropylene wax	3 parts
25	Iron compound (12)	1 part

A black fine powder (magnetic toner) with a
weight average particle diameter of $6.5 \mu\text{m}$ was



1 obtained by using the above materials in the same
manner as in Example 10.

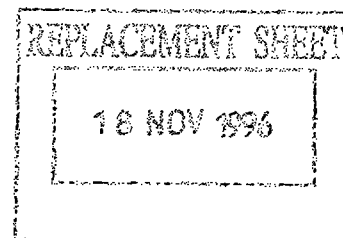
The magnetic toner had a saturation
magnetization of $32 \text{ Am}^2/\text{kg}$ and a coercive force of 120
5 oersteds.

100 Parts of the obtained magnetic toner and
1.0 part of hydrophobic silica (BET specific surface
area: $200 \text{ m}^2/\text{g}$) were mixed using a Henschel mixer to
obtain a one-component magnetic toner.

10 The one-component magnetic toner obtained was
applied to a commercially available laser beam printer
LBP-KT (trade name; manufactured by Canon Inc.) to
make 6,000 sheet printing test.

Sharp images with an image density of 1.42
15 were obtained from the initial stage of printing.
Even images after 6,000 sheet printing were sharp with
a density of 1.45. With regard to the resolution of
the images also, an initial value of 7.1 lines/mm was
maintained.

20 The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-16.3 \text{ } \mu\text{C/g}$. The coarse powder
with a particle diameter larger than $8.0 \text{ } \mu\text{m}$ was in a
quantity of 10% by weight before printing, and 12% by
25 weight after 6,000 sheet printing so that there was
little change. Restoration performance of the
quantity of triboelectricity of the magnetic toner in



1 the environment of high humidity is shown in Table 1.

Example 13

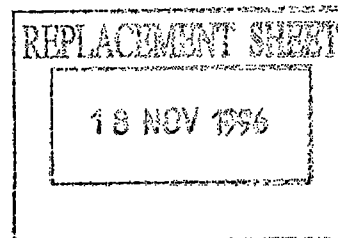
A one-component magnetic toner was obtained in the same manner as in Example 12 except that the
5 amount of the magnetic material was changed to 150 parts. This one-component magnetic toner had a saturation magnetization of $42 \text{ Am}^2/\text{kg}$ and a coercive force of 120 oersted.

The obtained one-component magnetic toner was
10 used to conduct a printing test in the same manner as in Example 12.

As a result, sharpe images with an image density of 1.34 were obtained from the initial stage of printing. Images after 6,000 sheet printing were
15 sharp with a density of 1.32. On the other hand, as to the resolution of the images, it was 7.1 lines/mm at the initial stage, but it lowered to 5.6 lines/mm after 6,000 sheet printing.

The quantity of triboelectricity of the
20 magnetic toner was measured by blowing-off to ascertain that it was $-12.1 \mu\text{c/g}$. The coarse powder with a particle diameter larger than $8.0 \mu\text{m}$ was in a quantity of 12% by weight before printing, and it increased to 17% by weight after 6,000 sheet printing,
25 between which there was a little increase.

Restoration performance of the quantity of triboelectricity of the magnetic toner in the



1 environment of high humidity is shown in Table 1.

Example 14

Styrene/butyl methacrylate copolymer 100 parts
(weight average molecular weight: 350,000)

5 (peak 1: molecular weight 8,000; peak 2:
molecular weight 150,000)

Magnetic material 80 parts
(average particle diameter: 0.2 μm ; coercive
force: 110 oersted)

10 Sasol wax 3 parts

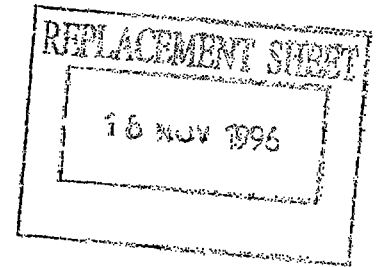
Iron compound (13) 3 parts

A black fine powder (negatively chargeable
magnetic toner) with a weight average particle
diameter of 7.5 μm was obtained by using the above
15 materials in the same manner as in Example 10.

The magnetic toner had a saturation
magnetization of 30 Am^2/kg and a coercive force of 110
oersted.

100 Parts of the obtained magnetic toner and
20 0.8 part of hydrophobic silica (BET specific surface
area: 200 m^2/g) were mixed using a Henschel mixer to
obtain a one-component magnetic toner.

The one-component magnetic toner obtained was
applied to a commercially available
25 electrophotographic copying machine NP-6060 (trade
name; manufactured by Canon Inc.) to make 20,000 sheet
copying test.



1 As a result, sharp images with an image
density of 1.38 were obtained from the initial stage.
Images after 20,000 sheet copying were also sharp with
a density of 1.40. With regard to the resolution of
5 the images also, an initial value of 6.3 lines/mm was
maintained.

 The quantity of triboelectricity of the
magnetic toner was measured by blowing-off to
ascertain that it was $-11.2 \mu\text{C/g}$. The coarse powder
10 with a particle diameter larger than $10.8 \mu\text{m}$ was in a
quantity of 33% by weight before printing, and 35% by
weight after 20,000 sheet copying, so that there was
little change. Restoration performance of the
quantity of triboelectricity of the magnetic toner in
15 the environment of high humidity is shown in Table 1.

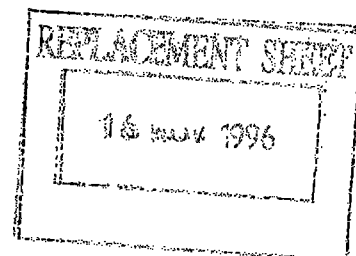
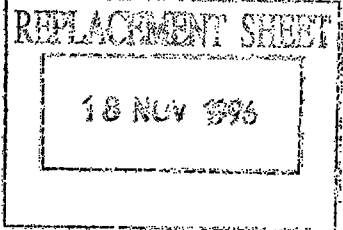


Table 1

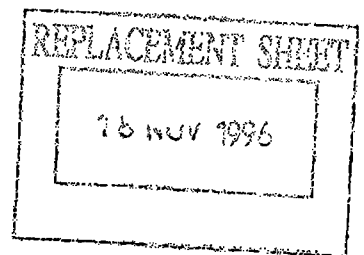
	Tribo- elec. 1)	Triboelectricity 2)					
		Shaken for 0 sec.		Shaken for 60 sec.		Shaken for 240 sec.	
		mC/kg	%	mC/kg	%	mC/kg	%
Example 1	-11.0	- 9.9	90	-11.0	100	-11.0	100
2	-10.2	- 9.2	90	-10.0	98	-10.2	100
3	-10.4	- 9.4	90	-10.2	98	-10.4	98
4	-10.3	- 8.8	85	- 9.6	93	- 9.9	96
5	- 9.4	- 7.8	83	- 9.4	100	- 9.4	100
6	- 9.2	- 7.5	81	- 8.2	90	- 8.6	93
7	- 9.6	- 8.6	90	- 9.6	100	- 9.6	100
8	-12.5	-11.4	91	-12.5	100	-12.5	100
9	-11.2	-10.2	91	-11.2	100	-11.2	100
10	-10.0	- 8.3	83	- 9.2	92	- 9.5	95
11	-10.2	- 8.5	83	- 9.4	92	- 9.7	95
12	-13.0	-10.4	80	-11.3	87	-12.0	92
13	- 9.6	- 7.5	78	- 8.2	85	- 8.8	92
14	- 8.9	- 7.2	81	- 7.8	88	- 8.3	93
Comparative Example 1	- 6.8	- 5.1	75	- 5.6	82	- 6.1	89
2	- 6.2	- 4.3	70	- 4.7	75	- 5.1	82
3	- 8.5	- 7.0	82	- 7.7	90	- 7.9	93
4	- 4.2	- 3.3	78	- 3.7	88	- 3.9	92

Triboelectricity 1) : Quantity of triboelectricity of magnetic toner which was allowed to stand for 2 days at high temperature and high humidity in an uncovered polyethylene container and thereafter shaken in a tumbling mixer for 240 seconds.

Triboelectricity 2) : Quantity of triboelectricity of magnetic toner which was further allowed to stand for 4 days at high temperature and high humidity and thereafter shaken in a tumbling mixer.

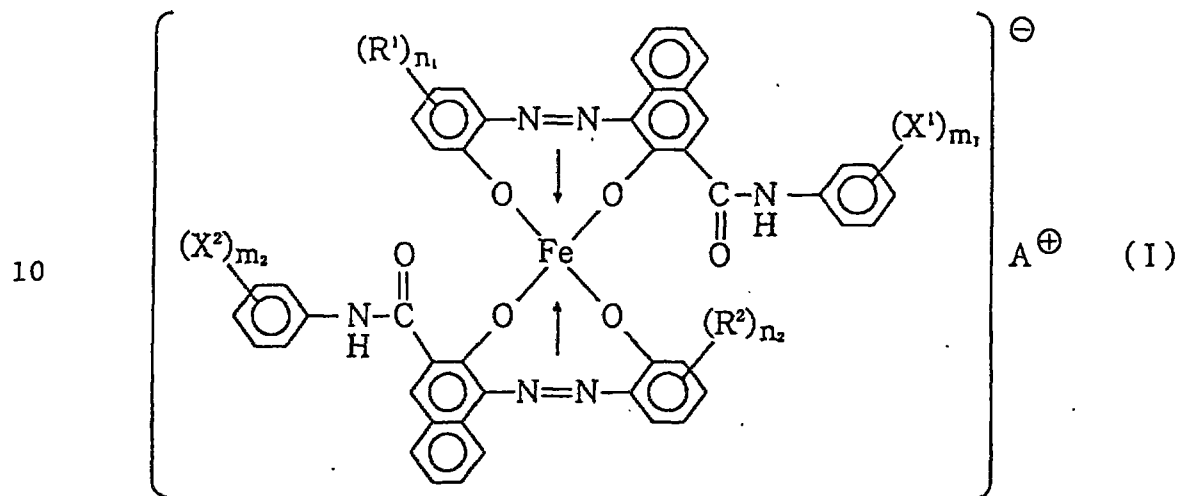


A magnetic toner for developing an electrostatic image is disclosed which has a binder resin, a magnetic material and an iron compound of the formula (I). The magnetic toner has a saturation magnetization of 20 to 50 Am²/kg and a coercive force of 40 to 200 oersted.



1 WHAT IS CLAIMED IS:

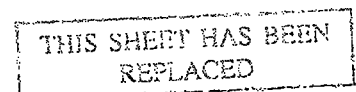
1. A magnetic toner for developing an electrostatic image, comprising a binder resin, a magnetic material and a compound represented by the following formula (I):



15 wherein R¹ and R² each represent a hydrogen atom, a sulfonic acid group, a carboxylic acid group, a carboxylate group, a hydroxyl group or a halogen atom, and may be the same or different; n₁ and n₂ each represent an integer of 1 to 4; X¹ and X² each
20 represent a hydrogen atom or a halogen atom; m₁ and m₂ each represent an integer of 1 to 3; and A[⊕] represents a hydrogen ion, an alkali metal ion or an ammonium ion;

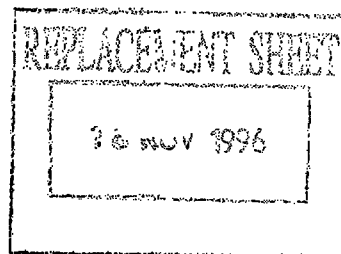
said magnetic toner having a saturation
25 magnetization of from 20 Am²/kg to 50 Am²/kg and a coercive force of from 40 oersted to 200 oersted.

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1 2. The magnetic toner according to claim 1,
wherein the alkali metal ion is selected from the
group consisting of sodium ion and potassium ion.

5 3. The magnetic toner according to claim 1,
wherein the magnetic material is contained in an
amount satisfying the following expression:

$$MT = -(10/3) \times d + (70 \pm 15)$$

10 wherein MT represents a content (% by weight) of the
magnetic material, and d represents a weight average
particle diameter (μm) of the magnetic toner, provided
that d is not more than 9 μm .

15 4. The magnetic toner according to claim 1,
wherein $A^{\oplus}$ comprises an ammonium ion and an alkali
metal ion.

20 5. The magnetic toner according to claim 4,
wherein $A^{\oplus}$ has 80 to 98 mol% of ammonium ion.

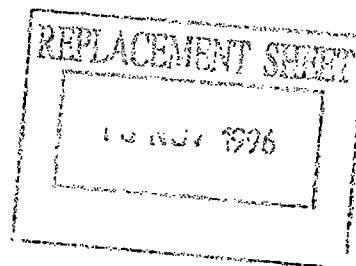
6. The magnetic toner according to claim 5,
wherein $A^{\oplus}$ has 85 to 95 mol% of ammonium ion.

25 7. The magnetic toner according to claim 1,
wherein $A^{\oplus}$ comprises an ammonium ion and an hydrogen
ion.

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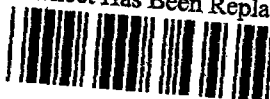


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- 1 8. The magnetic toner according to claim 7,
 wherein A[⊕] has 80 to 98 mol% of ammonium ion.
9. The magnetic toner according to claim 8,
5 wherein A[⊕] has 85 to 95 mol% of ammonium ion.
10. The magnetic toner according to claim 1,
 wherein A[⊕] comprises an ammonium ion, an alkali metal
 ion and an hydrogen ion.
- 10 11. The magnetic toner according to claim 10,
 wherein A[⊕] has 80 to 98 mol% of ammonium ion.
12. The magnetic toner according to claim 11,
15 wherein A[⊕] has 85 to 95 mol% of ammonium ion.
13. The magnetic toner according to claim 1,
 which has negative triboelectricity.
- 20 14. The magnetic toner according to claim 1,
 wherein the iron compound is contained in an amount of
 0.1 to 10 parts by weight based on 100 parts by weight
 of the binder resin.
- 25 15. The magnetic toner according to claim 1,
 wherein the iron compound is represented by the
 following formula:

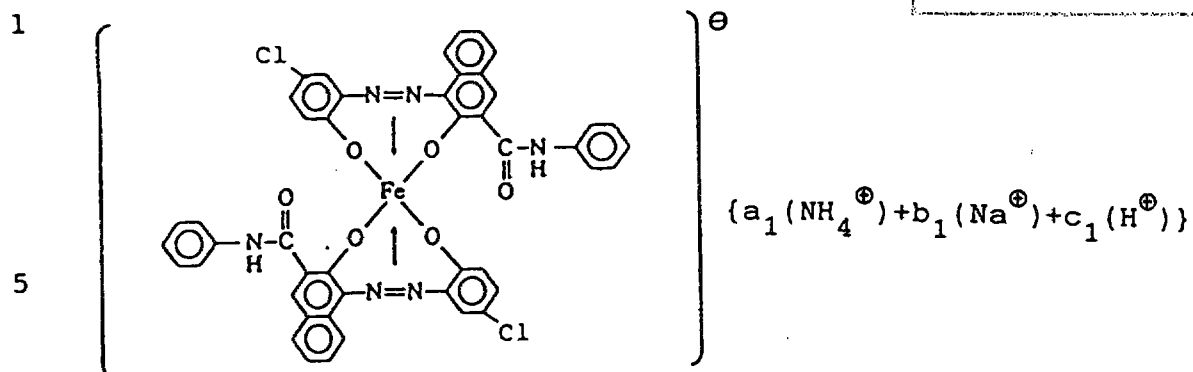
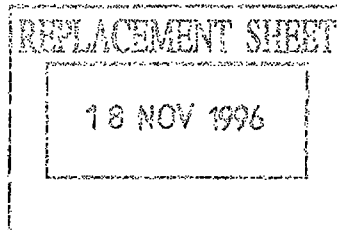
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10 wherein $a_1 + b_1 + c_1$ is 1.

16. The magnetic toner according to claim 15,
wherein a_1 is 0.8 to 0.98; b_1 is 0.01 to 0.19; and c_1
is 0.01 to 0.19.

15 17. The magnetic toner according to claim 16,
wherein a_1 is 0.85 to 0.95; b_1 is 0.01 to 0.14; and c_1
is 0.01 to 0.14.

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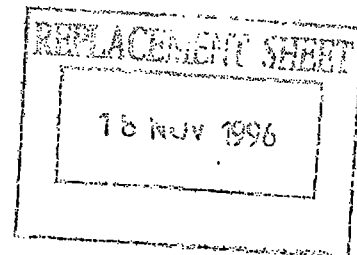


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REPLACED

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MAGNETIC TONER FOR DEVELOPING
ELECTROSTATIC IMAGE
ABSTRACT OF THE DISCLOSURE

A magnetic toner for developing an electrostatic image is disclosed which has a binder resin, a magnetic material and an iron compound of the formula (I). The magnetic toner has a saturation magnetization of 20 to 50 Am²/kg and a coercive force of 40 to 200 oersted.

FIGURE 1

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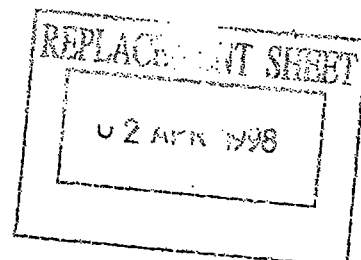
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MAGNETIC TONER FOR DEVELOPING
ELECTROSTATIC IMAGE

ABSTRACT OF THE DISCLOSURE

A magnetic toner for developing an electrostatic image is disclosed which has a binder resin, a magnetic material and an iron compound of the formula (I). The magnetic toner has a saturation magnetization of 20 to 50 Am²/kg and a coercive force of 40 to 200 oersted.

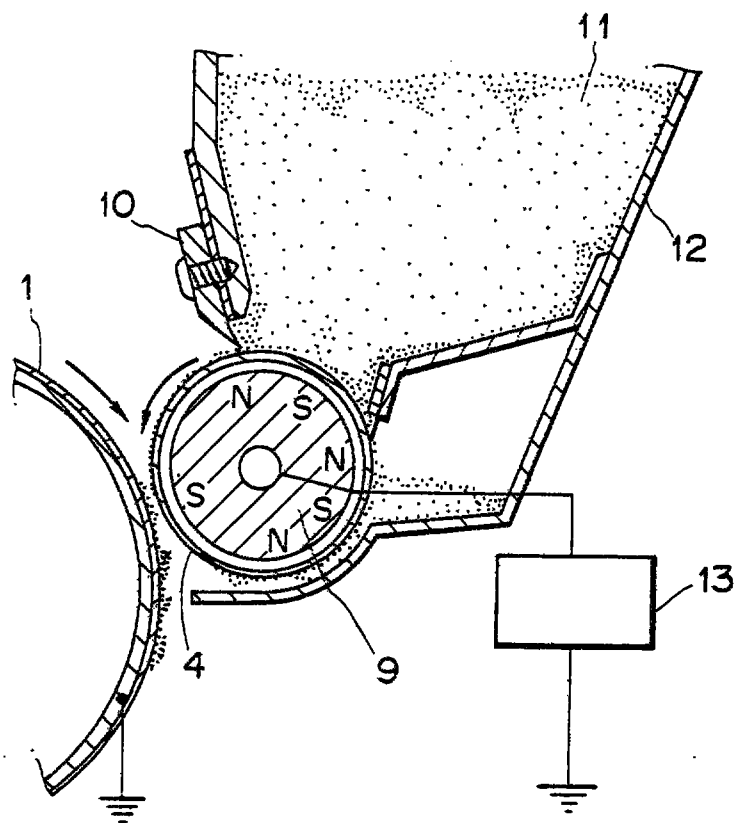
FIGURE 1

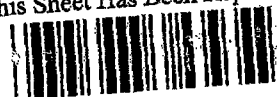


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/

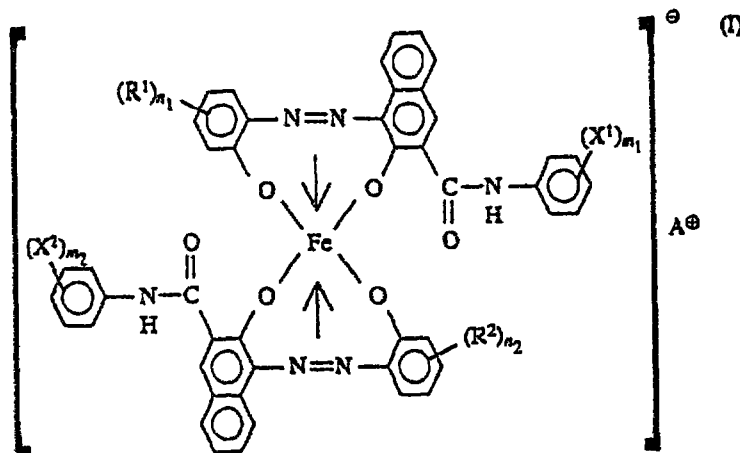
FIG. 1





What is claimed is:

1. A magnetic toner for developing an electrostatic image, comprising a binder resin, a magnetic material and a compound represented by the following formula (I):



wherein R^1 and R^2 are each a member selected from the group consisting of a hydrogen atom, a sulfonic acid group, a carboxylic acid group, a carboxylate group, a hydroxyl group and a halogen atom, and may be the same or different; n_1 and n_2 are each an integer of 1 to 4; X^1 and X^2 are each a member selected from the group consisting of a hydrogen atom and a halogen atom; m_1 and m_2 are each an integer of 1 to 3; and A^+ is a member selected from the group consisting of a hydrogen ion, an alkali metal ion and an ammonium ion;

said magnetic toner having a saturation magnetization of from 20 Am²/kg to 50 Am²/kg and a coercive force of from 40 oersted to 200 oersted, wherein the magnetic material is contained in an amount satisfying the following expression:

$$MT = -(10/3) \times d + (70 \pm 15)$$

wherein MT represents a content in % by weight of the magnetic material, and d represents a weight average particle diameter (μ m) of the magnetic toner, provided that d is not more than 9 μ m.

2. The magnetic toner according to claim 1, wherein the alkali metal ion is selected from the group consisting of sodium ion and potassium ion.

3. The magnetic toner according to claim 1, wherein A^+ comprises an ammonium ion and an alkali metal ion.

4. The magnetic toner according to claim 3, wherein A^+ has 80 to 98 mol % of ammonium ion.

5. The magnetic toner according to claim 4, wherein A^+ has 85 to 95 mol % of ammonium ion.

6. The magnetic toner according to claim 1, wherein A^+ comprises an ammonium ion and a hydrogen ion.



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7. The magnetic toner according to claim 6, wherein $A^{\oplus}$ has 80 to 98 mol % of ammonium ion.

8. The magnetic toner according to claim 7, wherein $A^{\oplus}$ has 85 to 95 mol % of ammonium ion.

9. The magnetic toner according to claim 1, wherein $A^{\oplus}$ comprises an ammonium ion, an alkali metal ion and an hydrogen ion.

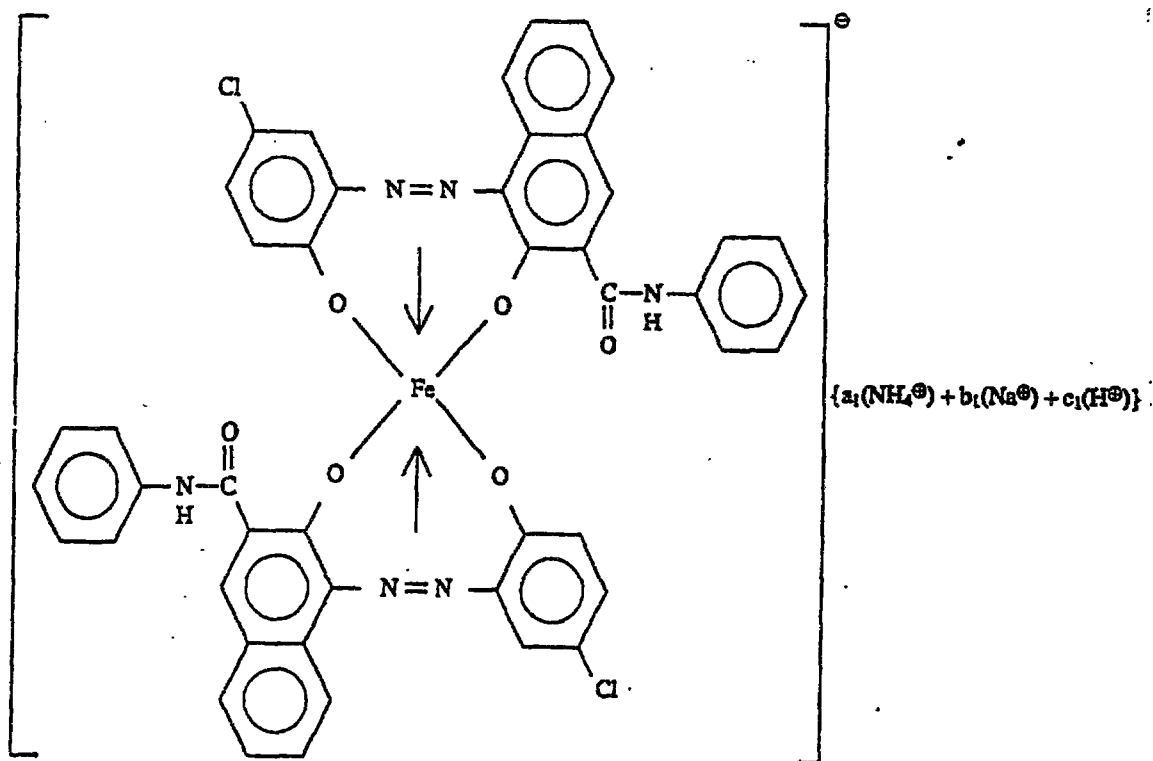
10. The magnetic toner according to claim 9, wherein $A^{\oplus}$ has 80 to 98 mol % of ammonium ion.

11. The magnetic toner according to claim 10, wherein $A^{\oplus}$ has 85 to 95 mol % of ammonium ion.

12. The magnetic toner according to claim 1, which has negative triboelectricity.

13. The magnetic toner according to claim 1, wherein the iron compound is contained in an amount of 0.1 to 10 parts by weight based on 100 parts by weight of the binder resin.

14. The magnetic toner according to claim 1, wherein the iron compound is represented by the following formula:



wherein $a_1 + b_1 + c_1$ is 1.

15. The magnetic toner according to claim 14, wherein a_1 is 0.8 to 0.98; b_1 is 0.01 to 0.19; and c_1 is 0.01 to 0.19.

16. The magnetic toner according to claim 15, wherein a_1 is 0.85 to 0.95; b_1 is 0.01 to 0.14; and c_1 is 0.01 to 0.14.

* * * * *

This Sheet Has Been Replaced



FIG. 1

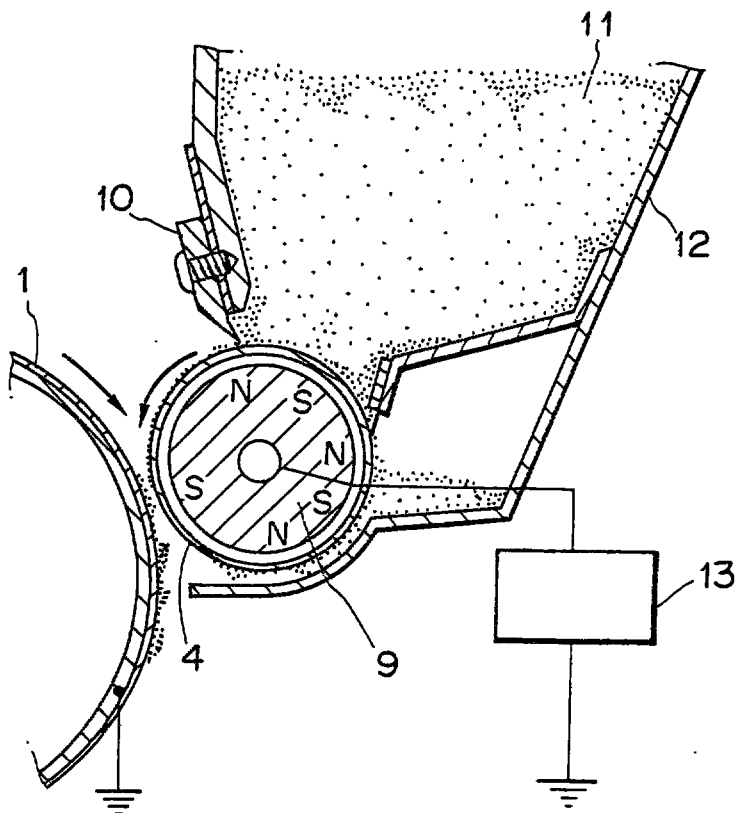


FIG. 2

