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(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650(US)

(72) Inventor: **Spence, John M., c/o EASTMAN KODAK COMPANY**
Patent Department 343 State Street
Rochester, New York 14650-2201(US)
Inventor: **Contois, Robert E., c/o EASTMAN KODAK COMPANY**
Patent Department 343 State Street
Rochester, New York 14650-2201(US)
Inventor: **DeMejo, Lawrence P., c/o EASTMAN KODAK COMPANY**
Patent Department 343 State Street
Rochester, New York 14650-2201(US)

(74) Representative: **Brandes, Jürgen, Dr.Rer.Nat. et al**
Wuesthoff & Wuesthoff, Patent- und Rechtsanwälte, Schweigerstrasse 2
W-8000 München 90(DE)

(54) Two-component magnetic developer for magnetic image character recognition.

(57) A two-component type magnetic developer and its use in electrostatographic processes for generating documents suitable for magnetic image character recognition is described. The developer comprises a mixture of a magnetic carrier and a magnetic toner comprising particles of a binder resin medium and a magnetic material dispersed in the binder resin medium. The magnetic carrier is composed of acicular magnetic stainless steel particles containing a chromium content of at least 9 percent by weight which have been passivated to form a chromium-rich, stable film on the particle surfaces. The magnetic carrier in the developer provides magnetic image character recognition images and characters of excellent magnetic image character recognition readable quality and developed images of excellent image density and sharpness.

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TWO-COMPONENT MAGNETIC DEVELOPER FOR MAGNETIC IMAGE CHARACTER RECOGNITION

This invention relates generally to a two-component type magnetic developer for developing electrostatically charged images in electrostatographic processes for generating documents suitable for magnetic image character recognition, and particularly to a two-component type magnetic developer for developing electrostatically charged images in electrostatographic processes for generating documents suitable for magnetic image character recognition which provides clear, sharp developed images having both excellent line and solid area development.

In July, 1956, the American Banking Association adopted magnetic ink character recognition as the common language for automatic reading of checks in order to ease the paper inundation which had grown steadily with manual methods. Magnetic ink character recognition involves the encoding of certain magnetic image character recognition information (MICR) in accordance with the American National Standards Institute (ANSI) standards for MICR reading at the bottom line of personal and commercial checks. The information involved, which is referred to as MICR characters, appears as the printed numbers and symbols in the somewhat unique "futuristic" font at the bottom line of each check. The checks are printed with a magnetic ink containing magnetizable particles. When the information contained on the document is to be read, the document is passed through a sorter/reader which first magnetizes the magnetizable particles and subsequently detects a magnetic field of the symbols resulting from the magnetic retentivity of the ink. Typically, the characters and symbols involved identify the bank, the bank branch or the issuing source, and/or the account affected by the transaction.

The extremely high reliability of the recognition of MICR information has made this banking industry standard attractive to the range of financial institutions which deal in large amounts of paper work.

Until recently however, extensive use of MICR was limited because of the cumbersome processes that were available to generate the MICR printing. Special printers had to be used to print the required magnetic ink on the document within the MICR placement accuracy. The printers were slow and the documents had to be printed in a number of sequential steps. This created additional handling problems which in turn generated related security concerns.

Recently, there was disclosed in Gruber et al, U.S. Patent No. 4,517,268, a non-impact printing process for generating MICR encoded documents which are recognizable to MICR readers. The method utilizes conventional electrostatographic imaging methods such as xerographic printing methods to generate MICR encoded documents in which images meeting current MICR standards are produced with a magnetic dry ink toner. As a direct result of this method, MICR encoded documents can now be produced for the first time at high speeds and in almost infinite quantities and at a comparatively low cost. For example, entire checks, in any quantity desired, can be printed in a single pass production including the form, variable fill-in data, serial number, logo, signature and MICR line staring out with plain blank safety paper. That is, checks containing MICR readable characters as well as normal text or graphics now can be produced in a single pass. This eliminates the need to manage and store pre-encoded blank check stock. Further, as many copies as are required on an individual basis can be printed thereby saving additional paper costs. Another advantage of the Gruber et al process resides in the flexibility which it provides in preparing the contents of the field on the document involved. That is, an almost limitless number of diverse forms having different fonts and logos containing different information in both MICR and non-MICR optical characters can be created and produced by this process. Of equal importance, a process now exists whereby MICR encoded documents of any type or sort in addition to personal and commercial checks can be produced in a fast and efficient manner and at a relatively low cost so that financial institutions other than banks throughout the entire financial industry may avail themselves of the advantages of this system.

In the process disclosed by Gruber et al in U.S. Patent No. 4,517,268 characters are imprinted on the desired document by known electrostatographic methods, particularly xerographic methods, with a high speed electronic printing device and developed with a magnetic developer composition comprising from 20 percent by weight to 70 percent by weight of magnetite particles, and from 30 percent by weight to 80 percent by weight of toner resin particles containing styrene copolymers, such as styrene butadiene copolymers, or styrene butylmethacrylate copolymers, styrene acrylate copolymers or polyesters, and carrier beads comprised of ferrite or steel cores coated with various polymeric compositions, including, for example, terpolymers of styrene, methylmethacrylate and a silane. Alternatively, the carrier particles can consist of uncoated ferrite substances.

In conventional xerographic printing, an electrostatic image of the desired hard copy is formed by selectively discharging a uniformly charged photoconductive surface, the photoreceptor, by a modulated scanned laser illuminator or light emitting diodes. A visible image is formed by delivering charged toner, made of a pigmented resin, to the photoreceptor surface in the development step. The charged toner adheres to the charged areas of the photoreceptor since the toner composition is selected such that the toner acquires a charge opposite in sign to the photoreceptor surface charge. The toner charging occurs through a triboelectric interaction between the toner and the carrier bead, a much larger magnetic particle, in which the particles rub together and acquire opposite electrostatic charges. The carrier serves the functions of charging the toner and transporting it to the photoreceptor under the control of magnetic fields in the developer housing. The developed image is subsequently transferred to paper by electric fields in the transfer station. The image on the paper is finally and permanently fixed in place by suitable fixing means such as a hot roll fuser while the photoreceptor is cleaned of any untransferred toner and uniformly discharged for reuse.

The method for applying the developer mix which is described above is well-known and is referred to as the "magnetic brush" process or technique. Such a process can utilize apparatus of the type described, for example, in U.S. Patent No. 3,003,462 and often comprises a nonmagnetic rotatably mounted cylinder having fixed magnetic means mounted inside. The cylinder is arranged to rotate so that part of the surface is immersed in or otherwise contacted with a supply of developer mix. The granular mass comprising the developer mix is magnetically attracted to the surface of the cylinder. As the developer mix comes within the influence of the field generated by the magnetic means within the cylinder, the particles of the developer mix arrange themselves in bristle-like formations resembling a brush. The bristle formations of developer mix tend to conform to the lines of magnetic flux, standing erect in the vicinity of the poles and lying substantially flat when the mix is outside the environment of the magnetic poles. Within one revolution the continuously rotating cylinder picks up developer mix from a supply source and then returns part or all of the material to the supply. This mode of operation assures that fresh mix is always available to the photoconductive surface at its point of contact with the brush. In a typical rotational cycle, the roller performs the successive steps of developer mix pickup, brush formation, brush contact with the photoconductive element, brush collapse and finally mix release. When this "magnetic brush" engages or contacts the electrostatic image bearing photoconductive surface, the toner particles are drawn from the brush, i.e. the toner particles are drawn away from the carrier particles, by the oppositely charged electrostatic image. If desired, more than one such magnetic roller device can be utilized in the process to apply the developer mix to the photoconductive element as in the case where large solid image areas such as logos and the like which require large amounts of toner are desired to be developed. The conductivity of the ferromagnetic carrier particles which form the "bristles" of the magnetic brush provides the effect of a development electrode having a very close spacing to the surface of the photoconductive or electrophotographic element being developed. By virtue of this development electrode effect it is to some extent possible to develop part of the toner in pictures and solid blacks as well as line copy. This ability to obtain solid area development with magnetic brush developing makes this mode of development advantageous where it is desired to print materials other than simple line copy. In the production of MICR encoded documents, this mode of development is particularly useful and suitable since magnetic toner particles must be used in the developer in order to provide MICR readable characters and symbols. That is, the developed characters must produce magnetic signals within defined limits when passed through a MICR reader so that the information can be read.

While the particular magnetic developer used by Gruber et al in their magnetic image character recognition process produces excellent MICR readable magnetic images and characters, it has been found that the print quality, i.e., the optical image density provided by the developer is somewhat lacking with respect to solid area development where a visible fringing effect can be observed in the developed image, particularly where the developer is employed in an electrostatographic process which utilizes a two-roller magnetic brush development system. That is, the images provided by the developer can be hollow in that solid areas are not completely filled. This is believed to be a result of the particular carrier component used in the two-component magnetic developer composition of Gruber et al which will be discussed in greater detail below.

An objective of this invention is to provide a magnetic developer which can be used in conventional electrostatographic processes for generating documents suitable for magnetic image character recognition which is capable of producing magnetic image character recognition images and characters of excellent MICR readable quality and overcomes the optical image density defect problems previously described.

This invention provides a two-component type magnetic developer that can be used in known electrostatographic processes for generating documents suitable for use in magnetic image character recognition that can simultaneously provide both MICR images and characters of excellent MICR readable quality and developed images having excellent image density and sharpness.

The two-component magnetic developer of the invention comprises a mixture of magnetic carrier particles composed of passivated acicular magnetic stainless steel particles containing at least 9 weight percent chromium, the surfaces of which comprise a thin protective layer that is rich in chromium, and a magnetic toner comprising particles of a binder resin medium and a magnetic material which is dispersed in the binder resin medium. Due to the particular magnetic carrier particles used in the developer compositions of the invention, there is provided a magnetic developer which can be used in known electrostatographic processes to generate documents which are suitable for magnetic ink character recognition which not only is capable of achieving high MICR image performance, i.e., high MICR readability, but a magnetic developer that also is capable of achieving high optical print quality, i.e., capable of providing developed images and characters of excellent image density and sharpness.

The two-component magnetic developer composition of the invention is characterized in that it is formed of a mixture of particles of a magnetic toner comprising a binder resin medium and a magnetic material or component, such as magnetite, which is dispersed in the binder resin medium and particles of a magnetic carrier comprising a mass of passivated acicular magnetic stainless steel particles containing at least 9 weight percent chromium, the surfaces of which comprise a thin protective layer that is high in chromium. When the magnetic toner particles are mixed with the specific magnetic carrier, that is, a magnetic carrier consisting of a mass of passivated acicular magnetic stainless steel particles containing at least 9 weight percent chromium and whose surfaces comprise a thin protective layer that is rich in chromium, and the resulting two-component developer is employed to develop electrostatically charged images in an electrostato- graphic process used to generate documents suitable for magnetic image character recognition, the solid area image density and hence the image quality is prominently improved over the solid area image density and image quality attainable by the use of a two-component magnetic developer consisting of a mixture of the same magnetic toner particles and a magnetic carrier consisting of an ordinary magnetic carrier such as the ferrite carrier particles which are disclosed in Gruber et al such as iron powder or iron oxide as being a suitable carrier material for use with a magnetic toner such as magnetite in a two-component magnetic developer composition for developing electrostatographically charged images in an electrostatographic process used to generate documents suitable for magnetic image character recognition.

Reflection density measurements of the formed images, which are provided below, show that when the specific magnetic carrier particles described herein are mixed with magnetic toner particles comprising a toner resin binder and magnetite dispersed within the binder, the image density is dramatically increased over the image density obtained when such carrier particles are not incorporated in the developer composition with the same magnetic toner but instead are replaced with an equivalent amount of uncoated sponge iron powder carrier particles. When an image is obtained by using a developer composed solely of a magnetic toner comprising particles of a toner resin binder composed of a styrene n-butylmethacrylate copolymer crosslinked with divinyl benzene and particles of magnetite dispersed therein and a magnetic carrier consisting of particles or beads of uncoated sponge iron powder is practically compared with a copied image obtained by using a developer of the invention comprising the same magnetic toner as described above and magnetic carrier particles composed of the previously described passivated acicular magnetic stainless steel particles of the invention, it is seen that the developer of the invention is advantageous in that the formed image is free of any fringe effect. Although not wishing to be bound by any particular theory, it is theorized that improved solid area image density and quality is achieved by the specific two-component developer of the invention due to an enhanced development electrode effect created by or resulting from the passivated stainless steel carrier particles used in the developer compositions described herein. As mentioned previously, the conductivity of the carrier particles which form the "bristles" of the magnetic brush used in the development of electrostatic images provides the effect of a development electrode having a very close spacing to the surface of the electrostatographic element being developed. The effect of the development electrode is to change the field configuration of the electrostatic image and increase the electric field in the space above large solid areas of charge. Under these conditions, the various parts of an electrostatic image will be developed-out more nearly in proportion to the electrical charge density on the plate surface rather than just at the voltage gradient along the edges so that edging or fringing effects which produce halos and give the developed copy a contrasting, or washed-out appearance are reduced or eliminated. A more detailed description of the development electrode is set forth in Schaffert, R.M. Electrophotography. London, Focal Press, 1980, pp. 35-36. In general, the higher the surface and bulk conductivity of the carrier particles which form the bristles of the magnetic brush used in the development of electrostatic images, the stronger the development electrode effect that is produced. A stronger development electrode effect results in better solid area development, i.e., better solid area image density. Accordingly, the passivated stainless steel particles described herein, being more electrically conductive (i.e., having a higher surface conductivity) due to passivation treatment than the iron or steel carrier particles of Gruber et al, produce a stronger development electrode effect than the carrier particles of Gruber et al and thereby provide better solid area development than the solid area development provided by the Gruber et al carrier particles. Further, not only are the carrier chains which are composed of the passivated stainless steel particles described herein more electrically conductive than the chains of carrier particles of Gruber et al due to passivation treatment, they are more electrically stable so that their conductivity remains stable for an extended period of time under development conditions. In addition, it is also theorized that the acicular or ansiotropic shape of the passivated stainless steel carrier particles used in the developer mixes described herein also contributes to the enhancement of the development electrode effect. As is commonly known, a long and narrow piece of magnetic material magnetizes along its length or long axis and has a stronger magnetic field than a spherical or bead-shaped piece of the same material. This is due to the smaller demagnetizing field in the long and narrow material resulting from the greater distance between the poles of the longer material. Acicular shaped carrier particles, being somewhat longer than they are wide, therefore, each possess a magnetic field stronger than the magnetic field possessed by a comparable spherical or bead-shaped carrier particle. Because of this, a stronger magnetic attraction exists from one acicular-shaped carrier particle to another in the carrier chain which forms the "bristles" of the magnetic brush in comparison to the magnetic attraction which exists from one spherical or bead-shaped carrier particle to another in a comparable chain.

Because the magnetic attraction of one acicular-shaped carrier particle for another is so strong, a strong magnetic contact between the individual particles in the carrier chain exists which also provides a good electrical contact between the particles so that a highly conductive pathway is established in the carrier chain. This helps to insure that increased electric fields will be provided in the spaces above the large solid areas of charge so that fringing effects will not be produced during the development of the electrostatic image and good solid area image density will result in the developed image. The strong magnetic contact between the individual carrier particles also is believed to prevent toner particles, which are insulative relative to the carrier particles due to the low conductive nature of the binder resin material which forms a part of the toner composition from working their way in between individual carrier particles at their points of contact as they would be expected to do in the case of the less tightly held spherically-shaped particles and increase the electrical resistance of the carrier chain.

The carrier component of the two-component magnetic developer of the invention comprises a mass of passivated particles of acicular magnetic stainless steel. The passivated steel surface comprises a thin, tightly adherent, chromium-rich layer. The particles of magnetic stainless steel are passivated, most suitably, by treatment with nitric acid. The passivation of stainless steel apparently rids its surface of free iron, enriching it in chromium which oxidizes to form a layer that is chemically stable and inert under electrostatographic development conditions. The resultant passivated stainless steel carrier particles are characterized as having improved conductivity and stability.

The term stainless steel designates a family of alloy steel of sufficiently high chromium content, e.g., at least 9 weight percent, to resist the corrosion or oxidation to which ordinary carbon steels are susceptible in a moist atmosphere. Not all stainless steels, however, can be used as carrier materials in the developer compositions described herein. The steel must be magnetic. Two types that meet this requirement are martensitic stainless steels, which contain from 10 to 18 weight percent chromium, and ferritic stainless steels, which contain from 15 to 30 weight percent chromium. Austenitic stainless steels contain a large amount of nickel (6 to 22 weight percent) and normally are nonmagnetic in the annealed condition.

Passivation of stainless steel consists of any treatment that forms a thin protective film or layer on the surface of the steel. This layer, which is transparent and microscopically thin, is rich in chromium relative to the untreated steel. The layer is more electrically conductive than the oxides of iron, and, being chemically stable, its conductivity remains stable for an extended period of time under development conditions. X-ray photoemission spectroscopy of the passivated surfaces indicates that the minimum thickness of the layer is 30 Å and that the ratios of Cr/Fe, O/Fe and C/Fe are increased at the surface as compared with the untreated steel. It also indicates the chromium in the surface layers is in the form $Cr(OH)_3$.

A particularly useful method of passivating the stainless steel is by treatment with nitric acid. Other passivating treatments are known, however, and any passivating treatment that forms on the steel a surface that remains free of copper in the standard copper plating test can be used. In this test, the sample of steel, typically a plate 2.5 cm x 5 cm x 0.16 cm is immersed in an acidified copper chloride solution containing 10 g of cupric chloride, 500 ml water and 5 ml hydrochloric acid at room temperature (20 °C). Plating of copper onto the steel shows that the steel has a reactive surface and has not been passivated. If the steel remains free of copper it is, by definition, passivated and is useful as a carrier in the developers described herein.

The reaction conditions for passivating with nitric acid or other passivating agents can vary depending on the composition and, to some extent, the particle size of the stainless steel. Whether or not certain conditions or passivating agents are suitable can readily be determined by the copper plating test. In any event, for economy and good results nitric acid is particularly useful as the passivating agent. Especially suitable conditions for nitric passivation of stainless steels of American Iron and Steel Institute (AISI) grades 410 and 434 include: aqueous nitric acid concentration from 18 to 22 volume percent, preferably 20 volume percent; temperature of 50 to 90° C, preferably 60 to 80° C, and reaction time is 5 to 30 minutes, preferably 15 to 25 minutes. Other conditions can be used if the copper plating test shows that they do not in fact passivate the stainless steel.

The acid treatment can be performed in different ways, including spraying and percolation. A particularly useful method is to form a slurry of the steel powder and the aqueous acid solution. The duration of this treatment will be influenced by the concentration of the acid, the temperature, the degree of agitation, and the particle size of the steel. When treating magnetic stainless steel powder of 100 to 400 microns average particle size, it is preferred to agitate the steel powder in a slurry of 20 volume percent nitric acid solution at 65° C for 20 minutes. After the steel has reached passivity, further immersion in the nitric acid solution has no apparent effect.

Following the nitric acid treatment the stainless steel powder is rinsed, preferably in water, and then any volatile water-visible solvent such as acetone or a lower alcohol such as methanol, ethanol or isopropanol. The rinsed carrier particles are dried, e.g., by agitating them in a current of warm air or nitrogen.

Some stainless steels, and especially stainless steel powders, contain a small amount of silicon. It is included by the manufacturers to improve the flow of the molten steel when it is spray-atomized to make steel powder. This silicon increases the resistivity of the steel. However, the silicon can be removed from the surfaces of the steel particles by washing them with an agent such as hydrofluoric acid before passivating them. If a steel contains silicon, treatment with hydrofluoric acid or other pickling solution before passivation will remove enough silicon to make the passivated steel particles sufficiently conductive for use in the developer compositions described herein.

Passivated stainless steel carrier particles having increased surface activity and stability are known as are the aforedescribed methods of passivating the stainless steel and are disclosed in Miskinis, U.S. Patent No. 4,310,611. Comparative tests demonstrating the chemical stability of the passivated stainless steel as compared with other steel or iron samples which have been treated in other ways, as well as comparative tests demonstrating the superior surface conductivity (i.e., lowered static resistance) of passivated stainless steel carriers over untreated stainless or sulfuric acid-treated stainless steel carriers or oxidized iron carriers, are set forth in aforementioned U.S. Patent No. 4,310,611 beginning at column 5, line 23 and continuing through column 6, line 68 and are reproduced in toto hereinbelow for convenience.

"COMPARATIVE TESTS

Test No. 1 demonstrates the chemical stability of passivated stainless steel as compared with other steel or iron samples which have been treated in other ways.

TEST NO. 1 - CHEMICAL STABILITY

Three plates of stainless steel and one of plain carbon steel (dimensions of plates: 2.5 cm x 5 cm x 0.16 cm) were washed with a particular acid or inert solvent and were then tested for chemical stability. The procedures were as follows:

Nitric Acid Wash-One stainless steel plate was washed with a 20 volume percent nitric acid solution for 20 minutes. It was then rinsed in water for 5 minutes, next in methanol for 5 minutes and then air dried.

Sulfuric Acid Wash-A second stainless steel plate was washed with sulfuric acid (5 vol. % solution) for 2 minutes and then air dried.

Solvent Wash-The third stainless steel plate and the carbon steel plate served as controls and were washed only in the inert solvent, dichloromethane.

The chemical stability of the washed plates was tested by dipping them in an acidified copper chloride solution containing 10 g cupric chloride, 500 ml water and 5 ml hydrochloric acid. All treatments were at room temperature (20° C). Analysis of the plates indicated that the stainless steel corresponded to AISI type 416 and contained iron as the major constituent and, by weight, 13.2% Cr, 0.23% Ni, 0.3% Mn, 0. 56% Mo, and 0.11% C; and that the carbon steel corresponded to AISI type 1006 and contained iron as the major constituent, less than 0.008% Cr, 0.32% Mn, 0.046% C and lesser amounts of other elements. The table below shows the results:

Table I

Plate		Wash Treatment	Dip Time	Copper Plating
A	Stainless Steel	20% HNO_3	12 min.	No
B	Stainless Steel	CH_2Cl_2	12 min.	Yes
C	Stainless Steel	%5 H_2SO_4	12 min.	Yes
D	Carbon Steel	CH_2Cl_2	30 sec.	Yes

No copper plating occurred with the nitric acid-treated stainless steel, indicating a stable non-reactive surface or, in other words, a passivated surface. The two other stainless steel plates and the plain carbon steel plate became copper plated, which indicates that their surfaces were reactive. The wash treatments to which they were subjected did not passivate them.

Test No. 2 which is next described, compares the electrical properties of untreated and of passivated stainless steel powders.

TEST NO. 2 - ELECTRICAL PROPERTIES

Four samples of stainless steel powder and a sample of sponge iron powder were pre-treated as follows:

Powder Sample	Composition	Pre-Treatment
F	Stainless Steel	No pre-treatment; tested as received from manufacturer.
G	Stainless Steel	Passivated by nitric acid treatment as in Test No. 1.
H	Stainless Steel	Sulfuric-acid treated as in Example 7 of U.S. 3,718,594; 5% sulfuric acid wash for 2 minutes, water wash (decant 12 times) and air dry.
I	Stainless Steel	Nitric-acid treated as in Test No. 1.
J	Iron (Hoeganaes EH sponge iron powder)	Fluidized bed oxidation as in U.S. 3,767,477.

The stainless steel and iron powders were products of Hoeganaes Corp. of Riverton, N.J. The steel, by analysis, was AISI type 410 L and contained iron as the major constituent and, by weight, 0.005% Al, 13.5% Cr, 0.025% Cu, <0.0015% Mg, 0.07% Mn, 0.006% Mo, 0.04% Ni, 1.0% Si, 0.025% Ag and <0.005% V.

The treated and untreated stainless steel powders were tested for static resistance and breakdown voltage. Static resistance was measured across a magnetic brush as follows: The brush was formed by attracting 15 grams of carrier particles to one end of a cylindrical bar magnet of 2.5 cm diameter. The magnet was then suspended with the brush-carrying end 0.5 cm from a grounded brass plate. The resistance of the particles in the magnetic brush was then measured between the magnet and the plate by means of a voltohmmeter. The breakdown voltage was measured under dynamic operating conditions in the manner described in the patent to Kasper et al U.S. Pat. No. 4,076,857 of Feb. 28, 1978.

The following table records the results of these tests:

TABLE II

Steel or Iron Powder Sample	Pre-Treatment	Static Resistance	Breakdown Voltage
F	None	1.1×10^9 ohms	75.1 volts
G	Nitric Acid	5.5×10^4 ohms	8.6 volts
H	Sulfuric Acid	1.5×10^8 ohms	82.3 volts
I	Nitric Acid	1.2×10^5 ohms	8.6 volts
J	Fluidized bed Oxidation	7.7×10^7 ohms	60.3 volts

These results show that the stainless steel carrier particles which were passivated by treatment with nitric acid (Samples G and I) were markedly lower in static resistance and in breakdown voltage than either the untreated or sulfuric acid-treated carriers or the oxidized iron carrier."

Also set forth in Miskinis, U.S. Patent No. 4,310,611 at column 8, lines 29 to 65 are tests demonstrating that the electrical resistance of stainless steel powder can be varied from 10^4 to 5 ohms by etching with hydrofluoric acid for varying periods of time. These tests are also set forth hereinbelow in toto for convenience.

"TEST NO. 4 - REMOVAL OF SILICON

Several samples of 410L stainless steel powder were etched for different periods of time with hydrofluoric acid (2.5 vol. % solution) then rinsed with water and methanol and allowed to dry. The dried particles were passivated with nitric acid (20 vol. % solution). The following table shows the static resistance of the samples of passivated stainless steel powder which had first been etched with hydrofluoric acid.

Etching time (2.5% HF)	Static Resistance (ohms)
0 sec	8.5×10^4
30 sec	4.5×10^4
60 sec	3.0×10^4
90 sec	2.0×10^4
120 sec	6.0×10^3
10 min	5.0×10^0

These results show that the electrical resistance of the 410L stainless steel powder can be varied from 10^4 to 5 ohms by varying the hydrofluoric acid treatment time. Further control of the silicon content of the stainless steel surfaces can be achieved by high temperature annealing of the steel under high vacuum followed by treatment with hydrofluoric acid. For instance by heating the steel particles at 850° C in a high vacuum, the surface silicon content can be significantly increased. Then by etching with hydrofluoric acid the silicon content and the electrical resistance of the particles can be reduced to the desired level. The particles are passivated to stabilize their conductivity after the hydrofluoric acid treatment. By vacuum annealing and acid treatments as described it is possible to provide a range of selected electrical resistances for the stainless steel particles."

As mentioned previously, it is believed to be important for the reasons given above that the passivated stainless steel particles have an acicular configuration.

The developer is formed by mixing the passivated, acicular particles of stainless steel described previously with a magnetic toner. Mixing can be accomplished, for example, by the known dry-blending method where the magnetic toner is supplied to a developer tank in an amount corresponding to the amount of the consumed magnetic toner and is mixed with the magnetic toner left in the tank whereby the developer is formed in situ. The developer normally will contain from 90 to 99 weight percent carrier and 10 to 1 weight percent toner.

Magnetic toner compositions useful in the invention comprise particles composed of a binder resin medium having a particle size of from 3 to 30 microns, typically 0.5 to 25 microns, and a magnetic component or magnetically attractable material such as magnetite, having a particle size of 1 micron, or smaller, typically between 0.02 microns and 1.0 micron, and more preferably having an average particle size of 0.1 to 0.6 microns which is dispersed in the binder resin medium. The magnetic materials used in the toner compositions described herein are magnetic in that they are attracted to a magnet, however, they are not necessarily magnets themselves.

Magnetite is a particularly useful magnetic material for use in the toner compositions of the invention. The shape of the particles is not particularly critical. Namely, fine cubic particles, amorphous particles, rounded particles and needle-like particles or combinations thereof may be used. Particularly useful magnetites are acicular magnetites commercially available from Pfizer Corporation as MO 4431 and MO 4232, cubical magnetites, MO 7029 commercially available from Pfizer Corporation, and Mapico Black, commercially available from Cities Service Company. Other useful magnetites which are commercially available include polyhedral magnetites, available from Hercules Incorporation as EX 1601 and XMT 100. As mentioned previously, the magnetic toner composition selected can contain mixtures of differently shaped magnetites. For example, mixtures comprised of acicular and cubic magnetites, that is, a mixture of hard magnetite and soft magnetite blends can be used. Generally, from 20 percent to 30 percent by weight of the hard magnetic substance can be selected and from 10 percent by weight to 30 percent by weight of a soft magnetic substance, such as Mapico Black, can be selected.

As the binder resin medium, there may be used polyamides, polyurethanes, epoxy, vinyl resins and polymeric esterification products of a dicarboxylic acid and a diol comprising a diphenol. Any suitable vinyl resin may be employed in the toners described herein including homopolymers or copolymers of two or more vinyl monomers. Typical of such vinyl monomeric units include styrene; vinyl naphthalene; ethylenically unsaturated mono-olefins such as ethylene, propylene, butylene, isobutylene and the like; vinyl ester such as vinyl chloride, vinyl bromide, vinyl fluoride, vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and like; esters of alpha-methylene aliphatic monocarboxylic acids such as methyl acrylate, ethyl atrylate, n-butyl acrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, 2-chloroethyl acrylate, phenyl acrylate methyl-alphachloroacrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and the like; acrylonitrile, methylacrylonitrile, acrylamide, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone, and the like; vinylidene halides such as vinylidene chloride, vinylidene chlorofluoride and the like; and N-vinyl compounds such as N-vinyl pyrrol, N-vinyl carbazole, N-vinyl indole, N-vinyl pyrrolidene and the like; and mixtures thereof.

Generally, toner resins containing a relatively high percentage of styrene are particularly useful since greater image definition and density is obtained with their use. The styrene resin employed may be a homopolymer of styrene or styrene homologs or copolymers of styrene with other monomeric groups containing a single methylene group attached to a carbon atom by a double bond. Any of the above typical monomeric units may be copolymerized with styrene by addition polymerization. Styrene resins may also be formed by the polymerization of mixtures of two or more unsaturated monomeric materials with a styrene monomer. The addition polymerization technique employed embraces known polymerization techniques such as free radical, anionic and cationic polymerization processes. Any of these vinyl resins may be blended with one or more other resins if desired, particularly other vinyl resins which insure good resistance against physical degradation. However, non-vinyl type thermoplastic resins may also be employed including resin modified phenolformaldehyde resins, oil modified epoxy resins, polyurethane resins, cellulosic resins, polyether resins and mixtures thereof. Also useful as toner resins include those materials that are polymeric esterification products of a dicarboxylic acid and a diol comprising a diphenol as described in U.S. Patent Number 3,590,000.

Especially useful resins are polystyrene resinous materials such as styrene butadiene resins, sstyrene butylmethacrylate copolymer resins, styrene acrylate copolymers, such as styrene butylacrylate copolymer resins, and the like. Particularly useful are toner resin particles containing from 55 percent by weight of styrene to 80 percent by weight of styrene, and from 20 percent by weight of n-butylmethacrylate to 45 percent by weight of n-butylmethacrylate, or styrene butadiene resins containing from 85 percent by weight to 95 percent by weight of styrene, and from 5 percent by weight to 15 percent by weight of butadiene.

There can also be incorporated into the magnetic toner compositions of the invention other known auxilliary addenda or components for developers. For example, a pigment such as carbon black and/or a dye such as Acid Violet may be added singly or in combination in amounts of from 0.5 to 5 percent by weight based on the total composition so as to improve the hue of the developer. Furthermore, a filler such as calcium carbonate or powdery silica may be added in an amount of up to 20 percent by weight based on the total composition to obtain a bulking effect. In the case where fixing is effected by a hot roll, an offset-preventing agent such as a silicon oil, a low-molecular weight olefin resin or wax may be used in an amount of 2 to 15 percent by weight based on the total composition. In the case where fixing is effected by means of a pressure roll, a pressure fixability-improving agent such as paraffin wax, an animal or vegetable wax or a fatty acid amide may be used in an amount of from 5 to 30 percent by weight based on the total composition. In order to prevent cohesion or agglomeration of developer particles and improve the flowability thereof, a flowability-improving agent such as a fine powder of polytetrafluoroethylene or finely divided silica (fumed silica) may be added in an amount of from 0.1 to 1.5 percent by weight based on the total composition.

It is particularly useful that the magnetic component or material, e.g., magnetite be present in an amount of from 20 percent by weight to 80 percent by weight, based on the sum of the amount of the binder medium and the magnetic material.

Any known method of toner particle formation may be utilized which results in toner of the desired properties. Typical of such methods are hot melt formation and mastication followed by attrition to the desired toner particle size. Instead of the above-mentioned method, there may be adopted another method in which the toner binder medium is dissolved in a polar organic solvent, for example, an aromatic solvent such as benzene, xylene, or ethylbenzene, ketone such as acetone, methylethyl ketone or methylisobutyl ketone or an ether such as tetrahydrofuran or dioxane. The magnetic material is dispersed in the solution and the dispersion is sprayed in drying air to effect granulation. In the latter method, if additional addenda is desired to be added to the composition, such as, for example, a colorant such as carbon black, the additional materials can be dispersed together with the magnetic component or dry-blended into the spray granulation product. In the former method, auxiliary addenda can be incorporated according to known recipes prior to mastication.

Although, as previously mentioned, magnetite is a particularly useful magnetic material for use in the toner compositions described herein, it is deemed that other magnetic materials can be used to form the stoner composition component of the invention as long as the particles which comprise the materials permit the achievement of the desired magnetic and electrical properties in the toner which is to be subsequently prepared and they are capable of providing images and characters that are MICR readable. Examples of such magnetic materials include magnetic pigments selected from alloys of iron, cobalt, nickel, or manganese and the like, such as hematite, ferrite and other ferromagnetic alloys.

Additionally, it is important to point out that the magnetic signal level is of substantial importance in magnetic image character recognition information systems since the amount of toner composition will vary in proportion to the signal level. Thus, for example, at a signal level of from 50 percent to 200 percent of nominal value, value of 100 percent, and preferably at a signal value of from 80 percent to 100 percent of nominal, there is deposited on the generated document, such as a personal check, desirable effective amounts of toner particles of the present invention.

The stainless steel carrier particles are larger than the toner particles, e.g., with an average particle size from 20 to 1000 microns and typically 40 to 500 microns. A convenient way of obtaining particles of the desired particle size range is by screening a mass of particles with the standard screens. Particles that pass through a 35 mesh screen and are retained on a 325 mesh screen (U.S: Sieve Series) are especially suitable.

By electrostatographic imaging methods or processes referred to herein is meant those methods or processes, including xerographic processes, where images or characters are generated on suitable ssubstrates such as checks, for example, which images are developed with the magnetic developer compositions disclosed herein and wherein the images are permanently affixed thereto by suitable fixing means such as heat.

The invention is further illustrated by the following examples and comparative tests.

Example 1

A toner composition was prepared as follows. A mixture containing 62 percent by weight of a poly-(styrene-co-n-butylacrylate-co-divinyl benzene) containing 77 percent by weight of styrene, 25 percent by weight n-butylacrylate and 6 percent by weight divinyl benzene, 28 percent by weight of acicular magnetic particles available from Pfizer Corporation as Magnetite MO 4232 and 10 percent by weight Regal 300 Carbon Black available from Cabot Corporation was melt-kneaded and dispersed by a hot two-roll mill. The mixture was then cooled and roughly pulverized to a coarse grind state (150 mm) by a rough pulverizer.

The mixture was finally pulverized in a fluid energy mill to obtain a toner having an average particle size of 9-11 microns by volume percent.

A developer composition was then prepared by blending together in a twin-cone blender for 5 hours, 3 percent by weight of the above-mentioned toner composition and 97 percent by weight of carrier particles consisting of sponge iron powder which were obtained commercially from Hoeganaes Corporation as Hoeganaes EH having an average particles size of 125 microns. The iron powder was oxidized by fluidized bed oxidation as in U.S. Patent No. 3,767,477 and had a static resistance of 8 x 10^7 ohm. The toner and carrier were then roll milled for one hour to form the developer.

Example 2

A second developer composition was prepared by blending together 3 percent by weight of the toner composition as prepared in Example 1 and 97 percent by weight of carrier particles consisting of the same Hoeganaes EH sponge iron particles as described in Example 1 except that the iron powder was not oxidized by fluidized bed oxidation and had a static resistance of 4 x 10^4 ohm.

Example 3

A third developer composition was prepared by blending together 3 percent by weight of the toner composition as prepared in Example 1 and 97 percent by weight of carrier particles consisting of stainless steel (AISI 410L) containing iron as the major constituent and, by weight, 0.005% Al, 13.5% Cr, 0.025% Cu, < 0.0015% Mg, 0.07%Mn, 0.006% Mo, 0.04% Ni, 1.0% Si, 0.25% Ag, and < 0.005% V obtained commercially from Hoeganaes Corporation. The carrier particles have a static resistance of 1 x 10^7.

Example 4

A fourth developer composition was prepared by blending together 3 percent by weight of the toner composition as prepared in Example 1 and 97 percent by weight of the stainless steel carrier particles described in Example 3 except that the stainless steel powder was etched for 10 minutes with hydrofluoric acid (2.5 volume percent solution), then rinsed with water and allowed to dry. The dried particles were then passivated with nitric acid (20 volume percent solution), for 20 minutes and rinsed in water for minutes, next in methanol for 5 minutes and air dried. The resulting carrier particles had a static sresistance of 5.0 x 10^0 ohm.

COMPARATIVE TESTS

The developer compositions as prepared in Examples 1-4 were incorporated into a copying machine (Ektaprint® 1392 Printer supplied by Eastman Kodak Company) and the copying operation was carried out. The average image densities of copies of one-half inch (1.27 cm) solid black squares, made with the developers of Examples 1-4, were measured using a commercially available reflection densitometer obtained from X-RITE Corporation. The image sharpness of the copies was also determined based on the sharpness of a line image area of the obtained copy. The results of the copying test are shown in Table I below.

TABLE I

Developer	Image Density	Sharpness
Example 1	0.7	Excellent
Example 2	0.8	Excellent
Example 3	0.8	Excellent
Example 4	1.3	Excellent

When the two-component type magnetic developer of the invention was used, sharp images having a high density were obtained. Furthermore, in the solid black portion, no fringing effect was observed at all, and the solid black portion had a sheer black color. However, when the two-component type magnetic developers of Examples 1, 2 and 3 were sused, all of which contained the same magnetic toner component as was present in the magnetic developer composition of the invention (Example 4) but contained, as a carrier material, oxidized iron particles (Example 1), non-oxidized iron particles (Examples 2) or stainless steel particles which had not been passivated in accordance with the teachings hereinabove (Example 3), image density decreased dramatically and an undesirable fringing effect was observed in the images produced from all three developers.

The two-component magnetic developer compositions of the invention have application for developing electrostatically charged images in any known electrostatographic processes used for generating documents suitable for magnetic image character recognition. The two-component magnetic developers of the invention can simultaneously provide both MICR images and characters of excellent MICR readable quality and developed images having excellent image density and sharpness.

Claims

1. A two-component magnetic developer comprising a mixture of magnetic toner particles comprising a binder resin medium and a magnetic material which is dispersed in the binder resin medium and magnetic carrier particles characterized in that the magnetic carrier particles are passivated acicular magnetic stainless steel particles containing at least 9 weight percent chromium the surfaces of which comprise a thin protective layer that is rich in chromium.
2. A developer of claim 1 wherein the steel is martensitic stainless steel and contains from 10 to 18 weight percent chromium.
3. A developer of claim 1 wherein the steel is ferritic stainless steel and contains from 15 to 30 weight percent chromium.
4. A developer of claim 1 wherein the stainless steel particles are passivated by treatment with nitric acid.
5. A developer of claim 1 wherein the stainless steel particles before being passivated are treated with hydrofluoric acid to remove silicon from the surfaces.
6. A developer of claim 1 wherein the magnetic toner material is magnetite.
7. A developer of claim 1 wherein the toner binder resin is a copolymer of styrene or lower alkyl styrene with alkyl acrylate or alkyl methacrylate or a styrene butadiene copolymer.
8. A developer of claim 11 wherein the toner resin binder is comprised of a styrene butadiene copolymer containing from 85 percent by weight to 90 percent by weight of styrene and from 10 percent by weight to 15 percent by weight butadiene.
9. A developer of claim 11 wherein the toner resin binder is comprised of a styrene n-butylmethacrylate copolymer wherein the styrene is present in an amount of from 40 percent by weight to 90 percent by weight and the n-butyl methacrylate is present in an amount of from 10 percent by weight to 60 percent by weight.
10. A developer of claim 1 wherein the magnetic material is present in an amount of from 20 percent by weight to 80 percent by weight based on the total weight of the toner binder medium and the magnetic material.