Abstract: The present invention relates to a toner and process for preparing a toner for reproduction of a metallic, preferably golden or silverly, hue by a printing process, especially for electrophotography. A congeneric process and/or a congeneric toner is preserved with regard to its metallic hue and at the same time not to impair the essential properties of the toner for the printing process in which it is to be used. At least one metallic pigment is provided with a coating of silicate and subsequently with an organic layer containing a charge control agent and optionally a colorant and combining the thus obtained particle with toner material.
METHOD FOR PREPARING TONER AND THE TONER

Reference is made to the co-pending, commonly assigned, U.S. Provisional Patent Application Serial No. 60/540,529 filed on January 30, 2004, entitled:

PREPARATION OF A TONER FOR REPRODUCING A METALLIC HUE AND THE TONER, the U.S. Patent Application Serial No. 60/540,529, entitled
PREPARATION OF A TONER FOR REPRODUCING A METALLIC HUE AND THE TONER and the WO Patent Application Serial No. PCT/US05/03459, entitled METALLIC HUE TONER AND ITS PREPARATION, the disclosure of all is incorporated herein by reference.

The present invention relates to a toner and a process for preparing a toner, for reproduction of a metallic, preferably golden or silvery, hue by a printing process, especially for electrophotography.

Printing processes serve not only to reproduce and transmit objective information, but also to convey esthetic impressions, for example when coffee-table books are printed or else in pictorial advertising. An immense problem here is posed in particular by the reproduction of metallic hues. Metallic hues are only imperfectly reproducible by a color mixture formed from primary colors, especially the colors cyan, magenta, yellow, and black (CMYK). A gold tone is particularly difficult to reproduce by means of such a color mixture. It has therefore already been proposed to incorporate metallic pigments or particles in the printing ink in order that a metallic color may be brought about directly. But in the case of toners, where magnetic and/or electrical and especially electrostatic properties are decisive, this is particularly problematic, since metallic constituents may have an adverse effect on these properties. Yet there have already been proposals to imbue toners with metallic constituents. For instance, U.S. Patent No. 5,180,650, issued on January 19, 1993, discloses providing a toner composition, which contains lightly colored metallic constituents, such as copper, silver or gold for example, in a coating, which in turn has been provided with an over-coating comprised of a metal halide.
But the appearance of prints in particular may be adversely affected by chemical reactions of the metallic constituents due to the halides, which can promote oxidations of the constituents for example. For instance, the tarnishing with which everyone is familiar from copper or silver objects may occur, making the metallic quality unattractive or disappear completely. Moreover, these toners are only lightly metallically colored, which is insufficient to reproduce a gold tone in printed matter. Further, when metallic constituents are incorporated in toners using conventional manufacturing processes, these metallic flakes are randomly oriented throughout the toner particles. This random orientation leads to the loss of metallic hue, and causes a dark appearance when such toners are fixed to a receiver sheet using heated rollers.

It is an object of the present invention to preserve a congeneric process and/or a congeneric toner with regard to its metallic hue and at the same time not to impair the essential properties of the toner for the printing process in which it is to be used, especially for electrophotography or electrography. It shall preferably be possible to fuse the toner to the printed stock in a non-contact manner, especially with the aid of microwaves, without disruption due to metallic constituents in the toner.

This object can be achieved according to the present invention by several methods. One involves first providing a metallic pigment with a coating of silicate, titanate, or aluminate and subsequently with an organic layer containing a charge control agent and optional colorant and combining the thus obtained particle with toner material including for example of: polymer, charge control agent, optional colorant, and fumed metal oxide like silica, titania, or alumina hydrophobically surface coated. Another approach involves providing a coating of an organic layer containing a charge control agent and optional colorant over the metallic pigment, and combining the resulting particle with toner material consisting of polymer resin, optional charge control agent, and optional fumed metal oxide particles that have been hydrophobized with a coating such as silica, titania, or alumina.
In further developments of the present invention, the organic layer utilizes at least one aliphatic acid, stearic acid, at least one amide of at least one acid, at least one salt of at least one acid, at least one olefinic material and/or at least one natural or synthetic wax. However, the use of stearic acid could give rise to the problem that the stearic acid will plasticize the toner material, and so would need to be done with particular care. The organic layer may include at least one polymer organic layer, such as a polyester, over the silicate, titanate, or aluminate layer. The organic layer could also include any of the polymers that are typically used as toner resins, as described in more detail hereinbelow. In addition, the metallic pigment may have only the organic layer as a coating, which may include at least one polymer, such as polyester.

The organic layer contains a charge control agent that is added to the organic coating material used in the coating process. In a different embodiment the charge control agent will be applied on the surface of the organic coating. Charge control agents for the use in toners are described e.g. in the Handbook of Imaging Materials, Second Edition, Marcel Dekker, Inc., New York, Basel, ISBN: 0-8247-8903-2, p.1 80ff and in references therein.

The organic layer may optionally contain a colorant as well. When the coating has an inherent color, this can lead to interesting color-varying effects with the metallic hue in a print or change the metallic hue as a whole. Optionally, the binder can be compounded with a colorant, i.e., a dye or pigment, either in the form of a pigment flush (a special mixture of pigment press cake and resin well-known to the art) or pigment-resin masterbatch, as well as any other desired addenda known to the art. If a developed image without modification of the original color of the pigment is desired, no colorant need be added. Normally, however, a colorant can be included and it can, in principle, be any of the materials mentioned in Colour Index, Vols. I and II, 2nd Edition (1987) or listed in the Pantone® Color Formula Guide, First Edition 2000-2001. The choice of colorants is described as well in e.g., proceedings of IS&T NIP 20: International Conference on Digital Printing Technologies, IS&T: The Society for Imaging Science and Technology, 7003 Kilworth Lane, Springfield, Virginia 22151 USA.
ISBN: 0-89208-253-4, p. 135. Carbon black can be especially useful while other
colorants can include pigment blue, pigment red, and pigment yellow. Specific
colorants can include copper phthalocyanine, and pigment blue sold under the
trade designation LUPRETON BLUE SEI 163. The amount of colorant, if used,
can vary over a wide range, e.g., from about 1 to about 25, and preferably from
about 3 to about 20 weight percent of the toner component. Combinations of
colorants may be used as well.

The colorant may have the function of a charge control agent and vice versa.

Otherwise, the process of the present invention can conform to any well-
known process for preparing dry toners wherein pigments are conventionally
incorporated in a toner core, i.e., for example by compounding, classifying and/or
grinding. Instead of embedding pigments in a toner core it is also possible, for
example, to utilize a shell construction wherein a pigment is applied to the surface
of a toner body, especially as part of a coating, optionally alone or mixed with
other ingredients, for example with polymers, waxes, or charge control agents.
Illustrative references are U.S. Patent No. 5,298,356, issued on March 29, 1994
and/or U.S. Patent No. 6,10,633, issued on August 29, 2000, the disclosures of
which are hereby incorporated by reference thereto.

Finally the inventive toner maybe coated with an additional component on
the surface consisting of hydrophobic fumed metal oxides like silica, aluminia, or
titania in concentrations of about 0.1% to about 3%.

The toners may be alternatively produced by so-called chemical toner
processes, called as well "chemically prepared toners", "polymerized toners" or
"in situ toners". The toners are not produced by grinding but by controlled
growth. Chemical process to be used are, among others, suspension
polymerization (e.g., DE 4202461, DE 4202462); emulsion aggregation (e.g., U.S.
Patent No. 5,604,076, issued on February 18, 1997); micro-encapsulation (e.g.,
DE 10011299); dispersion (e.g., U.S. Publication No. 2003/0087176 Al,
published on May 8, 2003); or chemical milling (e.g., proceedings of IS&T NIP
17: International Conference on Digital Printing Technologies, IS&T: The
Society for Imaging Science and Technology, 7003 Kilworth Lane, Springfield, Virginia 22151 USA ISBN: 0-89208-234-8, p. 345). The disclosures of all the above references are hereby incorporated by reference thereto.

In a further development of the present invention, the pigment is made platelet shaped. This is particularly advantageous for its adduction to a surface of a (larger) toner material particle.

Preferably, the metallic pigment can be coated with the silicate with the aid of a so-called sol-gel process. This can provide a particularly thin coating. It can be envisaged to this end to use stearic acid as lubricant and/or that the pigment is dispersed in a mixture of ethanol, water and a silica, titania, or alumina precursor. The silica precursor may be tetraethoxysilanes. The quantity of the silanes may of course be dependent on the particle size of the pigment. Preferably, a catalyst is used in addition.

In a further embodiment, the mixture is heated to speed a reaction in which the silica, titania, or alumina precursor is hydrolyzed and reacts to form a silicate, titanate, or aluminate, which deposits as a thin film on the pigment. A filtration may then be carried out to filter off undesirable by-products, for example the catalyst, metal compounds, or stearic acid.

It is possible to carry out drying and evaporation of solvent residues to achieve a pulverulent residue as a substance, which contains the silicate-coated pigment.

Preferably, the silicate, titanate, or aluminate comprises about 2% to about 10% of the weight of the metallic pigment.

The toner material can be clear/colorless or transparent or have an inherent color. When the toner material has an inherent color, this can lead to interesting color-varying effects with the metallic hue in a print or change the metallic hue as a whole.

The invention, and its objects and advantages, will become more apparent in the detailed description of the preferred embodiments presented below.

In a preferred embodiment of the process according to the present invention, the pigment is about 7 µm in size and toner particles of the toner
material are about 6-12 µm in size. As mentioned earlier, pigments may each be
disposed on one surface of a toner particle of the toner material.

The organic layer may include or consist of a polymer. Useful polymers
include vinyl polymers, such as homopolymers and copolymers of styrene. Styrene
polymers include those containing 40 to 100 percent by weight of styrene, or
styrene homologs, and from 0 to 40 percent by weight of one or more lower alkyl
acrylates or methacrylates. Other examples include fusible styrene-acrylic
copolymers that are covalently lightly crosslinked with a divinyl compound such
as divinylbenzene. Binders of this type are described, for example, in U.S. Reissue
Patent No. 31,072, which is incorporated in its entirety by reference wherein.
Preferred binders comprise styrene and an alkyl acrylate and/or methacrylate, and
the styrene content of the binder is preferably at least about 60% by weight.

Copolymers rich in styrene such as styrene butylacrylate and styrene
butadiene are also useful as binders, as are blends of polymers. In such blends, the
ratio of styrene butylacrylate to styrene butadiene can be 10:1 to 1:10. Ratios of
5:1 to 1:5 and 7:3 are particularly useful. Polymers of styrene butylacrylate and/or
butylmethacrylate (30 to 80% styrene) and styrene butadiene (30 to 80% styrene)
are also useful binders.

Styrene polymers include styrene, alpha-methylstyrene, para-chlorostyrene,
and vinyl toluene. Alkyl acrylates or methacrylates or monocarboxylic acids
having a double bond selected from acrylic acid, methyl acrylate, 2-ethylhexyl
acrylate, 2-ethylhexyl methacrylate, ethyl acrylate, butyl acrylate, dodecyl acrylate,
octyl acrylate, phenylacrylate, methacrylic acid, ethyl methacrylate, butyl
methacrylate and octyl methacrylate and are also useful binders.

Also useful are condensation polymers such as polyesters and copolyesters
of aromatic dicarboxylic acids with one or more aliphatic diols, such as polyesters
of isophthalic or terephthalic acid with diols such as ethylene glycol, cyclohexane
dimethanol, and bisphenols. Other useful resins include polyester resins, such as
may be obtained by the co-polycondensation polymerization of a carboxylic acid
component comprising a carboxylic acid having two or more valencies, an acid
anhydride thereof or a lower alkyl ester thereof (e.g., fumaric acid, maleic acid,
maleic anhydride, phthalic acid, terephthalic acid, trimellitic acid, or pyromellitic acid), using as a diol component a bisphenol derivative or a substituted compound thereof. Specific examples are described in U.S. Patent Nos. 5,120,631; 4,430,408; and 5,714,295, all incorporated herein by reference, and include propoxylated bisphenol - A fumarate, such as Finetone® 382 ES from Reichold Chemicals, formerly Atlac® 382 ES from ICI Americas Inc.

A useful binder can also be formed from a copolymer of a vinyl aromatic monomer with a second monomer selected from either conjugated diene monomers or acrylate monomers such as alkyl acrylate and alkyl methacrylate.

Colorants, and if necessary, release agents, fluidity improvers, charge controlling agents, magnetic substances, and cross-linking agents may be added to this polymeric binder.

Colorants may include such pigments or dyes as carbon black, for example, nigrosine dye, aniline blue, red oxide, acetylene black, monoazo dye, diazo dye, quinacridone, anthraquinone dye, chalco oil blue, copper phthalocyanine, indanthrene blue, benzene yellow, chrome yellow pigment, ultramarine yellow, duPont oil red, indanthrene blue, permanent brown FG, brilliant scarlet, malachite green oxalate, lamp black, rose Bengal, pigment green B, rhodamine B, and solvent 35.

The colorant to be used in the present invention may be one or a mixture of known dyes or pigments including Carbon Black, Lamp Black, Iron Black, ultramarine blue, Aniline Blue, Phthalocyanine Blue, Phthalocyanine Green, Hansa Yellow G, Rhodamine 6G Lake, Chalcooil Blue, Chrome Yellow, Quinacridone, Benzidine Yellow, Rose Bengal, triarylmethane dyes, monoazo and disazo dyes.

The above-mentioned colorants include, for example, carbon black, Nigrosine dye (Cl. No. 50415B), Aniline Blue (Cl. No. 50405), Charco Oil Blue (Cl. No. Azoic Blue 3), Chrome Yellow (Cl. No. 14090), Ultramarine Blue (Cl. No. 77103), Du Pont Oil Red (Cl. No. 26105), Quinoline Yellow (Cl. No. 47005), Methylene Blue Chloride (Cl. No. 52015), Phthalocyanine Blue (Cl. No.
74160), Malachite Green Oxalate (CI. No. 42000), Lump Black (CI. No. 77266), Rose Bengale (CI. No. 45435), the mixtures thereof. An addition rate of a colorant is preferably 1 to 20 parts by weight per 100 parts by weight of binder resins.

In the toner used in the present invention, various materials can be added for the purpose of coloring or electrostatic charge control. Such materials include, for example, carbon black, black iron oxide, graphite, Nigrosine, metal complexes of monoazo dyes, ultramarine blue, and all sorts of lakes such as Phthalocyanine Blue, Hanza Yellow, Benzo Yellow and Quinacridone. Examples of colorless charge control agents are quaternary ammonium salts, metal complexes for example with salicylic acid and hydrophobically-modified layered metal oxides. An addition rate of charge control agent or a mixture of charge control agents is preferably 1 to 20 parts by weight per 100 parts by weight of binder resins.

The metallic pigment preferably has a gold tone. This could be achieved with genuine gold. However, it is preferable to use a pigment, which contains copper and zinc, preferably in the form of an alloy, which could thus be referred to as brass or bronze, depending on the composition. Preferably, the ratio of copper and zinc fractions in the alloy varies from about 90:10 to about 70:30. As the zinc fraction in the alloy increases, the metallically golden hue changes from a more reddish to a more yellowish or even greenish gold tone. The color of the gold tone may possibly be intensified through a controlled oxidation of the metal.

The metallic pigment could alternatively have, for example, a silver tone which could result from the pigment containing among other possibilities, aluminum.

The present invention further provides a toner for reproduction of a metallic, preferably golden or silvery, hue by a printing process, especially for electrophotography, preferably prepared by the above-described process and; distinguished by at least one particle which comprises at least one metallic pigment, which has optionally been provided with a coat of silicate, and there-over with an organic layer. The advantages of such a toner have already been described in connection with the process of the present invention. The further developments
of the toner according to the present invention, which may specifically be contemplated as particular embodiments on their own or combined, envisage that the organic layer contains: at least one aliphatic acid; that the organic layer contains stearic acid, that the organic layer contains at least one amide of at least one acid, that the organic layer contains at least one salt of at least one acid, that the organic layer contains at least one olefinic material, that the organic layer contains at least one wax, that the wax is a natural wax, that the wax is a synthetic wax, that the pigment is platelet shaped, that the pigment has been coated with the silicate by a sol-gel process, that the toner is a pulverulent toner, that the silicate, titanate, or aluminate comprises about 2% to about 10% of the weight of the metallic pigment, that the pigment has been admixed to a toner material which is clear or transparent, that the pigment has been admixed to a toner material which has an inherent color, that the pigment is about 7 µm in size and that toner particles of the toner material are about 6-12 µm in size, that pigments are each disposed on a surface of a toner particle of the toner material, that the organic layer comprises a polymer, that the pigment is gold colored, that the pigment contains copper and zinc, that the pigment contains copper and zinc as constituents of an alloy, that the ratio of copper and zinc fractions in the alloy varies from about 90:10 to about 70:30, that the pigment is silver colored, and/or that the pigment contains aluminum.

The inventive toner maybe applied to a substrate by a digital printing process, preferably an electrostatic printing process, more preferably by an electrophotographic printing process as described in L. B. Schein, Electrophotography and Development Physics, 2nd Edition, Laplacian Press, Morgan Hill, California, 1996 (ISBN 1-885540-02-7); or, by a coating process, preferably an electrostatic coating process, more preferably by an electromagnetic brush coating process as described in U.S. Patent No. 6,342,273, issued on January 29, 2002, the disclosure of which is hereby incorporated by reference thereto. For fixing of the toner to the surface of the substrate a contact fusing method like roller fusing may be used, or preferably a non-contact fusing method like an oven, hot air, radiant, flash, solvent, or microwave fusing.
The process of the present invention and the toner of the present invention will now be more particularly described with reference to some examples which might reveal further inventive features, but to which the present invention is not restricted in its scope.

EXAMPLE 1:

A platelet-shaped brass pigment having a particle size of about 7 µm was initially provided with a silicate coating, followed by an organic coating of a bis-phenol A based polyester resin mixed with 3% of a charge control agents based on metal complexes with salicylic acid. This coated pigment was then intensively mixed in various concentrations with a clear toner consisting of polymeric binder, charge control agent, and fumed metal oxide having an average particle size of about 12 µm in a high speed mixer for two minutes to obtain a toner having a brass-coated surface.

Thereafter, these toners were mixed with a carrier, developed, and transferred to paper as usual for commercial printing. Finally, each toner was fixed on the paper surface by contactless fixation in an oven.

EXAMPLE 2:

Example 1 was repeated, except that the toner was fixed with a heated contact fixing apparatus, which comprised a hard roll surface and a Kapton film.

EXAMPLE 3:

Example 1 was repeated using a toner having a sharp melting point, known from U.S. Publication No. 2002/015010 Al, published on August 22, 2002, for example. Its 120°C melt viscosity was 12.4 Pa s.

EXAMPLE 4:

Example 3 was repeated except that a yellow toner was used instead of a clear toner.

EXAMPLE 5:

Example 4 was repeated using a magenta-colored toner.

EXAMPLE 6:

Example 5 was repeated using a cyan-colored toner.
EXAMPLE 7 (Comparative):

A gold-colored print was simulated in toner-based four-color printing. The match was poor. If anything, a dirty yellow was obtained that was devoid of the typical metallic shine.

EXAMPLE 8:

Example 1 was repeated, except that platelet-shaped brass pigment having a particle size of about 7 µm was initially provided with a silicate coating, followed by a 10% by weight organic coating consisting of bis-phenol A based polyester mixed with 3% of a charge control agents based on metal complexes with salicylic acid. This coated pigment was then intensively mixed in various concentrations with a clear toner consisting of polymeric binder, charge control agent, and fumed metal oxide having an average particle size of about 12 µm in a high speed mixer for two minutes to obtain a toner having a brass-coated surface. The concentration of the brass pigments was varied in 2% steps from 2% to 24%.

Thereafter, these toners were mixed with a carrier, developed, and transferred to paper as usual for commercial printing. Finally, each toner was fixed on the paper surface by contact-less fixation in an oven.

EXAMPLE 9:

Example 8 was repeated, except that the toner was fixed with a heated contact fixing apparatus, which comprised a hard roll surface and a Kapton film.

EXAMPLE 10:

Example 9 was repeated, except that that platelet-shaped brass pigment having a particle size of about 7 µm was directly provided with an organic coating consisting of bis-phenol A based polyester mixed with 3% of a charge control agents based on metal complexes with salicylic acid. The toner was fixed to the paper surface by contact-less fixation in an oven.

EXAMPLE II:

Example 1 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a charge control agent based on metal complexes with salicylic acid and 3% Pigment BLUE 15:3 via LUPRETON BLUE SEi 163 was added.
EXAMPLE 12:
Example 1 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a charge control agent based on metal complexes with salicylic acid and 3% Pigment Red 57:1 was added.

EXAMPLE 13:
Example 1 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a charge control agent based on metal complexes with salicylic acid and 3% Pigment Yellow 185 was added.

EXAMPLE 14:
Example 4 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a charge control agent based on metal complexes with salicylic acid and 3% Pigment Yellow 185 was added.

EXAMPLE 15:
Example 5 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a charge control agent based on metal complexes with salicylic acid and 3% Pigment Yellow 185 was added.

EXAMPLE 16:
Example 6 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a charge control agent based on metal complexes with salicylic acid and 3% Pigment Yellow 185 via LUPRETON BLUE 163 was added.

EXAMPLE 17:
Example 6 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a charge control agent based on metal complexes with salicylic acid and 3% Pigment Blue 15:3 via LUPRETON BLUE SEI 163 was added.

EXAMPLE 18:
Example 1 was repeated except that an organic coating of a bis-phenol A based polyester resin was mixed with 3% of a colored charge control agent based Nigrosine was added.
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.
WHAT IS CLAIMED IS:

1. A toner having a metallic hue and comprising a metallic pigment, said metallic pigment comprising:
   a) an organic layer selected from an aliphatic acid, an amide of at least one acid, a salt of at least one acid, an olefinic material, a natural wax, a synthetic wax, a polymer, and combinations thereof; which contains a charge control agent and optionally a colorant
   b) optionally, a coating of silicate, titanate, or aluminate,
   said toner optionally being coated with a hydrophobic fumed metal oxide.

2. The toner of claim 1, wherein said metallic pigment comprises either a combination of copper and zinc, or aluminum.

3. The toner of claim 2, wherein said metallic pigment comprises an alloy of copper and zinc in a ratio of from about 90:10 to about 70:30.

4. The toner of claim 1, wherein said metallic pigment is platelet-shaped.

5. The toner of claim 1, wherein said silicate, titanate, or aluminate comprises from about 2% to about 10%, by weight, of said metallic pigment.

6. The toner of claim 1, wherein said metallic pigment is present at a concentration of from about 5% to about 25%.

7. The toner of claim 1, wherein said metallic pigment is disposed on one surface of said toner.

8. The toner of claim 1, wherein said metallic pigment is about 7 microns in size.

9. The toner particle of claim 8, wherein said toner is from about 6 to about 12 microns in size.

10. The toner of claim 1, wherein said toner is surface coated with silica, titania, or aluminia at a concentration of from about 0.1% to about 3%.

11. A metallic pigment for use in toner, said metallic pigment comprising:
a) an organic layer selected from an aliphatic acid, an amide of at least one acid, a salt of at least one acid, an olefinic material, a natural wax, a synthetic wax, a polymer, and combinations thereof; which contains a charge control agent and optionally a colorant and

b) optionally, a coating of silicate, titanate, or aluminate in an amount of from 2% to about 10%, by weight, of said metallic pigment.

12. A process for the preparation of a toner having a metallic hue, said process comprising the steps of:

   a) providing a metallic pigment with
      i) an organic layer selected from an aliphatic acid, an amide of at least one acid, a salt of at least one acid, an olefinic material, a natural wax, a synthetic wax, a polymer, and combinations thereof, which contains a charge control agent and optionally a colorant and
      ii) optionally, a coating of silicate, titanate, or aluminate, whereby a coated metallic pigment is obtained;

   b) combining said coated metallic pigment with a toner material; and

   c) optionally surface coating the resulting toner material with a hydrophobic fumed metal oxide.

13. The process of claim 12, wherein said surface coating comprises coating the resulting toner material with silica, titania, or aluminia at a concentration of from about 0.1% to about 3%.

14. The process of claim 12, wherein the coating of step a)i) is silicate and is provided using a sol-gel process.

15. The process of claim 12, wherein said metallic pigment comprises either a combination of copper and zinc, or aluminum.
16. The process of claim 15, wherein said metallic pigment comprises an alloy of copper and zinc in a ratio of from about 90:10 to about 70:30.

17. The process of claim 12, wherein said metallic pigment is platelet-shaped.

18. The process of claim 12, wherein said silicate, titanate, or aluminate comprises from about 2% to about 10%, by weight, of said metallic pigment.

19. The process of claim 12, wherein said metallic pigment is present at a concentration of from about 5% to about 25%.

20. The process of claim 12, wherein said metallic pigment is disposed on one surface of said toner.

21. The process of claim 12, wherein said metallic pigment is about 7 microns in size.

22. The process of claim 21, wherein said toner is from about 6 to about 12 microns in particle size.
A. CLASSIFICATION OF SUBJECT MATTER

INV. G03G9/097 G03G9/09 C09C3/08 C09C1/60 C09C1/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G03G  C09C

Documentation searched other than minimum documentation & the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical search terms used)

EPO-Internal  WPI  Data,  PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>&amp; JP 09 160298 A (RICOH KK) 20 June 1997 (1997-06-20) abstract</td>
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Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents
  'A' document defining the general state of the art which is not considered to be of particular relevance
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'X' document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search
31 August 2006

Date of mailing of the international search report
19/09/2006

Name and mailing address of the ISA/
European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Piiwjik Tel (+31-70) 340-2040, Tx 31 651 epo nl, Fax (+31-70) 340-3016

Authorized officer
Vogt, Carol

Form PCT/ISA/210 (second sheet) (April 2005)
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