

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
31 July 2003 (31.07.2003)

PCT

(10) International Publication Number  
**WO 03/062927 A1**

- (51) International Patent Classification<sup>7</sup>: **G03G 9/08**
- (21) International Application Number: PCT/KR02/02430
- (22) International Filing Date:  
24 December 2002 (24.12.2002)
- (25) Filing Language: Korean
- (26) Publication Language: English
- (30) Priority Data:  
2001/86318 27 December 2001 (27.12.2001) KR
- (71) Applicant (for all designated States except US): **LG CHEM, LTD.** [KR/KR]; LG Twin Tower, Yoido-dong 20, Youngdungpo-ku, 150-721 Seoul (KR).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **LEE, Won-Sup** [KR/KR]; 103-203 Dasol apt., 395-3, Gung-dong, Yuseong-gu, 305-335 Daejeon-city (KR). **LEE, Chang-Soon** [KR/KR]; 109-1603 Cheonggunarae apt., 462-4, Jeonmin-dong, Yuseong-gu, 305-729 Daejeon-city (KR). **LIM, In-Hee** [KR/KR]; 10-1009 Suyubyeoksan apt., 205, Suyu 2-dong, Gangbuk-gu, 142-072 Seoul (KR).
- (74) Agent: **YOU ME PATENT & LAW FIRM**; Teheran Bldg., 825-33, Yoksam-dong, Kangnam-ku, 135-080 Seoul (KR).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 03/062927 A1**

(54) Title: MAGNETIC MONO-COMPONENT TONER COMPOSITION

(57) Abstract: The present invention relates to a magnetic mono-component toner composition, and more particularly to a mono-component toner composition that comprises magnetic toner particle comprising a binder resin, a magnetic component, and a charge control agent; a hydrophobic treated silica having a specific surface area of 20 to 80 m<sup>2</sup>/g; a hydrophobic treated silica having a specific surface area of 130 to 230 m<sup>2</sup>/g; and a metal oxide fine powder. A magnetic mono-component toner composition of the present invention has such good flowability that it provides smooth toner supply even when the developing roller surface has been worn due to long time use, and it has such excellent uniform chargeability that it prevents image deterioration ("wave" patterns of toner may form on developing roller, that is, magnetic sleeve) by forming a uniform toner layer on the developing roller.

## MAGNETIC MONO-COMPONENT TONER COMPOSITION

### BACKGROUND OF THE INVENTION

#### **(a) Field of the Invention**

The present invention relates to a magnetic mono-component toner  
5 composition, and more particularly to a magnetic mono-component toner  
composition having such good flowability that it provides smooth toner supply  
even when the developing roller surface has been worn due to long time use,  
and having such excellent uniform chargeability that it prevents image  
deterioration ("wave" patterns of toner may form on developing roller, that is,  
10 magnetic sleeve) by forming an uniform toner layer on the developing roller.

#### **(b) Description of the Related Art**

Generally, the dry-type developing methods of the electrophotography  
can be classified into two-component developing method using a  
two-component developer comprising a magnetic carrier and a toner, and  
15 mono-component developing method using a mono-component developer  
comprising a toner only without a carrier. In general, the mono-component  
developing method can realize smaller developing unit, lower manufacturing  
cost and easy maintenance. Therefore, the number of copiers and printers  
using the mono-component developing method has been spreading recently,  
20 and also the printing speed is improving significantly.

Differing from the two-component developing method using a

two-component developer comprising carrier particles that carry toner particle, the flowability of toner particle themselves greatly affects movement of toner in the magnetic mono-component toner.

The non-magnetic mono-component toner applies pressure on the  
5 developing roller using a blade made of metal or polymer to control the thickness of toner layer formed on the developing roller, and the two-component toner moves the toner particle by triboelectrification resulting from friction with the carrier particles. In magnetic mono-component developer, on the other hand, a toner regulating member (doctor blade)  
10 arranged so as to make contact with a developing roller, and the mono-component toner is triboelectrically charged by passing between toner regulating member and developing roller, and the charged toner is maintained on the surface of the developing roller by electrostatic force.

Accordingly, enough flowability to easily transport to the toner  
15 regulating member is required for a magnetic mono-component toner. If the surface of the developing roller (sleeve) is worn by long time use, that is, if the sleeve surface becomes relatively smooth, the triboelectrification becomes non-uniform and the toner particle may agglomerate to form a wave pattern on the surface of the developing roller, and thereby cause image deterioration.

20 To solve this problem, a method of reducing flowability of the toner to increase pressure applied to the toner when it passes through the toner

regulating member and to reduce formation of the wave pattern has been developed. However, this method inevitably worsens supply of toner and makes it impossible to obtain an uniform image density.

Accordingly, research on a magnetic mono-component toner having  
5 such good flowability that the toner is supplied without problems, and having such excellent uniform chargeability that an uniform toner layer is formed on the developing roller even after long time use, are highly required.

### **SUMMARY OF THE INVENTION**

An object of the present invention is to provide a magnetic  
10 mono-component toner composition having such good flowability that toner is supplied without problems, and having such excellent uniform chargeability that a uniform toner layer is formed on the developing roller even after long time use, which can prevent image deterioration due to a wave pattern on the sleeve.

15 In order to attain this object, the present invention provides a magnetic mono-component toner composition comprising:

a) magnetic toner particle comprising

i) a binder resin,

ii) a magnetic component, and

20 iii) a charge control agent;

b) a hydrophobic treated silica having a specific surface area of 20 to

80m<sup>2</sup>/g;

c) a hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g; and

d) a metal oxide fine powder.

5 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Hereinafter, the present invention is described in more detail.

The present inventors worked on a magnetic mono-component toner having excellent flowability and offering a uniform image. In doing so, they identified that if two species of hydrophobic silica having different specific  
10 surface areas are attached to magnetic toner particle, flowability can be improved and wave pattern formation on the developing roller due to insufficient triboelectrification can be prevented.

The present invention relates to a magnetic mono-component toner composition, which comprises magnetic toner particle comprising a binder  
15 resin, a magnetic component, and a charge control agent; a hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g; a hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g; and a metal oxide fine powder.

In the present invention, the binder resin may be used known resin  
20 materials for fixing. Particularly, a resin obtained by condensation or addition polymerization of alcohol components and carboxylic acid components is

preferred. Preferably, the binder resin may be used from 30 to 80wt% for the magnetic toner particle.

For the alcohol components, a diols or polyhydric alcohol or alcohol derivatives, such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, cyclohexane dimethanol, xylene glycol, bisphenol A, bisphenol A ethylene oxide, bisphenol A propylene oxide, sorbitol, and glycerin can be used alone or in combination. For the carboxylic acid components, a polybasic carboxylic acid or, carbonic acid derivatives, or a carboxylic anhydrides, such as maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, succinic acid, adipic acid, trimellitic acid, cyclopentane dicarboxylic acid, succinic anhydride, trimellitic anhydride, and maleic anhydride, can be used alone or in combination.

For the binder resin, preferably, acrylates, such as polyester, poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), poly(2-ethylhexyl acrylate), and poly(lauryl acrylate); methacrylates, such as poly(methyl methacrylate), poly(butyl methacrylate), poly(hexyl methacrylate), poly(2-ethylhexyl methacrylate), and poly(lauryl methacrylate); a copolymer of acrylates and methacrylates; a copolymer of a styrene monomer and acrylates or methacrylates; an ethylene polymer and a copolymer thereof, such as poly(vinyl acetate), poly(vinyl propionate), poly(vinyl lactate), polyethylene,

and polypropylene; a styrene copolymer, such as a styrene butadiene copolymer, a styrene isoprene copolymer, and a styrene maleic acid copolymer; poly(vinyl ether); poly(vinyl ketone); polyamide; polyurethane; rubber; epoxy resin; poly(vinyl butyral) rosin; modified rosin; phenol resin; and  
5 so forth are used alone or in combination. More preferably, polyester is used.

For the magnetic component, a ferromagnetic element, alloys, or mixtures thereof, a polyhedral type magnetic component, or an acicular type magnetic component can be used. Specifically, magnetite, hematite, ferrite, iron, cobalt, nickel, manganese, alloys or mixtures thereof, ferromagnetic  
10 alloys, or a magnetic oxide can be used. Preferably, the magnetic component is a fine powder having an average diameter smaller than 1 $\mu$ m, and it is preferably used from 20 to 70wt% of the magnetic toner particle.

For the charge control agent, metal complexes of azo dye compounds or salicylic acid compounds can be used for a negative charged toner, and  
15 nigrosine dye or quaternary ammonium salts can be used for a positive charged toner. The content of the charge control agent in the toner is not limited, but it is preferably used at 0.15 to 4wt% of the magnetic toner particle.

A release agent may be added to prevent offset of the magnetic mono-component toner particle. For the release agent, a variety of waxes  
20 and low-molecular-weight olefin resins can be used. To be specific, preferably, an olefin resin like polypropylene, polyethylene, and

propylene-ethylene copolymer is used, and more preferably, polypropylene is used. Preferably, the release agent is used at 0.05 to 5wt% for 100wt% of the binder resin.

The average diameter of the toner particle is not particularly limited, but toner particle having an average diameter of 5 to 30 $\mu$ m are preferably used. The toner particle may be prepared by melt blending/pulverization or polymerization.

The hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g prevents uniform triboelectrification due to agglomeration of toner particle, and improves uniform triboelectrification by making the toner passing the toner regulating member spread uniformly. Preferably, the specific surface area of the hydrophobic treated silica is from 20 to 80m<sup>2</sup>/g, and more preferably, from 30 to 50m<sup>2</sup>/g.

The hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g increases flowability, so that the toner rapidly transfer to the toner regulating member. As a result, unevenness of image density can be prevented. Preferably, the specific surface area of the hydrophobic treated hydrophobic silica is from 130 to 230m<sup>2</sup>/g, and more preferably, from 150 to 200m<sup>2</sup>/g.

Even when using b) the hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g, if the specific surface area of c) the hydrophobic



treated silica is below  $130\text{m}^2/\text{g}$ , flowability of the toner does not improve much, and uneven may form on the solid images due to unevenness of the toner layer if many solid images are printed. Otherwise, if the specific surface area exceeds  $230\text{m}^2/\text{g}$ , the hydrophobic silica having large specific surface area  
5 embedded to the surface of the toner particle, so that flowability of the toner does not improve much.

In addition, even when using c) the hydrophobic treated silica having a specific surface area of  $130$  to  $230\text{m}^2/\text{g}$ , if the specific surface area of b) the hydrophobic treated hydrophobic silica is below  $20\text{m}^2/\text{g}$ , wave pattern may  
10 form on the developing roller surface due to agglomeration of the toner particle. This may cause image deterioration by forming a wave pattern on the printed image. Otherwise, if it exceeds  $80\text{m}^2/\text{g}$ , pressure applied to the toner when it passes through the toner regulating member may be lowered due to hydrophobic silica having small specific surface area. As a result, frictional  
15 electrification may be insufficient, and image density may be reduced.

Preferably, c) the hydrophobic treated silica having a specific surface area of  $130$  to  $230\text{m}^2/\text{g}$  is attached to the surface of the toner particle in a larger amount than b) the hydrophobic treated silica having a specific surface area of  $20$  to  $80\text{m}^2/\text{g}$ . More preferably, the hydrophobic treated silica having  
20 a specific surface area of  $20$  to  $80\text{m}^2/\text{g}$  is used at  $0.5$  to  $1.5\text{wt}\%$  and the hydrophobic treated silica having a specific surface area of  $130$  to  $230\text{m}^2/\text{g}$  is

used at 0.5 to 2.5wt% for 100wt% of the toner particle.

If the hydrophobic silica having the smaller specific surface area is used in a larger amount than the hydrophobic silica having the larger specific surface area, frictional electrification may become unevenness and the image density may be reduced due to insufficient triboelectrification of the toner.

Even when c) the hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g is used at 0.5 to 2.5wt% for 100wt% of the toner particle, if b) the hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g is used at less than 0.5wt%, a wave pattern may form on the developing roller surface due to agglomeration of the toners. Otherwise, if it is used at more than 1.5wt%, extra silica not attached to the surface of the toner particle reduces fusing ability at fixing and fusing process in electrophotographic processes.

Additionally, even when b) the hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g is used at 0.5 to 1.5wt% for 100wt% of the toner particle, if c) the hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g is used at less than 0.5wt%, image density becomes nonuniform because the toner transfer to the toner regulating member becomes difficult due to insufficient flowability. Otherwise, if it is used at more than 2.5wt%, frictional electrification is insufficient when the toner passes through the toner regulating member, and therefore image blurring or a

decrease in image density appears.

Hydrophobic treatment can be done by coating or attaching a silane coupling agent or silicone oil to the silica particles.

For the silane coupling agent, dimethyldichlorosilane,  
5 trimethylchlorosilane, methyltrichlorosilane, arylphenyldichlorosilane,  
benzyl dimethylchlorosilane, bromomethyl dimethylchlorosilane,  
*p*-chlorophenyltrichlorosilane, 3-chloropropyltrimethoxysilane,  
vinyltriethoxysilane, vinyltriacetoxysilane, divinylchlorosilane, or  
hexamethylenedisilazane can be used.

10 Also, silicone oil can be used for hydrophobic treatment to reduce  
fogging (image deterioration due to transfer of toner to non-image area). For  
example, dimethylsilicone oil, methylphenylsilicone oil, methylhydrogen  
silicone oil, alkyl modified silicone oil, fluorine modified silicone oil, alcohol  
modified silicone oil, amino modified silicone oil, epoxy modified silicone oil,  
15 epoxy/polyether modified silicone oil, phenol modified silicone oil, carboxyl  
modified silicone oil, mercapto modified silicone oil, and so forth having a  
viscosity of 50 to 10000 cps (centipoise) at 25 °C can be used.

The hydrophobic treatment can be done by adsorbing silicone oil on  
the inorganic powder surface. For example, silica is put in a mixer, silicone oil  
20 diluted in a solvent is sprayed into the mixer, and the silica is then heated and  
dried in the mixer while continuing to agitate by magnetic stirrer.

The hydrophobic silica can be adsorbed on the surface of the toner particle using a common mixer, such as a turbine mixer, a Henschel mixer, or a super mixer, or by using surface modification equipment (Nara Hybridization System; Nara MFG Co.). The hydrophobic silica may be adsorbed on the  
5 toner particle weakly or strongly with part of it embedded in the surface thereof.

The present invention uses two kinds of hydrophobic silica, each having a different specific surface area, that is, b) the hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g, and c) the hydrophobic treated silica having area of 130 to 230m<sup>2</sup>/g, to prevent nonuniform  
10 electrification and wave pattern formation on the sleeve surface by smooth the surface and preventing agglomeration of toner particle, and thereby prevents image deterioration due to wave patterns.

The metal oxide fine powder prevents the toner from adsorbing on the photoconductive drum surface when many images are printed for a long time,  
15 and greatly improves the PCR(Primary Charge Roller) contamination.

Preferably, the average particle diameter of the metal oxide fine powder is from 50 to 500nm, and more preferably, 60 to 300nm. If the average particle diameter is below 50nm or over 500nm, flowability and durability is remarkably decreased.

20 For the metal oxide fine powder, titanium dioxide, aluminum oxide, zinc oxide, magnesium oxide, cerium oxide, iron oxide, copper oxide, tin oxide, and

so forth can be used. Considering modification and availability, titanium dioxide is preferable. It is more preferable to use pure titanium dioxide including tin than not including tin.

Preferably, the metal oxide fine powder is used at 0.3 to 1.5wt% for  
5 100wt% of the toner particle, and more preferably at 0.5 to 1.2wt%. If the content is below 0.3wt%, the durability cannot be improved, and if it exceeds 1.5wt%, the fusing ability may be reduced.

In the present invention, the specific surface area of the silica refers to a value determined by the BET method. It can be measured with  
10 commercially available high-precision automatic gas absorption equipment, etc. This equipment uses inert gas, particularly nitrogen gas, as an adsorption gas to measure the BET specific surface area ( $S$ ;  $m^2/g$ ) from the gas adsorption amount required to form a single molecular layer on the surface of the hydrophobic silica particles.

15 Hereinafter, the present invention is described in more detail through Examples and Comparative Examples. However, the following Examples are only for the understanding of the present invention, and the present invention is not limited by the following Examples.

## EXAMPLES

### 20 Example 1

(Preparation of toner particle)

100wt% of polyester resin as a binder resin, 95wt% of iron oxide as a magnetic component, 2wt% of organo-azo complex as a charge control agent, and 5wt% of low-molecular-weight polypropylene as a release agent were mixed in a Henschel mixer. The above mixed ingredients were melt kneaded  
5 through a twin-screw extruder heated at 165°C. It was then crushed with a jet mill and classified with a pneumatic classifier to obtain toner particle having a weight-average particle diameter of 6.7µm.

(Preparation of magnetic mono-component toner composition)

For 100wt% of the toner particle, 1.0wt% of hydrophobic silica having a  
10 specific surface area of 20m<sup>2</sup>/g treated with hexamethyldisilazane (HMDS), 0.5wt% of hydrophobic silica having a specific surface area of 130m<sup>2</sup>/g treated with dimethyl silicone oil, and titanium dioxide having an average particle diameter of 120nm as a metal oxide fine powder were mixed in a Henschel mixer for 3 minutes. The mixture was attached onto the surface of the toner  
15 particle to obtain a magnetic mono-component toner composition.

#### Examples 2 to 54 and Comparative Examples 1 to 10

The procedure of Example 1 was carried out with the content and compositions shown in the following Table 1.

Table 1

Classification	Hydrophobic silica having a specific surface area of 20 to 80m <sup>2</sup> /g		Hydrophobic silica having a specific surface area of 130 to 230m <sup>2</sup> /g	
	Specific surface area	Content (wt%)	Specific surface area	Content (wt%)
Example 2	130	1.0	20	0.5
Example 3	130	1.0	20	1.0
Example 4	130	2.5	20	0.5
Example 5	130	2.5	20	1.0
Example 6	130	2.5	20	1.5
Example 7	180	0.5	20	0.5
Example 8	180	1.0	20	0.5
Example 9	180	1.0	20	1.0
Example 10	180	2.5	20	0.5
Example 11	180	2.5	20	1.0
Example 12	180	2.5	20	1.5
Example 13	230	0.5	20	0.5
Example 14	230	1.0	20	0.5
Example 15	230	1.0	20	1.0
Example 16	230	2.5	20	0.5
Example 17	230	2.5	20	1.0

Classification	Hydrophobic silica having a specific surface area of 20 to 80m <sup>2</sup> /g		Hydrophobic silica having a specific surface area of 130 to 230m <sup>2</sup> /g	
	Specific surface area	Content (wt%)	Specific surface area	Content (wt%)
Example 18	230	2.5	20	1.5
Example 19	130	0.5	40	0.5
Example 20	130	1.0	40	0.5
Example 21	130	1.0	40	1.0
Example 22	130	2.5	40	0.5
Example 23	130	2.5	40	1.0
Example 24	130	2.5	40	1.5
Example 25	180	0.5	40	0.5
Example 26	180	1.0	40	0.5
Example 27	180	1.0	40	1.0
Example 28	180	2.5	40	0.5
Example 29	180	2.5	40	1.0
Example 30	180	2.5	40	1.5
Example 31	230	0.5	40	1.5
Example 32	230	1.0	40	0.5
Example 33	230	1.0	40	1.0



Classification	Hydrophobic silica having a specific surface area of 20 to 80m <sup>2</sup> /g		Hydrophobic silica having a specific surface area of 130 to 230m <sup>2</sup> /g	
	Specific surface area	Content (wt%)	Specific surface area	Content (wt%)
Example 34	230	2.5	40	0.5
Example 35	230	2.5	40	1.0
Example 36	230	2.5	40	1.5
Example 37	130	0.5	80	0.5
Example 38	130	1.0	80	0.5
Example 39	130	1.0	80	1.0
Example 40	130	2.5	80	0.5
Example 41	130	2.5	80	1.0
Example 42	130	2.5	80	1.5
Example 43	180	0.5	80	0.5
Example 44	180	1.0	80	0.5
Example 45	180	1.0	80	1.0
Example 46	180	2.5	80	0.5
Example 47	180	2.5	80	1.0
Example 48	180	2.5	80	1.5
Example 49	230	0.5	80	0.5
Example 50	230	1.0	80	0.5

Classification	Hydrophobic silica having a specific surface area of 20 to 80m <sup>2</sup> /g		Hydrophobic silica having a specific surface area of 130 to 230m <sup>2</sup> /g	
	Specific surface area	Content (wt%)	Specific surface area	Content (wt%)
Example 51	230	1.0	80	1.0
Example 52	230	2.5	80	0.5
Example 53	230	2.5	80	1.0
Example 54	230	2.5	80	1.5
Comp. Example 1	180	1.0	20	0.4
Comp. Example 2	180	1.0	20	16
Comp. Example 3	180	0.4	40	1.0
Comp. Example 4	180	2.6	40	1.0
Comp. Example 5	-	-	40	0.5
Comp. Example 6	-	-	40	1.0
Comp. Example 7	-	-	40	1.5

Classification	Hydrophobic silica having a specific surface area of 20 to 80m <sup>2</sup> /g		Hydrophobic silica having a specific surface area of 130 to 230m <sup>2</sup> /g	
	Specific surface area	Content (wt%)	Specific surface area	Content (wt%)
Comp. Example 8	180	0.5	-	-
Comp. Example 9	180	1.0	-	-
Comp. Example 10	180	2.5	-	-

#### Test Example

Magnetic mono-component toner compositions prepared in Examples 1 to 54 and Comparative Examples 1 to 10 were used to print 5,000 sheets of paper using a non-contact, magnetic mono-component developing type printer (LaserJet 4000; Hewlett-Packard Company) under normal temperature and humidity (20°C; 55±5% RH). The image density, fogging, wave pattern, and PCR contamination were determined by the following method. The results are shown in the following Table 2:

- a) Image density (I.D) – Solid area image was determined with a Macbeth reflection densitometer RD918 (I.D value larger than 1.30 is approved).

b) Fogging (background) – The non-image area was observed with an optical microscope.

○: No fogging was observed.

△: Obscure fogging was observed.

5        ×: Clear fogging was observed.

c) Wave pattern – Magnetic mono-component toners prepared in Examples 1 to 54 and Comparative Examples 1 to 10 were used to print half-tone images on 100 sheets of paper. The printed half-tone images and surface of the developing sleeve were observed by eye.

10        ○: No wave pattern.

△: Wave pattern was observed on page 1, but disappeared on page 100.

×: Wave pattern was observed on all pages.

d) PCR contamination (contamination of developing drum) – A transparent tape was attached to the toner remaining on the PCR surface after transferring. The tape was observed with an optical microscope.

15        ○: No PCR contamination was observed.

△: Obscure PCR contamination was observed.

×: Clear PCR contamination was observed.

Table 2

Classification	Image Density	Fogging	Wave Pattern	PCR Contamination
Example 1	1.35	○	△	△
Example 2	1.38	○	○	△
Example 3	1.42	△	○	△
Example 4	1.39	○	△	○
Example 5	1.43	○	○	○
Example 6	1.45	△	○	○
Example 7	1.48	○	△	○
Example 8	1.51	○	○	○
Example 9	1.52	△	○	○
Example 10	1.33	○	○	△
Example 11	1.34	○	○	△
Example 12	1.37	△	○	△
Example 13	1.35	○	△	○
Example 14	1.39	○	○	○
Example 15	1.41	△	○	○
Example 16	1.43	○	△	○
Example 17	1.45	○	○	○
Example 18	1.46	△	○	○
Example 19	1.33	○	○	△
Example 20	1.35	○	○	△

Classification	Image Density	Fogging	Wave Pattern	PCR Contamination
Example 21	1.37	△	○	○
Example 22	1.36	○	○	△
Example 23	1.38	○	○	△
Example 24	1.39	△	○	○
Example 25	1.41	○	△	○
Example 26	1.42	○	○	○
Example 27	1.44	△	○	○
Example 28	1.32	○	△	○
Example 29	1.34	○	○	○
Example 30	1.36	△	○	○
Example 31	1.35	○	○	△
Example 32	1.37	○	○	△
Example 33	1.38	△	○	△
Example 34	1.40	○	△	○
Example 35	1.43	○	○	○
Example 36	1.45	△	○	○
Example 37	1.31	○	△	○
Example 38	1.32	○	○	○
Example 39	1.35	△	○	○
Example 40	1.34	○	△	○
Example 41	1.36	○	○	△

Classification	Image Density	Fogging	Wave Pattern	PCR Contamination
Example 42	1.38	△	○	○
Example 43	1.42	○	○	○
Example 44	1.45	○	○	○
Example 45	1.50	△	○	○
Example 46	1.33	○	△	○
Example 47	1.35	○	○	○
Example 48	1.37	○	○	○
Example 49	1.35	○	△	○
Example 50	1.38	○	○	○
Example 51	1.39	△	○	○
Example 52	1.43	○	△	○
Example 53	1.46	○	○	△
Example 54	1.49	○	○	○
Comp. Example 1	1.35	△	×	×
Comp. Example 2	1.43	×	×	△
Comp. Example 3	1.32	△	×	×
Comp. Example 4	1.50	×	×	△
Comp. Example 5	1.44	△	×	○
Comp. Example 6	1.32	×	×	○
Comp. Example 7	1.45	△	×	○
Comp. Example 8	1.30	×	×	○

Classification	Image Density	Fogging	Wave Pattern	PCR Contamination
Comp. Example 9	1.40	△	×	○
Comp. Example 10	1.29	×	×	△

As seen in Table 2, magnetic mono-component toner compositions prepared in Examples 1 to 54, which comprise magnetic toner particle comprising a binder resin, a magnetic component, and a charge control agent; a hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g; a hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g; and a metal oxide fine powder according to the present invention, show a sufficient image density (I.D) of over 1.30 and have less image fogging (background), image deterioration due to wave pattern on the developing roller surface, and PCR contamination. On the contrary, magnetic toners prepared in Comparative Examples 1 to 10 show severe image deterioration due to wave patterns and image fogging.

As seen above, a magnetic mono-component toner composition of the present invention has such a good flowability so as to provide smooth toner supply even when the developing roller surface has become worn due to long time use, and it has such excellent uniform chargeability that it prevents image deterioration by forming a uniform toner layer on the developing roller.



While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended

5 claims.

**WHAT IS CLAIMED IS:**

1. A magnetic mono-component toner composition, which comprises:
  - a) magnetic toner particle comprising:
    - i ) a binder resin;
    - 5 ii ) a magnetic component; and
    - iii) a charge control agent;
  - b) a hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g;
  - c) a hydrophobic treated silica having a specific surface area of 130 to 10 230m<sup>2</sup>/g; and
  - d) a metal oxide fine powder.
2. The magnetic mono-component toner composition according to Claim 1, which comprises:
  - a) 100wt% of magnetic toner particle comprising:
    - 15 i ) 30 to 80wt% of a binder resin (for 100wt% of magnetic toner particle);
    - ii ) 20 to 70wt% of a magnetic component (for 100wt% of magnetic toner particle); and
    - iii) 0.15 to 4wt% of a charge control agent (for 100wt% of magnetic 20 toner particle);
  - b) 0.5 to 1.5wt% of a hydrophobic treated silica having a specific

surface area of 20 to 80m<sup>2</sup>/g;

c) 0.5 to 2.5wt% of a hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g; and

d) 0.3 to 1.5wt% of a metal oxide fine powder.

5           3. The magnetic mono-component toner composition according to Claim 1, wherein a) i ) the binder resin is one or more selected from the group consisting of polyester, poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), poly(2-ethylhexyl acrylate), poly(lauryl acrylate), poly(methyl methacrylate), poly(butyl methacrylate), poly(hexyl methacrylate),  
10 poly(2-ethylhexyl methacrylate), poly(lauryl methacrylate), a copolymer of acrylates and methacrylates, a copolymer of a styrene monomer and acrylates or methacrylates, poly(vinyl acetate), poly(vinyl propionate), poly(vinyl lactate), polyethylene, polypropylene, a styrene butadiene copolymer, a styrene isoprene copolymer, a styrene maleic acid copolymer, poly(vinyl ether),  
15 poly(vinyl ketone), , polyamide, polyurethane, rubber, epoxy resin, poly(vinyl butyral) rosin, a modified rosin, and a phenol resin, which are obtained by condensation or addition polymerization of alcohol components and carboxylic acid components.

          4. The magnetic mono-component toner composition according to  
20 Claim 1, wherein a) ii ) the magnetic component is one or more selected from the group consisting of alloys or mixtures of magnetite, hematite, ferrite, iron,

cobalt, nickel, or manganese; ferromagnetic alloys; and a magnetic oxide.

5 5. The magnetic mono-component toner composition according to Claim 1, wherein a) iii) the charge control agent is a metal complex azo dye or a salicylic acid compound for a negative charged toner, and a nigrosine dye or a quaternary ammonium salt for a positive charged toner.

6. The magnetic mono-component toner composition according to Claim 1, wherein a) the magnetic mono-component toner particle further comprise iv) 0.05 to 5wt% of release agent for 100wt% of the binder resin.

10 7. The magnetic mono-component toner composition according to Claim 1, wherein average diameter of a) the toner particle is 5 to 30 $\mu$ m.

8. The magnetic mono-component toner composition according to Claim 1, wherein b) the hydrophobic treated silica having a specific surface area of 20 to 80m<sup>2</sup>/g and c) the hydrophobic treated silica having a specific surface area of 130 to 230m<sup>2</sup>/g are hydrophobic treated by coating or attaching  
15 a silane coupling agent or silicone oil on the silica particles.

9. The magnetic mono-component toner composition according to Claim 1, wherein d) the metal oxide fine powder is one or more mixtures selected from a group consisting of titanium dioxide, aluminum oxide, zinc oxide, magnesium oxide, cerium oxide, iron oxide, copper oxide, and tin oxide.

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/KR02/02430

**A. CLASSIFICATION OF SUBJECT MATTER**  
**IPC7 G03G 9/08**  
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)  
IPC7 G03G 9/08, G03G 9/09, G03G 9/087, G03G 15/08, G03G 9/083

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Kr, JP: classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NPS, ESPACENET, DELPHION etc.,

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**



Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2000-75541 A (CANON INC) Mar. 14. 2000 See the whole document	1
A	JP 1998-333359 A (CANON INC) Dec. 18. 1998 See the whole document	1 - 9
A	JP 1999-305480 A (TODA KOGYO CORPORATION) Nov. 05. 1999 See the whole document	1 - 9
A	JP 2000-206731 A (CANON INC) Jul. 27. 2000 See the whole document	1 - 9

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	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 26 MARCH 2003 (26.03.2003)	Date of mailing of the international search report 27 MARCH 2003 (27.03.2003)
---	--

Name and mailing address of the ISA/KR  Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer KIM, Hyun Sook Telephone No. 82-42-481-5584 
---	---

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR02/02430

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2000-75541 A	Mar. 14. 2000	US 6077636 A CN 1237723 A EP 933685 A1	06. 20. 2000 12. 08. 1999 08. 04. 1999
JP 1998-333359 A	Dec. 18. 1998	US 6013406 A DE 69802323 T2 EP 864930 A1 EP 864930 B1 DE 69802323 CO KR 261054 B1	01. 11. 2000 07. 11. 2002 09. 16. 1998 11. 07. 2001 12. 13. 2001 07. 01. 2000
JP 1999-305480 A	Nov. 05. 1999	US 6416864 BA EP 864930 A2 EP 864930 A3 US 6379855 BA	07. 09. 2002 08. 18. 1999 11. 17. 1999 04. 30. 2002
JP 2000-206731 A	Jul. 27. 2000	NONE	