Magnetic Toner Prepared by the Suspension Polymerization Method

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Abstract

Magnetic toner prepared by the suspension polymerization method was investigated. Magnetic powder is inherently hydrophilic. The magnetic toner made by suspension polymerization shows insufficient electrostatic properties because of the low electrical resistivity of the toner surface. Hydrophilic magnetic powders were interfaced between monomer and water during suspension polymerization, giving rise to a shell structure. The dispersion in the toner particles was improved by hydrophobic treatment of the magnetic powders. As hydrophobic reagents, a coupling agent and a polymerization initiator plus monomer were investigated. Using the latter reagent, the magnetic powder was dispersed well. The toner improved the dispersion of the magnetic powder, had higher electrical resistivity, and showed better electrophotographic properties. Influence of the particle size of the magnetite and the mechanism of surface treatment are also discussed.

Introduction

Recently smaller particle size toners have been used for fine images in electrophotographic printers.[1] Smaller size toner particles can be produced by a conventional pulverization method or by a polymerization method. On the other hand, monocomponent magnetic toner has been used for the compact print engine, which is a system without toner concentration control. In a previous study we prepared a small particle size nonmagnetic toner by suspension polymerization and compared the polymerized spherical toner with a toner prepared by the purlverization method.[2] The polymerized spherical toner had better flow properties and longer life in a dual-component developer mixture, but was not suitable for a blade cleaning system.

Therefore we tried to make a magnetic toner by suspension polymerization and to evaluate the characteristics for electrophotography. It was difficult to disperse magnetic powder into the toner particles because of the hydrophilic property of the magnetic powder. It has no affinity to styrene monomer. If the monomer suspension was polymerized with the magnetic powder, interfaced monomer and water acted as the suspension stabilizer.[3] In this case, the polymer particle may be covered with magnetic powder. The characteristics of this particle may not have adequate morphology for toner with lower electrical resistivity and charge ability.

These properties can be modified by overcoating of toner particles. However, the fixation property cannot be improved by this overcoating method. To apply the polymerized magnetic toner in a heat roller fixation system, it is necessary to disperse magnetic powder inside of the toner particles. In the present study, several surface treatments of the magentic powders were investigated. The relationship between the method of surface treatment, dispersibility of the toner particles, and toner characteristics will be reported.

Materials

Commercial grade magnetite powders (octahedra, 0.1 ~ 0.5 μm) and styrene monomer were used in these experiments without further purification.

Hydrophobic treatment of magnetite was performed by two methods: (1) by coupling agent; magnetite was dispersed in water at 343 K. Coupling agent was added and this slurry was stirred for 2 hr. After that it was filtered and vacuum dried. (2) By *in-situ* method; benzoyl peroxide (polymerization initiator) was added to the monomer mixture during the dispersing process.

Suspension Polymerization

Monomers (styrene: 90.9 mol %, 2-ethyl-hexyl acrylate: 9.0 mol %, divinyl benzene: 0.1 mol %) 55 wt %, magnetite 44.5 wt %, and charge control agent (chrome azo type dye) 0.5 wt % were ball milled for 12 hr at room temperature. This monomer mixture and azobis-2,4-dimethylvaleronitrile (radical initiator) were added to water containing SiO_2 powder as the suspension stabilizer. Then the mixture was homogenized by a mechanical homogenizer. This suspension was polymerized at 343 K for 8 hr under N_2 atmosphere with 3 sec^{-1} stirring by a paddle. Af-

ter the polymerization, the suspension stabilizer was removed by reaction with sodium hydroxide. The polymerized particles were filtered, rinsed with water, and vacuum dried.

Measurement

The water contact angle was used as a measure of the hydrophobicity of the magnetite powder by dropping purified water onto a plate of pressed magnetite powder. The modification of the magnetite surface was evaluated by infrared spectroscopy (FT-IR), using the KBr tablet method with base line correction. For IR spectroscopy, the hydrophobic treated magnetite was washed by organic solvent in an ultrasonic cleaner. Electrical resistivity was calculated from the current through tapped toner in the vessel with parallel flat electrode and guard ring electrode in a 10 kV/cm electric field. Mean particle size of the toner was measured by a TA-II Coulter counter.

Imaging

Image characteristics of the polymerized magnetic toners were evaluated in a laser printer (Panasonic KXP4620), using 6.5 g of toner and 15 g of ferrite carrier (Hitachi Metals, Ltd. KBN-100 Ba-Ni-Zn type 74 ~ 149 μm). Triboelectric charge of the developer mixture was measured by the blow-off method (Toshiba Chemical Co., Ltd. TB-200). Reflective image density (IDR) of the solid black areas in the test pattern was measured by densitometer (Sakura PDA-65). Background soil of white areas was detected by a color differential meter (Nippon Denshoku $\sum$ 80) as the Hunter whiteness deficiency (dWh) of the paper after printing. Fixation property was evaluated by an adhesive tape (Scotch 810) peeling method as the residual reflective image density of a solid black area after peeling.

Hydrophobic Treatment of Magnetite

The hydrophobic treatment of magnetite by a coupling agent and the treatment called the *in-situ* method, were examined. We used two typical coupling agents, anilino silane (γ-anilino propyl trimethoxy silane) and titanate TTS (isopropyl triisostearic titanate). The *in-situ* method is intended to accomplish the hydrophobic treatment of magnetite and to disperse it in the monomer at the same time, using the initiator benzoyl peroxide and the ball mill. The *in-situ* treated magnetite sample was separated from the monomer mixture after the dispersing process. Figure 1 shows photographs of the water contact angle tests for the untreated and treated magnetite. These hydrophobic treated magnetites showed high water contact angles.

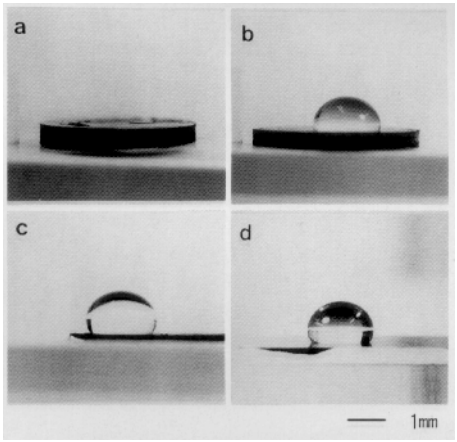

Figure 1. Photomicrographs showing the water contact angle for pressed magnetite. (a) Untreated, (b) anilino silane, (c) titanate TTS, and (d) in-situ *method.*

Suspension Polymerized Toner

The polymerization test results with these magnetites are shown in Table I. In this test, anilino silane, titanate, and *in-situ* treatment gave higher water contact angles, but the toner made from magnetite treated by a coupling agent did not show sufficient electrical resistivity and image quality. The best results were obtained by the *in-situ* method.

To understand these results, we checked the dispersibility of these magnetites into toner particles. Optical micrographs of the cross sections of the toners are shown in Figure 2. In the case of untreated magnetite, the magnetite particles existed around the toner particles. Hydrophobic treated magnetite was dispersed into the toner particles. However, in the case of the coupling agent treatment, few magnetite particles were found inside the toner particles. Only the *in-situ* treated magnetites were well dispersed into the toner particles. This toner also showed higher electrical resistivity and higher image density.

Scanning electron micrographs of these toners are shown in Figure 3. The toners that have poor magnetite dispersion have rough surfaces, but the toners in which magnetite is well dispersed have smooth surfaces.

The reason why higher water contact angle was associated with lower electrical resistivity of toner is not clear. We could treat the agglomeration of magnetite by making it hydrophobic, but could not treat each magnetite particle with coupling agent. Otherwise the dispersibility was responsive to the property of the coupling agent.

Table 1. Characteristics of the Polymerized Toner with Untreated and Hydrophobic Treated Magnetite

	Magnetite		Toner				
Example no.	Treatment	Water contact angle(°)	Particle size (μm)	E.R.* (Ω-m)	T.E.C.† (μC/g)	Image density (OD)	Background (dWh)
T-1	None	0	7.0	7.10 E + 12	– 12.2	0.77	2.1
T-2	Anilino silane	85	7.1	7.30 E + 10	– 15.1	1.18	0.2
T-3	Titanate TTS	130	8.2	6.70 E + 06	– 25.6	0.53	0.6
T-4	None + BPO	125	7.1	1.70 E + 13	– 24.3	1.32	0.2

* E.R.: electrical resistivity. † T.E.C.: triboelectric charge.

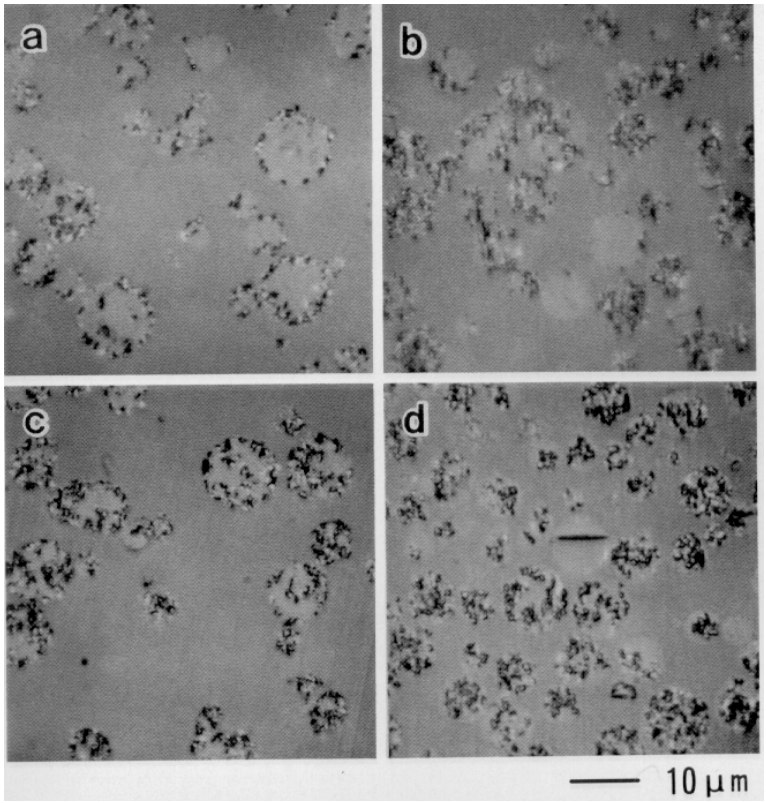

Figure 2. Optical micrographs of the cross sections of suspension polymerized toners with untreated and hydrophobic treated magnetite. (a) Untreated, (b) anilino silane, (c) titanate TTS, and (d) in-situ method.

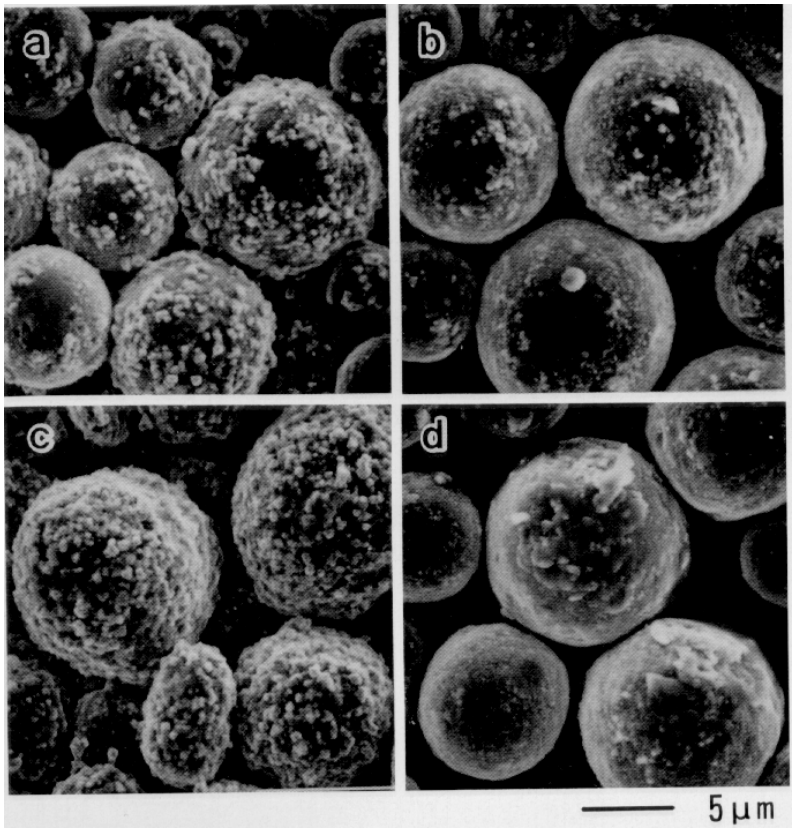

Figure 3. Scanning electron micrographs of the suspension polymerized toners with untreated and hydrophobic treated magnetite. (a) Untreated, (b) anilino silane, (c) titanate TTS, and (d) in-situ method.

Table 2. Characteristics of Polymerized Toner with Different Size Magnetite Particles

	Magnetite		Toner					
Example no.	Particle size (μm)	Surface area (m^2/g)	Particle size (μm)	E.R.* (Ω-m)	T.E.C.† (μC/g)	Image density (OD)	Background (dWh)	Fixation (%)
T-5	0.5	3.5	5.3	1.62 E + 13	– 39.5	1.02	0.1	82.3
T-6	0.2	7.0	6.3	2.40 E + 13	– 18.8	0.66	0.3	59.1
T-7	0.1	11.6	6.2	9.67 E + 09	– 8.8	0.55	1.2	36.1
T-8	0.1	10.6	6.4	2.42 E + 10	– 9.6	0.35	0.1	42.9

* E.R.: electrical resistivity.
† T.E.C.: triboelectric charge.

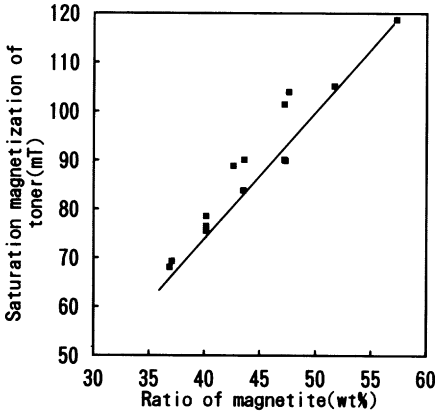

Figure 4. Relationship between the ratio of magnetite in the monomer mixture and saturation magnetization of the toner.

Magnetization of Polymerized Toner

In the development process of an electrophotographic printer, magnetic toner is developed by the balance of electrostatic force and magnetic force. Magnetization of the toner is one of the most important factors for print quality. There are many machines using toners with different magnetization. Therefore, it is important to control the magnetization.

We made several polymerized toners with different magnetite contents and measured the magnetization of the toner. The relationship between the ratio of the magnetite added into the monomer mixture and the saturation magnetization of the toner is shown in Figure 4. The magnetization of polymerized toner increased linearly with the magnetite content of monomer mixture. It is clear that the magnetization of the suspension-polymerized toner could be controlled.

Properties of Magnetite

There are many magnetites with different properties. We process magnetite with octahedral, needle, and spherical shapes which may be used for toner. Magnetite properties influenced by the mean particle size and the dispersibility were investigated. Characteristics of polymerized toners using magnetite with different particle sizes are shown in Table II. The larger particle size magnetite gave the better toner properties: higher electrical resistivity, triboelectric charge, and image density.

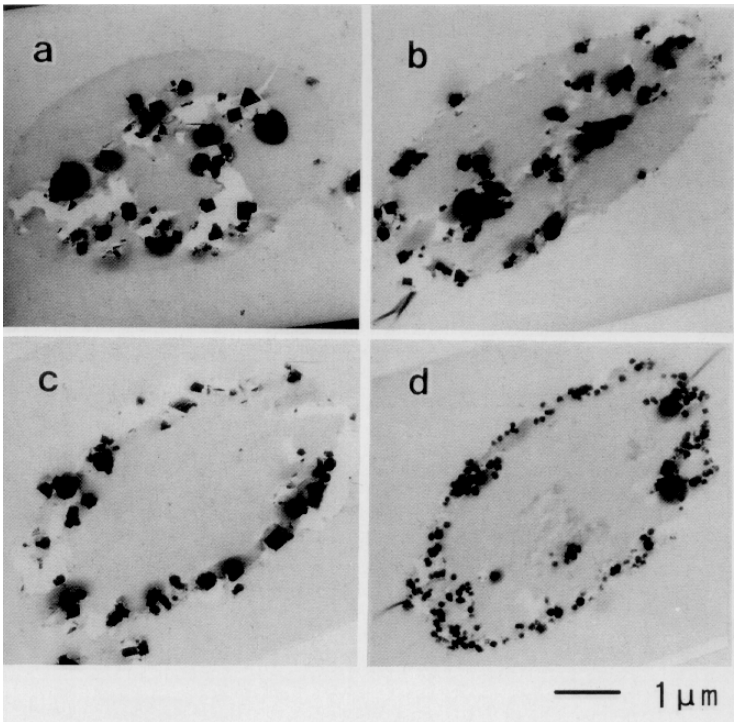

Figure 5. TEM cross sections of the polymerized magnetic toners. Specimens were prepared wtih a microtome. (a) T-5, (b) T-6, (c) T-7, and (d) T-8.

Table 3. Characteristics of Polymerized Toner with Different Conditions of Magnetite Treatment

	Magnetite	Reagent		Toner					
Example no.	Particle size (μm)	BPO (mol%)	Coupling agent	Particle size (μm)	E.R.* (Ω-m)	T.E.C.† (μC/g)	Image density (OD)	Background (dWh)	Fixation (%)
T-9	0.1	0.6	—	6.4	1.66 E + 13	– 24.3	0.60	0.1	41.7
T-10	0.1	1.2	—	6.8	1.30 E + 13	– 32.2	1.15	0.1	61.8
T-11	0.5	1.2	Anilino Si	7.1	3.07 E + 13	– 30.8	1.10	0.2	74.0
T-12	0.5	1.2	TTS	6.5	4.13 E + 13	– 19.7	1.18	0.1	79.2

* E.R.: electrical resistivity.
† T.E.C.: triboelectric charge.

To check the reason for these properties, the dispersibility of magnetite was observed. Transmission electron micrograph (TEM) cross sections of the polymerized magnetic toner are shown in Figure 5. Specimens were prepared with a microtome. The larger size magnetites were dispersed into the toner particles, but the smaller size magnetites were not well dispersed. The toner covered with small sized magnetite seems to show lower electrical resistivity, charge ability, and image density. In the fixation property, well dispersed magnetite toner gave the higher fixation ratio, and vice versa. The difficulty in dispersing the small size magnetite into the toner may have been caused by the difficulty in providing hydrophobic treatment to all of the magnetite particles because of the large total surface area.

Improvement of the Dispersibility of Small Size Magnetite

In the first experiments small size magnetite was not well dispersed in toner particles (T-7, T-8). Here the benzoyl peroxide (BPO) content was 0.3 mol % of monomer mixture in each test. However, if the BPO content were increased in the monomer mixture, small size magnetite might also be able to disperse and show better toner properties. We therefore tried to increase the BPO content of the monomer mixture. The results of these experiments are shown in Table III (T-9 and T-10).

With increasing BPO content, small size magnetite was also dispersed in toner and gave higher electrical resistivity and charge ability. Furthermore, when BPO and coupling agent were used together, dispersibility was still further improved (T-11 and T-12 in Table III). Figure 6 shows SEM micrographs of the toners listed in Table III. The better magnetite dispersibility was recognized by the smooth surfaces of these toners in Figure 6.

Mechanism of *In-Situ* Treatment

In the suspension polymerization to produce magnetic toner, the importance of the magnetite dispersibility was clarified. The *in-situ* treatment method was effective in making toners with characteristics acceptable for electrophotographic printers.

We tried to elucidate the mechanism of the *in-situ* treatment by FT-IR. The magnetite powder was separated from the monomer mixture after ball milling for 12 hr. was

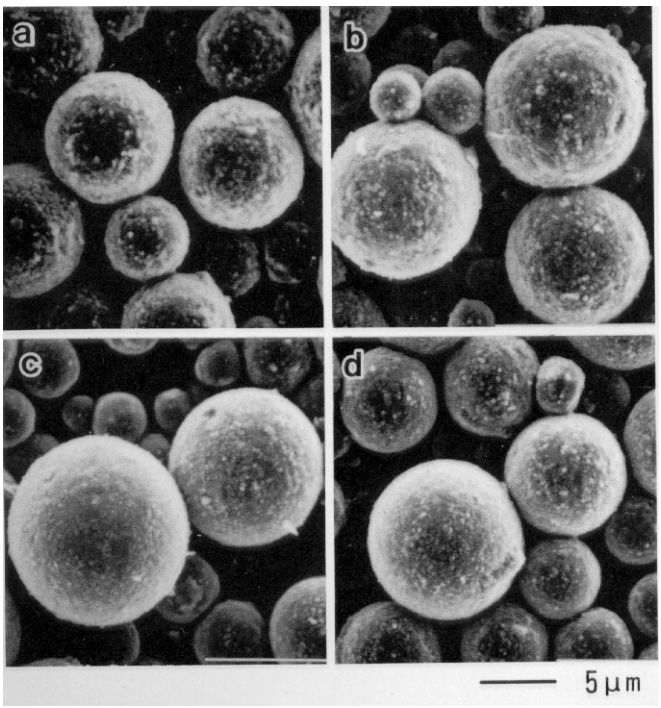

Figure 6. Scanning electron micrographs of the suspension polymerized toners with increased BPO content, and with use of coupling agent together with BPO. (a) T-9, (b) T-10, (c) T-11, and (d) T-12.

washed by toluene and acetone, then was measured by FT-IR spectroscopy. The FT-IR spectra of *in-situ* treated magnetite, untreated magnetite, and styrene acrylic copolymer are shown in Figure 7. Even though it had been washed by organic solvent, *in-situ* treated magnetite still had some absorption peaks of the styrene acrylic copolymer. This result indicated that a part of the monomer had been polymerized by the initiator BPO during the dispersing process in the monomer mixture. Despite the fact that BPO has a very slow decomposition speed or is inactive at room temperature, polymer seems to have grown on the magnetite surface.

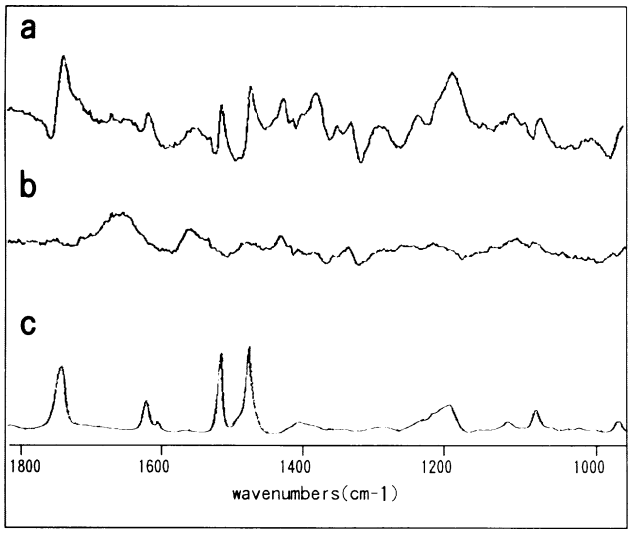

Figure 7. FT-IR spectra of the magnetites. (a) in-situ treated magnetite, (b) magnetite, and (c) styrene acrylic copolymer.

Print Image by Polymerized Magnetic Toner

Polymerized magnetic toner with well-dispersed magnetite has been discussed. From the characteristics of the small size spherical toner, better flowability and finer print images with high resolution are expected. We compared the print quality of this polymerized magnetic toner and the pulverization method toner in an electrophotographic printer. Photomicrographs of these print image samples are shown in Figure 8. The small size polymerized toner gave a better image with less edge roughness than ordinary size pulverized toner.

Conclusions

The method of producing magnetic toner by suspension polymerization was investigated, and the following results were obtained.

1. Hydrophobic treatment of magnetite by a coupling agent gave poor dispersion into the toner.
2. Magnetite prepared by the *in-situ* treatment by BPO in the dispersing process gave better dispersibility and toner characteristics.
3. It was easy to disperse large size magnetite into the toner particles. Small size magnetite was dispersed by increasing BPO content.
4. During *in-situ* treatment, polymer grew on the magnetite surface.

Acknowledgment

The authors would like to thank Professor M. Takeuchi of Ibaraki University for useful discussions.

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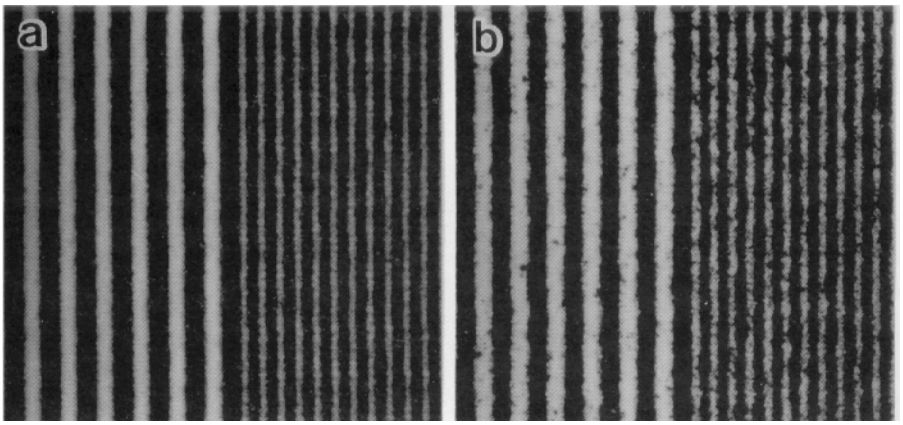

Figure 8. Photomicrographs of print images obtained by polymerized magnetic toners. (a) 6-μm polymerized toner and (b) 10-μm pulverization method toner.