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The Influence of Particle Size, Shape and Particle Size Distribution on Properties of Magnetites for the Production of Toners

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A wide range of iron oxides is used for the production of toners for copiers and laser printers. However, the properties of the toner have to be tailored to the needs of each particular printing system. The precipitation process allows control of particle size, shape and particle size distribution of magnetic iron oxides. The influence of these parameters on magnetic and other data of the magnetite and the toner is discussed.

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Introduction

Monocomponent toners that are widely used in copiers and laser printers contain about 40 wt % of magnetic iron oxide (magnetite Fe_3O_4) that makes the use of an additional magnetic ferrite carrier obsolete. This allows the construction of compact and relatively inexpensive machines. Some of the dual component toners also contain magnetite to facilitate dust control. Because the properties of the toners are tailored according to the needs of the copier or printer machine, a variety of iron oxides with different magnetic properties are used. While the saturation magnetization influences mainly the image density, coercivity and remanence have an impact on the resolution. Many laser printers operate with toners in the 4.8 kA/m range while many copier toners have a coercivity of approximately 8 kA/m. In this article we give an overview of the properties and the production of iron oxide pigments that are used in the toner industry.

Methods for the Production of Magnetites

Magnetite was first synthesized during the early years of this century. Four main methods are in use today to produce magnetite on a commercial scale:

Spray Roasting Process
Laux Process
Penniman Process
Precipitation Process

In the spray roasting process, known as the Ruthner process, ferrous chloride is hydrolyzed and oxidized at high temperatures. This method is widely used for the regeneration of ferrous or ferric chlorides to produce iron oxides and hydrochloric acid. Spray roasted hematites serve as raw material for hard and soft ferrites. Patents that describe the preparation of spray roasted magnetites for the use in toners have been filed.[1–3] However, today these grades have no significant market share in the toner industry due to their broad particle size distribution.

The Laux process was developed by the IG Farben Industries in Krefeld–Uerdingen, Germany during the 1920s. It was the first large-scale process for the production of synthetic iron oxides. In this process nitrobezene is reduced with metallic iron yielding iron oxide and aromatic amines. Main application for black Laux grades is the coloring of paints and construction materials. The Bayer AG introduced the first Laux magnetite for the production of monocomponent toners in 1980. Laux grades are successfully used in some toner formulations. However, only a limited remanence and coercivity range is available. A review of the Laux process and related methods of the production of iron oxides is given in Ref. 4.

In the Penniman process metallic iron is dissolved in acid, hydrolyzed and oxidized to yield iron oxides (Fig. 1). It is widely applied to produce yellow FeOOH, however, this process is not well suited to prepare magnetites, because the process has to be performed at a pH between 5 and 11 where the dissolution of metallic iron significantly slows down.

The most frequently used process for the production of monocomponent toner oxides is the precipitation process that was first described in a patent filed in 1905 (US 808.928). There are three different ways to prepare magnetites by this process:

Neutralization
Two-step precipitation
One-step precipitation

The neutralization process employs ferrous and ferric iron and an alkaline component to precipitate magnetite directly at a low temperature. Most frequently, mixtures of $FeCl_2$ and $FeCl_3$ are treated with ammonia

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Iron Oxide Production:
Penniman Process

(1) Production of nuclei by precipitation

$$2FeSO_4 + 4NaOH + 1/2\ O_2 \rightarrow 2\ \alpha\text{-}FeOOH + 2Na_2SO_4 + H_2O$$

(2) Growing of FeOOH on nuclei

$$\begin{array}{ll} 2Fe + 2H_2SO_4 & \rightarrow 2FeSO_4 + 2H_2 \\ 2FeSO_4 + 1/2\ O_2 + 3H_2O & \rightarrow 2\ \alpha\text{-}FeOOH + 2H_2SO_4 \\ \hline 2Fe + 1/2\ O_2 + 3H_2O & \rightarrow 2\ \alpha\text{-}FeOOH + 2H_2 \end{array}$$

Raw material: blank iron scrap

Figure 1.

Iron Oxide Production:
Precipitation Process

One - step Precipitation

$$2FeSO_4 + 6NaOH + 1/2\ O_2 \rightarrow Fe_3O_4 + 3Na_2SO_4 + 3H_2O$$

Two - step Precipitation

$$2FeSO_4 + 4NaOH + 1/2\ O_2 \rightarrow 2\ \alpha\text{-}FeOOH + 2Na_2SO_4 + H_2O$$

$$2FeOOH + FeSO_4 + 2NaOH \rightarrow Fe_3O_4 + Na_2SO_4 + 2H_2O$$

Figure 2.

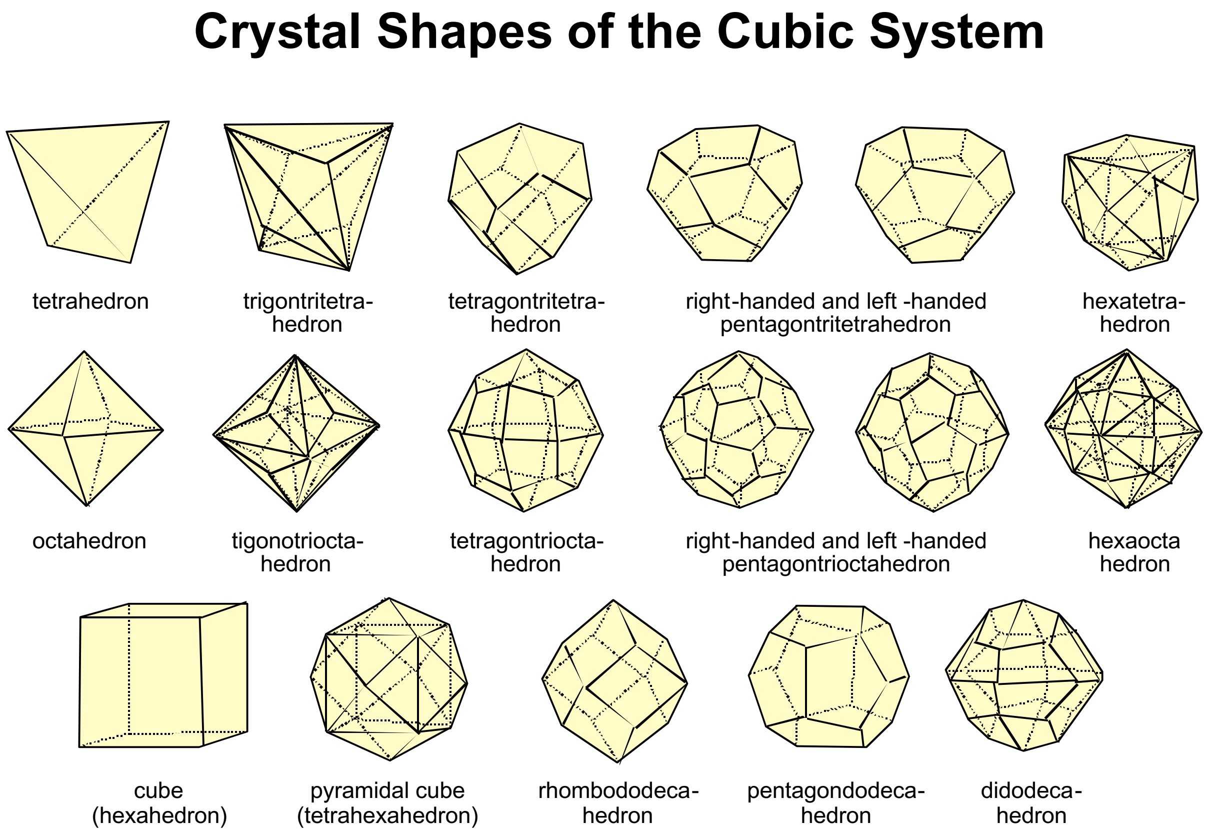

Figure 3.

to get the desired magnetites. This process leads to nanoscale particles and is therefore not suitable for the production of toner oxides.[5–7]

In the two-step procedure an iron(III) oxide or oxyhydroxide, a liquid ferrous component, and an alkaline compound are reacted at a temperature above 70°C (Fig. 2). This process is very well suited for the production of magnetites with tailor made properties, narrow particle size distribution and controllable particle shape. On the other hand, the production costs are rather high due to the use of synthetic iron oxide as one component. It is only feasible if cheap iron oxide pigments are available. More details are found in Refs. 8 through 10.

Since the development of the monocomponent toners, mostly by Canon, the one-step precipitation process became the predominant method to produce magnetites for toners. Because only two chemicals are needed (a ferrous salt solution and an alkaline component), production costs are lower compared to the two component process.

Almost any shape of the cubic system (Fig. 3) can be prepared. Particle size distribution is very narrow if appropriate reactors are employed. A broad range of particle sizes are available. Tailor made magnetites for almost every application in the toner industry can be made. Furthermore, the introduction of additives, e.g., Si, Al etc., or post treatment with organic or inorganic

Raw materials for the production of toner oxides

- ○ Fe-component
  - — $FeSO_4$
  - — $FeCl_2$
  - — Other Fe-II-salts
- ○ Alkaline Component
  - — Ammonia (gaseous or dissolved in water)
  - — NaOH
  - — KOH
  - — CaO
  - — MgO
  - — Na_2CO_3
  - — K_2CO_3
  - — $MgCO_3$
  - — $CaCO_3$
- ○ Oxidizing Agents
  - — Air
  - — Oxygen
  - — Ozone
  - — Chlorine
  - — Nitrates
  - — Nitric Acid
  - — Organic Nitro-compounds
  - — Chlorates (I), (V), (VII)
- ○ Additives
  - — Silicates (Na-, K-silicate)
  - — Aluminates or $Al_2(SO_4)_3$
  - — $TiOSO_4$ or Titanates (inorganic)
  - — Zn as $ZnSO_4$
  - — P as Na-Phosphate
  - — Organic Si-Compounds
  - — Organic Ti-Compounds (Esters)
  - — Fatty-acids and derivatives
  - — Polyacrylates
  - — Polyalcohols (PVA etc.)

Figure 4.

compounds can easily be achieved. The post treatments adjust electrical properties (e.g. conductivity and triboelectric charge) and improve thermal stability. Many patents[11–18] describing post treatment and addition of Si, Al and other inorganic compounds are known.

Precipitation Process

The fundamental process consists of the following steps:

- Introducing the alkaline component (or the ferrous component) to the reactor
- Heating to precipitation temperature
- Adding the ferrous component (or the alkaline component)
- Oxidizing until the reaction is completed

Ferrous components $FeSO_4$ or $FeCl_2$ are widely used. Typically, these compounds are by-products from the steel industry (pickling of steel strip with H_2SO_4 or HCl) or titanium dioxide production.

Some manufacturers prepare solutions of ferrous salts by dissolving metallic iron scrap in the appropriate acid. An additional purification step (filtration) may be necessary.

Caustic soda is often used as the alkaline component. The use of ammonia, soda, lime, limestone, magnesia or $MgCO_3$ is also possible and can offer an advantage of getting a valuable by-product (e.g. ammonium sulfate) or a cost advantage if less expensive limestone or lime is used. Oxidation is usually performed with air but other oxidizing agents such as nitrates, various chlorates, chlorine, or hydroperoxides are also suitable.

Typically, the magnetites are prepared in stirred tank reactors either continuously or batchwise. Figure 4 gives a summary of the raw materials that can be employed in this process. Figure 5 shows a typical flow chart of the production process.

Additives are quite frequently employed. Silicates, aluminum compounds and various other metals are cited in the patent literature. However, only silicates and aluminum compounds are common.[14–18] They stabilize the magnetite against oxidation and exhibit positive effects on fluidity and triboelectric charge. Some manufacturers offer surface treated grades with improved dispersibility and stability. Because of the use of expensive organic compounds, these grades sell for higher prices than untreated products.

There are several process parameters used to control particle shape, particle size and particle size distribution. Table I gives an impression of the most important means to control the process.

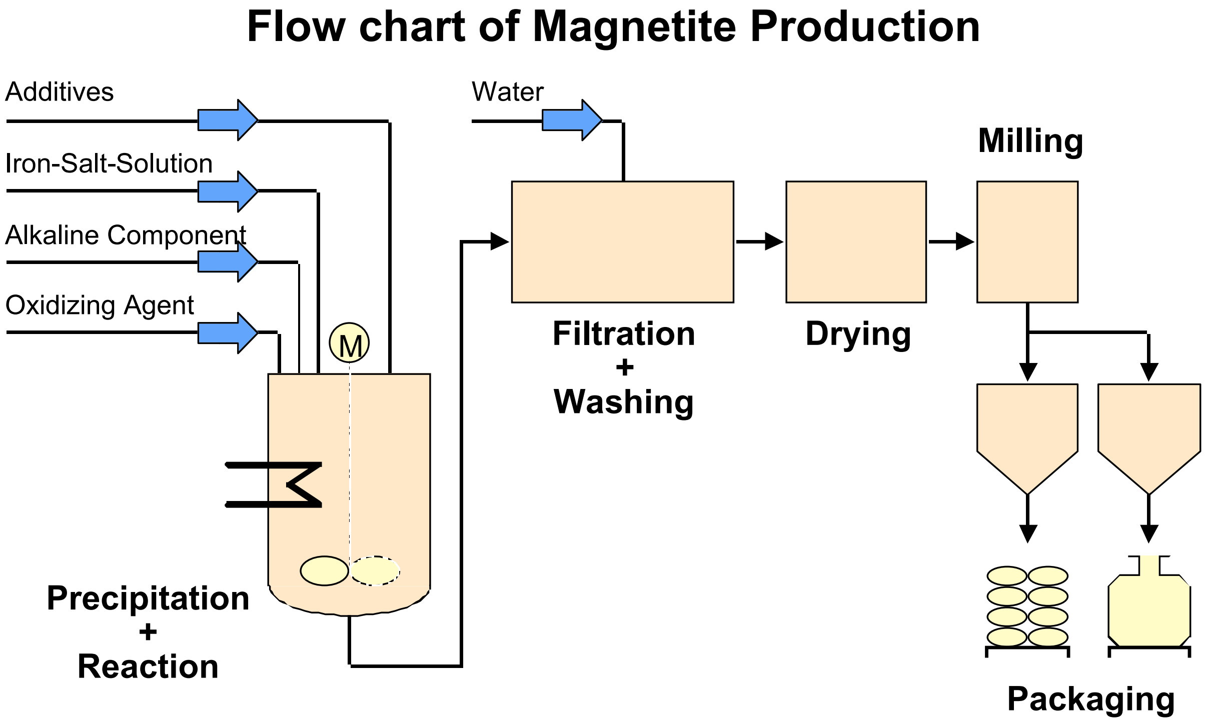

Figure 5.

TABLE I. Process Control Parameters

Process Parameter	Acts on	Effect	Effect
Temperature 50 – 95°C	Particle size 0.01 – 2 µm	Lower temperature Finer particles	Very strong
Ratio Fe/alkaline 0.6 – 0.4	Particle shape, particle size 0.1 – 1 µm	Lower ratio gives Octahedra; High ratio spheres	Very strong
Air about 1 l/h • mole Fe	0.1 – 1 µm	Particle size Finer particles	Higher airflow gives Strong
Agitator	Particle size Distribution	Some agitators lead to sharper particle size distribution	Strong
CFe-Compound	Particle size	Lower concentration gives finer particles	Medium
Si-addition	Particle shape	Improves sphericity	Medium

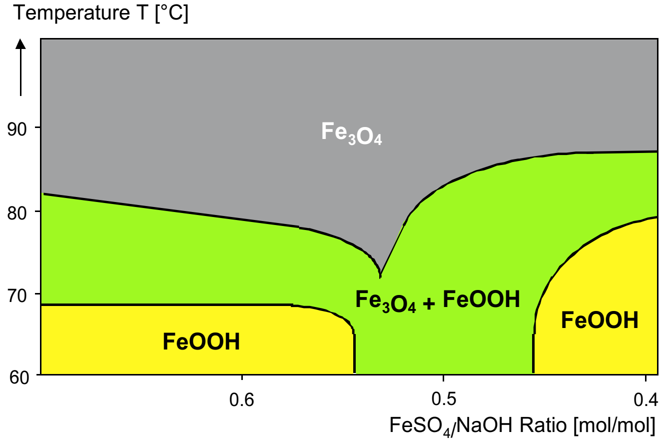

Figure 6.

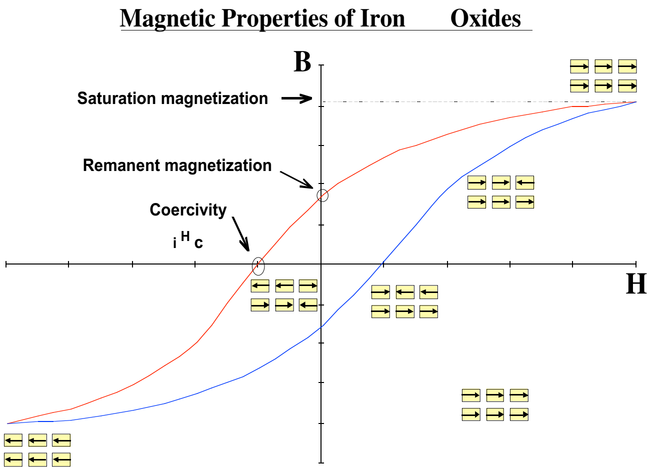

Figure 7.

It is very important for a magnetite producer to know the phase diagram of the various iron oxides and oxyhydroxydes that exist. The formation of magnetite is favored kinetically, but not thermodynamically, i.e., under certain conditions the precipitation of magnetite is the fastest reaction.

As illustrated in Fig. 6 it is not possible to prepare magnetite at a low temperature, at a high Fe/NaOH as well as at a low Fe/NaOH ratios with the one step precipitation process. Between 25 to 100°C hematite (α-Fe_2O_3) and goethite (α-FeOOH) are thermodynamically more stable than magnetite; α-FeOOH is formed at low temperatures (25 – 50°C) in acidic or strongly alkaline region. α-Fe_2O_3 is formed in acidic region at temperatures above 80°C. Some additives also favor the formation of either magnetite or goethite.

Particle Shape, Particle Size, Particle Size Distribution and its Effects on the Magnetic Properties

Magnetite crystallizes in the cubic crystal system with the space group Fd3m with the spinel structure. Figure 3 shows the various shapes of crystals that are available in the cubic crystal system. From these shapes, cubes, octahedra, rhombododecahedra, capped cubes, trunctuated octahedra and spheres are most widely known. The so-called spheres often observed in the preparation of magnetites actually consist of agglomerates of cubes of different particle size.

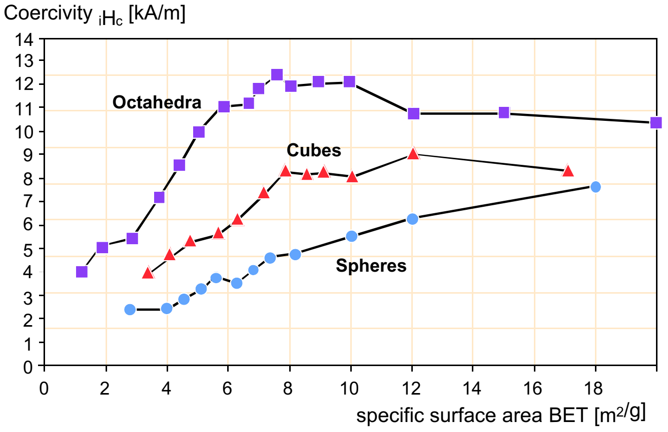

Figure 8.

The particle shape determines the axes of the crystal, and thus its magnetic properties, which are illustrated in Fig. 7. Assuming equal particle size and particle size distribution, the coercivity decreases in the following sequence:

Spheres < cubes < octahedra

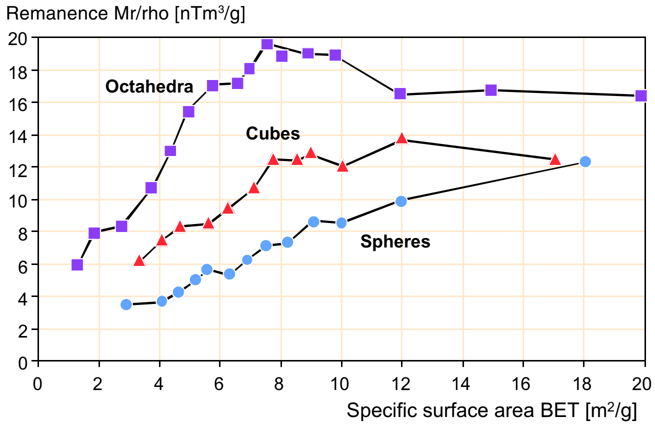

Figure 9.

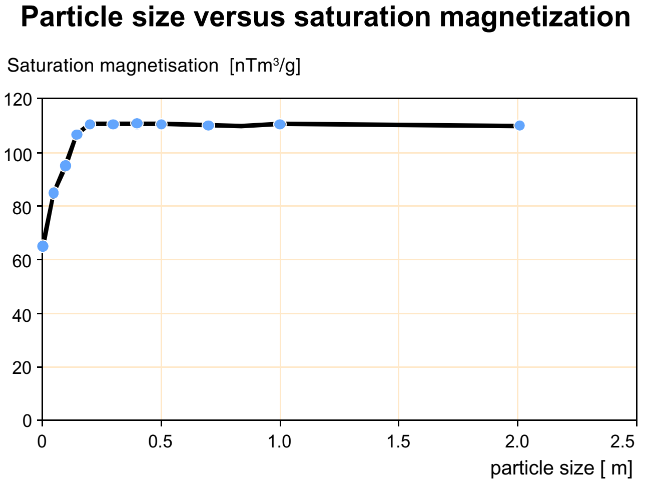

Figure 10.

This is due to the number of magnetic axes, which is undefined for spheres, 6 for cubes and 8 for octahedra. The particle size itself has a rather strong effect on the magnetic properties too. The smaller the particles are the higher is their coercivity and remanence. Figure 8 shows the influence of the particle size and shape on the coercivity for spherical, cubical and octahedral magnetites. The influence on the remanence is visualized in Fig. 9.

The saturation magnetization is independent of the particle size over a wide range (Fig. 10) and is mainly influenced by the FeO-content Fe(II) (Fig. 11) and the total iron oxide content. As the particle size becomes lower than 0.05 µm, magnetites tend to become increasingly more superparamagnetic. The superparamagnetic particles exhibit low coercivity, remanence and saturation magnetization.[19–23] Figures 12, 13 and 14 show three electron micrographs of magnetites with spherical, cubic and octahedral shapes, respectively.

Particle size distribution itself does not exhibit a macroscopic effect on the magnetic parameters of the magnetites, but it influences dispersibility and triboelectrical properties of the particles. Very large particles and hard agglomerates should be avoided anyway because they cause severe quality problems in the finished toner. Therefore, a narrow particle size distribution is

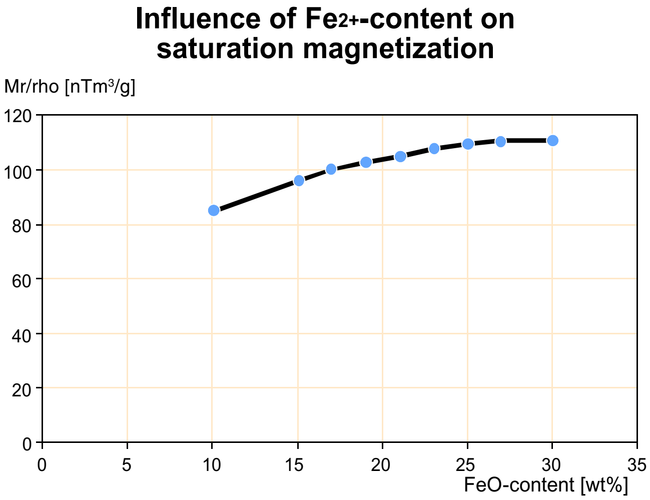

Figure 11.

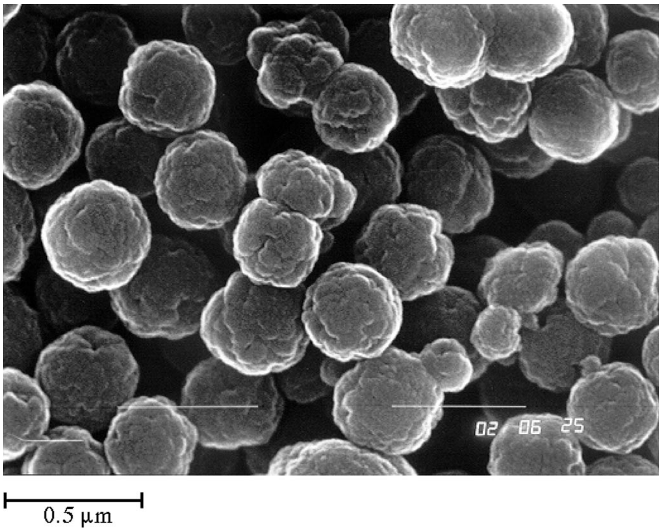

Figure 12.

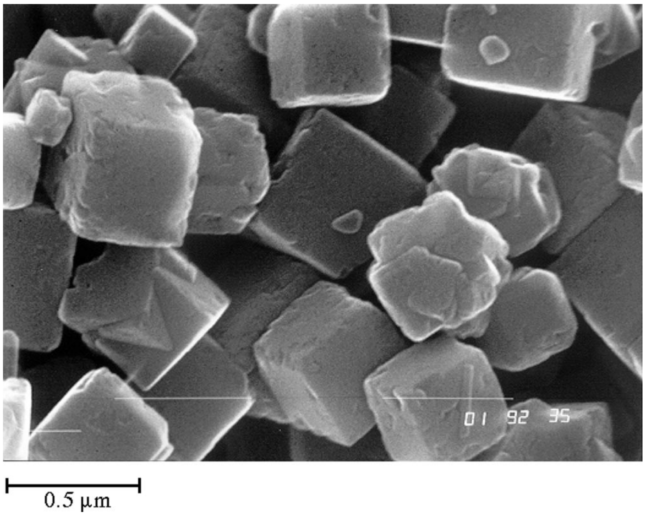

Figure 13.

TABLE II. Magnetic Properties of Representative Toners

	H.P. 4000	Canon NP 8530	Ricoh FT 2050	Turbon MT 90 X
Coercivity [kA/m]	5.1	8.8	8.0	10.2
Remanence [nTm^2/g]	1.3	3.8	5.0	6.3
Saturation Magnetization [nTm^2/g]	45	31	45	58
Iron Oxide Loading [wt %]	~ 45	~ 34	~ 46	~ 56

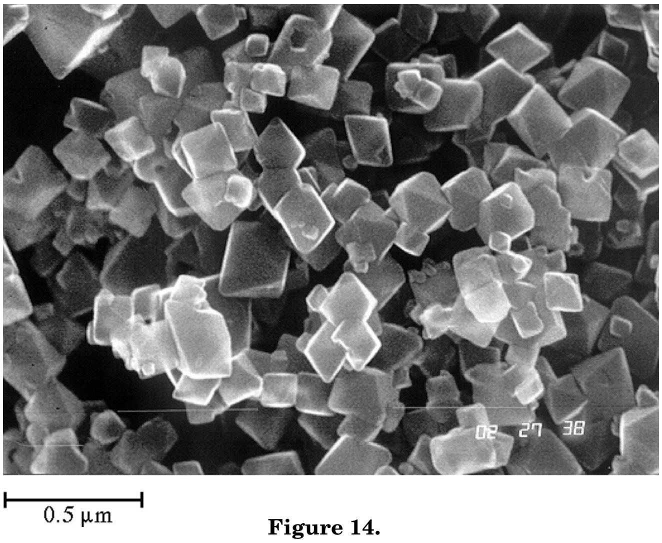

Figure 14.

always more desirable. Using all parameters to influence particle size and shape tailor made magnetite particles exhibiting coercivities between 2.4 and 20 kA/m and BET-surfaces between 1.0 and 25 m^2/g can be produced.

If the neutralization process is applied, even finer magnetites that can reach the superparamagnetic region can be prepared. These particles have a particle size as low as 10 nm and, a BET-surface well above 100 m^2/g. By adding various compounds that influence not only the magnetic properties and stability, it is possible to produce almost every magnetite the toner industry needs. Due to specialized drying and milling steps, the dispersibility of these magnetites is usually very good. To improve the fluidity of the magnetites and to prepare dust free powders, the preparation of granules is also possible.

Table II summarizes the properties of some popular toners. In a copier or laser printer, the magnetic force that holds the toner to the magnetic brush development system has to be balanced with the electrostatic attraction of the photoconductor drum. The magnetic force is mainly influenced by the saturation magnetization of the toner and thus determined by the iron oxide content of the formulation. Depending on the construction of the copier or printer engine, the required range can vary significantly as illustrated above. The construction of the engine also determines the coercivity and thus the remanent magnetization. Toners with a low coercivity in the 5 kA/m range contain spherical iron oxide particles. For higher coercivities, octahedrons or cubes are used. The typical iron oxide particle size is between 0.1 and 0.5 µm.

Review articles dealing with the topics discussed in this article can be found in Refs. 24 through 33. Basic information about magnetism and physical properties of ferrites can be found in Ref. 34.

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