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

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## Abstract

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 to control 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 being discussed.

## Introduction

Mono component toners that are widely used in copiers and laser printers contain about 40% of magnetic iron oxide (magnetite Fe3O4) that makes the use of an additional magnetic ferrite carrier obsolete. This allows the construction of compact and relative cheap machines. Some of the dual component toners contain magnetite too 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 60 Oe range while many copier toners have a coercivity of approximately 100 Oe. Toners with a coercivity of approximately 300 Oe are used for MICR applications (e.g. magnetically readable cheques).

In the present paper we give an overview about 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. 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 an aromatic nitro-compound 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 range of magnetic properties are available.

In the Penniman process metallic iron is dissolved, hydrolized and oxidized to yield iron oxides.

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 mono component toner oxides is the precipitation process which was first described in a patent filed in 1905 (US 808.928).

There are three different ways to prepare magnetites by this process:

One-step precipitation
Two-step precipitation
Neutralization.

The neutralization process employs ferrous and ferric iron and an alkaline component to precipitate magnetite directly at a low temperature. Most frequently, mixtures of FeCl2 and FeCl3 are treated with ammonia to get the desired magnetites. This process leads to nanoscale particles and is therefore not suitable for the production of toner oxides.

In the two-step procedure an iron-III-oxide or oxihydroxide, a liquid ferrous component and an alkaline compound are reacted at a temperature above 70°C. 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.

Since the development of the mono-component 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.4) can be prepared. Particle size distribution is very narrow if appropriate reactors are employed. A broad range of particle sizes is 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 the post treatment with organic or inorganic compounds can easily be achieved.

Therefore, this paper deals only with the one-step precipitation process that is most widely used for the precipitation of toner oxides. We discuss the preparation of magnetites with well defined magnetic properties, particle size, particle shape and particle size distribution.

## The Precipitation Process

The fundamental process consists of the following steps:

- Filling 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.

As ferrous components FeSO4 or FeCl2 are widely used. Typically, these compounds are by-products from the steel industry (pickling of steel strip with H2SO4 or HCl) or the 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 alkaline component. The use of ammonia, soda, lime, limestone, magnesia or MgCO3 is also possible and can offer an advantage by getting a valuable by-product (e.g. ammonium sulfate) or a cost advantage if cheap limestone or lime is used. Oxidation is usually performed with air but other oxidation agents such as nitrates, various chlorates, chlorine or hydro-peroxides are also suitable.

Typically, the magnetites are prepared in stirred tank reactors either continuously or batchwise.

Additives are quite frequently employed. Silicates, aluminium compounds and various other metals are cited in the patent literature. However, only silicates and aluminium compounds are common. They stabilize the magnetite and exhibit positive effects on fluidity and triboelectric charge of the magnetites. 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.

Fig. 1 gives a summary of the raw materials that can be employed in this process.

**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
  - $Na_2CO_3$
  - $K_2CO_3$
  - $MgCO_3$
  - $CaCO_3$
- Additives
- Oxiding Agents
  - Air
  - Oxygen
  - Ozone
  - Chlorine
  - Nitrates
  - Nitric Acid
  - Organic Nitro-compounds
  - Chlorates (I), (V), (VII)
- 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 1.*

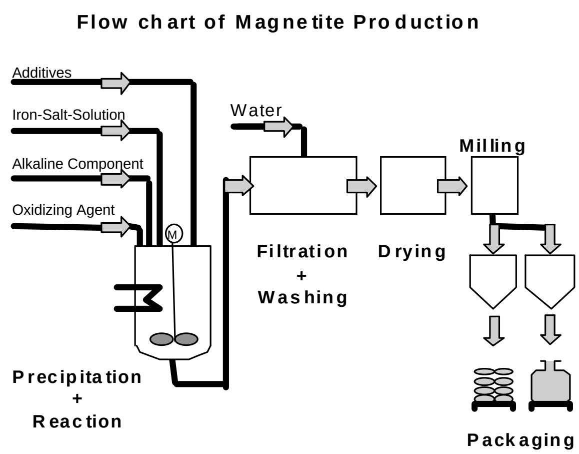


*Figure 2.*

Figure 2 shows a typical flow chart of the production process.

There are several process parameters used to control particle shape, particle size and particle size distribution.

The table shown below gives an impression of the most important means to control the process.

It is very important for a magnetite producer to know the phase diagram of the various iron oxides and oxihydroxydes that exist. Magnetite is not stable at room temperature. Therefore, the formation of magnetite is not favored thermodynamically. However, under certain conditions the formation of magnetite is the fastest reaction so that it is precipitated due to kinetic reasons.

| Process Parameter | Acts on | Effect | Effect |
|---|---|---|---|
| Temperature | Particle size | Lower temperature Finer particles | Very strong |
| Ratio Fe/alkaline | Particle shape, particle size | Lower ratio gives Octahedra; High ratio spheres | Very strong |
| Air | Particle size | Higher air gives Finer particles | Strong |
| Agitator | Particle size Distribution | Some agitators lead To better particles Size distribution | Strong |
| CFe-Compound | Particle size | Lower concentration gives finer particles | Medium |
| Si-addition | Particle shape | Improves sphericity | Medium |

Therefore, it is not possible to prepare magnetite at a low temperature, at a high Fe/NaOH as well at a low Fe/NaOH ratio with the one step precipitation process. Between 25 to 100°C hematite (alpha-Fe2O3) and Goethite (alpha-FeOOH) are thermodynamically more stable than magnetite. These compounds are formed under certain conditions.

Fig. 3 gives an impression on the phase diagram of magnetite. Some additives favor the formation of either magnetite or goethite which has to be kept in mind if additives are used.

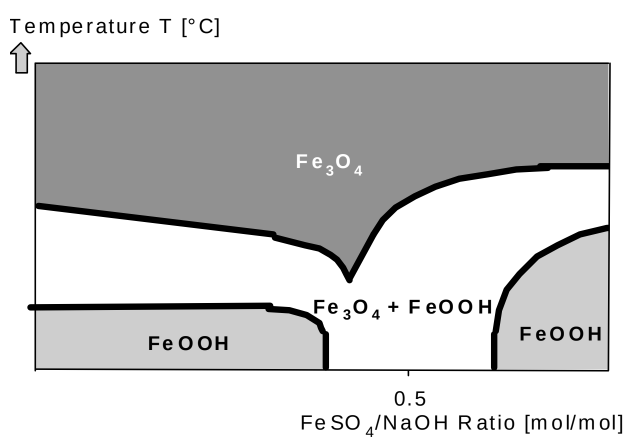


*Figure 3.*

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

Magnetite cystallizes in the cubic crystal system with the space group F d3m with the spinel structure. Figure 4 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 really consist of agglomerates of cubes of different particle size.

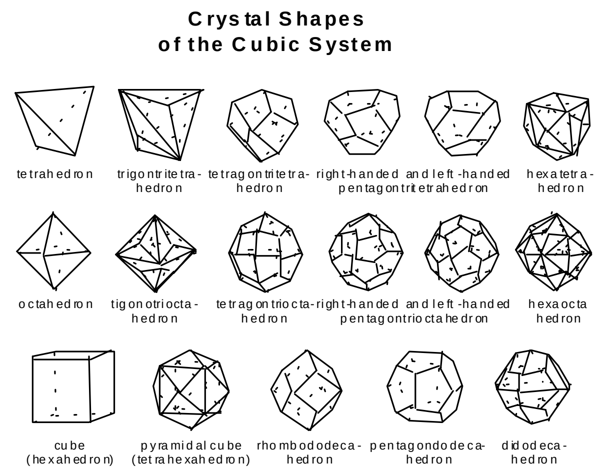


*Figure 4.*

The particle shape determines the easy axes of the crystal and thus its magnetic properties. Assuming equal particle size and particle size distribution the coercivity decreases in the following sequence:

*Spheres < cubes < 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 the remanence. Figure 5 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. 6.

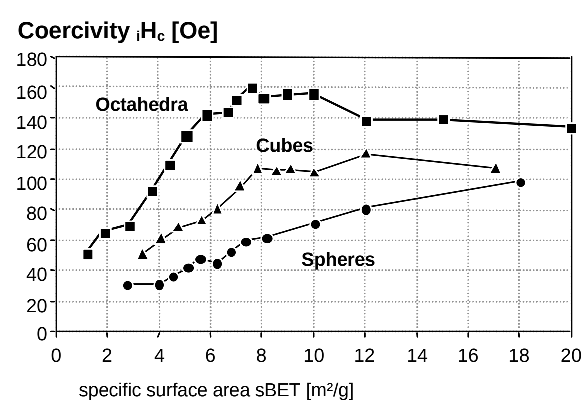


*Figure 5.*

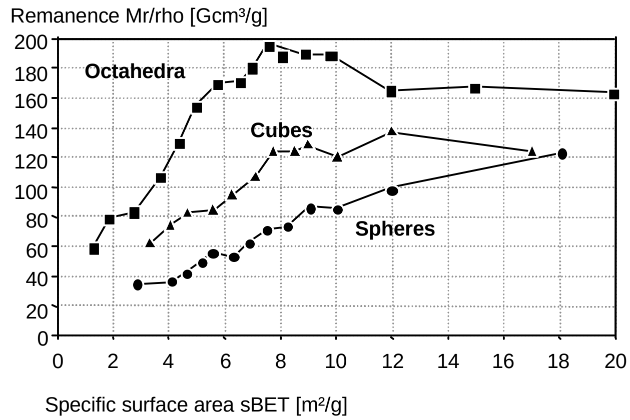


*Figure 6.*

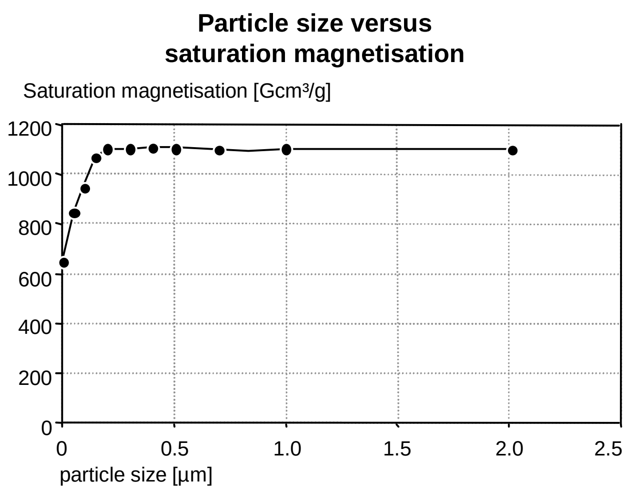


*Figure 7.*

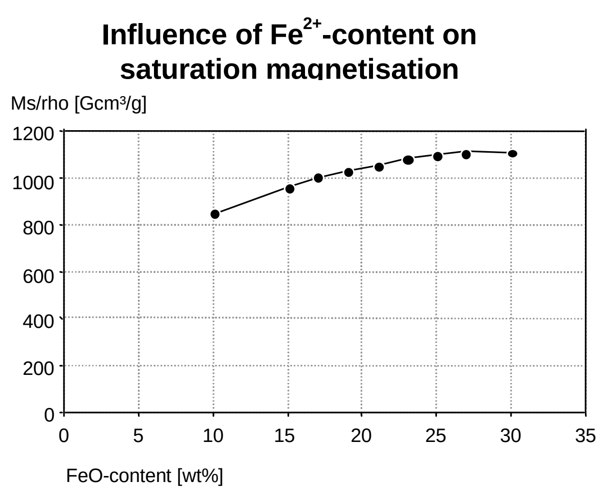


*Figure 8.*

The saturation magnetization is independent on the particle size over a wide range and is mainly influenced by the FeO-content (Fe2+)(Fig. 7 and 8) and the total iron oxide content.

In order to illustrate this effect, figures 9-14 show six electron micrographs of magnetites with various spherical, cubic and octahedral shape and different particle size.

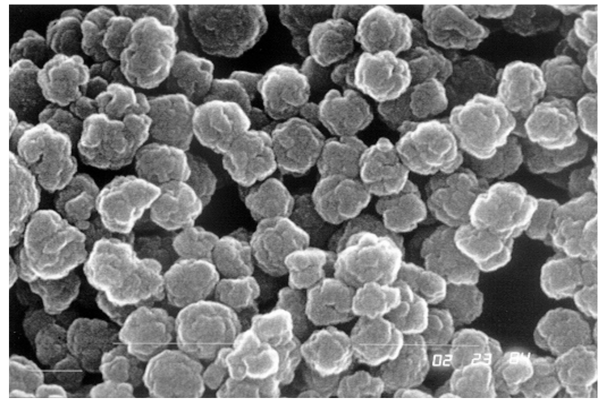

*Figure 9. Magnification 60000 : 1*

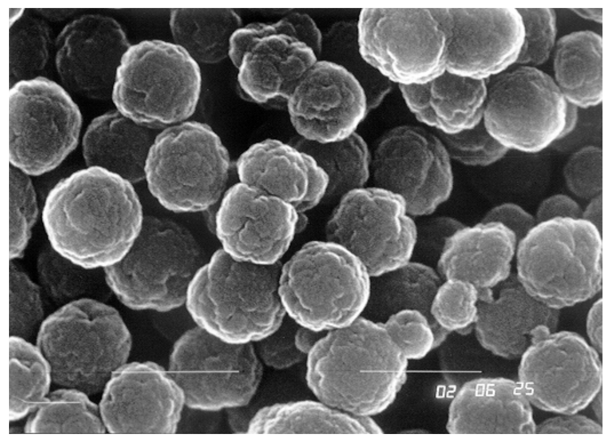

*Figure 10. Magnification 60000 : 1*

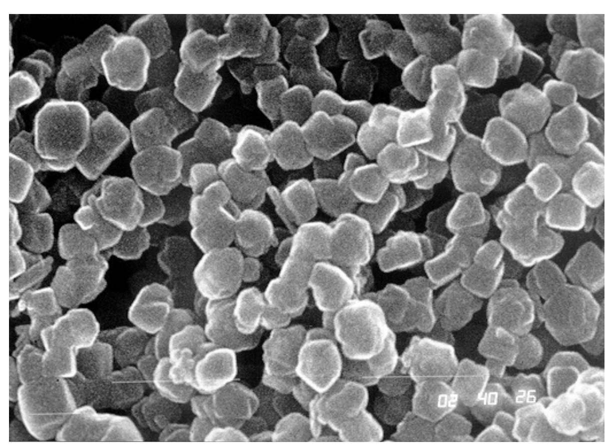

*Figure 11. Magnification 60000 : 1*

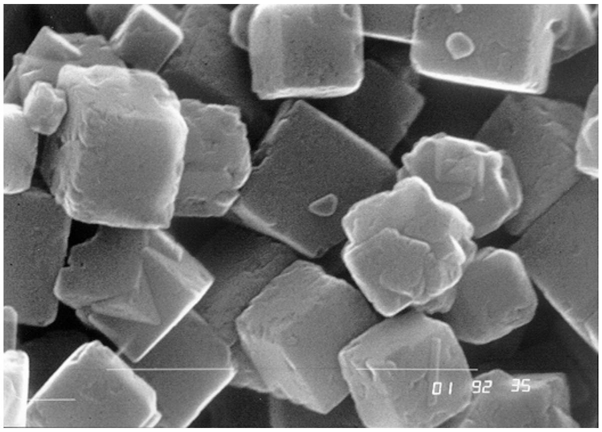


*Figure 12. Magnification 60000 : 1*

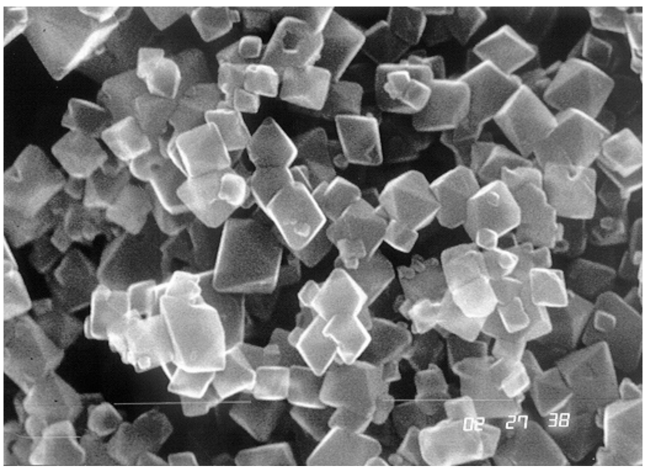


*Figure 13. Magnification 60000 : 1*

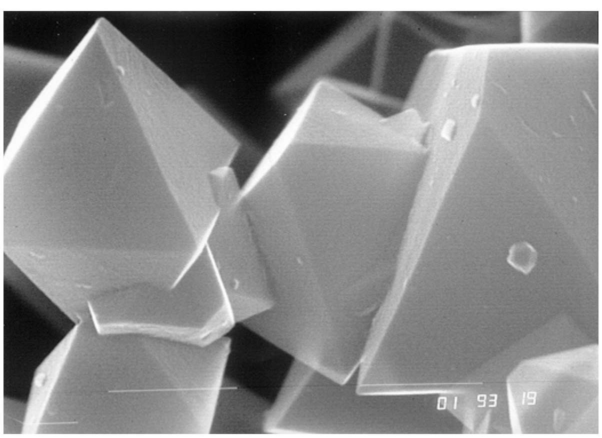


*Figure 14. Magnification 60000 : 1*

Particle size distribution itself does not exhibit a macroscopical effect on the discussed 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 sharp particle size distribution is always very desirable.

Using all parameters to influence particle size and shape tailor made magnetite particles exhibiting coercivities between 30 and 250 Oe 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 $m^2/g$. 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 possible.

## Biography

**Ulrich Meisen** was born 1955 in Wuppertal. Studies of Chemistry and computer science from 1975 to 1984 at the universities of Dortmund, Freiburg and Münster. Graduated 1981 at Dortmund university in the field of inorganic solid state chemistry. From 1981 to 1984 Ph. D. thesis at Dortmund university in the same field.

Research chemist at BAYER AG from 1984 on. Areas of work:
- magnetic iron oxides
- barium ferrites
- iron oxides for color pigments

Head of research team toner oxides from 1988 on.

**Hendrik Kathrein** received his Diplom degree in mineralogy from the University of Cologne in 1979 and a Ph.D. in solid state chemistry in 1982. Since 1983 he has worked for BAYER in various positions in R&D, production and marketing in Germany and the USA. His work has primarily focused on iron oxides for magnetic tapes and inorganic oxides for toners and other technical applications.