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*EVALUATION OF IRON OXIDES FOR
FERRITE MANUFACTURE*

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Evaluation of Iron Oxides for Ferrite Manufacture

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ABSTRACT

Iron oxides intended for use in ferrite manufacture are described in terms of physical properties such as surface area, particle size and shape, and tap density. Results are presented of a study of the barium hexaferrite formation reaction, using X-ray Diffraction, Differential Thermal and Thermogravimetric Analyses and, based thereon, the possibility of including a reactivity parameter in the description of an iron oxide is suggested.

Introduction

The physical and chemical properties of iron oxides have a major influence on the magnetic properties and on the microstructure of any ferrite made using them. The techniques used in the evaluation of iron oxides are of interest to manufacturers both of iron oxides and of ferrites. The present paper deals mainly with some of the methods used in assessing the physical

properties of iron oxides intended for use in ferrite manufacture.

The presence of impurities in an iron oxide can easily obscure the effect of variation of any of the physical properties. The ferrite industry, however, has been fortunate in being able to obtain high-purity synthetic iron oxides from the pigment industries, thereby enabling variables due to the presence of impurities to be kept to a minimum.

Generally, an iron oxide is described in terms of its particle shape, particle size distribution and surface area. Other related parameters such as tap density, apparent density, compressibility, oil absorption, average particle size and shrinkage on sintering have also been used to indicate the physical characteristics of the iron oxide.

In the present paper, an attempt is made to relate the physical properties of iron oxides with their reactivity behaviour in the formation of barium hexaferrite. X-ray diffraction analysis and the thermal behaviour were employed in the reactivity studies.

Experimental

1. Particle size and shape measurements: Iron oxides intended for ferrite

manufacture usually have a distribution of particle sizes in the range of 0.1 to 10 microns. Electron microscopy is the best technique to yield information regarding the shape and surface characteristics of such iron oxides. In Figure 1, electron micrographs of two different types of iron oxide are shown, one with acicular shape and the other with irregular shape.

Electron microscopy and, in some cases, optical microscopy can be used for particle size distribution determinations. Sedimentation and centrifugal methods also can be used for particle size analysis, although care must be taken in interpreting such results, since neither method will distinguish between a single particle and an agglomerate of equal size. In Figure 2, the particle size distributions of four different oxides, as determined with an Eagle-Picher photosedimentometer, are depicted. The results are comparable with those obtained using an Andreasen Pipette. The analysis can be completed in two hours. However, sedimentation methods were not sufficiently sensitive to show differences between fairly similar oxides that could, in fact, be distinguished from

one another by thermo-analytical methods, when the oxides were incorporated into ferrite compositions.

2. Surface Area Measurements: The surface areas of the iron oxides were determined using a Perkin-Elmer Sorptometer. In Figure 3, the relationship between the surface area of the iron oxides, and their tap density and average particle size, and also the degree of shrinkage of barium carbonate/iron oxide mixes on sintering, are shown. The percent diametral shrinkage represents the shrinkage of a pressed pellet of a $\text{BaCO}_3:5.5\text{Fe}_2\text{O}_3$ (molar) mixture after firing at 1250°C for two hours. In general, the tap density and average particle size decrease with increasing surface area, while the diametral shrinkage increases, although there are certain anomalous results.

3. Reactivity of barium ferrites — a. Sample preparation: Mixtures having molar compositions of $\text{BaCO}_3:6.0\text{Fe}_2\text{O}_3$ and $\text{BaCO}_3:5.5\text{Fe}_2\text{O}_3$ were employed to study the barium ferrite formation reaction, in order to evaluate the reactivity characteristics of a range of types and grades of iron oxide and to relate them to the surface area of the oxides. Table I gives a summary of the samples used in this investigation.

Two techniques were employed in the preparation of mixtures. In one, a Waring Blender was used to wet-blend Fisher "Technical Grade" barium carbonate with the appropriate Northern Pigment iron oxide. In the second method, the mixing was done by precipitating barium carbonate on to suspended iron oxide particles by slowly adding an ammonium bicarbonate solution to a constantly-stirred slurry of iron oxide in barium nitrate solution. A 0.3M solution of Fisher "Reagent Grade" barium nitrate was used for this purpose. After the precipitation was complete, the slurry was filtered and the residue washed. This method yielded a more intimate mixture of iron oxide and barium carbonate than the wet-blending procedure.

From surface area measurements, it was found that the barium carbonate obtained using the precipitation process was much finer than the technical grade barium carbonate. The two different types of mixtures were examined by optical microscopy as shown in Figures 4a and 4b. The barium carbonate particle agglomerates in the precipitated mixtures were of equant shape with a size range of three to six microns (See Figure 4a). In contrast, in the wet-mixed samples, the barium carbonate particle agglomerates exhibited a different shape, as illustrated in Figure 4b and appeared as long needles, up to 20 microns long with a cross dimension of one to four microns. The barium carbonate particles were of the same size for the various mixtures prepared by a given method and it can thus be supposed that any variations in the reactivity

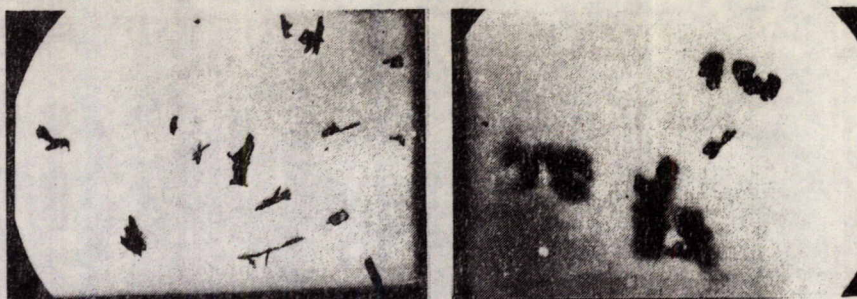


Fig. 1. Electron micrographs of two types of iron oxide: (a) a acicular shape; (b) irregular shape. (Magnification: X 10,000)

observed following a given method of mixing, are attributable mainly to the variations in the physical characteristics of the iron oxides.

Iron oxides of acicular particle shape — but of three different grades (used in Mixtures A, C and H), an iron oxide of irregular particle shape (D), and a hydrated iron oxide of acicular shape (E), were used in the preparation of 12 different mixtures using either the wet-blending or the precipitation techniques. Samples of the mixtures were heated to temperatures of 750°C , 1000°C , 1100°C for 30 min., and to 1200°C for two hours; they were then subjected to x-ray diffraction examination, to differential thermal analysis and to thermogravimetric analysis, in order to assess the extent of reaction that had taken place.

It is believed that surface area measurements on the calcined samples provide a very good indication of the behaviour of the material in the later stages of processing(1). Surface area measurements were again done on the various samples after heat treatment using a Perkin-Elmer Sorptometer, while the average particle size was determined using a Fisher Subsieve Sizer. Some of the results are shown in Figures 5a and 5b, respectively. In each case, the surface area of the mixture after the heat treatment at

750°C was lower than that of the original iron oxide used in the mixture.

b. Differential thermal analyses and x-ray diffraction examinations: Differential thermal analysis was done using an equipment constructed by one of us (R.H.L.) at the Mines Branch,

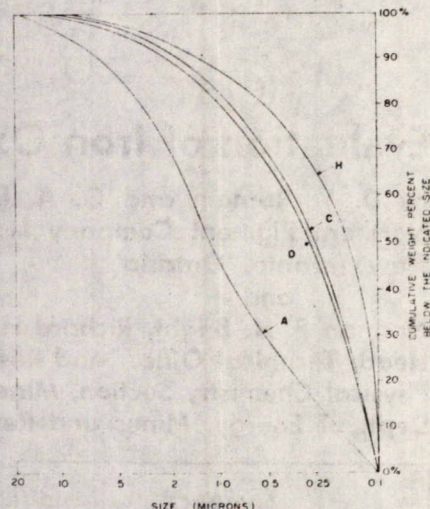


Fig. 2. Particle size distribution of four grades of iron oxide used in various compositions. (The letters on the curves indicate the mixes in which the particular oxides were used).

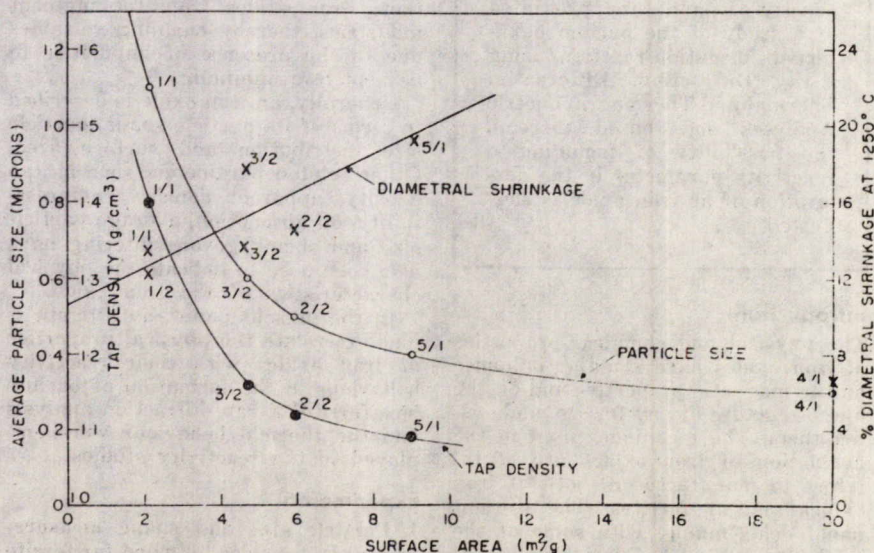


Fig. 3. Variation in average particle size and tap density of iron oxides and of diametral shrinkage of $\text{BaCO}_3:5.5\text{Fe}_2\text{O}_3$ Pellets when fired at 1250°C for 2 hours as functions of the surface area of the iron oxides. (The figures alongside each experimental point indicate the grade and lot number of the oxide used, as per Table 1).

Ottawa. A heating rate of 12 deg. C per minute up to 1100°C was employed. From the DTA traces, the decomposition of BaCO₃, the disappearance of Fe₂O₃ and the formation of BaO.6Fe₂O₃ could be followed semi-quantitatively. The amount of barium carbonate still present was estimated from the area of the endothermic $\alpha \rightarrow \beta$ crystal transition peak observed at about 830°C. The Néel temperature of 690°C for hematite and the Curie Point of 460°C for barium hexaferrite both gave rise to small endothermic peaks. The areas under these various peaks, corrected to a constant weight of sample, gave semi-quantitative estimates of the amount of each constituent present.

In the X-ray diffraction work, the height of one prominent diffraction peak for each constituent was used to give a rough estimate of the amount of the phase causing the peak. The prominent lines chosen have the "d" spacings of 4.17 Å for Fe₂O₃.H₂O, 3.71 Å for BaCO₃, 2.69 Å for Fe₂O₃, and 2.77 Å for BaO.6Fe₂O₃.

In Figures 6a and 6b, semi-quantitative estimates of the several constituents at various temperatures on the basis of the DTA and X-ray examinations, respectively, are given for two samples. Samples G and I were made from irregular-shaped and acicular-shaped iron oxides, respectively. It will be seen that the greater disappearance of Fe₂O₃ and BaCO₃ in sample G as compared with sample I, is accompanied by the formation of a larger proportion of ferrite. Since the iron oxides used in the samples G and I have about the same surface area, the results might indicate that the irregular vs. acicular shape could have been more of a factor in controlling the reactivity than was the difference in surface area.

It might be mentioned that, in samples E, F, H and I, containing either a hydrated iron oxide or the finer grade of acicular iron oxide, hematite was prominent up to 1100°C while, in samples such as J and K using a coarser acicular iron oxide, hematite was present only in small quantities even at 1000°C.

c. Thermogravimetric analyses: In the present study, the only information that could be gleaned from an examination of the TGA traces was from the weight change due to CO₂ loss at various temperatures which yielded a quantitative estimate of the extent of the barium carbonate decomposition. A Stanton Thermobalance was used with a heating rate of 6 deg. C per minute in an air atmosphere, up to 1200°C. Samples, untreated and calcined at a range of temperatures, were examined on the thermobalance. From the TGA traces, the percentage of barium carbonate decomposed in the original calcinations at temperatures of 750°C and 950°C was determined for each sample. By 950°C the barium carbonate had been decomposed to the extent of 94-97% of

TABLE I
Details of Sample Mixtures Studied

Sample Mix Identification	Iron Oxide Details					Molar Ratio of BaCO ₃ :Fe ₂ O ₃ used	Mixing Technique used for ferrite formation	Diametral Shrinkage of BaCO ₃ :Fe ₂ O ₃ pellet when heated to 1250°C for 2 hours (%)
	Grade	Lot	Particle Shape	Average Particle Size (μ)	Surface Area (m ² /g)			
A	#1	#1	Acicular	1.1	2.1	1:6	Precipitation	—
B	#1	#2	Acicular	1.1	2.1	1:6	do	—
C	#2	#1	Acicular	0.5	5.9	1:6	do	—
D	#3	#1	Irregular	0.6	4.7	1:6	do	—
E	#4	#1	Acicular	0.3	20.0	1:6	do	6.5
F	#4	#1	Acicular	0.3	20.0	1:5.5	do	6.0
G	#3	#2	Irregular	0.6	4.6	1:5.5	do	17.7
H	#5	#1	Acicular	0.4	9.0	1:5.5	do	19.3
I	#2	#2	Acicular	0.5	5.9	1:5.5	do	14.6
J	#1	#2	Acicular	1.1	2.1	1:5.5	do	13.5
K	#1	#1	Acicular	1.1	2.1	1:5.5	do	13.7
L	#1	#2	Acicular	1.1	2.1	1:5.5	Wet Blending	12.3
M	#3	#2	Irregular	0.6	4.6	1:5.5	do	13.7

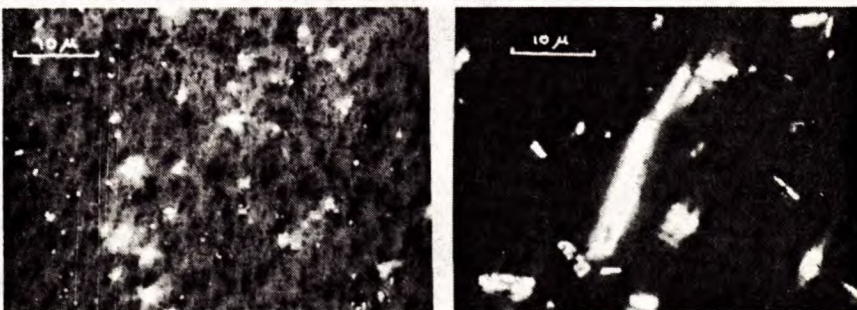


Fig. 4. Optical photomicrographs of BaCO₃/Fe₂O₃ mixes made by: (a) Precipitation mixing; (b) Wet-mixing in Waring blender. Magnification as indicated. Partly polarized light use.

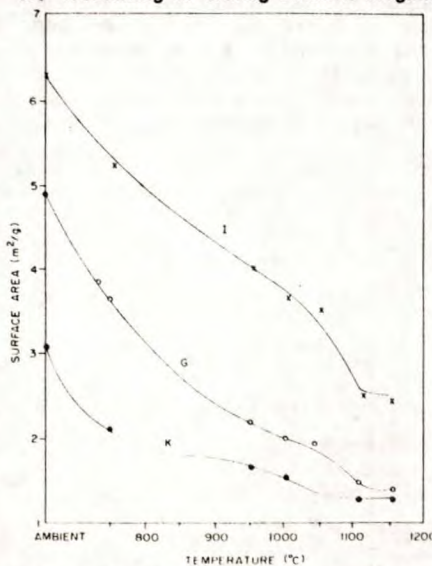


Fig. 5a. Plot showing the variation of surface area of BaCO₃ · 5.5 Fe₂O₃ Compositions with calcination temperature.

the original BaCO₃ present; it was considered that a valid comparison could no longer be made between the various samples on the basis of such a small amount of residual carbonate. In computing the amount of barium carbonate decomposed in the mixtures containing the hydrated iron oxide, it was assumed that all the water of hydration was given up by 700°C, and that any weight loss occurring

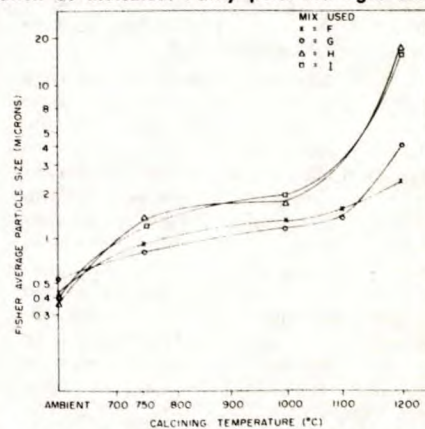


Fig. 5b. Plot showing the variation of average particle size of BaCO₃ · 5.5 Fe₂O₃ Compositions with calcination temperature.

above this temperature was due to CO₂ loss from the barium carbonate. This assumption, although probably not strictly true, was considered to give at least a very good approximation to the correct figures.

Discussion

The aim of the investigation was to correlate the physical characteristics of particle shape and size distribution and related parameters such as surface area, average particle size and tap density, with the results obtained in the reactivity studies, as indicated by X-ray diffraction and by the thermo-analytical techniques. Consid-

erable experimental work has been reported dealing with solid state reactions in ferrites. From thermal investigations of barium carbonate and iron oxide mixtures, Sadler (2) reported that an equation of the type:

$$Y^2 = 2kt + \text{constant},$$

where Y = thickness of product layer,
 t = time of reaction,
 and k = reaction rate constant,

representing Fick's diffusion law, could be applied to the rate of decomposition of barium carbonate in the barium ferrite formation reaction. Barium carbonate alone does not decompose appreciably below 1000°C. However, in the presence of iron oxide, noticeable decomposition was observed at a temperature of 750°C. It is believed that the initial reaction responsible for the decomposition of the carbonate is due to the diffusion of ions from Fe_2O_3 into the BaCO_3 lattice and, hence, that the decomposition rate is probably controlled by the diffusion rate of these ions. At higher temperatures, barium oxide is supposed to be the major diffusing species. In the x-ray analyses, however, the presence of BaO was not evident; also, in the samples calcined at 750 and 950°C, some diffraction lines were found that could not be attributed to any known compounds. It is suspected that barium ferrites of higher molar $\text{BaO}:\text{Fe}_2\text{O}_3$ ratio than 1:6 might have been formed. A phase study of this system is in progress in the Mines Branch Laboratories; it is hoped that this study may enable these compound(s) to be identified.

On the basis of the assumption that the points of contact between iron oxide and barium carbonate are the starting points for reaction, it can be supposed that a greater interface area between barium carbonate and iron oxide would promote greater decomposition of the carbonate. In the present series of experiments, this supposition was borne out by the much higher percentage weight losses obtained using compositions prepared by precipitation mixing than was obtained with comparable wet-mixed compositions. For example, using the same iron oxide, a precipitation-mix sample G gave a weight loss after heating the mixture to 750°C, indicating the decomposition of 63% of the original barium carbonate present as compared with 26% for wet-mixed sample M. Another factor causing differences in the interface area and, probably, in the percentage weight loss, is the particle size distribution of the iron oxide. Using the same precipitation-mixing technique, the percentage weight loss, indicating decomposed BaCO_3 , varied between 32 and 65% over the samples E to K, inclusive, when heated at 750°C.

In Figure 7, various parameters are plotted for the range of iron oxides and mixtures studied; these include the average particle size in microns and the surface area in m^2/g for the

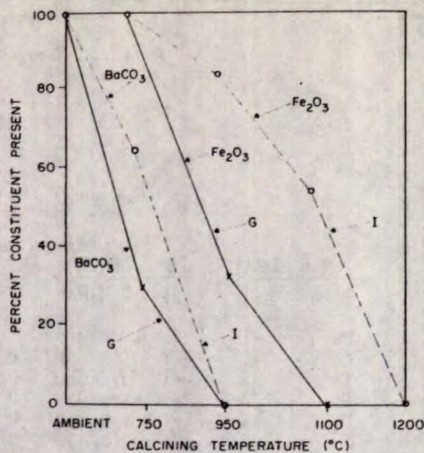


Fig. 6a. Plot showing the disappearance of BaCO_3 and Fe_2O_3 with temperature as indicated from the DTA results.

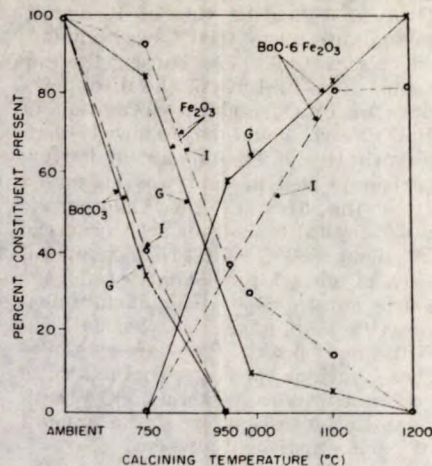


Fig. 6b. Plot showing the disappearance of BaCO_3 and Fe_2O_3 and the formation of $\text{BaO} \cdot 6 \text{Fe}_2\text{O}_3$ with temperature, as indicated by the X-ray diffraction results.

various oxides, the diametral shrinkage of pellets formed from the barium carbonate/iron oxide mixtures and fired at 1150°C, and the percentage of original barium carbonate decomposed after the $\text{BaCO}_3/\text{Fe}_2\text{O}_3$ mixed powders had been heated to 750°C for 30 minutes, as determined from the TGA observations. From these graphs, it can be seen that, in general, the shrinkage increased with increasing surface area of the oxide used. There were certain apparent anomalies that will be mentioned shortly. Using a given sample of iron oxide, the precipitation-mixed sample gave a higher shrinkage than the corresponding wet-mixed sample. The shrinkage was increased by 4% by resorting to precipitation mixing in the case of irregularly-shaped iron oxides (samples G and M, respectively), while the

increase was only 1.2% with acicular oxides (samples J and L, respectively).

In considering the various trends apparent from Figure 7, it is apparent that the shrinkage values, in general, increased with increasing surface area. It was interesting to note the anomalous shrinkage values for samples E and F. This is attributed to the fact that the iron oxide used in sample mixtures E and F was in the hydrated form. Samples C and I, which were made using two different lots of the Grade #2 oxide, showed disproportionately low reactivities as judged by the percentage of barium carbonate decomposed at 750°C, whereas, from their surface areas and other properties, one would have ex-

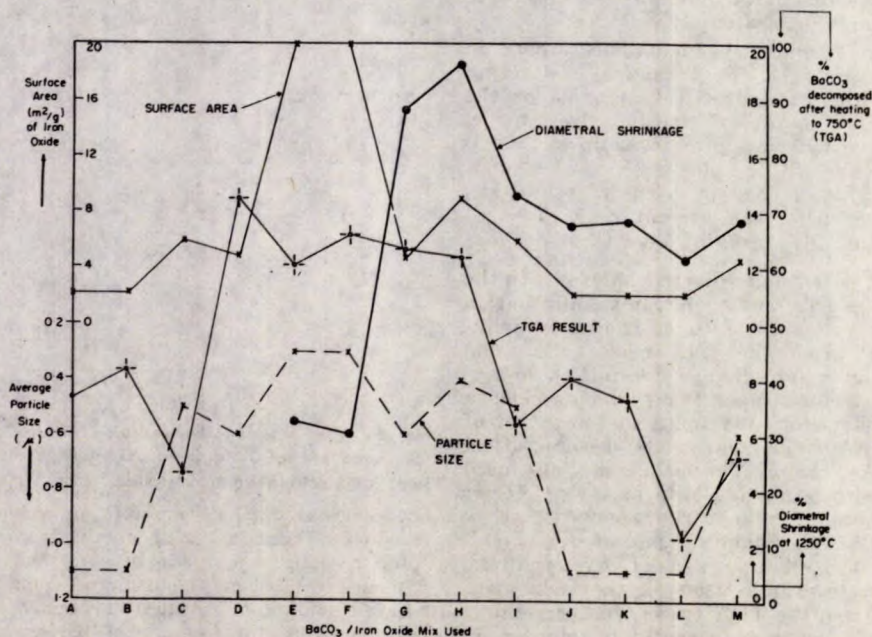


Fig. 7 Plot showing the variations in average particle size and surface area of the iron oxide, the % diametral shrinkage at 1150°C of $\text{BaCO}_3 : 6 \text{Fe}_2\text{O}_3$ Pellets, and % of original BaCO_3 decomposed after calcination at 750°C, for the various iron oxide samples. x.....x surface area (m^2/g).....% diametral shrinkage x.....x average particle size μ% original BaCO_3 decomposed

pected substantially higher figures. These low reactivity figures were strongly supported by the semi-quantitative x-ray diffraction results on these samples. The sample I, which contains an iron oxide of surface area 5.9 m²/g, showed a weight loss corresponding to 32.0% decomposition at 750°C of the original BaCO₃ present in the mix, whereas samples J and K, containing an oxide of surface area only 2.1 m²/g, gave weight-loss figures corresponding to 36-40% decomposition of the original BaCO₃.

The method of preparation of the mix also affects the percentage weight-loss figures obtained. Thus, samples J and L, which contain the same lot and grade of iron oxide in the same molar proportions, gave weight-loss figures corresponding, respectively, to 40.3% and 11.2% decomposition at 750°C of the original BaCO₃ present; sample J was made by precipitation mixing, whereas sample L was made by wet mixing.

Samples A and K were prepared using the precipitation-mixing technique and contain the same iron oxide but with different molar ratios, viz., 1:6.0 in A and 1:5.5 in K. The weight losses were 36.2% and 36.4%, respectively. In samples B and J, using the same oxide, the weight losses were 41.5% and 40.3%, respectively. These indicate a good degree of reproducibility of the test. The significance of the weight-loss parameter is also apparent from the comparison of the weight-loss figures 36.2% and 41.5%, or 36.4% and 40.3%, between iron oxide samples of the same grade, but from two different lots, namely samples A and B or K and J, respectively. Surface area and tap density measurements did not show any significant difference between these two pairs of samples.

From the above discussion of the results of the TGA tests, it would seem that the percentage weight loss corresponding to the decomposition of a proportion of the original barium carbonate at 750°C would be a useful parameter for comparing the reactivities of various grades of iron oxide and also among various lots of the same grade, insofar as the term "reactivity" is used to denote the barium carbonate decomposition in the presence of iron oxide.

Economos and Clevenger(3), and Blum and Li(4) studied nickel ferrite formation by measuring the saturation

magnetization with the aim of studying the influence of particle size on the reactivity of iron oxides. They could not obtain any function relating particle size and reactivity. Economos and Clevenger also noted that two of the mixtures, somewhat coarser than the finest mixture, yielded about 10% more ferrite. Their conclusions were that size, in itself, does not affect the activation energy of the ferrite formation, but that size distribution does appear to have an effect.

In the present study, the hematite phase had disappeared to a considerable extent at 1000°C in the samples using the coarser grades of acicular iron oxides, while, in the samples using a finer grade of oxide, the hematite phase was still present in significant amounts even at 1100°C. Using the much finer, hydrated iron oxides, the hematite phase was present in significant amount even in material that had been heated to 1200°C. This result showed a distinct similarity to the above-mentioned observation by Economos and Clevenger and may be another manifestation of the effects of an acicular vs. an irregular particle shape.

It is apparent that an oxide which could be termed highly reactive from the weight-loss experiment does not necessarily yield a greater proportion of barium ferrite at 1200°C. However, it may be assumed that the differences in the weight loss from one sample to another reflect the differences in the interface activation of the mixtures, caused by variations in the size distribution and surface activity of the iron oxides under consideration. While the size distribution and surface activity characteristics may not correspond quantitatively to the reactivity of the ferrite formation, they may have some relation to the subsequent steps in the processing and to the final microstructure of the ferrite and its magnetic properties.

Conclusions

From the above study, it is seen that surface area and related parameters, such as tap density and average particle size, for a given type of iron oxide, need not necessarily represent the reactivity characteristics of the iron oxide, either in association with the barium carbonate decomposition or in the final ferrite formation.

The application of thermogravimetry to determine the extent of de-

composition of barium carbonate during the barium ferrite formation appears to be a sensitive and reasonably reliable method of indicating the surface properties that influence the reactivity of the iron oxide in ferrite formation, dependent mainly on the particle shape and size distribution, which control the surface area. This method gives a reproducible comparison between various types of iron oxide, between various grades of the same type, and also between various lots of the same grade. Investigations are being continued with additional grades of iron oxide with a view to substantiating the above work.

From the above study, it is, however, evident that there is, as yet, no means of completely characterizing an iron powder so that its properties can be used to predict with certainty the final microstructure and magnetic properties of a ferrite made from it. Fabrication techniques can affect the final properties of a ferrite as much as the chemical and physical properties of the powder constituents. It is proposed to extend the study of ferrite formation to cover these facets of the problem.

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