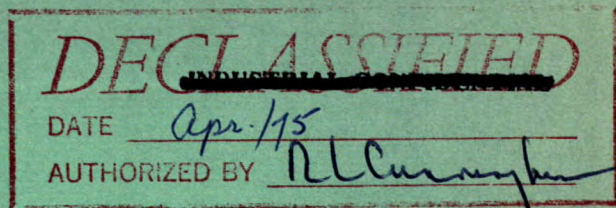


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OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 67-64

**THE EVALUATION OF IRON OXIDES FOR  
'HARD' FERRITE MANUFACTURE ON  
BEHALF OF THE NORTHERN PIGMENT  
COMPANY LIMITED,  
NEW TORONTO, ONTARIO**

by

**NORMAN F. H. BRIGHT,  
JOHN F. ROWLAND AND RICHARD H. LAKE  
MINERAL SCIENCES DIVISION**

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Norman F.H. Bright, John F. Rowland and Richard H. Lake\*

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SUMMARY OF RESULTS

Iron oxides manufactured by Northern Pigment Company Limited, New Toronto, 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. A group of iron oxides from competitive manufacturers was examined similarly and found, in general, to give equivalent performance to various Northern Pigment grades. A final assessment of all the oxides must await the results of magnetic tests.

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## INTRODUCTION

As mentioned in an earlier Mines Branch Investigation Report<sup>(1)</sup>, considerable interest was expressed by Northern Pigment Company Limited, New Toronto, Ontario, manufacturers of iron oxides for pigments and other purposes, during the latter half of 1964, in having a programme of work on iron oxides, intended for use as raw materials in ferrite manufacture, initiated in the Mines Branch in order to provide a centre of "know-how" concerning ferrite technology in Canada. It was felt that such a programme, if initiated, should preferably be a co-operative one, with Northern Pigment personnel contributing some portions of the experimental work involved, and with Mines Branch personnel being responsible for other facets of the study. The division of labour would be decided upon by mutual agreement among the persons concerned and would be dependent upon the experimental facilities available at the two locations involved. At that time, however, certain more immediate "ad hoc" problems at Northern Pigment intruded themselves and the solution of these problems<sup>(1)</sup> prevented any attack then on the wider programme.

Early in 1966, however, it became possible to embark upon this programme and a "modus operandi" was decided upon by discussions involving the senior author of this report and the technical personnel of Northern Pigment. It was decided to divide the work into two main categories: (a) that related to the technology of "hard" or permanent-magnet-type ferrites, based upon the barium hexaferrite composition, and (b), that related to the technology of "soft" ferrites, based upon the mono-ferrite or spinel-type structure and composition. This report represents, in large measure, the completion of the Mines Branch contribution to phase (a) of this programme. It was found possible during the course of work, to make a public presentation and publication of some of the results of the work at the 1967 Annual Meeting of the Canadian Ceramic Society<sup>(2)</sup>. The present report will be an amplification and completion of the work presented on that occasion, and will also include certain material which was not conveniently presentable at such an occasion.

Concurrently with this work, a more fundamental and largely independent study of ferrite science and technology has been in progress in the Mines Branch. One publication and several reports on this work have already been prepared and others are envisaged ultimately<sup>(3, 4, 5, 6, 7)</sup>. It was felt that the co-operative Northern Pigment/Mines Branch programme on iron oxides for ferrite technology and the "in-house" Mines Branch programme would be of mutual benefit to one another.

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\*For references, see pages 36 and 37.

Certain aspects of the co-operative programme, and, in particular the magnetic testing of the samples prepared, which is to be conducted by Northern Pigment, are not yet completed. The results of this will be made available to the recipients of this document in supplement form.

The main objective of the work has been to investigate the variation of reactivity of various grades of iron oxide, of both Northern Pigment and competitive manufacture, in the formation of barium hexaferrite, and to determine, if possible, some means of assessing this reactivity without the necessity of going through the process of making and testing magnetically a finished ferrite ceramic piece. It was hoped to define the desirable parameter(s) in an iron oxide that would make it a satisfactory raw material for the manufacture of "hard" ferrites.

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, thus, of interest to manufacturers both of iron oxides and of ferrites. The present report deals mainly with some of the methods used in the Mines Branch in assessing the physical and chemical behaviour of iron oxides intended for use in "hard" 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 at various times to indicate the physical characteristics of iron oxides.

In this work, an attempt has been made to relate the physical properties of iron oxides with their chemical reactivity behaviour in the formation of barium hexaferrite. X-ray diffraction analysis and the thermal behaviour were employed as the main experimental tools in studying the variation of reactivity from one sample to another. Surface area and particle size and shape measurements, along with certain other parameters, were included within the scope of the study for correlation purposes.

The work, which has extended over the past year-and-a-half, may be divided into three main sections. The first deals with tests made on a group of four different sets of Northern Pigment oxides, each set containing samples that had received a range of calcination treatments, the second with a group of nine further sets of Northern Pigment oxide samples, one being a duplicate of an earlier set, included for comparison and consistency-

of-behaviour assessment. The third group of sets of samples was made mostly using iron oxides from competitive manufacturers, namely, C.K. Williams Ltd., and Columbian Carbon; again, a set incorporating the same Northern Pigment oxide was included for comparison purposes. A description will first be given of the experimental techniques used in the investigation; the results of the tests made will be presented. The report concludes with the deductions to be drawn from the results of the tests.

## EXPERIMENTAL TECHNIQUES EMPLOYED

These techniques can be divided into three categories, viz., those applied to the iron oxides or to barium carbonate as individual raw materials, those applied in the preparation of the mixes and calcines, and those applied to the iron oxides in admixture with barium carbonate, i. e., the mixes used in the preparation of barium ferrite.

### A. Tests on the Raw Materials

#### 1. Measurements of Size and Shape of Iron Oxide Particles

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.

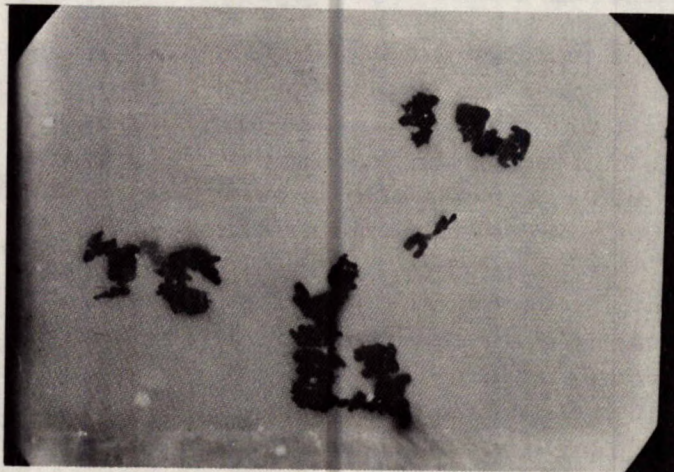
Electron microscopy and, in some cases, optical microscopy have been used for particle-size distribution determinations. Sedimentation and centrifugal methods also can be used for particle-size analysis, although care must be taken in interpreting such results, since neither method will distinguish between 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. The procedure consists of:

- (a) Preparing a well-dispersed suspension of the iron oxide, using an alkyd resin and xylene.
- (b) Transferring to a sedimentation cell.
- (c) Noting the variation of the per cent absorption values with time as the suspended particles fall through 1.25 cm.



(a)



(b)

Figure 1. Electron micrographs of two types of iron oxide:

(a) acicular shape

(b) irregular shape

(Magnification: X10,000)

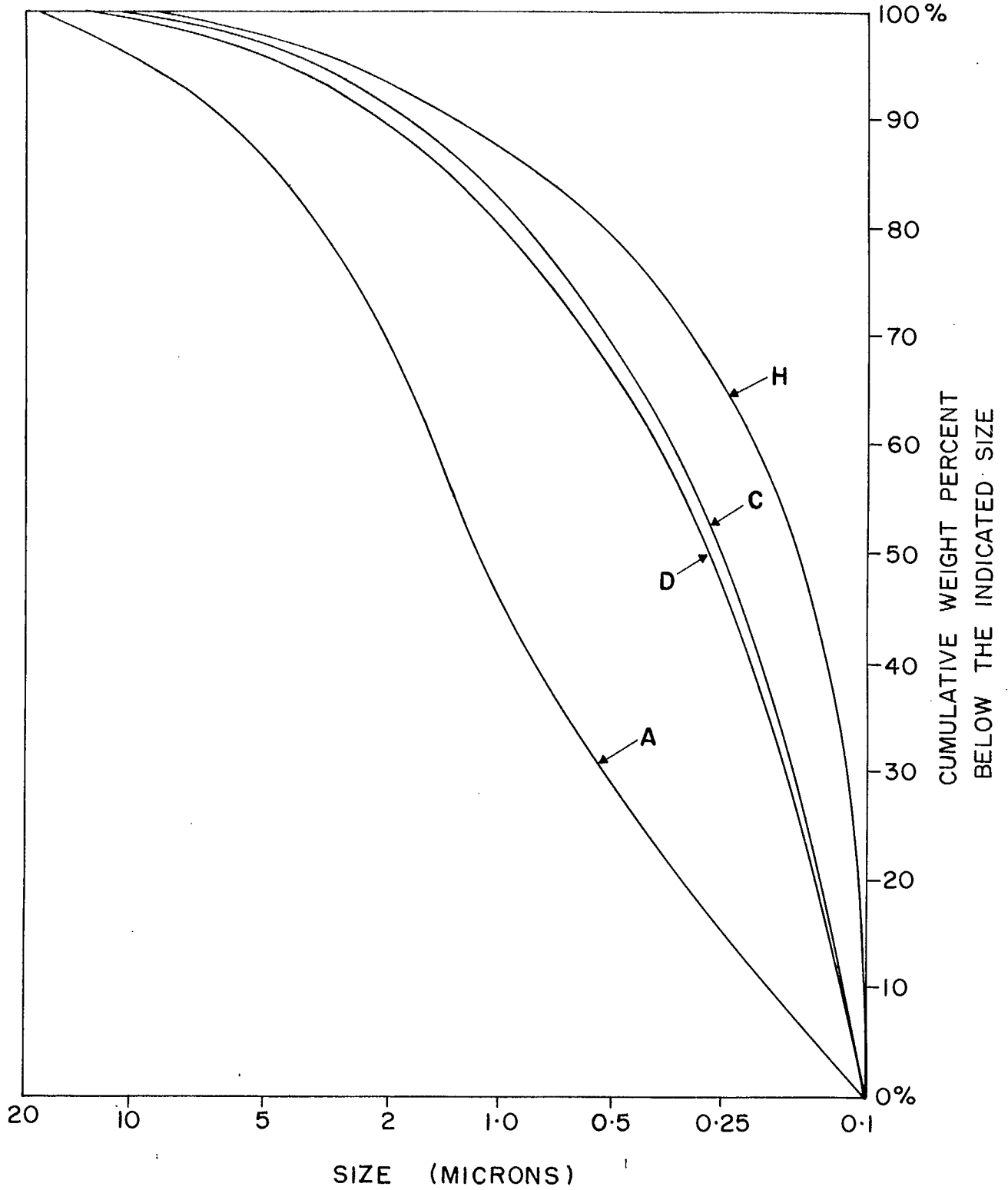


Figure 2. Particle-size Distribution of Four Grades of Iron Oxides Used in Various Compositions .  
(The letters on the curves indicate the mixes in which the particle oxides were used).



Using this particular apparatus, the per cent light-absorption reading, corresponding to a 0.5 micron particle diameter, is obtained in about seventy minutes.

The principles involved in this technique of particle-size determination are:

- (a) In the suspension, the particles fall at rates in proportion to their size (Stokes' Law).
- (b) The particles fall as though they were spheres of the same weight.
- (c) The light obscured by a given weight of particles in suspension has a definite relation to the size of the particles.

The method does not yield absolute values but merely relative figures, useful for practical applications.

Sedimentation methods were not sufficiently sensitive, however, to show differences between fairly similar oxides that could, in fact, be distinguished from one another by thermoanalytical methods, when the oxides were incorporated into ferrite compositions, as will be seen later in this report.

## 2. Barium Carbonate Particle-Size Measurement

Arising out of the discussions in the course of the work, it was pointed out that the use of differential thermal analysis (D.T.A.), thermogravimetric analysis (T.G.A.), or other techniques for assessing the relative reactivities of various grades of iron oxides vis-à-vis barium carbonate in the formation of barium hexaferrite, would only be valid if the barium carbonate itself could be treated as a constant factor and, in particular, did not show any significant variation in particle or aggregate size when precipitated in the presence of various grades of iron oxides. It was, therefore, thought advisable to conduct some high-magnification microscopy on the various mixes to see whether there was any significant variation in the barium carbonate size or shape. The results showed that there was, in fact, no significant variation in particle size and shape. The precipitated barium carbonate particles were all of more or less equant dimensions and exhibited a particle size that lay very largely in the 3-6 micron range. Details of the results obtained will be given later.

## 3. Surface-Area Measurements

The surface areas of the iron oxides were determined using a Perkin-Elmer Sorptometer by Mr. A.A. Winer, Mineral Processing Division, Mines Branch.

#### 4. Tap Densities

The tap density of certain grades of the iron oxides was determined by standard procedures in the Northern Pigment laboratories. No experimental results are quoted in the present report.

#### B. Preparation of the Mixes

Two techniques were employed in the preparation of the mixes. This work was done in the Northern Pigment laboratories.

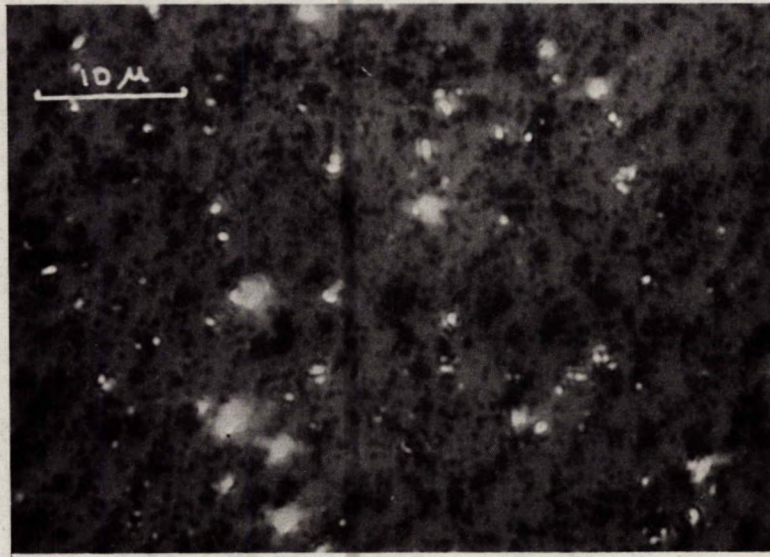
##### (1) Wet-mixing Method

Stoichiometric quantities of either  $\text{BaCO}_3/6 \cdot 0\text{Fe}_2\text{O}_3$  or  $\text{BaCO}_3/5 \cdot 5\text{Fe}_2\text{O}_3$ , as desired, were mixed for fifteen minutes in a Waring Blender. Fisher "Technical Grade" barium carbonate and the appropriate Northern Pigment or competitive iron oxide were used. The quantities employed were 200 g of solids and 500 ml of water.

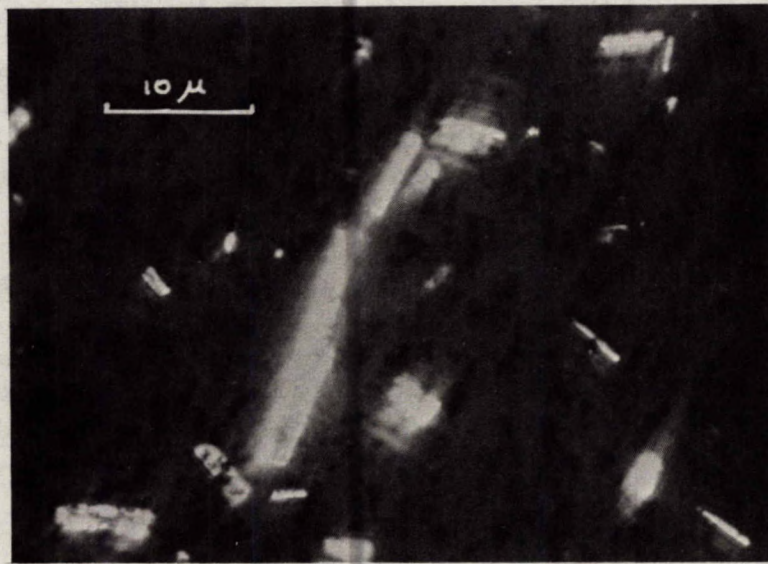
##### (2) Precipitation Method

In this method, a stream of  $\text{CO}_2$  was passed through a constantly-stirred slurry of the appropriate iron oxide in the desired quantity in a 0.3 M solution of Fisher "Reagent Grade" barium nitrate. After several tests, it was found that, by maintaining a pH value of 9 or 10 by ammonia addition, faster precipitation rates could be achieved. Alternatively, an ammonium bicarbonate solution could be used as the precipitant. About 90 minutes were required to precipitate a 200 g mixture. After the precipitation was complete, as determined by the absence of any  $\text{Ba}(\text{NO}_3)_2$  in the solution, the slurry was filtered through a No. 1 Whatman filter on a Buchner funnel; the precipitate was washed thoroughly and dried overnight in an oven at  $120^\circ\text{C}$ . This method yielded a more intimate mixture of iron oxide and barium carbonate than did 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 3a and 3b. The barium carbonate particle agglomerates in the precipitated mixtures were of equant shape with a size range of 3 to 6 microns (See Figure 3a). In contrast, in the wet-mixed samples, the barium carbonate particle agglomerates appeared as long needles, up to twenty microns long with a cross dimension of 1 to 4 microns, as illustrated in Figure 3b. 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 observed following a given method of mixing, are attributable mainly to the variations in the physical characteristics of the iron oxides.



(a)



(b)

Figure 3. Optical photomicrographs of  $\text{BaCO}_3/\text{Fe}_2\text{O}_3$  mixes made by:

(a) Precipitation mixing

(b) Wet-mixing in Waring Blender

Magnification as indicated  
Partly polarized light used

### (3) Calcination of the Mixes

The mixes, after drying, were calcined at a range of temperatures, including, in various instances, 750°C, 950°C, 1000°C, and 1100°C for 30 minutes, or at 1200°C for 2 hours. The calcinations were conducted in air in a Globar-heated kiln. The heating rate employed was 200 to 250 deg C per hour, while the cooling rate was about 40 deg C per hour. The calcinations were done in the Northern Pigment laboratories. Samples of all products were sent to the Mines Branch for examination there, while other portions of the same materials were retained at Northern Pigment for magnetic testing, etc., at a later date.

### C. Tests on the Mixes

#### (1) X-ray Diffraction Studies

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  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , 3.71 Å for  $\text{BaCO}_3$ , 2.69 Å for  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ . This procedure is not better than semi-quantitative insofar as accuracy is concerned, since it is really the peak area that is a measure of the material producing it; any shape factor has thus been neglected. In addition, any materials present at less than 5% of the total sample may very well not be detected at all, and certainly could not be estimated, even semi-quantitatively. The magnitude of the peaks, thus determined and detailed later, should be compared only for one given compound at a time. There is no relation between the size of the peaks of different compounds, either within one sample or from sample to sample. This arises from the different scattering powers of various atoms for X-rays and from the differences in crystal symmetry of the various compounds involved. In all cases, the figures should be considered as relative only within one set of samples and for one particular compound, at the various calcination temperatures.

At one stage in the investigation, it was the hope of the Northern Pigment personnel that the X-ray line-broadening technique might be used as a means of estimating the barium ferrite crystallite size and, perhaps, thus provide additional information on the relative reactivity of various grades of iron oxide. In reply to this enquiry, the following excerpt from a letter dated November 24, 1966 by one of us (J.F.R.) indicates that little success in this regard was to be expected.

"With regard to your question as to whether line-broadening has been observed in the recent X-ray diffraction studies of samples from the Ferrite Manufacture program, the answer is no. It is difficult to assess this phenomenon in peaks of low intensity, but no evidence of line-broadening was observed in any of the peaks that are clearly resolved from the background."

"Our previous experience with correlating line-broadening with crystal size has been limited to the interpretation of powder films, and this work was not too fruitful. It is probable that the use of diffraction charts would make a similar investigation even less reliable, due to the interference of background variations with broadened and depressed peaks. These difficulties, combined with the absence of detectable line-broadening in the samples already examined, suggest that this technique would not be useful."

"It is probable that the use of electron diffraction methods would be useful for crystal-size determinations, although we are not certain whether you refer to electron microscope photographs or electron diffraction patterns. The former technique has been used successfully for similar problems at the Mines Branch."

The use of dark-field electron microscopy for the measurement of crystallite size in ferrite samples has been discussed by Smith and Sutarno<sup>(4)</sup>.

In the X-ray powder diffraction work, it was observed that, in the samples calcined at 750°C and at 950°C, lines were present that could not be attributed to any known compound(s). It is suspected that these compound(s) might well be barium ferrites of  $\text{BaO}:\text{Fe}_2\text{O}_3$  molar ratio intermediate between 1:1 and 1:6 e.g., 1:2 or 1:4, possibly. There are insufficient data at present to solve this aspect of the problem but such an explanation would, at least in part, account for the fact that the barium carbonate starts to disappear from the mixture sooner than the barium hexaferrite appears to be formed.

It was agreed that a study of the  $\text{BaO}-\text{Fe}_2\text{O}_3$  phase system and, in particular, the examination of the existence of ferrites intermediate between  $\text{BaO}.\text{Fe}_2\text{O}_3$  and  $\text{BaO}.6\text{Fe}_2\text{O}_3$ , the two well-established compounds in this system, would be worthwhile. A start has been made on this study using the co-precipitation technique. It is reasonably certain that some intermediate compound(s) exists, but the composition is not yet known. It is known that there are significant differences between the three systems that give rise to commercially interesting hexaferrites, namely  $\text{PbO}-\text{Fe}_2\text{O}_3$ ,  $\text{SrO}-\text{Fe}_2\text{O}_3$  and  $\text{BaO}-\text{Fe}_2\text{O}_3$ . This study will be made at the Mines Branch as time and opportunity permit.

## 2. Differential Thermal Analysis (D.T.A.)

Differential thermal analysis was done using an equipment constructed by one of us (R.H.L.) at the Mines Branch, Ottawa. A heating rate of 12 deg C per minute up to 1200°C was employed. All tests were done in an air atmosphere. In the D.T.A. work also, an attempt was made to put the results on a semi-quantitative basis by estimating the size of certain diagnostic peaks, correcting to a constant weight of sample, and using the area of the peak as a measure of the amount of compound causing it. The peaks used were:-

- (i) The lower of two crystal-transition endothermic peaks that occur with barium carbonate. The upper-temperature peak, at 978°C, observable with barium carbonate alone, was not used here, since, when the appropriate temperature is reached, most if not all of the barium carbonate has reacted. The peak used occurs in the 825-835°C range. The difficulty in this case is the uncertainty of the choice of a base line from which to measure the size of the peak. The profile of the peak was cut out and weighed as a measure of its area.
- (ii) For estimating the amount of  $\alpha$ -hematite present, the small endothermic, Néel-temperature peak at about 690°C was used. This corresponds to the anti-ferromagnetic→paramagnetic transition in the hematite lattice. This is only a very small peak and, hence, the accuracy obtainable is low.
- (iii) For estimating the amount of ferrite formed, the small, endothermic Curie-temperature peak, occurring at about 460°C, was used. This again is a very small peak, resulting in only poor accuracy of estimation.

Again, in comparing the results, one should consider as valid only the relative values for a given compound for a given set of samples at the various temperatures studied. The absolute values quoted later in this report are not significant.

### 3. Thermogravimetric Analysis (T.G.A.)

In the thermogravimetric tests on these materials, a Stanton Thermobalance was used with a heating rate of 6 deg C per minute in an air atmosphere, up to about 1250°C.

The only information obtainable from the thermogravimetric studies of these mixes is the weight loss which each sample undergoes at various temperatures as it is gradually heated. Except for those mixes involving the uncalcined hydrated iron oxide 319X (see later), it has been assumed that the weight loss at any given temperature was due entirely to CO<sub>2</sub>-loss from barium carbonate, and thus represented the proportion of barium carbonate decomposed in that heating of the sample.

One must be careful here to distinguish between the barium carbonate present in the sample as supplied to the Mines Branch, which is the material that will give rise to the weight losses in the T.G.A. tests, and the barium carbonate that had already been decomposed in the calcinations conducted at Northern Pigment before sending to the Mines Branch for T.G.A. examination. The total CO<sub>2</sub> loss of the uncalcined materials is a measure of the barium carbonate originally present in the mix. The difference between this figure and the T.G.A. loss obtained in the Mines Branch test will, therefore, represent the amount of barium carbonate that has reacted during the calcination. Since it was shown that, in the main, the barium carbonate itself, in the precipitation mixes at least, is a constant factor, it follows that the variations

of weight loss from one sample to another after a given calcination treatment will be a measure of the reactivity of the grade of iron oxide used in that particular mix. It should be borne in mind, however, that this is only one means of assessing this reactivity and does not, in fact, represent the rate of formation of ferrite, merely the rate of disappearance of the barium carbonate. An accurate measure of the rate of formation of ferrite, and its variation from sample to sample, could be obtained only from the magnetic measurements that are to be conducted later by Northern Pigment.

Thus, T.G.A. is the only technique that can be considered as giving any accurate quantitative estimate of amount of reaction, but it must be remembered that this estimate refers only to the barium carbonate and gives no information whatsoever concerning the disappearance of the iron oxide or of the formation of the barium hexaferrite, both of which processes occur without change of weight.

Reference has been made above to the hydrated Northern Pigment oxide Grade 319X. In interpreting the T.G.A. results obtained with mixes containing this oxide, a special procedure was necessary.

This oxide was assigned the nominal formula of  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  since it was found by X-ray diffraction to be composed of goethite ( $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). On examination by D.T.A., it was found to lose its water of combination in two closely-overlapping stages, proceeding at their greatest velocity at about  $350^\circ\text{C}$ . The water-loss appeared to be complete below  $500^\circ\text{C}$ . On examination by T.G.A., however, there appeared to be an indication of a further small weight loss taking place at around  $700^\circ\text{C}$ . According to the D.T.A. test, the dehydration apparently yielded some  $\gamma$ -hematite, which, at higher temperatures, reverted to  $\alpha$ -hematite. It may be that this "higher-temperature" weight loss is due to this  $\gamma \rightarrow \alpha$ -hematite reaction, since it has been widely held that  $\gamma$ -hematite is not, in fact, an anhydrous  $\text{Fe}_2\text{O}_3$ , but rather a slightly hydrated body, possibly having a formula such as  $\text{H}_2\text{O} \cdot 5\text{Fe}_2\text{O}_3$ . In support of this, it is known that  $\text{H}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ , or  $\gamma$ -alumina, has a spinel-type structure very closely similar to that of  $\gamma$ -hematite, which is crystallographically related to magnetite,  $\text{Fe}_3\text{O}_4$ , but, chemically, behaves as hematite,  $\text{Fe}_2\text{O}_3$ . These observations point out the need for an accurate knowledge of the true degree of hydration of this yellow oxide 319X, if it is to be used as a basis for ferrite manufacture. Such a knowledge is necessary for the accurate control of the stoichiometry of any mix involving it.

In this work, in making calculations involving the stoichiometry of mixes containing this oxide, the arbitrary assumption was made that all loss of weight below  $500^\circ\text{C}$  was due to  $\text{H}_2\text{O}$  from the oxide, and that all loss of weight from the  $\text{BaCO}_3$ /iron oxide mix above  $500^\circ\text{C}$  was due to  $\text{CO}_2$  loss from the carbonate. The former is most probably strictly true; the latter is probably not strictly true but the use of this assumption will not lead to results that are seriously in error. Samples, untreated and also calcined

at a range of temperatures, were examined on the thermobalance. From the TGA charts, 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 the original BaCO<sub>3</sub> present, and valid comparisons could no longer be made among the various samples on the basis of such a small amount of residual carbonate. By 1000°C, no barium carbonate remained undecomposed in any of the mixes; it was therefore, not necessary to conduct TGA tests on any of the samples that had been calcined either at this temperature or at 1100°C or 1200°C.

### EXPERIMENTAL RESULTS

As mentioned earlier in this report, a group of four sets of samples was examined first. These were all Northern Pigment oxides, as follows:-

- (1) Grade 533V, Lot No. 505.
- (2) Grade 533V, Lot No. 628.
- (3) Grade E-41, Lot No. 5050.
- (4) Grade 4000, Lot No. 178.

These were all made into 1/6.0 BaCO<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> mixes by the precipitation method, which were labelled A, B, C and D, respectively.

In the second group of nine sets of samples, the following Northern Pigment oxides were included, the mix labels being as indicated.

- (1) Grade 319, Lot No. 520; Mix E
- (2) Grade 319, Lot No. 520; Mix F

Note: Mix F and the remaining members of both this and the later groups were all made at a nominal 1/5.5 BaCO<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> ratio, instead of at the 1/6.0 value, as heretofore.

- (3) Grade 4000, Lot No. 16; Mix G
- (4) Grade 403, Lot No. 543; Mix H
- (5) Grade E-41, Lot No. 609; Mix I
- (6) Grade 533V, Lot No. 628; Mix J

Note: This is the mix that was included for comparison purposes against the behaviour of the same material in Mix B.

- (7) Grade 533V, Lot No. 505; Mix K

Note: This may also be used for comparison against Mix A.



(8) Grade 533V, Lot No. 628; Mix L

(9) Grade 4000, Lot No. 16; Mix M

Note: These last two mixes, L and M, were made by the wet-blending procedure, in contradistinction to all the others, which were made by precipitation-mixing.

The details of the particle size and shape, and surface area of the oxides, and of certain characteristics of the mixes made containing these oxides, are given in Table 1.

In Table 2, the corresponding details for the competitive oxides are supplied, where these are known. These samples were as follows:

(1) C.K. Williams, Grade 1265; Mix N

(2) C.K. Williams, Grade 3098; Mix O

(3) C.K. Williams, Grade 5098; Mix P

(4) C.K. Williams, Grade 9998; Mix Q

(5) Northern Pigment Oxide, Grade 533V, Lot No. 628; Mix R

(6) Columbian Carbon, Grade 110-2; Mix S

Note: Mix R was again included for comparison purposes.

In this series of experiments, the calcinations at 1000°C and 1100°C were each split into two portions, one portion being calcined for 15 minutes and the other for one hour, as compared with the 30-minute figure used in the earlier series. This was done in the hope of assessing the effects, if any, of time of calcination on the various grades.

The results of the X-ray examinations for Samples A to M, inclusive, are given in Table 3, while those for Samples N to S, inclusive, are given in Table 4. It will be noted that no samples having received 30 minutes calcination at 950°C were supplied for the latter group of oxides and, hence, no comparisons with the behaviour of the earlier sets at this temperature are possible. The figures given in Table 4 are the sum of two completely independent sets of measurements. Since these figures represent relative intensities only, this is a quite legitimate procedure. In general, the reproducibility between the two sets was good and exhibited a high degree of self-consistency.

The D. T. A. results obtained with the first two groups of samples are given in Table 5, while Table 6 gives the equivalent results for the more recent group of samples incorporating the competitive oxides. It will be observed in Table 6 that, for the Sample S, three sets of results are recorded for the  $\text{Fe}_2\text{O}_3$  contents; this was done in order to substantiate the somewhat unusual behaviour of this mix, in that the presence of significant amounts of  $\text{Fe}_2\text{O}_3$  persisted even up to the highest temperatures and longest times of calcination.

T A B L E 1

Details of Sample Mixtures Studied

Sample Mix Identification	I r o n   O x i d e   D e t a i l s					Molar Ratio of $\text{BaCO}_3:\text{Fe}_2\text{O}_3$ used	Mixing Technique used for ferrite formation	Diametral Shrinkage of $\text{BaCO}_3:\text{Fe}_2\text{O}_3$ pellet when heated to $1150^\circ\text{C}$ for 2 hours (%)
	Grade	Lot	Particle Shape	Average Particle Size ( $\mu$ )	Surface Area ( $\text{m}^2/\text{g}$ )			
A	533V	505	Acicular	1.1	2.1	1:6.0	Precipitation	Not determined
B	533V	628	Acicular	1.1	2.1	1:6.0	do	do
C	E-41	5050	Acicular	0.5	5.9	1:6.0	do	do
D	4000	178	Irregular	0.6	4.7	1:6.0	do	do
E	319	520	Acicular	0.3	20.0	1:6.0	do	6.5
F	319	520	Acicular	0.3	20.0	1:5.5	do	6.0
G	4000	16	Irregular	0.6	4.6	1:5.5	do	17.7
H	403	543	Acicular	0.4	9.0	1:5.5	do	19.3
I	E-41	609	Acicular	0.5	5.9	1:5.5	do	14.6
J	533V	628	Acicular	1.1	2.1	1:5.5	do	13.5
K	533V	525	Acicular	1.1	2.1	1:5.5	do	13.7
L	533V	628	Acicular	1.1	2.1	1:5.5	Wet Blending	12.3
M	4000	16	Irregular	0.6	4.6	1:5.5	do	13.7

TABLE 2

## Details of Competitive Iron Oxide Samples Studied

Sample Mix Identification	Iron Oxide Details						Molar Ratio of BaCO <sub>3</sub> :Fe <sub>2</sub> O <sub>3</sub> used	Mixing Technique used for ferrite Preparation	Diametral Shrinkage of BaCO <sub>3</sub> :Fe <sub>2</sub> O <sub>3</sub> pellet when heated to 1250°C for 2 hours (%)
	Manufacturer	Grade	Lot	Particle Shape	Average Particle Size (μ)	Surface Area (m <sup>2</sup> /g)			
N	C.K. Williams	1265	-	Spherical		6.0	1:5:5	Precipitation	
O	C.K. Williams	3098	-	Spherical		7.0	1:5:5	Precipitation	
P	C.K. Williams	5098	-	Spherical		5.1	1:5:5	Precipitation	
Q	C.K. Williams	9998	-	Spherical		2.4	1:5:5	Precipitation	
R	Northern Pigment	533V	628	Acicular	1.1	2.1	1:5:5	Precipitation	13.5
S	Columbian Carbon	110-2	-	Spherical		5.4	1:5:5	Precipitation	

TABLE 3 - X-ray Diffraction Examination of Ferrite Samples

Heat treatment given to sample	Constituent estimated and X-ray line used	A	B	C	D	E	F	G	H	I	J	K	L	M	
Mix as received	BaCO <sub>3</sub> (3.71 Å) Fe <sub>2</sub> O <sub>3</sub> (2.69 Å)	24	22	22	23	17	19	28	26	22	18	21	17	13	
No heat treatment	Fe <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O(4.17 Å) BaO.6Fe <sub>2</sub> O <sub>3</sub> (2.77 Å)	50	47	45	47	Probably nil	Probably nil	52	48	49	56	38	53	47	
30 min at 750°C	BaCO <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O BaO.6Fe <sub>2</sub> O <sub>3</sub>	17	13	17	5	Present?	Present?	9	9	19	16	17	19	15	
		50	47	46	41	39	38	44	44	46	43	49	58	52	
		-	-	-	-	-	3	-	-	-	-	-	-	-	
		-	-	2	2	-	-	-	-	-	-	-	-	-	
30 min at 950°C	BaCO <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O BaO.6Fe <sub>2</sub> O <sub>3</sub>	-	5	9	12	5	16	22	10	24	15	9	21	27	
		-	-	-	-	-	-	-	-	-	-	-	-	4	
		32	32	25	32	27	33	29	21	18	24	18	9	30	
30 min at 1000°C	BaCO <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O BaO.6Fe <sub>2</sub> O <sub>3</sub>	-	5	3	5	7	13	7	5	17	16	-	4	-	
		-	-	-	-	-	-	-	-	-	-	-	-	-	
		35	34	34	35	37	45	33	33	21	32	26	43	30	
30 min at 1100°C	BaCO <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O BaO.6Fe <sub>2</sub> O <sub>3</sub>	No Samples Prepared				-	12	9	3	5	7	-	2	-	
		No Samples Prepared				-	39	46	43	46	42	35	39	52	44
2 hours at 1200°C	BaCO <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O BaO.6Fe <sub>2</sub> O <sub>3</sub>	No Samples Prepared				-	11	2	-	-	-	-	-	-	-
		No Samples Prepared				-	48	50	51	38	37	37	23	50	35

These figures reported represent peak heights in arbitrary units.

TABLE 4. X-ray Diffraction Examination of Ferrite Samples  
Made from Competitive Oxides

Note: Ferrite =  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ ; 3.71 Å line used for  $\text{BaCO}_3$ ; 2.69 Å line used for  $\text{Fe}_2\text{O}_3$ ; 2.77 Å line used for ferrite

Heat treatment given to sample		Constituent estimated	N	O	P	Q	R	S
Mix as received;		$\text{BaCO}_3$	21	21	24	28	23	32
No heat treatment		$\text{Fe}_2\text{O}_3$	52	46	50	58	51	53
		Ferrite	-	-	-	-	-	-
30 min at		$\text{BaCO}_3$	16	1	8	20	19	11
750°C		$\text{Fe}_2\text{O}_3$	47	41	51	57	61	41
		Ferrite	-	-	-	-	-	-
1000°C	15 min	$\text{BaCO}_3$	-	-	-	-	-	-
		$\text{Fe}_2\text{O}_3$	15	-	5	10	7	10
		Ferrite	34	40	40	35	44	28
1000°C	1 hour	$\text{BaCO}_3$	-	-	-	-	-	-
		$\text{Fe}_2\text{O}_3$	6	-	-	2	-	3
		Ferrite	37	38	33	35	45	31
1100°C	15 min	$\text{BaCO}_3$	-	-	-	-	-	-
		$\text{Fe}_2\text{O}_3$	7	-	-	-	-	6
		Ferrite	47	42	39	43	41	34
1100°C	1 hour	$\text{BaCO}_3$	-	-	-	-	-	-
		$\text{Fe}_2\text{O}_3$	-	-	-	-	-	4
		Ferrite	49	44	41	43	40	33
2 hours at		$\text{BaCO}_3$	-	-	-	-	-	-
1200°C		$\text{Fe}_2\text{O}_3$	-	-	-	-	-	2
		Ferrite	34	39	40	44	46	30

The figures reported represent peak heights in arbitrary units.

TABLE 5. D.T.A. Examination of Ferrite Samples

(Note: All peaks have been scaled to a 600 mg sample. All units are arbitrary).

Heat treatment given to sample	Peak examined	A	B	C	D	E	F	G	H	I	J	K	L	M		
Mix, as received No heat treatment	BaCO <sub>3</sub> (X)	346	390	344	344	136	132	185	119	196	220	153	190	175		
	Fe <sub>2</sub> O <sub>3</sub>	0	0	0	0	7	5	16	7	10	14	17	25	14		
	Ferrite	0	0	0	0	0	0	0	0	0	0	0	0	0		
30 minutes at 750°C	BaCO <sub>3</sub> (Y)	244	184	263	67	25	20	51	28	124	127	118	194	125		
	Fe <sub>2</sub> O <sub>3</sub>	0	0	0	0	23	22	16	17	14	26	24	27	19		
	Ferrite	0	0	0	0	0	0	0	0	0	0	0	0	0		
30 minutes at 950°C	BaCO	0	0	0	0	0	0	0	0	0	0	0	0	0		
	Fe <sub>2</sub> O <sub>3</sub>	0	0	0	0	13	10	5	10	12	7	13	15	0		
	Ferrite	29	28	34	37	17	15	15	9	15	15	10	9	15		
30 minutes at 1000°C	BaCO <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	0		
	Fe <sub>2</sub> O <sub>3</sub>	0	0	0	0	7	6	5	10	12	0	5	0	0		
	Ferrite	35	40	41	40	18	20	14	14	16	20	16	15	17		
30 minutes at 1100°C	BaCO <sub>3</sub>	No Samples Prepared				0	0	0	0	0	0	0	0	0	0	
	Fe <sub>2</sub> O <sub>3</sub>					4	3	0	6	9	0	0	0	0	0	0
	Ferrite					14	24	17	15	13	21	15	20	19		
2 hours at 1200°C	BaCO <sub>3</sub>	No Samples Prepared				0	0	0	0	0	0	0	0	0		
	Fe <sub>2</sub> O <sub>3</sub>					0	0	0	0	0	0	0	0	0	0	0
	Ferrite					16	20	13	11	15	14	14	16	12		
% of original BaCO <sub>3</sub> left after 750°C calcination [ = $\frac{(Y)}{(X)} \times 100$ ] %		70.5	47.2	76.4	19.5	18.4	15.2	27.5	23.5	63.3	57.7	77.1	100+	71.5		

TABLE 6. DTA Results on Ferrite Mixes Containing Competitive Oxides

(Note: All peaks have been scaled to a 600 mg samples. All units are arbitrary.)

Heat treatment given to sample		Peak examined	N	O	P	Q	R	S
Mix as received No heat treatment	BaCO <sub>3</sub> (X)	148		218	202	192	182	181
	Fe <sub>2</sub> O <sub>3</sub>	8	7	18	13	9	9, 8, 8	
	Ferrite	-	-	-	-	-	-	
30 minutes at 750°C	BaCO <sub>3</sub> (Y)	37	7	46	84	79	31	
	Fe <sub>2</sub> O <sub>3</sub>	20	17	22	17	20	19, 20, 20	
	Ferrite	-	-	-	-	-	-	
1000°C	15 minutes	BaCO <sub>3</sub>	-	-	-	-	-	-
		Fe <sub>2</sub> O <sub>3</sub>	7	4	4	7	-	11, 12, 12
	Ferrite	19	22	19	23	25	13	
1000°C	1 hour	BaCO <sub>3</sub>	-	-	-	-	-	-
		Fe <sub>2</sub> O <sub>3</sub>	4	-	1	3	-	9, 7, 7
	Ferrite	16	16	21	20	20	15	
1100°C	15 minutes	BaCO <sub>3</sub>	-	-	-	-	-	-
		Fe <sub>2</sub> O <sub>3</sub>	3	-	-	-	-	6, 6, 5
	Ferrite	16	19	22	18	19	14	
1100°C	1 hour	BaCO <sub>3</sub>	-	-	-	-	-	-
		Fe <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	6, 8, 6
	Ferrite	16	22	21	17	19	18	
2 hours at 1200°C	BaCO <sub>3</sub>	-	-	-	-	-	-	-
	Fe <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	4, 4, 4	
	Ferrite	17	15	11	18	20	14	
% of original BaCO <sub>3</sub> left after 750°C calcination			25.0	3.2	22.8	43.8	43.4	17.1
[ = $\frac{(Y)}{(X)} \times 100$ ] %								

TABLE 7. T.G.A. Results on Ferrite Samples

Heat treatment given to sample	Assessment of Barium Carbonate present	A	B	C	D	E	F	G	H	I	J	K	L	M
Mix, as received	% BaCO <sub>3</sub> originally present, based on anhydrous weight of final ferrite	17.80	17.94	18.16	18.70	18.88	20.63	20.90	21.26	19.24	18.79	19.33	19.10	20.36
No heat treatment	Determined as % CO <sub>2</sub> % of original BaCO <sub>3</sub> still present in sample as supplied	3.97	4.00	4.05	4.17	4.21	4.60	4.66	4.74	4.29	4.19	4.31	4.26	4.54
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
30 minutes at 750°C	% BaCO <sub>3</sub> present, based on anhydrous weight of final ferrite	11.35	10.49	14.04	5.20	7.49	7.09	7.71	8.12	13.05	11.21	12.29	16.95	14.98
	Determined as % CO <sub>2</sub> % of original BaCO <sub>3</sub> still present in sample as supplied	2.53	2.34	3.13	1.16	1.67	1.58	1.72	1.81	2.91	2.50	2.74	3.78	3.34
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	63.8	58.5	77.3	27.8	39.7	34.3	37.0	38.2	68.0	59.7	63.6	88.8	73.7
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	36.2	41.5	22.7	72.2	60.3	65.7	63.0	61.8	32.0	40.3	36.4	11.2	26.3
30 minutes at 950°C	% BaCO <sub>3</sub> present based on anhydrous weight of final ferrite	0.49	0.40	1.26	0.58	1.17	1.17	1.08	1.12	1.03	0.54	0.49	0.58	1.12
	Determined as % CO <sub>2</sub> % of original BaCO <sub>3</sub> still present in sample as supplied	0.11	0.09	0.28	0.13	0.26	0.26	0.24	0.25	0.23	0.12	0.11	0.13	0.25
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	2.78	2.25	6.92	2.70	6.2	5.7	5.2	5.3	5.4	2.9	2.6	3.1	5.5
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	97.22	97.75	93.08	97.30	93.8	94.8	94.8	94.7	94.6	97.1	97.4	96.9	94.5



TABLE 8. T. G. A. Results on Mixes Containing Competitive Oxides

Heat treatment given to sample	Assessment of Barium Carbonate present	N	O	P	Q	R	S
Mix as received	% BaCO <sub>3</sub> originally present, based on anhydrous weight of final ferrite	20.14	19.33	18.88	18.52	19.19	19.42
	Determined as % CO <sub>2</sub>	4.49	4.31	4.21	4.13	4.28	4.33
No. heat treatment	% of original BaCO <sub>3</sub> still present in sample as supplied	100.0	100.0	100.0	100.0	100.0	100.0
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	0.0	0.0	0.0	0.0	0.0	0.0
Calcined for 30 min at 750°C	% BaCO <sub>3</sub> present, based on anhydrous weight of final ferrite	6.77	4.13	6.23	8.83	9.06	5.52
	Determined as % CO <sub>2</sub>	1.51	0.92	1.39	1.97	2.02	1.23
	% of original BaCO <sub>3</sub> still present in sample as supplied	33.6	21.4	33.0	47.7	47.2	28.4
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	66.4	78.6	67.0	52.3	52.8	71.6
Calcined for 15 min at 1000°C	% BaCO <sub>3</sub> present, based on anhydrous weight of final ferrite	0.00	0.49	0.94	0.40	No	0.63
	Determined as % CO <sub>2</sub>	0.00	0.11	0.21	0.09		0.14
	% of original BaCO <sub>3</sub> still present in sample as supplied	0.0	2.5	5.0	2.2	Sample	3.2
	% of original BaCO <sub>3</sub> decomposed in Northern Pigment calcination	100.0	97.5	95.0	97.8	Available	96.8

The T.G.A. results obtained with the first two groups of samples are given in Table 7, while Table 8 gives the equivalent results for the more recent group of samples.

The results presented in the various tables will be discussed in the following section of the report. In the course of the earlier studies, involving Mixes A, B, C and D, the DTA and TGA examinations and the calcination tests were conducted only up to about 1000°C, whereas, in the case of all later mixes, the tests were extended to 1200°C. As a consequence, certain interesting phenomena were observed that were not encountered in the earlier work, viz., in the DTA tests on several grades of barium carbonate/iron oxide mixes and on their calcination products, peaks were observed as follows:-

1. A very small exothermic peak at about 820°C, observable only in the tests on those mixes that had been calcined to 1000°C or higher, in which the BaCO<sub>3</sub> was all decomposed. This peak, therefore, could not be due to the crystal-inversion of residual BaCO<sub>3</sub>.
2. An endothermic peak of varying size (from extremely small to moderate), occurring at 1180°C on heating the sample.
3. An exothermic peak, slightly less sharp in shape, but of equivalent size, occurring at about 1120°C on cooling the sample.

These peaks were attributed to the presence of barium sulphate in the sample; peak 1, above, representing the formation of the BaSO<sub>4</sub> from the barium carbonate (or oxide) and any sulphate impurity. Peaks 2 and 3 represent the α ↔ β crystal transition in BaSO<sub>4</sub>, known to occur at about 1150°C. The magnitude of these peaks varied from sample to sample, depending on the grade of iron oxide used and was as follows.

<u>Mix</u>	<u>Grade of Iron Oxide</u>	<u>Magnitude of BaSO<sub>4</sub> peaks</u>
E.	319X(base stock for 533V)at 1/6 mol. ratio	Fairly large
F.	319X( ditto )at 1/5.5 mol. ratio	Moderately large
G.	4000, Lot 16	Very small
H.	403, Lot 543	Moderate
I.	E-41, Lot 609	} N.B.: - E to K inclusive } were all precipitation } mixes } Made at 1/5.5 mol. ratio } by wet mixing
J.	533V, Lot 628	
K.	533V, Lot 505	
L.	533V, Lot 628	
M.	4000, Lot 16;	
		Very small
		Extremely small
		Nil
		Extremely small
		Extremely small

Although the detection of the presence of barium sulphate in the samples as detailed above was of interest to Northern Pigment, it apparently did not give rise to any serious concern since they were aware that sulphates were present on occasion and that they did not, apparently, seriously affect the behaviour of the product, particularly in the 1/5.5 mol. ratio mixes, which contain a slight excess of BaO over that required for the stoichiometric

hexaferrite. The extreme stability of barium sulphate was considered to be the reason for the lack of deleterious effects due to its presence. The main disadvantage of its presence was that it acted as a slight diluent on the hexaferrite and slightly disturbed the intended Ba:Fe stoichiometry. No action was felt to be necessary at this stage to deal with it.

## DISCUSSION OF RESULTS

In this section of the report, an account will first be given of the interpretation put upon the results obtained with the first group of samples, viz., A to D, inclusive. Any extension or modification of these interpretations and conclusions that became evident from a consideration of the results on samples E to M, inclusive, will next be given. Finally, a comparison between the results obtained with the various grades of competitive oxides, contained in samples N, O, P, Q and S, with the results obtained with Northern Pigment oxides will be given.

Insofar as the results on the first group of samples are concerned, it can be stated that it was possible, from the DTA results, to obtain a reasonable semi-quantitative assessment of the extent to which the barium carbonate had been decomposed at the various calcination temperatures. Somewhat less accurate assessments of the proportions of barium hexaferrite that had been formed and of the disappearance of the hematite at these same temperatures were also obtained.

In general, one may say that, with all samples, little, if any, ferrite had been formed at 750°C, but that, by 950°C, a very substantial amount of ferrite had been formed, while by 1000°C, a still greater amount of ferrite was present. There was, however, a considerable variation from sample to sample in the extent to which this reaction had proceeded. There was an even greater variation in the amount of barium carbonate that had decomposed in the samples calcined at 750°C. A small amount of residual barium carbonate was detectable at 950°C but none at 1000°C in any sample. In the case of Grade 4000, the barium carbonate was already about 72% decomposed in the 750°C-calcined sample, whereas only about 23% was decomposed in the E-41 Grade sample calcined at this temperature. The two samples of the 533V Grade showed intermediate behaviour, with Lot #505 showing more residual BaCO<sub>3</sub> present in the 750°C-calcined sample than did Lot #628. The amount of ferrite formed at 950°C, as compared with that formed at 1000°C being considered as 100% (although the reaction is admittedly incomplete at that temperature), showed that the reaction was most complete for Grade 4000 at 950°C; the variations between the other three grades were less significant.

The X-ray diffraction results confirmed the DTA findings completely insofar as valid comparisons could be drawn. An estimation

of the heights of various diagnostic diffraction peaks was used to give an assessment of the abundance of the various compounds present. With all grades, there was still a small amount of residual hematite, even at 1000°C, confirming the above-mentioned incompleteness of reaction. The Grade E-41 material appeared to show the least degree of ferrite formation and the largest amount of residual hematite in the 950°C-calcined sample.

In the thermogravimetric work, the loss in weight was taken as a measure of CO<sub>2</sub> released from residual barium carbonate. The samples had been dried at 120°C and, therefore, should contain no water; they were never heated to a sufficiently high temperature for measurable oxygen to be lost from the iron oxide. This procedure therefore, gives a quantitative measure of the same factor as was given semi-quantitatively by the DTA and the results obtained by the two techniques were consistent.

It appeared that the thermogravimetric analysis of those samples that had been calcined for 30 minutes at 750°C, yielded a weight-loss figure which provided the best means of classifying the various grades of oxide, since this particular parameter gave by far the greatest spread over the samples tested.

On the basis of the tests performed on Samples E to M, inclusive, there was little, if any, reason to change the foregoing discussion referring to the earlier samples, A to D, inclusive. The hypotheses advanced still appeared to be valid and the most convenient criterion for distinguishing the relative reactivities of various iron oxides in the formation of barium hexaferrite was still considered to be the weight loss as determined by T.G.A. on the samples that had been calcined to 750°C at Northern Pigment.

Insofar as comparisons can be drawn amongst the results obtained by the three techniques, as reported in Tables 3, 5 and 7, it will be seen that the results are almost completely consistent when allowance is made for the inevitable errors and limitations of the various techniques.

Certain aspects of the results are worthy of comment, as follows:

a) Reproducibility of Tests

A survey of the results on the earlier sets of samples, A to D, and of those on the later sets, E to M, shows that there are several direct comparisons of the same lot of the same grade being tested in both groups. The only difference was the use of a 1/6.0 mol. ratio of BaO:Fe<sub>2</sub>O<sub>3</sub> in the earlier sets and a 1/5.5 ratio in the later. Considering the percentage of the original BaCO<sub>3</sub> in the samples decomposed after calcination at 750°C as the measure of reactivity, the higher the figure, the higher being the reactivity of the mix, we see from Table 7 that the following comparisons can be drawn:-

		<u>% BaCO<sub>3</sub> decomposed (TGA)</u>
533V Grade, Lot 505	A	36.2%
ditto	K	36.4%
533V Grade, Lot 628	B	41.5%
ditto	J	40.3%

This indicates a surprisingly good degree of reproducibility of test and strongly validates the test as a means of assessing reactivity of one mix as compared with that of another.

b) Reproducibility of Behaviour of Various Lots of a Given Grade

Since, from the earlier remarks, the test itself has been shown to be valid and reproducible, it can be legitimately used as a criterion of variability within one grade of iron oxide. The comparisons that can be drawn are as follows:

		<u>% BaCO<sub>3</sub> decomposed (TGA)</u>
533V, Lot 505	A	36.2%
ditto	K	36.4%
533V, Lot 628	B	41.5%
ditto	J	40.3%
#4000, Lot 178	D	72.2%
#4000 Lot 16	G	63.0%
E41, Lot 5050	C	22.7%
E41, Lot 609	I	32.0%

It will be seen that there is substantially more variation from one lot to another of a given grade than can be accounted for by the variation to be expected among several tests on a given material. Hence, there is a certain degree of variability of reactivity within any one grade of oxide that should be improved, if possible.

c) Technique of Mixing

The reactivity of a given lot of a given grade of oxide, when mixed with barium carbonate, depends on the mixing technique. Comparison between the reactivities in precipitation mixes and in wet-blending mixes are as follows:-

				% BaCO decomposed (TGA)	
533V. Grade,	Lot 628, 1/5.5 ratio.	Precipitation mix	J		40.3%
	ditto	Wet mix	L		11.2%
#4000	, Lot 16, 1/5.5 ratio.	Precipitation mix	G		63.0%
	ditto	Wet mix	M		26.3%

This gives a strong indication of the enhanced degree of reactivity obtained in the precipitation-mixing technique and is a reflection of the greater intimacy of contact of the reacting species.

Considerable previous experimental work has been reported dealing with solid state reactions in ferrites. From thermal investigations of barium carbonate and iron oxide mixtures, Sadler<sup>(8)</sup> reported that an equation of the type:

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

where  $Y$  = the thickness of the product layer,  
 $t$  = the 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 this compound 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 ferrite(s) richer in BaO than corresponds to the ratio 1:6 might have been formed.

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 this second series of experiments, this supposition was borne out by the much higher percentage weight losses obtained using samples prepared by precipitation mixing than was obtained with wet-mixing of comparable composition.

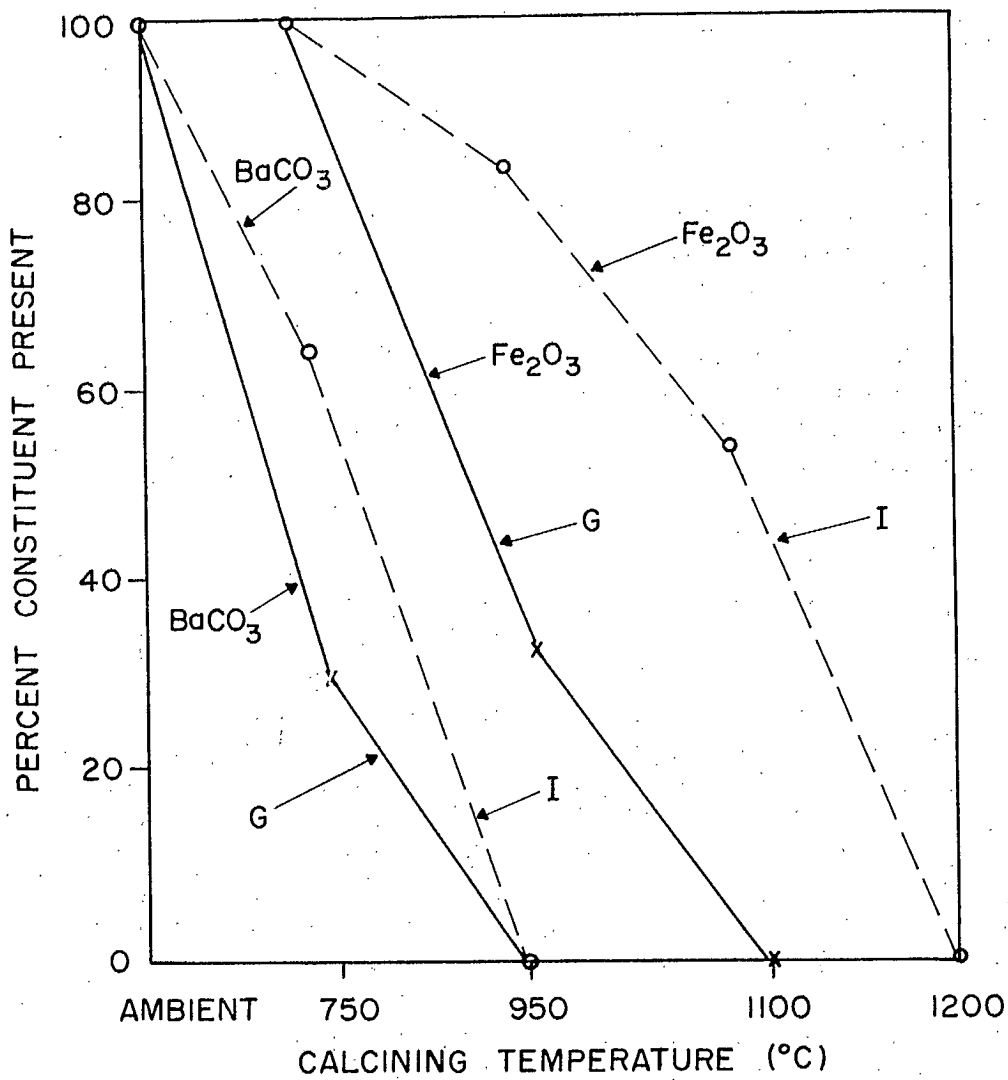


Figure 4a. Plot Showing the Disappearance of BaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> with Temperature as Indicated from the DTA Results.

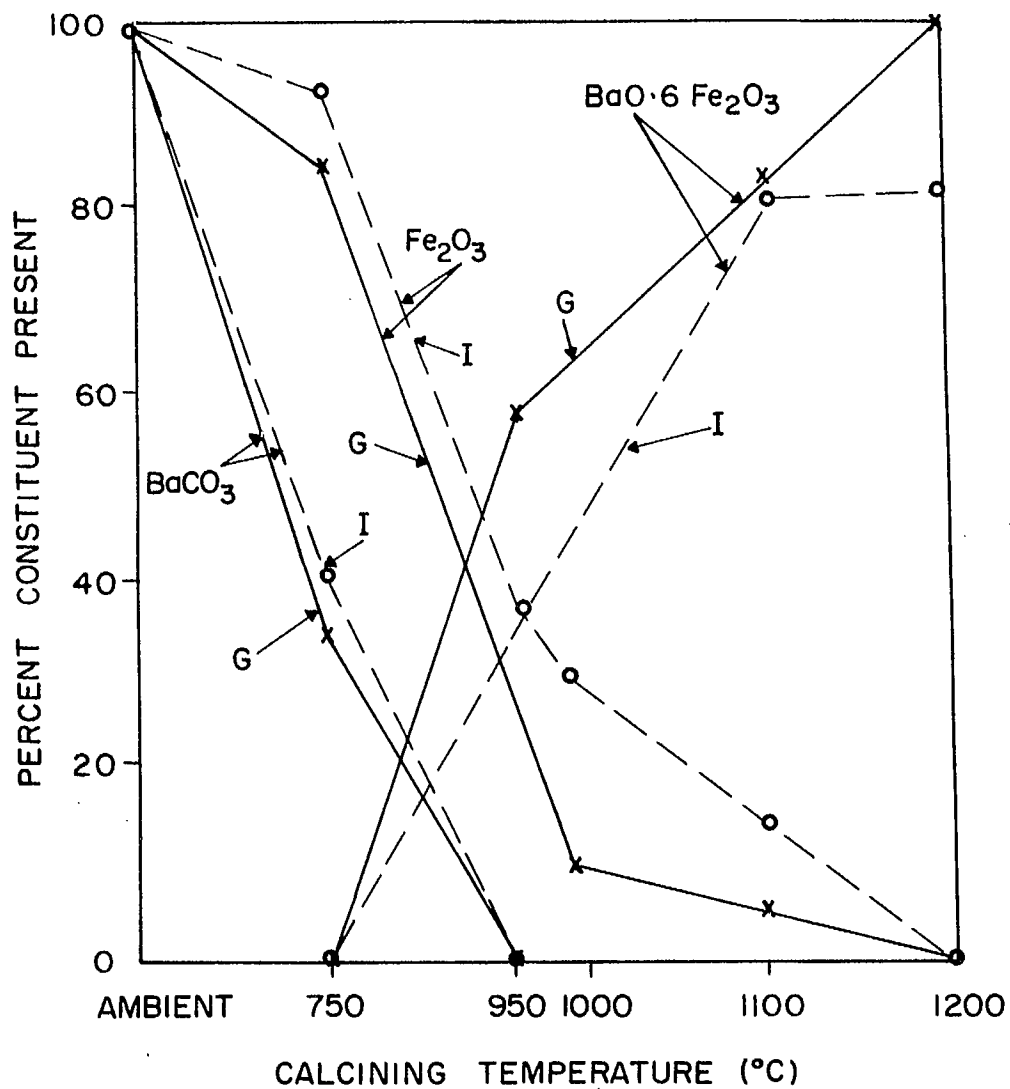


Figure 4b. Plot Showing the Disappearance of BaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> and the Formation of BaO·6Fe<sub>2</sub>O<sub>3</sub> with Temperature, as Indicated by the X-ray Diffraction Results.



(d) Correlation of Results from Samples A to M, Inclusive

In Figures 4a and 4b, 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 typical sets of samples. These mixes, G and I, were made from irregular-shaped (Grade 4000) and acicular-shaped (Grade E-41) iron oxides, respectively. It will be seen that the greater disappearance of  $\text{Fe}_2\text{O}_3$  and  $\text{BaCO}_3$  in Mix I is accompanied by the formation of a larger proportion of ferrite. Since the iron oxides used in the Mixes G and I have about the same surface area (see Table I, page 15), 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 Mixes E, F, H and I, containing either a hydrated iron oxide (Grade 319) or the finer grades of acicular iron oxide (Grades 403 and E-41, respectively), hematite was prominent up to  $1100^\circ\text{C}$  while, in mixes such as J and K, using a coarser acicular iron oxide (Grade 533V), hematite was present only in small quantities even at  $1000^\circ\text{C}$ . It would thus appear that neither size alone nor particle shape alone is the overall controlling factor in determining reactivity.

In Figure 5, 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  $\text{m}^2/\text{g}$  for the various oxides, the diametral shrinkage of pellets formed from the barium carbonate/iron oxide mixtures and fired at  $1150^\circ\text{C}$ , 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  $750^\circ\text{C}$  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 anomalies that will be mentioned shortly. Using a given type of iron oxide, the precipitation mix gave a higher shrinkage than the corresponding wet mix. The shrinkage was increased by 4% by resorting to precipitation mixing in the case of irregularly-shaped iron oxides (Mixes G and M, respectively), while the increase was only 1.2% with acicular oxides (Mixes J and L, respectively).

In considering the various trends apparent from Figure 5, it appears that the shrinkage values, in general, increased with increasing surface area. It was interesting to note the anomalous shrinkage values for Mixes E and F. This is attributed to the fact that the iron oxide (Grade 319) used in Mixes E and F was in the hydrated form.

Mixes C and I, which were made using two different lots of the Grade E-41 oxide, show disproportionately low reactivities as judged by the percentage of barium carbonate decomposed at  $750^\circ\text{C}$ , whereas, from their surface areas and other properties, one would have expected substantially higher figures. These low reactivity figures were strongly supported by

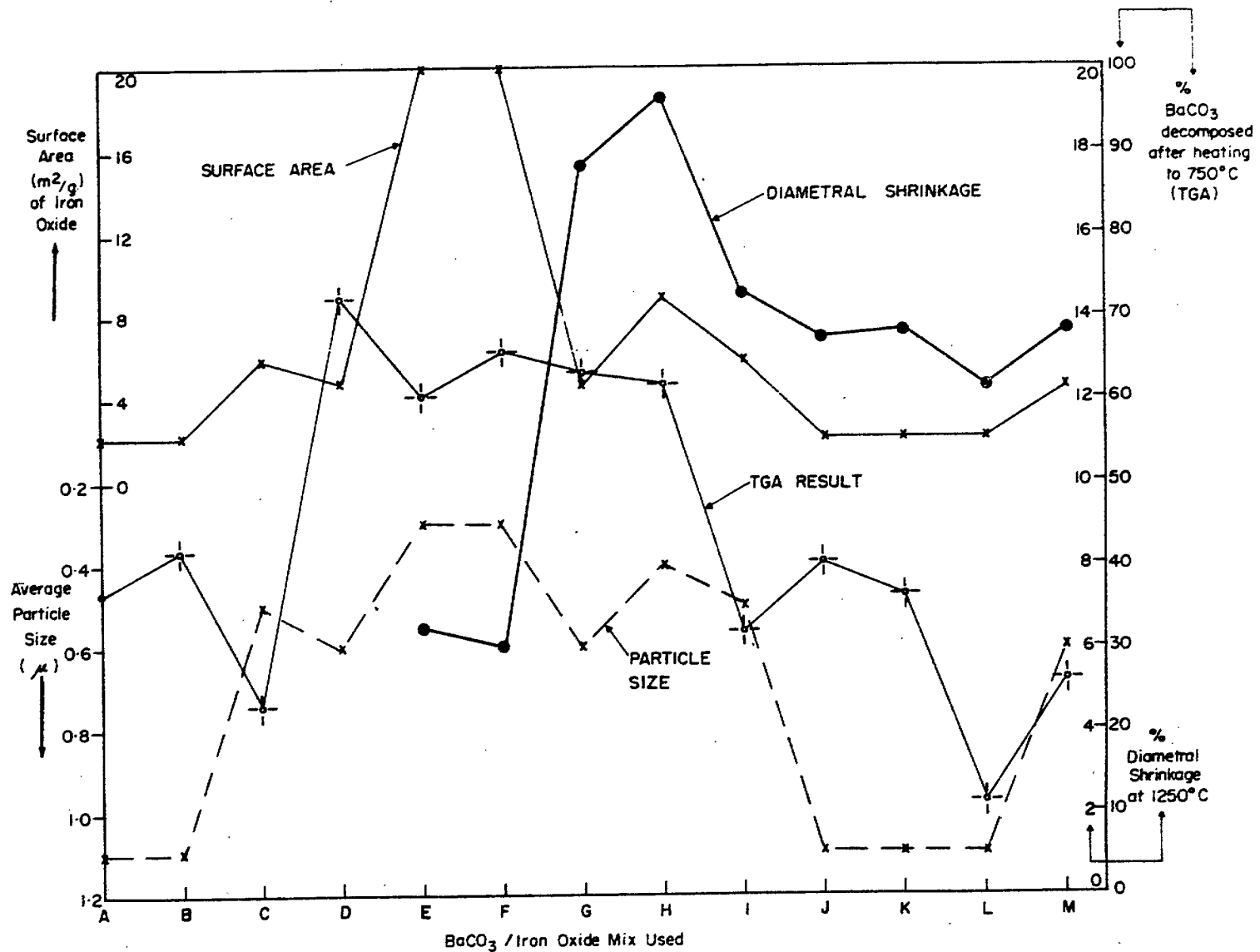


Figure 5. Plot Showing the Variations in Average Particle Size and Surface Area of the Iron Oxide, the % Diametral Shrinkage at 1150°C of BaCO<sub>3</sub>:6Fe<sub>2</sub>O<sub>3</sub> Pellets, and % of Original BaCO<sub>3</sub> Decomposed After Calcination at 750°C, for the Various Iron Oxide Samples.

x——x      Surface Area (m<sup>2</sup>/g)                      ●——●      % Diametral Shrinkage  
 x-----x      Average Particle Size (μ)                      +---+      % Original BaCO<sub>3</sub> Decomposed

the semi-quantitative X-ray diffraction results on these samples. The samples of Mix I, which contains an iron oxide (F-41) of surface area  $5.9 \text{ m}^2/\text{g}$ , showed a weight loss corresponding to 32.0% decomposition at  $750^\circ\text{C}$  of the original  $\text{BaCO}_3$  present in the mix, whereas those of Mixes J and K, containing an oxide of surface area only  $2.1 \text{ m}^2/\text{g}$ , (533V), gave weight-loss figures corresponding to 36-40% decomposition of the original  $\text{BaCO}_3$ .

e) Discussion of Results Obtained with Competitive Oxides

At the outset of this section, it may be stated that the pattern of results exhibited by the mixes made incorporating the various competitive oxides follows very closely that already observed and discussed for the range of Northern Pigment oxides, insofar as the figures that are available permit comparisons to be made.

In Figure 6 are plotted the following parameters:

- (1) Surface area of the oxide in  $\text{m}^2/\text{g}$ , as given in Table 2.
- (2) The intensity of the  $\text{BaCO}_3$  peak in the X-ray diffraction pattern of the sample supplied after calcination for 30 min at  $750^\circ\text{C}$ , as given in Table 4.
- (3) The proportion of  $\text{BaCO}_3$  present in these same samples, as assessed by the relative sizes of the DTA peaks corresponding to the  $\text{BaCO}_3$  crystal inversion observed for the  $750^\circ\text{C}$ -calcined material and for the uncalcined material. These data are taken from Table 6.
- (4) The proportion of  $\text{BaCO}_3$  present in these same samples, as assessed from the ratio of the  $\text{CO}_2$  losses obtained in the TGA tests on the  $750^\circ\text{C}$ -calcined material and in the uncalcined material. These data are taken from Table 8.

In order to emphasize the correlation between these parameters, it will be observed that the surface area has been plotted in the inverse sense from the other three factors. The virtually perfect correlation between these four sets of results is immediately apparent.

As mentioned for the earlier sets of samples, the presence of a low proportion of  $\text{BaCO}_3$  in the  $750^\circ\text{C}$ -calcined sample, as supplied, implies that a high proportion of the barium carbonate has reacted with the  $\text{Fe}_2\text{O}_3$  during the calcination at Northern Pigment. Since the  $\text{BaCO}_3$  itself has been demonstrated to be a substantially constant factor, and since the other preparation conditions have all been standardised, then the conclusion is that these sets of results are directly related to the reactivity of the grade of  $\text{Fe}_2\text{O}_3$  in the mix. This relation is in the sense that a high surface area and a low residual  $\text{BaCO}_3$  content after the  $750^\circ\text{C}$  calcination, indicate the presence of a highly reactive iron oxide, and vice versa. This,

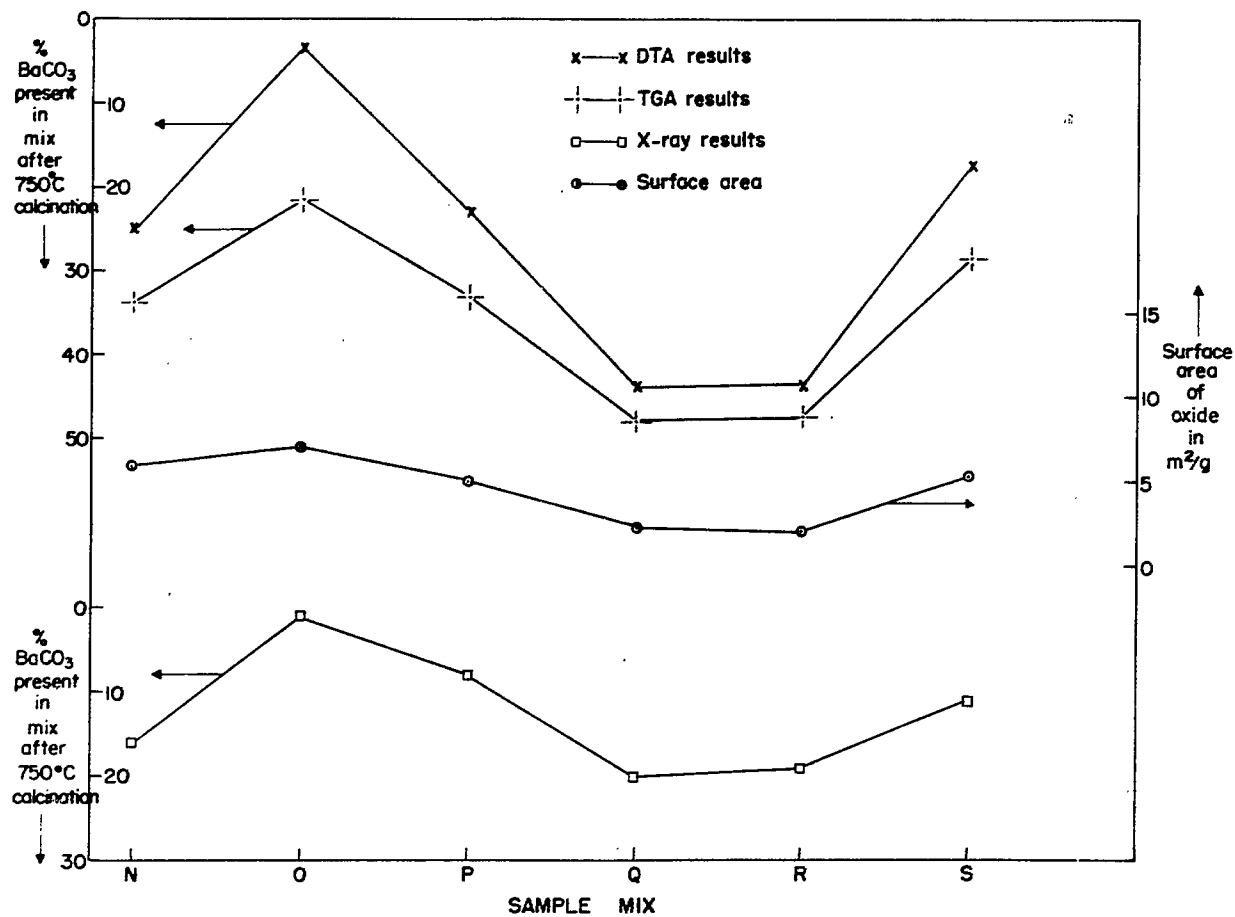


Figure 6. Plot Showing the Variations in Surface Area of the Iron Oxide, and the % of Original BaCO<sub>3</sub> Present in the Mix After Calcination at 750°C, as Determined by X-ray Diffraction, Differential Thermal Analysis and Thermogravimetric Analysis for the Various Competitive Iron Oxide Samples.

of course, accords closely with the conclusions drawn from the results on the earlier tests, where valid comparisons can be made. It must be remembered that the earlier series were less homogeneous in respect of the type of oxide used.

It will be seen that the Northern Pigment oxide 533V, Lot #628 (Mix R), behaves in a very similar way to the C.K. Williams Grade 9908 oxide, and both can be regarded as only moderately reactive materials. This is true in spite of the fact that the Northern Pigment oxide has an acicular shape, while the competitive oxide has a spherical shape.

The results of the tests on the Columbian Carbon 110-2 oxide (Mix S) indicate that this material has a somewhat different and rather less satisfactory behaviour than any of the other oxides used in these groups of samples. While the surface area of this oxide is reasonably high ( $5.4 \text{ m}^2/\text{g}$ ) and the residual  $\text{BaCO}_3$  in the  $750^\circ\text{C}$ -calcined sample is intermediate in value by comparison with the other mixes of these groups, it was noticeable, both from the X-ray and DTA results, that the amount of ferrite formed, even after calcination at  $1200^\circ\text{C}$  for two hours, was less than for all other mixes. In addition, a significant quantity of the iron oxide remained unreacted under these conditions. One may conclude that this oxide would be a less desirable raw material for barium ferrite manufacture than almost any other oxide examined. This, of course, does not imply that this 110-2 oxide would be inferior in performance in other contexts.

A consideration of the results obtained with the various samples that had been calcined for 15 minutes and for 60 minutes at  $1000^\circ\text{C}$  and at  $1100^\circ\text{C}$ , leads to the conclusion that, as expected, the longer time of calcination at each temperature produces a more complete reaction. In most instances, the additional time at  $1000^\circ\text{C}$  provides a product equivalent in composition to that obtained by the shorter calcination at the higher temperature. Where a slight difference is apparent, it is usually in the sense that the shorter calcination at  $1100^\circ\text{C}$  is rather more efficacious than the longer calcination at  $1000^\circ\text{C}$ . Whether or not this is an economically acceptable condition will depend, of course, on the relative costs of longer times and higher temperatures in the calcination kilns employed. It does, however, seem to be indicated, both in the earlier sets of samples and in the more recent sets, that the use of  $1100^\circ\text{C}$  for calcination produces the highest proportion of barium hexaferrite in the product; in many instances, the proportion of ferrite observed in the samples calcined for 2 hours at  $1200^\circ\text{C}$  was inferior to that indicated by the  $1100^\circ\text{C}$  figures, even when this temperature was employed for only 15 minutes. This observation from the DTA results appears to be statistically significant. It is not, however, known whether this is a real effect or whether it has been caused as some artifact of the DTA technique.

## CONCLUSIONS

From the foregoing studies, 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 decomposition of barium carbonate during the barium ferrite formation appears to be a sensitive and reasonably reliable method of indicating the surface properties of the iron oxide, 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 with competitive grades of iron oxide indicate that they are subject to the same range of variation of properties as the Northern Pigment oxides, and that equivalent grades could readily be selected. Certain competitive grades, however, were seen to exhibit anomalous behaviour.

From the study, it is, however, evident that there is, as yet, no means of completely characterizing an iron oxide 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. The final assessment of the performance of a particular grade of oxide must await the results of the magnetic testing to be conducted by Northern Pigment. A judgment may then be made, based on the correlation (or lack of it) between the magnetic performance of the finished ferrites and the physical and chemical properties of the oxides and the mixes containing them, as presented herein.

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APPENDIX

ELECTRONIC CERAMICS

ECRDC RESEARCH PROJECT C 73

Identification of Mines Branch Personnel  
Advisory Committee

Ian F. Wright MPD\*, Chairman  
W.A. Gow EMD  
Dr. N.F. Bright MSD  
J.G. Brady MPD  
V.A. McCourt N

Operational

Function

V.M. McNamara EMD	Pilot plant ceramic powder preparation
J.C. Ingles EMD	Control analyses
Dr. A.H. Webster MSD	Sintering and structural studies
V.A. McCourt N	Lapidary and electroding
Ian F. Wright MPD	Ceramic engineering
T.B. Weston MPD	Electronic test methods and component evaluation
R.C. McAdam	Wet chemical analytical methods and analyses
Dr. A.H. Gillieson MSD	Spectrographic analyses
Dr. E.H. Nickel MSD	Sample preparation for petrographic studies
Dr. Sutarno	Ferrite Research Programme

- \* MPD - Mineral Processing Division  
EMD - Extraction Metallurgy Division  
MSD - Mineral Sciences Division  
N - Preparation and Properties of Materials Laboratory  
of the Mineral Processing Division

Ian F. Wright,  
Project Co-ordinator

John Convey,  
Director, Mines Branch