Sept. 27, 1960 H. C. WESTCOTT 2,954,303

PRODUCTION OF FERROMAGNETIC OXIDE

Filed April 17, 1956

FIG. 1.

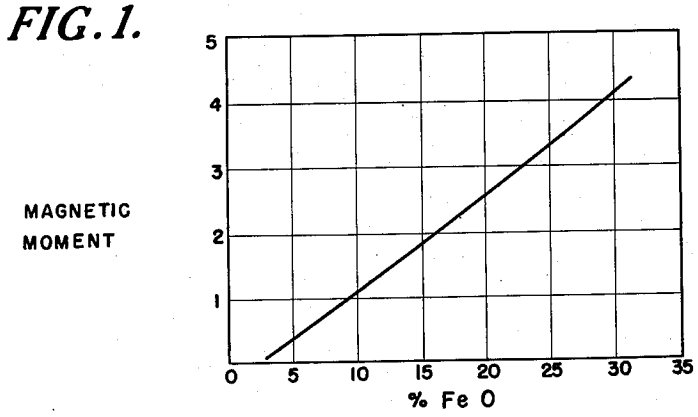


FIG. 2.

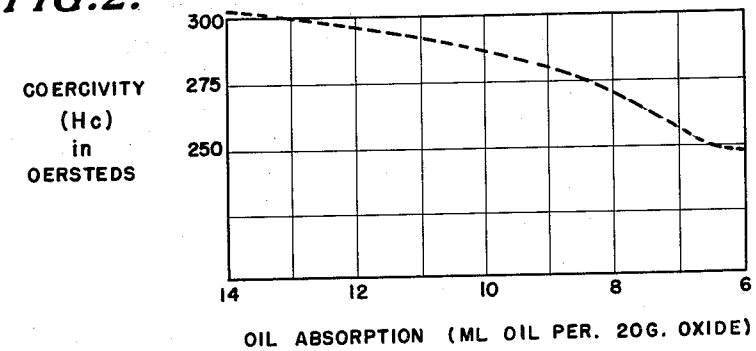
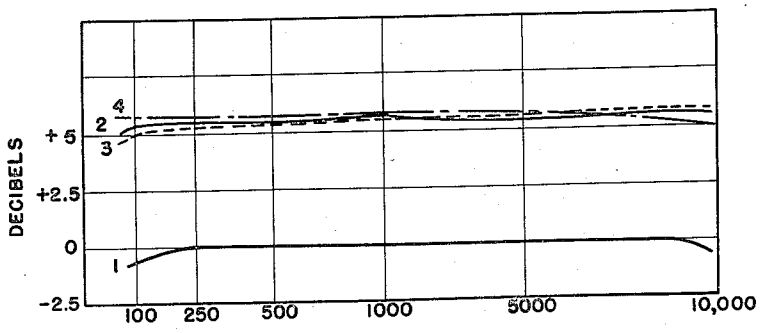


FIG. 3.



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PRODUCTION OF FERROMAGNETIC OXIDE

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15 Claims. (Cl. 117—161)

This invention relates to improved ferromagnetic oxide and to a process for the production of the same. More particularly, the invention relates to the preparation of an improved ferromagnetic oxide material for use in a magnetic record member comprising a base or carrier, such as a tape, ribbon, disc, cylinder, or the like, of a non-magnetic material coated or impregnated with my magnetic material, and a binder.

This application is a continuation-in-part of my application Serial No. 533,863, filed September 12, 1955, and now abandoned.

The method of the invention primarily comprises providing a quantity of iron oxide, grinding said oxide, either per se or in the presence of a grinding medium as discussed hereinafter, into particles of such fine size and smooth surface, the latter to increase density by imparting an oil absorption characteristic to said particles substantially lower than the oil absorption characteristic of the unground iron oxide and the former to improve short wave length response, thereby imparting superior magnetic recording and reproducing properties to the ground particles upon magnetization thereof by reduction and oxidation. Ferromagnetic oxide produced in accordance with this method may comprise ground particles substantially completely of the gamma form of ferric oxide, Fe_2O_3, said ferric oxide having been ground to such fine size and smooth surface, as noted above, to have an oil absorption characteristic not greater than about 0.45 ml. of oil per gram of oxide, and having a coercivity of not greater than about 300 oersteds. No specific lower limit of oil absorption characteristic is contemplated, but the commercially practical limit is about 0.23 ml. of oil per gram of oxide. However, as will be more fully explained hereinafter, depending upon the density and particle size of the iron oxide starting material and upon the degree of oxidation carried out, if the ferric oxide is ground to an extremely high density, undesirable effects and, particularly, lowering of the coercivity below about 180 oersteds by excessive densification (the lower limit presently attributed to magnetic recording machines on today's market) results thereby yielding poor short wave length response.

In connection with the above, it should be stressed that gamma ferric oxide, Fe_2O_3, is preferably contemplated for an end product. Nevertheless, the method of my invention is also applicable to other forms of magnetic oxides such as ferrosoferric oxide, $Fe_2O_3.FeO$. In the case of this latter oxide, however, chemical instability is present because of the tendency of such compound to oxidize at room temperature. In view of this instability, I prefer to produce treated gamma ferric oxide, Fe_2O_3, to the extent permitted by factors such as density and particle size of the starting material, and the degree of densification by grinding, without exceeding minimum coercivity limits. In this respect, it should be preliminarily noted that oxidation also has the effect

of increasing density thus lowering coercivity of ferromagnetic oxide, as will be fully detailed hereinafter.

Magnetic sound record tapes, cylinders, and discs may be made with a non-magnetic backing, such as paper, plastic, rubber, or the like, and with a coating thereover, or an impregnation thereof of a magnetic oxide of iron. Magnetic oxides of iron heretofore used for this purpose have not been satisfactory, because such magnetic oxides do not possess properties, particularly, physical properties, suitable for being adapted to magnetic recording purposes. Such prior oxide coatings have exhibited a ratio of B_r (remanent induction) to B_s (induction at saturation) substantially less than one which results in low sensitivity. In addition, B_s of such prior oxide coatings has been relatively low in value, thus limiting potential B_r thereof.

With reference to the foregoing, it should be understood that B_s represents the saturated flux density of material in the presence of an applied magnetic field, and B_r represetnts the flux density at zero magnetization or remanent induction after applied magnetic field is removed from said material. As can be appreciated, in order to realize maximum sensitivity for any given material, B_r should approach the value of B_s. Of course, B_s should be as high as possible in order to maximize potential B_r of the material.

It should also be pointed out that for any magnetizable material in a state of random dispersion, B_r will be approximately equal to 0.5 B_s for such material. In order to increase B_r and, therefore, more nearly approach the B_s of such material, random dispersion should be oviated, i.e., orientation of the particles of oxide should be carried out.

Magnetic oxides of iron used heretofore are of such density because of their configuration and surface characteristics, as to limit the amount thereof that can be applied to any given area of, for example, magnetic tape. In other words, it can be appreciated that magnetic oxide particles of high absorbent surface characteristics are not capable of being incorporated to a preferred degree in a particular oxide/binder combination on, for example, a given area of non-magnetic backing tape in a magnetic sound record element. This yields undesirable results for magnetic recording purposes in that B_s of the oxide/binder combination is relatively low, and therefore, maximum signal from the coated magnetic surface subsequent to exposure to a magnetic field is not achieved.

Furthermore, these prior magnetic oxides were incapable of substantially complete magnetic orientation and accompanying high B_r:B_s when incorporated to said preferred degree in a particular oxide/binder combination. As noted heretofore, in order to realize maximum B_r with resulting increased sensitivity, magnetic particles must be aligned in a preferred direction constituting orientation. The magnetic oxides of iron utilized heretofore, being of relatively low density and uneven surface characteristics made impossible the achievement of any substantial degree of orientation due to the very characteristics just noted. One uneven particle would act against another such particle approximate thereto and interfere with the inclination to orient in one direction. Thus, many particles of magnetic oxides used heretofore would remain crosswise, or substantially crosswise to preferred direction even after orienting forces were applied thereto for the purpose of orientation.

I have now found that it is possible to produce an iron oxide, or mixture of iron oxides, possessing properties that are much more desirable for magnetic recording purposes. As noted heretofore, magnetic material of my invention has greatly improved physical properties,

and particularly, density, affording maximum sensitivity. In addition, as will be noted hereinafter, particle size, coercivity and magnetic moment are controlled to insure maximum sensitivity and optimum overall frequency response.

The particle size, coercivity and magnetic moment of my novel magnetic material are influenced by a number of factors. These factors are (*a*) the density and particle size characteristics of the iron oxide starting material, (*b*) the degree of oxidation of the magnetic oxide following reduction thereof, and (*c*) the degree of grinding to which the material is subjected. Basically, my process involves utilization of controlled dehydration, reduction, oxidation, and grinding of non-magnetic hydrated ferric oxide, $Fe_2O_3.H_2O$, of selected density and particle size. As will be made evident hereinafter, the sequence of these steps is subject to variation, but the end result, in any event, is the transformance of the non-magnetic ferric oxide into magnetic material which displays optimum particle size, density, coercivity and magnetic moment.

With the above in mind, the primary object of this invention is the provision of ferromagnetic oxide possessing improved physical and magnetic properties such as particle size, density (low oil absorption), and accompanying maximum sensitivity, and optimum and controllable coercivity and magnetic moment.

Another object of this invention is to provide ferromagnetic oxide in the form of particles of such fine size and smooth surface as to impart low oil absorption characteristics (density) and yielding magnetic properties superior to heretofore known magnetic oxides of iron.

A further object of my invention is to provide ferromagnetic oxide adapted to form an element of a magnetic record member comprising ground particles substantially completely of the gamma form of ferric oxide, Fe_2O_3, said particles having been ground to such fine size and smooth surface as to have an oil absorption characteristic not greater than about 0.45 ml. of oil per gram of oxide, and the treatment of these particles being such that the coercivity thereof is not greater than about 300 oersteds.

A more specific object of my invention is to provide a magnetic record member comprising my novel magnetic material in combination with suitable binders, said magnetic material comprising ground particles of magnetic oxides of iron including both ferric and ferrosoferric oxides and mixtures thereof, particles having been ground to such fine size and smooth surface as to have an oil absorption characteristic not greater than about 0.45 ml. of oil per gram of oxide, and the treatment of such particles being such that the coercivity thereof is not greater than about 300 oersteds, thereby providing a record member having enhanced magnetic recording properties and better oriented magnetic material therein.

A further object of my invention is to provide a commercially economical process for the production of improved magnetic material from non-magnetic iron oxide of selected density and particle size.

Still another object is the provision of a process for making improved magnetic material which comprises providing a quantity of iron oxide of selected density and particle size, heating said iron oxide to dehydrate the same, reducing said dehydrated iron oxide to ferrosoferric oxide, $Fe_2O_3.FeO$, at least partially oxidizing said ferrosoferric oxide, and grinding the particles to such fine size and smooth surface as to impart an oil absorption characteristic to said particles substantially lower than the oil absorption characteristic of the unground oxide and imparting superior magnetic recording and reproducing properties to the ground particles when used as an element in a record member.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that the detailed description and specific examples, while indicating the preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

Reference is made to the accompanying drawings wherein:

Figure 1 is a graph representing magnetic moment plotted against percent reduction of heated ferric oxide monohydrate thereby illustrating the criticality of FeO content in the reduction of said heated monohydrate;

Figure 2 is a graph of oil absorption expressed in mls. of oil per gram of oxide against coercivity expressed in oersteds, for several samples of magnetic material embodying my invention. This graph illustrates the effect of decreasing oil absorption (increasing density) by grinding the magnetic iron oxide; and

Figure 3 illustrates increased sensitivity by using an increased amount of my novel oxide per given amount of binder.

My method of grinding iron oxide in order to enhance the magnetic properties thereof constitutes a novel improvement of itself and can be utilized at any time prior to the magnetization of the iron oxide or subsequent thereto. In any event, the basic steps involved in improving the magnetic properties must be controlled thereby controlling the coercivity of the end product within desired limits set by electronic recording apparatus with which my material is primarily used.

The density and particle size of the iron oxide starting material also plays its part as a variable in controlling end product coercivity. In connection with these characteristics of the iron oxide starting material, it should be noted that a denser iron oxide of larger particle size is more cheaply produced so that, for certain purposes, it would be preferred to use this cheaper material. However, it should be stressed that, bearing in mind the necessity for stabilizing by oxidation with accompanying reduction in coercivity, the starting material should be of as great a density and of as small a particle size as practicable.

In order to more clearly explain the manner in which the foregoing variables influence my invention, it should be reiterated that the grinding step decreases coercivity by densifying the material being ground. To a great extent, such densification is the inevitable result of decreasing the particle size. Bearing in mind that a lower coercivity limit is prevent in the circumstances as noted heretofore and that an end product of as fine a particle size as practicable is desired, it can be appreciated that the density of the starting material is quite important.

Specifically, a relatively expensive low density iron oxide of fine particle size could be ground to a great extent, thus decreasing particle size even more without increasing the density to such an extent as to exceed the lower coercivity limit set by recording apparatus presently on the market. On the other hand, the cheaper grade iron oxide having relatively high density and of larger particle size could not be ground to as great a degree because the rate of densification would exceed the diminution of particle size to such an extent as to lower the coercivity to the minimum value before optimum particle size is reached.

Oxidation is also a factor in the reduction of coercivity, as noted heretofore. In addition, substantially complete oxidation of the reduced iron oxide should preferably be carried out in order to arrive at a chemically stable end product. With this in mind, it can be appreciated that the extent of reduction of coercivity by densification through grinding is governed by the amount of oxidation necessary to insure a substantially stable end product.

Thus, in utilizing my invention, I must (*a*) select a starting material of as low density and as fine a particle size as practicable, commensurate with the cost of pro-

duction which the end product price can bear, (*b*) control the extent of grinding so as to control lowering of coercivity by densification, yet without sacrificing the advantages achieved by greatly decreased particle size and accompanying low oil absorption (densification), and (*c*) control the degree of oxidation of the reduced iron oxide so as to control lowering coercivity, yet without sacricifing the advantages achieved by having a chemically stable end product.

With the above in mind, the following alternative sequences of steps are presented, although it should again be noted that my method of grinding the ferromagnetic oxide produced, constitutes a novel improvement of itself and will be separately amplified upon hereinfater.

A quantity of ferric oxide monohydrate of a particular density and particle size, either before or after grinding in accordance with my invention, is heated to dehydrate the same. Coincidently with dehydration, the ferric oxide monohydrate is reduced, for example, in a reducing atmosphere such as hydrogen, carbon monoxide, or a combination of such gases. A preferred composition of gas can constitute 30% hydrogen, 20% carbon monoxide, and the balance of the gas being substantially all nitrogen. Slow reduction at a temperature of about 650° F. provides a more uniform material. It should be understood and appreciated that reduction can be carried out in a number of recognized ways.

Substantially complete reduction is always carried out until, by chemical analysis, there is obtained ferrosoferric oxide having the structural formula $Fe_2O_3.FeO$, where the FeO content is 31.0 to 31.4%. This percentage, which is achieved by substantially complete reduction imparts improved magnetic properties to the material in that magnetic moment of a particle is maximized, thereby maximizing B_s for the material. Reference is made to Figure 1, which shows a graph wherein magnetic moment is plotted against percent reduction. The following table sets forth values of magnetic moment for specified samples having a varying percentage FeO.

TABLE I

Percent FeO:	Magnetic moment
8	0.75
11	1.25
15	1.75
18	2.25
21	2.75
26	3.5
30.5	4.0
31.5	4.25

From the graph and table it can be seen that when the FeO content is about 31%, the greatest magnetic moment is realized.

Following reduction, the magnetic material is preferably oxidized in order to impart chemical stability although it can be appreciated that such oxidation step can be entirely omitted if a chemically unstable end product is capable of utilization on a commercial basis. Oxidation is normally accomplished by using dry air as the oxidizing medium.

As fully noted heretofore, it is desirable to continue oxidation until the $Fe_2O_3.FeO$ is substantially all converted to the stable gamma form of Fe_2O_3. However, the character of the starting material along with the degree of grinding carried out (if grinding precedes reduction and oxidation) or to be carried out (if grinding follows reduction and oxidation) influences the degree of oxidation that can be done. In any event, oxidation should be controlled so that coercivity of the end product does not exceed the minimum coercivity desired, yet with the accompanying achievement of a reasonable degree of chemical stability.

In connection with the foregoing, two situations are presented.

(*a*) If grinding is first carried out, then the particle size and density of the starting material and the amount of grinding must be controlled to realize a potential coercivity (prior to reduction) of such a value as to permit reduction of coercivity by oxidation without exceeding the minimum coercivity value desired and yet with the achievement of some reasonable degree of chemical stability.

(*b*) If grinding follows reduction and oxidation, then the burden of initial control is shifted to the oxidation step, i.e., oxidation should not be carried out to such an extent as to make impractical the degree of grinding necessary to achieve desired particle size, magnetic coercivity and accompanying value of oil absorption (densification). Here again, it should be recognized that the amount of oxidation that can be carried out will be influenced by the character of the starting material. For example, if the starting material is of very low density and fine particle size, then substantially complete oxidation could be carried out with accompanying substantially complete chemical stability, yet without forestalling the ability to significantly diminish the particle size and increase the density of the oxide through grinding thereby obtaining an end product of near optimum magnetic recording utility but of a density such that the coercivity has not been lowered below the minimum.

The following table is presented in order to illustrate the effect of oxidation upon coercivity of ferromagnetic oxide.

TABLE II

Coercivity:	Percent FeO
400	31
396	26
392	21
386	15
380	12
374	10
360	8
345	6
330	4
315	2
300	1

In connection with the foregoing sequence of steps involving dehydration, reduction, and preferably oxidation, it is, of course, generally known in the art to utilize the same to produce a ferromagnetic oxide material, i.e., gamma ferric oxide, Fe_2O_3 (with oxidation) and ferrosoferric oxide (with partial or no oxidation). However, the criterion of carrying out substantially complete reduction to the indicated percent FeO content and the accompanying maximized magnetic moment and control of coercivity were not appreciated heretofore and constitute improvements over prior processes.

The material resulting from dehydration, reduction and oxidation per se can be used of itself, for example, as an element in a magnetic record member. However, this material is still deficient both as to magnetic properties and physical characteristics in that maximum sensitivity is not achieved.

As noted heretofore, in order to attain such maximum sensitivity, and, in addition, attain improved short wave frequency response, however, I have found that an additional step should be carried out in the preparation of the magnetic material. This additional step comprises grinding the iron oxide, either before or after reduction and oxidation, at normal temperature and pressure with, for example, a ball mill, into particles of very fine size and smooth surface (high density).

Ferromagnetic oxide such as gamma Fe_2O_3 not subjected to my grinding step does not possess optimum properties. First, only a limited amount of this oxide can be added to any binder. This is because an excess of previously used low density oxides, in any given part, will result in rapid deterioration of oxide-binder strength, and insufficient orientation of the magnetic particles in

said binder, upon subjecting the same to orientation treatment in a magnetic field.

Nevertheless, it can be appreciated that it is of advantage to maximize, within practical limits, the proportion of magnetic oxide added to a suitable binder. A large amount of magnetic oxide per given amount of binder results in a maximum amount of magnetic oxide on any given area of, for example, a magnetic record member when such oxide and binder are used to coat or impregnate the record track of said record member. This in return maximizes B_s for said given area.

In order to achieve the above and yet insure maximum magnetic orientation with resulting increased B_r, as well as adequate oxide-binder strength, each particle should be smooth and fine and separated from each and every other particle by a minute layer of binder so as to permit freedom of movement of each particle to orient. By grinding the magnetic oxide to a fine size and smooth surface (high density), I facilitate the encapsulation of each particle with binder so as to facilitate orientation and yet permit significantly greater amount of the high density magnetic oxide to be included in a given portion of binder without sacrifice of strength. The end effect is greater sensitivity. B_s is maximized due to the fact that more particles are present per given area of, for example, magnetic tape, and total B_r per given area is maximized by the greater degree of orientation.

To specifically illustrate the advantages achieved through maximizing B_s and B_r by my process, in, for example, magnetic tape recording, it can be appreciated that, at any given instant, due to the higher density (low oil absorption) and better orientation, a greater amount of B_r is available under a magnetic recording head for reproduction of signal on the tape. Thus, a higher volume of signal is realized on playback. Alternatively, the tape can be slowed down with attainment of the same volume of signal on playback that is realized with present day magnetic recording tapes.

The foregoing advantage is of particular importance in video work. Present day magnetic recording tapes require a tremendous speed of travel (about 40 feet per second) in order to provide enough particles under the recording head to register the signal at short wave lengths and yet provide a usable signal of sufficient volume.

Also, because of the fine size of the material of my invention, a far greater decibel value of signal can be obtained at high frequencies (short wave lengths) and this high value can be used to significantly slow the tape down and still obtain decibel values equivalent to those of currently used magnetic recording tape. This concept is substantially linear so that, for example, by using the fine sized magnetic material of my invention and thus double the number of particles under a recording head at any given time, I can halve the speed of the tape.

The densification which I impart to the iron oxide by "grinding" can be best expressed in terms of a quantitative measurement known as oil absorption. The iron oxide particles before treatment are of a porous nature. In other words, they have a high oil absorption as evidenced by their readiness to reduction and oxidation and to absorption of moisture. This oil absorption is best expressed in terms of the amount of oil required to bring a stipulated amount of oxide to a plastic state.

A porous particle requires a substantial amount of oil to achieve such plastic state. Bearing in mind that magnetic oxide/binder formulations should be well dispersed to provide maximum efficacy in, for example, a magnetic record member, it can be appreciated that lowering the porosity should lower the amount of binder required to achieve a dispersion, i.e., lower the "oil absorption."

Accordingly, I conceived the step of grinding the oxide material so as to provide particles of fine size and smooth surface. The fine size achieves advantages noted heretofore and the smoothing of the surface effectively lowers the oil absorption of such particles, i.e., increases density, and, as noted, among other beneficial results, permits significantly greater amounts of treated particles to be included in a given amount of binder, in turn maximizing B_s. Also, as noted heretofore, upon utilization of such oxide/binder mixture as an element in, for example, a magnetic record member, greater degrees of orientation with accompanying increased B_r are realized because the treated particles being of small size and smooth surface tend to line up without conflict and, significantly, despite the fact that a greater amount of the same are present per given area of magnetic material carried.

The following table illustrates decreasing oil absorption by grinding with or without the presence of a grinding medium as noted hereinafter, in accordance with my invention. As stated heretofore, decreasing oil absorption according to my process permits more oxide to be combined per given amount of binder, increasing B_s yet with excellent orientation thus maximizing B_r and yielding greater sensitivity.

TABLE III

Time of grinding in minutes:	Oil absorption in ml./ 20 grams of oxide
0	13.0
10	10.5
20	8.4
30	8.0
40	7.4
50	7.1
60	6.9
70	6.5
80	6.2
90	6.1

NOTE.—Twenty gram samples of gamma ferric oxide were used and grinding was carried out with a ball mill.

The optimum physical characteristics are approached after about 1–1½ hours of grinding, since, at that time, 4.0 parts of ground oxide can be combined with one part of binder, yet with approximately optimum orientation, as represented by B_r. Gamma ferric oxide and a vinyl resin binder were used in arriving at the above figures. However, these figures are applicable to any binder that is used in the normal manufacture of magnetic recording media.

With respect to the amount of oxide that can be added per given amount of binder, there is a certain critical point beyond which one cannot proceed. Practical considerations dictate a limit of about 8.5 parts oxide per 1.5 parts binder, i.e., 85%–15%, respectively, beyond which maximum orientation and accompanying maximum B_r cannot be achieved. Of course, this inability to properly orient is caused because of the inclusion of such a great mass of oxide per given amount of binder, with accompanying inadequate dispersion in the binder. Even with ground oxide it is possible to reach such a point where the particles interfere with each other, thus preventing optimum orientation. Further, such improved dispersion causes agglomeration and gives rise to high inherent noise level in the system.

In line with the above, it can also be appreciated that too great an amount of oxide per given amount of binder will result in inadequate oxide-binder strength. The binder must function to adhere the oxide to the backing in, for example, a magnetic tape and an insufficient amount of such binder will cause crumbling. However, in any event, not less than about 50% oxide is contemplated.

Turning to Figure 2, the fact that coercivity is decreased by grinding is illustrated. This effect on coercivity is, in addition to and separate from that previously noted in the reduction and oxidation stages.

The following table sets forth values of coercivity in oersteds per given degree of oil absorption. Twenty grams of gamma ferric oxide were used and raw linseed

oil was utilized to determine oil absorption. A ball mill was used for grinding.

TABLE IV

Oil absorption in ml. of oil per 20 grams or oxide:	Coercivity (H_c) in oersteds
16	310
13	300
10.5	287.5
8.4	275
8	265
7.4	262
6.9	255
6.5	250
6.2	250
6.1	250

The graph of Figure 2, as well as Table IV clearly shows that coercivity is decreased by grinding. In addition, it might be noted that most of the change in oil absorption took place after the first hour of grinding. The decreased coercivity through grinding can be best explained by appreciating the fact that the particles are made denser and smaller.

Although the fact that coercivity is decreased to a controlled extent by grinding is not of the significance attributable to increased oxide:binder ratio and improved orientation, nevertheless, it constitutes a part of my invention. Of course, as noted heretofore, the degree of lowering of coercivity through decreasing of oil absorption is directly related to the particle size and density of the starting material and to the degree of oxidation being carried out. On the basis of magnetic recording machine designs presently in commercial use, coercivity of the final product should not go below about 180 oersteds, because of resulting poor frequency response.

It should be stressed at this point that, conceivably, further magnetic recording apparatus will be designed to operate with magnetic recording members of coercivity characteristics lower than 180 oersteds. In that event, my process would be utilized accordingly on the basis of the new lower coercivity limit. The advantages presented by such circumstances would include the ability to use a cheaper starting material of higher density and larger particle size; the ability to decrease oil absorption of such starting material by grinding to a greater degree of density; and the ability to substantially completely oxidize material of such increased density.

As noted heretofore, grinding can be achieved by use of a ball mill or any other standard equipment which will produce the effect of mortar and pestle, i.e., increase apparent density of the material. Other types of standard equipment would include, of course, a differential two-roll mill or a Banbury type of mixer, both of which are capable of "grinding" in the sense used in this application and of the effect achieved by mortar and pestle. In addition, it can be stated that both wet and dry grinding are contemplated by my invention, however, dry grinding is preferred.

With reference to both dry and wet grinding, the exact conditions are variable depending on the grinding medium involved, the ratio of grinding medium to material being ground, and the like. It can be appreciated, of course, that the grinding medium can constitute any organic solvent or, when commercially desirable, the binder itself, e.g., grinding can be carried out in a differential two-roll mill upon a mixture of unground oxide and resinous binder such as polyvinyl chloride, thereby combining both the grinding and dispersion steps in one operation. The exact time of grinding is also variable in accordance with the foregoing. It should be understood that my invention is not limited to any precise method or equipment for accomplishing such grinding so long as desired oil absorption and coercivity are achieved.

Figure 3 is set forth to illustrate increased sensitivity

by using an increased amount of my novel oxide per given amount of binder. The graphs shown in Figure 3 show the decibel readings, over the indicated frequency range for the oxide/binder sample 1 (2 parts untreated oxide to 1 part polyvinyl chloride), sample 2 (3.0 parts treated oxide of 0.29 oil absorption to 1 part polyvinyl chloride) and samples 3 and 4 (like sample 2 only with slight changes in coating thickness).

The signal levels noted heretofore were measured over a frequency of 100 cycles—10 kilocycles. It must be understood that in audio recording, it is desired to record and reproduce every frequency within the range of the human ear with equal intensity. Of course, this same concept is applicable to the higher frequencies of video recording.

Examples

A more complete understanding of the new products and procedures of my invention, as described above, may be had by referring to the following specific examples of actual operation in accordance with the said invention.

Example I

Ten grams of hydrated ferric oxide having a length of approximately 0.8 micron, a diameter of approximately 0.2 micron and a density, designated by oil absorption, of 0.65 ml. of oil per gram of oxide were subjected to dry grinding in a ball mill for 1½ hours until an oil absorption of 0.23 ml. of oil per gram of oxide was obtained. At that point, the particle size was less than 0.5 micron.

The ground oxide was then placed in a reducing atmosphere while being subjected to heat. The reducing atmosphere constituted 30% hydrogen, 20% carbon monoxide, and 50% substantially all nitrogen. The temperature provided was about 650° F.

The hydrated ferric oxide was thus reduced to a composition having structural formula $Fe_2O_3.FeO$. The FeO content was 31%, which indicated substantially complete reduction. Coercivity was measured to be approximately 340 oersteds.

The material was then fully oxidized (to less than 1% FeO) in air at 450° F. and gamma ferric oxide was obtained. By magnetic measurement, the coercivity of this ferric oxide was shown to be 240 oersteds.

Example II

The material of Example I was later combined with a vinyl resin, i.e., polyvinyl chloride, and a suitable plasticizer such as di-octyl phthalate in solvent solution and adhered to a recording backing tape. While the oxide-binder was still in fluid form, the tape was passed through a unidirectional magnetic field to suitably orient the magnetic particles.

A total of 4 parts of gamma ferric oxide per 1 part of binder were utilized. Upon magnetic measurement, it was noted that this combination yields a ratio of B_r/B_s of 0.9, which is considered excellent with respect to sensitivity.

The magnetic recording tape thus produced utilized a starting material of very fine particle size and low density. It exhibited best performance at short wave lengths both in audio recording and video recording. Because of the high density and fine size of particles present on the tape, it was possible to obtain satisfactory video recordings at tape speed of about 20 feet per second, to wit, speeds of less than half the speeds necessary for magnetic record tapes previously used.

Example III

Ten grams of hydrated ferric oxide having a length of approximately 0.8 micron, a diameter of approximately 0.2 micron and a density, designated by oil absorption, of 0.65 ml. of oil per gram of oxide, were placed in a reducing atmosphere while being subjected to heat. The reducing atmosphere constituted 30% hy-

drogen, 20% carbon monoxide, and 50% substantially all nitrogen. The temperature provided was about 600° F.

The hydrated ferric oxide was thus reduced to a composition having a structural formula $Fe_2O_3.FeO$. The FeO content was 31%, which indicated substantially complete reduction. Coercivity was measured to be approximately 400 oersteds.

The material was then fully oxidized (to less than 1% FeO) in air at 450° F. and gamma ferric oxide was obtained. By magnetic measurement, the coercivity of this ferric oxide was shown to be 300 oersteds.

The gamma ferric oxide was then subjected to dry grinding in a ball mill for 1½ hours until an oil absorption of 0.23 ml. of oil per gram of oxide was obtained. At that point, the coercivity was measured to be 240 oersteds and the particle size was less than 0.5 micron.

Example IV

The material of Example III was later combined with a resin, i.e., chlorosulphonated polyethylene to form a self-supporting medium for magnetic recording. While the mixture thus formed was still in a plastic state, the magnetic particles were suitably oriented by calendering into a thin film.

A total of 4 parts of gamma ferric oxide per 1 part of polyethylene were utilized. Upon magnetic measurement, it was noted that this combination yields a ratio of B_r/B_s of 0.8, which is considered excellent with respect to sensitivity.

As with Example II, the recording member yielded excellent results particularly in video recording. Best performance was realized at short wave lengths. Thus, particularly, for video work, high density and fine sized magnetic material achieved by using a starting material of low density and fine particle size, whether grinding takes place initially or subsequently, is best.

Example V

Ten grams of hydrated ferric oxide having a length of approximately 1.6 microns, a diameter of approximately 0.3 micron, and a density, designated by oil absorption, of 0.5 ml. of oil per gram of oxide, were subjected to dry grinding in a ball mill for 1½ hours until an oil absorption of 0.26 ml. of oil per gram of oxide was obtained. At that point, the particle size was 0.7 micron.

The ground oxide was then placed in a reducing atmosphere while being subjected to heat, as in Example I.

After substantially complete reduction was carried out, coercivity was measured to be approximately 315 oersteds. The materal was then partially oxidized (to about 6.5% FeO content) in air at 450° F. and the resulting material was a mixture of gamma ferric oxide and ferrosoferric oxide having a coercivity of 240 oersteds.

Example VI

The material of Example V was later combined with a vinyl resin, i.e., polyvinyl chloride, and a suitable plasticizer such as di-octyl phthalate in solvent solution and adhered to a recording backing tape. While the oxide-binder was still in a fluid form, the tape was passed through a unidirectional field to suitably orient the magnetic particles.

A total of 7.5 parts of the mixture of gamma ferric oxide and ferrosoferric oxide per 2 parts of binder were utilized. Upon magnetic measurement, it was noted that this combination yields a ratio of B_r/B_s of 0.75.

As can be appreciated, although the density is substantially the same, the particle size of the end product is greater than that realized by using a starting material having lower density and finer particle size. The result is lower sensitivity at short wave lengths because of the inability to incorporate as great a number of particles per given portion of recording tape. Although such product is not preferred for video recording, it can be used for audio recording because of the longer wave lengths involved even at audio high frequencies.

In addition, it should be noted that the end magnetic recording material of this example is not as chemically stable as that of the previous examples because only partial oxidation was carried out. As with the disadvantage involved in limited amount of grinding, the resultant disadvantage of slight chemical instability is appreciated, but the ability to use a cheaper starting material warrants such disadvantages in the end product under some circumstances. In instances such as home audio recorders, magnetic tape of only average sensitivity at short wave lengths and of slight chemical instability might still be used to great advantage, and, in this respect, it should be stressed that the use of my novel material would make such tapes far better performers than their equivalents presently on the market.

On the general question of chemical instability, fully oxidized ferric oxide is, of course, the most stable form. However, ferrosoferric oxide with FeO content of from about 1% to 15% is substantially stable at normal ambient temperatures and only likely to reoxidize at elevated temperatures.

Example VII

Ten grams of hydrated ferric oxide having a length of approximately 1.8 microns, a diameter of approximately 0.25 micron, and a density, designated by oil absorption, of 0.4 ml. of oil per gram of oxide, were placed in a reducing atmosphere while being subjected to heat. The reducing atmosphere constituted 30% hydrogen, 20% carbon monoxide, and 50% substantially all nitrogen. The temperature provided was about 650° F.

The hydrated ferric oxide was thus reduced to a composition having structural formula $Fe_2O_3.FeO$. The FeO content was 31%, which indicated substantially complete reduction. Coercivity was measured to be approximately 300 oersteds.

The material was then oxidized in air at 450° F. to an FeO content of about 9.5%. The resultant material constituted a mixture of gamma ferric oxide and ferrosoferric oxide having a coercivity of about 220 oersteds.

This magnetic material was then subjected to dry grinding in a ball mill for about 1½ hours until an oil absorption of 0.3 ml. of oil per gram of oxide was obtained. At that point, the coercivity was measured to be 200 oersteds and the particle size was 1 micron in length.

Example VIII

The material of Example VII was combined with chlorosulphonated polyethylene to form a self-supporting medium for magnetic recording. While the mixture thus formed was still in a plastic state, the magnetic particles were suitably oriented by calendering into a thin film.

A total of 7 parts of the said material per 3 parts of polyethylene were utilized. Upon magnetic measurement, it was noted that a ratio of B_r/B_s of 0.7 was realized.

The resulting end product is not of maximum sensitivity at short wave length because of the larger particle size thereof. In addition, the stability is not optimum, since only partial oxidation was carried out. Both of these factors were necessitated by the relatively higher density and larger size of the starting material.

By my novel process I have succeeded in producing an improved ferromagnetic oxide, which, upon utilization in, for example, a magnetic record member, yields results not heretofore achieved, and, particularly, improved overall sensitivity and frequency response. The superior magnetic properties of my magnetic iron oxide material are easily demonstrated by comparison of the recording and reproducing performance of previous iron oxides.

In connection with this invention, I have already noted

that any binder material can be used. Such binder must merely be acceptable in the normal manufacture of magnetic recording elements.

It should also be stressed that my novel grinding step can be carried out at any time in the process. Normally, such grinding takes place either prior to dehydration, reduction, and oxidation, or subsequent thereto. However, as can be readily appreciated, grinding can be carried out at any other time such as following dehydration and before reduction, or following reduction and prior to oxidation.

It is evident from the foregoing that "grinding" contemplates the effect achieved by mortar and pestle. In other words, the desired reduction in particle size and oil absorption characteristics of the oxide being treated is dependent upon a shearing, rolling, or impact type of action, all of which have been generally designated "grinding."

Throughout this specification, I have emphasized the effect of density and particle size characteristics of the starting material on the operating conditions applied to my general method of production. These starting material characteristics govern the degree of grinding and oxidation that can be carried out within stipulated minimum coercivity limits. Therefore, by suitably controlling such factors within the general framework of my novel process, I can successfully produce an end product capable of yielding maximum operating performance for various applications in both audio and video recording apparatus.

The novel principles of this invention are broader than the specific embodiments recited above, and rather than unduly extending this disclosure by attempting to list all the numerous modifications that have been conceived and reduced to practice during the course of this development, these novel features are defined in the following claims.

I claim:

1. The method of making improved ferromagnetic oxide which comprises providing a quantity of ferric oxide monohydrate, dehydrating said ferric oxide monohydrate and fully reducing the same by gaseous reduction to magnetically anisotropic ferrosoferric oxide, $Fe_2O_3.FeO$, grinding the oxide under non-aqueous conditions into particles of such fine size and smooth surface as to impart an oil absoprtion characteristic to said particles of not greater than 0.45 ml. of oil per gram of oxide, and a coercivity of not greater than 300 oersteds, said magnetically anisotropic ground oxide being capable upon orientation of yielding a B_r/B_s value ranging from 0.5 to 0.9.

2. The method of claim 1 wherein the oxide is dry ground.

3. The method of claim 1 wherein the oxide is ground into particles having an oil absorption characteristic of not less than 0.23 ml. of oil per gram of oxide.

4. The method of claim 1 wherein said grinding step is a ball milling step and the time of grinding is between 1 hour and 1½ hours.

5. The method of claim 1 wherein at least a part of said ferrosoferric oxide $Fe_2O_3.FeO$ is at least partially oxidized, thereby facilitating control of coercivity of the final ferromagnetic oxide product.

6. The method of claim 5 wherein said ferrosoferric oxide $Fe_2O_3.FeO$ is substantially completely oxidized to gamma ferric oxide Fe_2O_3.

7. The method of claim 6 wherein the grinding step follows the oxidation step.

8. Magnetically anisotropic, gaseously reduced ferromagnetic oxide adapted to form an element of a magnetic record member and having a coercivity of not greater than about 300 oersteds, comprising ground particles of at least one magnetic synthetic iron oxide selected from the group consisting of ferrosoferric oxide $Fe_2O_3.FeO$ and gamma ferric oxide Fe_2O_3, said iron oxide having been ground under non-aqueous conditions to such fine size and smooth surface as to have an oil absorption characteristic of not greater than 0.45 ml. of oil per gram of oxide and being capable upon orientation of yielding a B_r/B_s value ranging from 0.5 to 0.9.

9. Magnetically anisotropic ferromagnetic oxide as claimed in claim 8 having an oil absorption characteristic of not less than 0.23 ml. of oil per gram of oxide.

10. Magnetically anisotropic ferromagnetic oxide as claimed in claim 8 wherein said oxide is ferrosoferric oxide $Fe_2O_3.FeO$ having an FeO content of 31.0% to 31.4%.

11. Magnetically anisotropic ferromagnetic oxide as claimed in claim 8 wherein said oxide is a mixture of ferrosoferric oxide $Fe_2O_3.FeO$ and gamma ferric oxide Fe_2O_3.

12. Magnetically anisotropic ferromagnetic oxide as claimed in claim 8 wherein said oxide is gamma ferric oxide Fe_2O_3.

13. A magnetic record member having a non-magnetic carrier and a magnetic track adherently bonded thereto of magnetic material and binder composition, said magnetic material having a coercivity of not greater than about 300 oersteds and comprising ground particles of at least one magnetically anisotropic, gaseously reduced synthetic iron oxide selected from the group consisting of ferrosoferric oxide $Fe_2O_3.FeO$ and gamma ferric oxide Fe_2O_3, said iron oxide having been ground under non-aqueous conditions to such fine size and smooth surface as to have an oil absorption characteristic not greater than about 0.45 ml. of oil per gram of oxide, and being capable upon orientation of yielding a B_r/B_s value ranging from 0.5 to 0.9.

14. A magnetic record member as claimed in claim 13 wherein the magnetic material is in amount of at least 50% but not more than about 85% by total weight of magnetic material and binder composition.

15. A magnetic record member as claimed in claim 13 wherein said binder composition is polyvinyl chloride.

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