

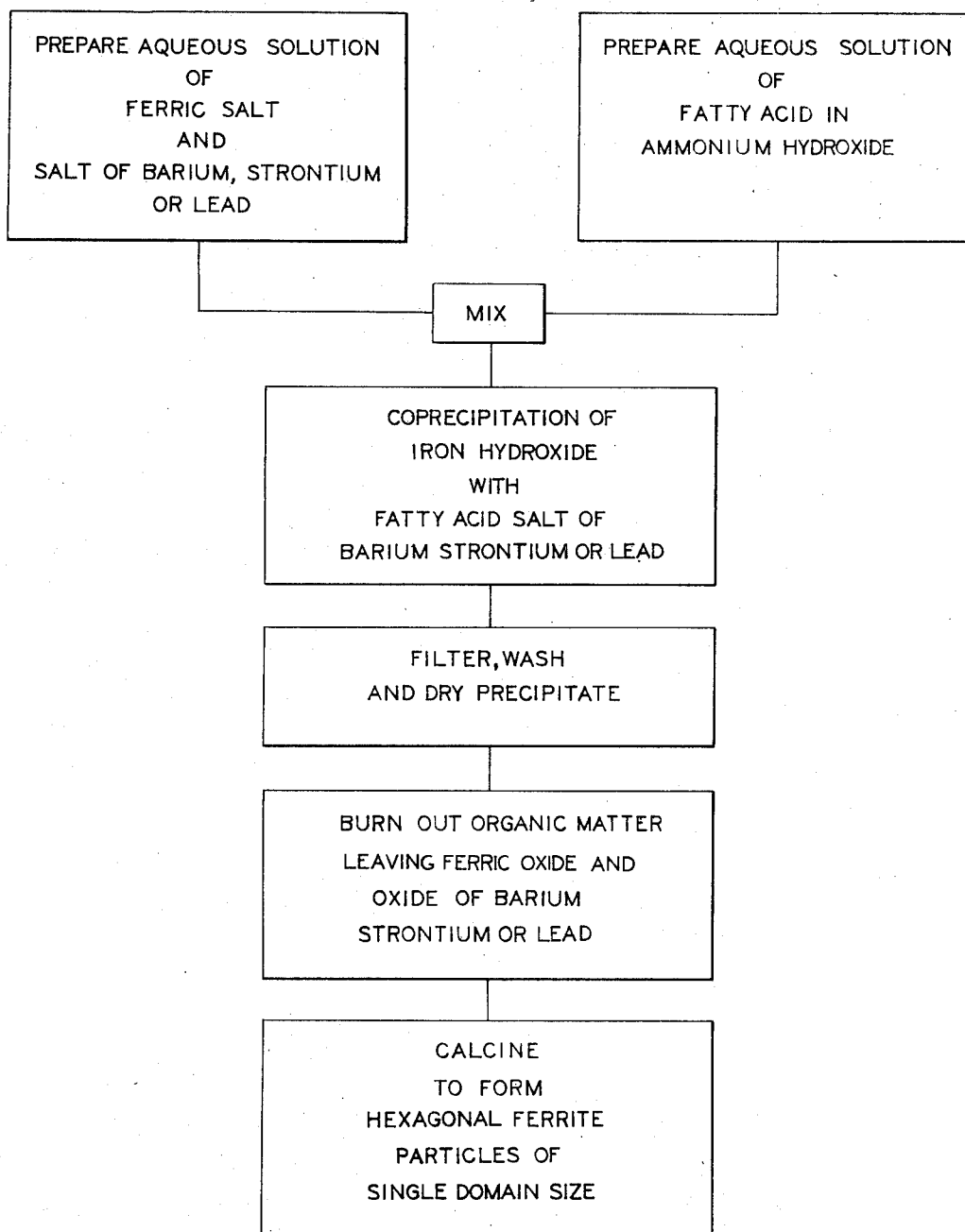
Jan. 11, 1972

A. L. MICHELI

3,634,254

METHOD OF COPRECIPITATING HEXAGONAL FERRITES

Filed June 16, 1969



INVENTOR

Adolph L. Micheli

BY

George A. Grove

ATTORNEY

1

3,634,254

METHOD OF COPRECIPITATING HEXAGONAL FERRITES

Adolph L. Micheli, Royal Oak, Mich., assignor to General Motors Corporation, Detroit, Mich.
Filed June 16, 1969, Ser. No. 833,447

Int. Cl. C04b 35/26

U.S. Cl. 252—62.63

3 Claims

ABSTRACT OF THE DISCLOSURE

A method is disclosed for coprecipitating chemical constituents of ferrites as intimately mixed, finely divided particles which may be readily calcined to form ferrimagnetic bodies. In a preferred embodiment, iron is precipitated as its hydroxide from aqueous solution and barium, strontium or lead is coprecipitated therewith as the respective laurate salt. The finely divided precipitated particles are intimate mixtures of the iron and coprecipitated element so that upon the drying and calcining a dense, hexagonal ferrite of single domain size is formed.

This invention relates to the manufacture of ferrites and more particularly it is related to a method of chemically coprecipitating iron hydroxide and a long chain fatty acid salt of barium, strontium or lead as finely divided particles which may be readily converted into dense, highly efficient ferrites.

While ferromagnetism is commonly recognized as a property of certain metals, a similar effect known as ferrimagnetism has been observed in certain compounds of metals such as the ferrites. It is known that the reaction products of oxides of iron and oxides of other suitable metals possess ferrimagnetic properties. These complex oxides are known as ferrites and, depending upon the composition and particular treatment of the ferrites, their magnetic properties may be either soft or hard. Since some commercially important ferrite compositions do not occur in nature, it is necessary that they be manufactured. Ferrites have been formed by mechanically mixing powders of Fe_2O_3 and oxides or carbonates of other metals such as cobalt, manganese, zinc, magnesium, barium, and strontium and lead. If mixed in the proper known proportions and suitably sintered, the resulting particles are ferrimagnetic. However, it is realized that the method of forming ferrites by mechanically mixing the oxide constituents produces a product having magnetic properties less desirable than those theoretically obtainable. This has been attributed, in part, to incomplete mixing which may cause a product of slightly low density to be formed. Moreover, it is quite difficult to produce ferrite particles uniformly of single domain size by mechanical means. Although the mechanically formed powders may be milled, it is extremely difficult to achieve uniform powder mixture of about one micron particle size which is approximately the single domain size of hexagonal ferrites.

A very useful and commercially important class of ferrites are the hexagonal ferrites such as barium ferrite, ideally $\text{BaFe}_{12}\text{O}_{19}$ (or $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$) strontium ferrite ($\text{SrFe}_{12}\text{O}_{19}$) and lead ferrite ($\text{PbFe}_{12}\text{O}_{19}$). They are hard ferrites which means that they are difficult to demagnetize. In order for these hexagonal ferrites to possess near optimum magnetic properties the individual particle size must closely approximate the single domain size which is believed to be approximately one micron. Unfortunately, a domain size of this dimension is within the range where hard ferrite precursor powders fabricated by conventional mechanical techniques normally have their mean particle diameter. In the fabrication of highly

2

effective permanent ferrite magnets it is important to be below this critical diameter in the preparation of the ferrite precursor powders because of subsequent grain growth during the sintering operation. Since it is extremely difficult to classify or separate particles of micron size, commercial sintered hexagonal ferrites typically contain grains which are larger than the single domain size and therefore leave something to be desired as far as magnetic properties are concerned.

It is an object of the present invention to provide a useful, readily performed chemical coprecipitation process yielding finely divided ferrite precursor powder containing an intimate mixture of a suitable compound of iron and of an element selected from the group consisting of barium, strontium and lead. The precipitated powder is calcined to form ferrite particles of substantially critical domain size or slightly smaller.

In accordance with a preferred embodiment of my invention a hexagonal ferrite such as barium ferrite, strontium ferrite or lead ferrite is formed by a chemical coprecipitation technique. An aqueous solution of suitable proportions of a suitable iron salt and a suitable salt of barium (or strontium or lead) is prepared. A second aqueous solution of ammonium hydroxide and the ammonium salt of a fatty acid such as lauric acid or stearic acid is formed. The composition of the ammonium hydroxide-ammonium salt of fatty acid solution is adjusted so that there is just enough of the fatty acid salt present to precipitate barium, the iron being precipitated by the ammonium hydroxide. The two solutions are mixed at room temperature and a very finely divided precipitate is formed. The precipitate particles each contain an intimate mixture of iron hydroxide and barium-fatty acid salt. The proportion of iron and barium in the precipitate is the same as that initially present in the solution. The precipitate is filtered from the mother liquor, washed with water and dried. The precipitated powder is heated to decompose the barium-fatty acid salt and yields barium oxide. The burned-out powder is then calcined to form ferrite particles which are substantially uniformly one micron particle size. These particles are found to have excellent magnetic properties very closely approaching those determined theoretically obtainable in dense crystals of the ferrite of domain size.

Other objects and advantages of my invention will become more apparent from a detailed description thereof which follows.

The drawing is a flow diagram depicting basic steps in a preferred embodiment of the process which have been described briefly and will now be described in more detail.

A specific example of the invention will more clearly describe a preferred technique of carrying out my method. A water solution of reagent grade barium nitrate and ferric nitrate of the correct molar ratio 1Ba^{++} to 12Fe^{+++} was prepared. The solution comprised 155 grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 8.55 grams of $\text{Ba}(\text{NO}_3)_2$ and sufficient distilled water to provide a total solution volume of 500 ml. A second water solution of lauric acid dissolved in ammonium hydroxide was prepared. Twenty (20) grams of lauric acid and 100 grams (112 ml.) of reagent grade ammonium hydroxide solution (28%–30% NH_3) were added to a sufficient quantity of distilled water to provide a clear solution having a total volume of 2000 ml. and a pH of about 10.8. The water solution of barium nitrate and ferric nitrate was added to the ammonium laurate-ammonium hydroxide solution to completely precipitate all the barium and iron. The solution of ammonium laurate-ammonium hydroxide was rapidly stirred during the precipitation and the pH accurately monitored. The precipitation should not be continued below a pH of 8

as barium laurate is not suitably precipitated below this pH value. Preferably the precipitation is accomplished at a pH of 8.5.

The brown precipitate was filtered at room temperature from the mother liquor and washed four times with distilled water to remove soluble ammonium salts formed during the double decomposition reactions. The filtered and washed precipitate was then dried at 200° F. in air overnight. The dry precipitate powder was analyzed and found to consist of barium laurate and hydrated ferric oxide. The finely divided precipitate was heated at 200°–250° C. to burn out or decompose the barium laurate in the mixture to barium oxide and to fully dehydrate the ferric oxide. X-ray analysis of the fine powder revealed a fine particle mixture of magnetic Fe₂O₃ and BaO. The particle size of powder at this point was in the range of 100 to 500 angstroms. Small portions of the barium oxide-magnetic ferric oxide powder were calcined at varying temperatures between 570° C. and 1190° C. for one hour each. Measurements were then made on each of the specimens with a magnetometer at room temperature to evaluate the hysteresis properties of the respective calcined specimens. In connection with these measurements the maximum intrinsic coercive force of each of the specimens was noted. In the table is summarized the maximum intrinsic coercive force for each of the specimens which had been heated for one hour at the stated temperature.

TABLE

Specimen number	Calcining temperature, ° C.	Coercive force, (H _{ci}) oersteds
1.....	570	100
2.....	625	100
3.....	680	3,250
4.....	700	4,500
5.....	800	4,750
6.....	970	5,500
7.....	1,090	4,500
8.....	1,190	2,500

For uniform heating periods of one hour it was found that a temperature of approximately 600° C. was required to form a hexagonal ferrite. This was determined by X-ray analysis. It is noted in the above table that the values of maximum intrinsic coercive force increased as the calcining temperatures were increased up to a temperature of about 970° C. This appears to be due to the fact that the uncalcined powder was considerably smaller than single domain size for barium ferrites (about one micron or 10⁴ angstroms) and some grain growth was necessary to achieve the required domain size. In fact, the specimens which were calcined at temperatures substantially below 970° C. demonstrated superparamagnetic properties which was apparently due to their ultra fine particle size. Superparamagnetism in these specimens was determined by a Mossbauer study. However, the calcining of the powder at 970° C. for one hour produced barium ferrite particles of approximately single domain size having a maximum intrinsic coercive force of 5500 oe. This value of intrinsic coercive force is in good agreement with that reported in the literature for single domain barium ferrite powder (H_{ci}=5350 oe.). It is also in the range which fits a theoretical value for single domain barium ferrite published in the literature of H_{ci}=5900 oe. This latter value is based on a coherent rotating model of single domain uninteracting particles when shape and crystal anisotropy are both taken into account.

Since the ferrite precursor powders produced in accordance with my method are typically smaller than the single domain size of most ferrites, it will be appreciated that there is ample opportunity to control the calcining temperature and period to achieve a desired particle size. The coreaction of the ferrite precursors and the grain growth are both time and temperature dependent. The

optimum particle size may vary somewhat with different ferrite compositions but the optimum calcining conditions may be determined experimentally as was done in connection with the above example with respect to barium ferrite.

In general, my method may be employed both to coprecipitate iron with barium, strontium or lead to form the simple hexagonal ferrites as described and it may be employed to form more complex ferrite-precursor mixtures of iron, barium (strontium and lead) and any of a number of other metals such as manganese, magnesium, zinc, cobalt and the like. In these situations the iron and the other metals except for barium, strontium and lead are precipitated as the respective hydroxides, and the latter elements are precipitated as fatty acid salts. For the precipitation of barium, strontium and lead long chain saturated or unsaturated fatty acids containing preferably ten to twenty carbon atoms are employed. I consider it desirable to employ a fatty acid of at least ten carbon atoms to assure substantially complete precipitation of barium, strontium or lead in the ammonium hydroxide environment. Fatty acids containing more than twenty carbon atoms add little to the completeness of the precipitation, and may themselves be difficult to dissolve in ammonium hydroxide. Lauric acid and stearic acid are examples of readily available, substantially pure fatty acids which may be employed in my process. For best results, it is necessary that only sufficient fatty acid be used in the coprecipitation process to effect the precipitation of barium, strontium or lead. All other materials should be precipitated as their respective hydroxide salt. I find it necessary to use the fatty acid salt of barium, cobalt or lead to bring about a true coprecipitation of these metals with iron hydroxide. However, if all ferrite precursor metals in a given formulation are precipitated as stearates, which is, of course, usually possible, the precipitate tends to coalesce and melt during burn out of the fatty acid and the desired ultra fine particle size is lost.

Accordingly, my invention provides a technique of coprecipitating iron and other suitable metals with barium, strontium or lead. The three last named metals are precipitated as long chain fatty acid salts and all other metals are precipitated as the respective hydroxides. Although the preparation of barium ferrite was described in a specific embodiment, strontium ferrite, lead ferrite and other ferrites may be formed by substantially the same process.

Thus, it will be appreciated that other modes of my described method could be adapted by one skilled in the art and accordingly the scope of my invention should be considered limited only by the following claims.

I claim:

1. A method of forming a ferrite comprising coprecipitating ferric hydroxide and a fatty acid salt of an element selected from the group consisting of barium, strontium and lead from an aqueous solution of an ammonium hydroxide and a fatty acid to form finely divided particles wherein said iron hydroxide and said fatty acid salt are intimately mixed, said fatty acid containing at least ten carbon atoms in its molecule,

separating the precipitated particles from the aqueous mother liquor,

drying said particles,

burning out the fatty acid organic material from said particles to leave a residue comprising an intimate mixture of ferric oxide and the oxide of said element, and

further heating said particles thereby coreacting said oxides to form a particulate crystalline ferrite composition comprised of iron, oxygen and an element taken from the group consisting of barium, strontium and lead, said coreacted particles being of substantially the single domain size of the desired ferrite composition or smaller.

5

2. A method of forming a ferrite comprising preparing a first aqueous solution comprising a suitable salt of iron and of at least one element selected from the group consisting of barium, strontium and lead, preparing a second aqueous solution comprising a fatty acid containing from ten to twenty carbon atoms in its molecule in aqueous ammonium hydroxide, mixing said first and said second aqueous solutions to coprecipitate iron hydroxide with a fatty acid salt of said element to form a finely divided precipitate wherein said iron hydroxide and said fatty acid salt are intimately mixed, filtering said precipitate from the mother liquor, drying the precipitate, burning out the fatty acid organic material from said particles, the residue comprising an intimate mixture of ferric oxide and the oxide of said element, and calcining said particles to form a crystalline ferrite composition comprising iron, oxygen and an element taken from the group consisting of barium, strontium and lead, said particles being of substantially the single domain size of the desired ferrite composition or smaller.

3. A method of forming a hexagonal ferrite comprising preparing a first aqueous solution containing a suitable ferric salt and a salt of at least one element selected from the group consisting of barium, strontium and lead, preparing a second solution comprising a fatty acid containing from ten to twenty carbon atoms in its molecule in aqueous ammonium hydroxide, the amount of said fatty acid in said second solution

6

being substantially chemically equivalent to the amount of said element in said first solution, the amount of said ammonium hydroxide being in excess of the amount which is chemically equivalent to said ferric salt, mixing said first and said second aqueous solutions to coprecipitate iron hydroxide with the fatty acid salt of said element to form a finely divided precipitate wherein said iron hydroxide and said fatty acid salt are intimately mixed, filtering said precipitate from the mother liquor, drying the precipitate, burning out the fatty acid organic material from said particles at a temperature of about 200°–250° C., the residue comprising an intimate mixture of ferric oxide and the oxide of said element, the particle size of said particles being 500 angstroms or less, and calcining said particles to coreact said ferric oxide and the oxide of said element to form a hexagonal ferrite and to effect the growth of said particles whereby particles of substantially the single domain size of the desired hexagonal ferrite composition are obtained, said single domain size being in the order of one micron.

References Cited

UNITED STATES PATENTS

3,019,189	1/1962	Albers-Schoenberg	252—62.63
3,049,404	8/1962	Wade	252—62.63

ROBERT D. EDMONDS, Primary Examiner