

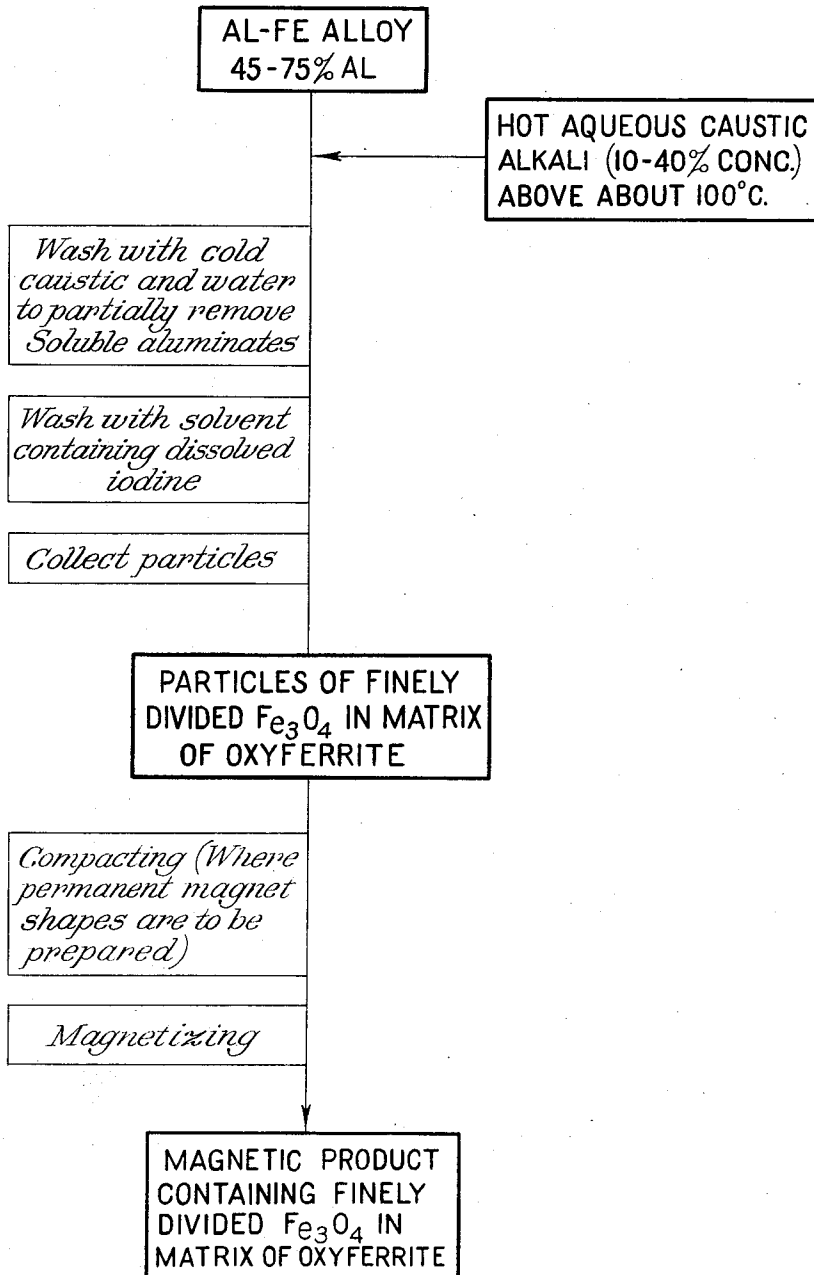
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MAGNET MATERIAL AND METHOD OF PREPARING THE SAME

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MAGNET MATERIAL AND METHOD OF
PREPARING THE SAME

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12 Claims. (Cl. 175-21)

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This invention relates to magnet material and to a method of preparing the same, reference being made to the accompanying drawing which forms a part of this specification. More particularly, the invention relates to the preparation of permanent magnet material from aluminum-iron alloys by treatment of such alloys with caustic alkali to dissolve away the aluminum and leave an undissolved, finely divided residue consisting largely of well dispersed, finely divided Fe_3O_4 , in a matrix of oxyferrite. The material so produced has been found to possess good magnet properties, adapting it for use in the manufacture of permanent magnets and permanent magnet material.

It has heretofore been proposed to treat alloys of aluminum and a metal of the iron group, such as nickel or cobalt, with caustic soda to produce finely divided nickel, or cobalt, suitable for use as a catalyst in hydrogenation processes. Neither nickel nor cobalt produced by such method, however, possesses magnetic properties that make either of them suitable for use as permanent magnet material. If, instead of starting with aluminum-nickel or aluminum-cobalt alloys, one starts with aluminum-iron alloys and treats the same with caustic soda in a manner similar to that described for the preparation of catalytic nickel, or cobalt, the resulting iron product possesses magnetic properties that are in no way superior to those possessed by the magnetic oxide of iron, Fe_3O_4 . For instance, the energy product of the iron produced in the same way as the nickel and cobalt catalysts will be in the neighborhood of 200,000, or less.

In accordance with the method of my present invention, the composition of the aluminum-iron alloy used as the starting material is such, and the conditions of treatment are so selected and controlled, that a different product from that resulting from the method of making a catalyst from aluminum alloys of metals of the iron group is produced. Furthermore, the product of my method possesses magnetic properties that peculiarly adapt it for use in the making of permanent magnets and permanent magnet materials. Its energy product, for instance, is in excess of 500,000 and may be in excess of 1,100,000 when prepared in accordance with the preferred method of my invention.

I have found that in order to obtain the best permanent magnet properties, the aluminum-iron alloy used as the starting material should be between 50 and 60% by weight of aluminum. It is possible, however, to obtain less satisfactory

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results within the broader range of from 45 to 75% aluminum content by weight of the starting alloy. Some increase in magnetic properties, especially for alloys lying within the range of from 50 to 54% of aluminum by weight, is realized if the alloy is heat treated at around 2000° F. for several hours and then air cooled, since such heat treatment appears to homogenize the alloy.

The original particulation size of the aluminum-iron alloy subjected to the caustic alkali leaching is also important in its effect upon the magnetic properties of the final product. The alloy should be in a finely divided form such that it will pass through a 40-mesh screen, and it should preferably be of fairly uniform particle size. I have found it advantageous to ball-mill the aluminum-iron alloy so as to pass through a 100-mesh screen before subjecting the alloy to the caustic alkali leaching step.

In the leaching of the aluminum-iron alloy rather close control of the conditions of the leaching and subsequent washing step is necessary in order to develop the desired magnetic properties in the final product. For instance, the concentration of the caustic alkali solution, for best results, should be between 25 and 35% of caustic alkali by weight of the solution, with an optimum of 30%. With some sacrifice in magnetic properties of the product, the concentration range can be broadened within the limits of from 10 to 40% of caustic alkali by weight of the solution.

The temperature at which the leaching operation is carried out is also important. Poorer magnetic properties are obtained if the finely divided aluminum-iron alloy is added to the aqueous caustic alkali solution in the cold than if the solution is hot at the time of such addition. Preferably, the caustic alkali solution is at about its boiling point at the time of the addition of the finely divided aluminum-iron alloy, and is kept at around that temperature until the substantial completion of the dissolution or leaching out of the aluminum from the alloy. With a solution having a caustic alkali concentration within the range of 25 to 35% of caustic alkali, by weight, this will mean a temperature of over 100° C. and generally in the neighborhood of 110 to 120° C. The time of the leaching operation should be as short as possible, and under the conditions mentioned as preferred, the time may be as short as twenty minutes, or even shorter.

I have found that if the undissolved residuum from the leaching operation is allowed to age in

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the leaching solution for any considerable length of time, there is some loss in the magnetic properties of the product. There is even more loss in magnetic properties if the undissolved particles are washed with water in a prolonged washing operation, or if the undissolved particles are largely freed from the leaching solution or from the wash water and allowed to stand around exposed to the air. In fact, upon drying out, the residual particles from the leaching operation are so highly oxidizable as to be pyrophoric.

Accordingly, I have found that the residual particles from the leaching operation should be washed with as little delay as possible after the completion of the leaching operation and, if shaped permanent magnets are desired, the particles should then be compacted into the desired shape without any intermediate complete drying of the particles. The washing is preferably carried out with cold aqueous caustic alkali solution, followed with water washing, if desired, to remove soluble aluminates, but without complete removal of the aluminate film that may surround the residual particles.

Compacting of the washed particles remaining from the leaching and washing steps is carried out at pressures in excess of one hundred thousand pounds per square inch, and preferably at pressures above one hundred sixty thousand pounds per square inch. The pressure must be applied rather slowly in order to permit the escape of water from the particles. After being compacted, the material is hard enough to scratch glass. In general, the hardness is considerably in excess of that of pure iron, being greater than 200, and usually being above 300 units, when measured on a Vickers-Amsler hardness tester under a 1.5 kilogram load diamond penetrator, 20 seconds duration.

As to the magnetic properties of the compacted material, test bars show an energy product, $B_d H_d$ Max. in excess of five hundred thousand, and frequently in excess of one million. The higher figures compare favorably with some grades of "Alnico."

On the other hand, if the material is to be used in the coating of a carrier to make a magnetic impulse member, such a magnetic tape for a magnetic sound recorder, it is not necessary to go through the compacting step.

It is, therefore, an important object of this invention to provide novel magnet material comprising iron in the form of oxyferrite as the matrix, with Fe_3O_4 in finely divided, sub-microscopic form well dispersed throughout the matrix.

It is a further important object of this invention to provide a method of making magnet material starting with an aluminum-iron alloy, dissolving out the aluminum content with an aqueous caustic alkali solution of such concentration and under such conditions as to leave undissolved particles consisting largely of oxyferrite containing well dispersed, sub-microscopic particles of Fe_3O_4 , washing the excess of soluble aluminates from such particles and without completely drying said particles or exposing the same to the atmosphere, either compacting said particles under high pressure into shapes capable of being permanently magnetized as such or pulverizing the particles to provide suitable magnetic material for use in the making of magnetic sound records and the like.

It is a further important object of this invention to provide a method of making magnetic

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material having good magnetic properties for use as permanent magnets or in pulverulent form for the coating of magnetic impulse record members, the material consisting largely of oxyferrite containing Fe_3O_4 in a sub-microscopic state of division well dispersed throughout the oxyferrite.

It is a further important object of this invention to provide magnetic material in the form of compacted shapes or in a fine state of subdivision, the material consisting largely of finely divided Fe_3O_4 well dispersed throughout oxyferrite, as a matrix.

Other and further important objects of the invention will become apparent from the following description and appended claims.

The attached sheet of drawings contains a detailed flow chart of a process according to the present invention. A more detailed explanation of each of the steps of the process will be hereinafter presented.

As a starting material for use in the method of my invention, an aluminum-iron alloy having an aluminum content between 50 and 60% by weight, and preferably the beta form of the alloy in which the aluminum content is between 53 and 56% by weight, is employed. Aluminum-iron alloys in which the aluminum content lies between 45 and 75%, by weight, can be used with less satisfactory results. The aluminum-iron alloy can be used in its as-cast condition, or it can be first subjected to a heat treatment to homogenize the alloy, as by holding the alloy at around 2000° F. for from four to five hours and then air-cooling. The heat treatment step is particularly effective in the case of alloys running between 50 and 54% of aluminum, by weight, within which range the increase in magnetic properties is especially noticeable.

In preparing the aluminum-iron alloy for leaching with caustic alkali solution, the alloy is first broken up and ground to a relatively fine size, such that the particles will pass through a 40-mesh screen. Preferably, the particle size should be such that the major portion of the ground material will pass through an 80- or even a 100-mesh screen. Ball milling of the pulverized alloy may be employed, if desired.

In the leaching of the pulverized alloy, an aqueous caustic alkali solution of a concentration of between 10 and 40% by weight, and preferably between 25 and 35% by weight is used to dissolve away the aluminum. Because of its relative cheapness, caustic soda is selected, but caustic potash could also be used. The aqueous caustic alkali solution is brought to a temperature around its boiling point, and preferably 100° C., before the finely divided alloy is introduced into the solution. If the alloy were added to a cold caustic alkali solution, even though the reaction is strongly exothermic and would therefore heat up the solution, the final product would not have so good magnetic properties as where the alloy is added to an initially hot solution of caustic alkali. The temperature of the caustic alkali, after the addition of the aluminum-iron alloy, is maintained at around its boiling point, which will lie between 100 and 125° C. for the broad concentration range of from 10 to 40% by weight of caustic alkali, and between 110 and 120° C. for the narrower preferred range of between 25 and 35% concentration of caustic alkali. The optimum concentration of caustic alkali by weight is 30%. The ratio of caustic soda (NaOH) to alloy should be between 1 to 1 and 4 to 1 by weight, and preferably about 2½ to 1.

The addition of the finely divided alloy to the hot solution of caustic alkali is made rapidly and the leaching operation carried out in as short a time as possible. With the caustic alkali solution at the boil at the time of addition of the alloy, a very vigorous reaction takes place. The reaction is allowed to proceed until substantially all of the aluminum content of the alloy has been dissolved. Hydrogen gas is evolved as a result of the reaction that takes place. Reaction is substantially complete within twenty minutes or so from the start of the addition of alloy, but may be brought to completion in a matter of seconds.

With as little delay as possible after the completion of the reaction, the residual undissolved particles are washed to remove the greater part of the soluble aluminates associated with the particles and in solution in the leach. As soon as the reaction has stopped, the leach solution is decanted off of the undissolved residue, and the residue washed two or more times in cold 25% caustic soda solution and finally two or more times with cold water. The residue after the washing treatment is a friable spongy material, which, if allowed to dry, is strongly pyrophoric. Consequently, the material should not be permitted to dry out nor should it be exposed to the atmosphere any more than possible in a semi-dried condition. The washing is carried out as expeditiously as possible and only to an extent necessary to remove a large proportion of the soluble aluminates produced in the leaching operation. Ordinarily, the product has been sufficiently washed when the pH of the wash water has been reduced below 9, and preferably within the range of 8 to 8.5.

If the leached material is to be used for the coating of a non-magnetic carrier, as in the making of coated paper tape for magnetic impulse record members, it is not necessary to compact the material. The material, after being washed with cold caustic soda solution, or water, or both, is washed with alcohol. The first alcohol wash may be with cold alcohol (denatured 95% ethyl alcohol), and then with hot alcohol, heated to from about 65° C. up to the boiling point, stirring thoroughly and decanting after each wash. Approximately four volumes of alcohol to one of the paste is used each time.

Following the alcohol wash the material is washed with a like volume of acetone and finally with acetone containing about 1/2 to 1% by weight of iodine dissolved in the acetone. The iodine apparently serves to reduce some of the oxides that are present. The resulting material is then mixed with a binder, such as a vinyl resin, and ball milled to make a coating composition for coating paper tape or other non-magnetic carrier. The ratio of the magnetic material to resinous binder should be as high as possible, and in general, in the neighborhood of 2 1/2 to 1, by weight.

If permanent magnet compacts are to be made, the leached and water washed material is sufficiently freed from water, as by means of an alcohol wash or an acetone wash containing dissolved iodine, and the material in the form of a wet paste then placed in a die. Pressure is applied slowly at the start until most of the liquid is expelled. Thereafter, the pressure can be applied more rapidly until it reaches a maximum of at least 50 tons per square inch. The pressure is held at that figure, or above, for five minutes or more to allow any remaining water to escape, after which the pressure may be raised to as high as 160,000 pounds per square inch or higher. The

sodium aluminate remaining in association with the magnetic material appears to serve as a bond for the particles during the compacting operation. In the final compact, the bond is apparently an oxide bond uniting the oxyferrite particles as a homogeneous whole. The compacts may be made into bar form, or other shapes.

The compacted material is very hard and brittle, but fairly strong under tension or compression. It is hard enough to scratch glass and exhibits a hardness well in excess of 200 on a Vickers-Amsler machine, using a 1.5 kilogram load diamond penetrator applied over 20 seconds duration. Depending upon the pressure used in compacting the material, the hardness may run as high as 300, or over. Such a degree of hardness, in itself, indicates that the product is not ordinary iron, which has a hardness not in excess of 200 on the same scale.

A chemical analysis of the magnetic product of my invention shows some aluminum, probably present as sodium aluminate, with the aluminum content running up to 1 or 2% and usually between 0.5 and 5% at the outside. The sodium content may run from 0.1 to 1.0% and more generally between 0.2 and 0.4. Analysis by vacuum diffusion at 1650° F. shows an oxygen content that may vary between 4 and 11%. The lower the oxygen content, in general, the better the magnetic properties of the material within these limits.

Microscopic analysis of the product indicates that it consists largely of iron in the form of oxyferrite, with Fe₃O₄ in very finely divided and mostly a sub-microscopic state of sub-division, well distributed in the oxyferrite, as the matrix. The iron gives a very distorted lattice under X-ray diffraction, indicating a possible reason for the unusual magnetic properties. The effective Fe₃O₄ present is spread through the matrix of oxyferrite in sub-microscopic particles. The agglomerated Fe₃O₄, if present with the finely dispersed Fe₃O₄, can be considered as impurity. The effective oxygen in dispersed Fe₃O₄ should not be more than about 5% in weight and the total oxygen (O₂) not more than 11%. However, a minor percentage, possibly a few tenths of a per cent of oxygen, is dissolved in the iron itself.

The following table indicates the properties of the test bars pressed at around 144,000 pounds per square inch:

Peak magnetic force, H _p —3060 Oersteds
Peak induction B _p —14,560 gauss
Residual induction B _r —7810 gauss
Coercive force H _c —365 Oersteds
Max. energy product B _a H _a max. 1,150,000

The following example will serve to illustrate a preferred embodiment of my method, but it should be understood that my invention is not limited to the specific conditions given.

Example

An aluminum-iron alloy having an aluminum content of 54.4% and an iron content of 45.6% was ground to pass a 60-mesh screen and the material held on an 80-mesh screen was selected. 224 parts of the aluminum-iron powder so obtained were added a little at a time to an aqueous caustic alkali solution at its boiling temperature, or around 110° C. The caustic soda solution was prepared by dissolving 400 grams of caustic soda (NaOH) in 1200 grams of water, to produce a concentration of 25% NaOH by weight. The total time of the leaching operation was around five minutes.

After washing twice with 25% NaOH solution (cold) and twice with water, the residue from the leaching operation, in the form of a wet paste, was compacted in a die under a pressure of about 144,000 pounds per square inch to form a bar having a weight of 12 grams and having dimensions of 0.81 x 0.586 x 5.11 cm., giving a density of 4.96 g/cm³. When tested after one hour the following magnetic test data were obtained from the bar:

Peak magnetic force, H_p —3100 Oersteds
Peak induction B_p —13,890 gauss
Residual induction B_r —7460 gauss
Coercive force H_c —395 Oersteds
Energy product $B_a H_a$ max. 1.125×10^6
Induction for max. energy 4500 gauss

This is a continuation-in-part of my application Serial No. 610,671, filed August 13, 1945, now abandoned.

I claim as my invention:

1. The method of making permanently magnetizable material, which comprises adding a finely divided aluminum-iron alloy of between 45 and 75% by weight of aluminum to an initially hot aqueous caustic alkali solution of from 25 to 35% concentration, maintaining said solution at around its boiling point until substantially all the aluminum has been dissolved away, washing remaining undissolved particles to partially remove soluble aluminate therefrom and compacting said particles without completely drying and without substantial exposure of said particles to the atmosphere.

2. A permanent magnet, comprising a magnetized compact consisting largely of well dispersed finely divided Fe_3O_4 in a matrix of oxyferrite, the hardness of the compact being in excess of 200 (Vickers-Amsler diamond Vickers, 1.5 kg. load, 20 secs. duration), said compact having been prepared by the compacting of particles resulting from reacting a finely divided aluminum-iron alloy containing between 45% and 75% aluminum by weight with a hot aqueous solution of a caustic alkali containing 10% to 40% by weight concentration to dissolve away substantially all of the aluminum, and collecting the undissolved particles.

3. A permanent magnet, comprising a magnetized compact consisting largely of well dispersed, finely divided Fe_3O_4 in a matrix of oxyferrite, the hardness of the compact being in excess of 200 (Vickers-Amsler, 1.5 kg. load, 20 secs. duration), said compact having an energy product, $B_a H_a$ max. in excess of 0.5×10^6 , said compact having been prepared by the compacting of particles resulting from reacting a finely divided aluminum-iron alloy containing between 45% and 75% aluminum by weight with a hot aqueous solution of a caustic alkali containing 10% to 40% by weight concentration to dissolve away substantially all of the aluminum, and collecting the undissolved particles.

4. The method of making permanent magnet material, which comprises reacting an aluminum-iron alloy containing between 45 and 75% by weight of aluminum with a hot aqueous caustic soda solution of between 10 and 40% concentration until the dissolution of aluminum is substantially complete, washing the undissolved residue first with an aqueous medium and then with a water-miscible organic solvent containing dissolved iodine and collecting the washed residue.

5. The method of making permanent magnet material, which comprises reacting an aluminum-

iron alloy containing between 45 and 75% by weight of aluminum with a hot aqueous caustic soda solution of between 10 and 40% concentration until the dissolution of aluminum is substantially complete, washing the undissolved residue first with an aqueous medium and then with acetone containing dissolved iodine and collecting the washed residue.

6. The method of making a magnetic material which comprises reacting particles of an aluminum-iron alloy containing between 45% to 75% aluminum by weight with an aqueous caustic alkali having a concentration of 25% to 35% caustic by weight, at substantially the boiling point of said caustic solution until substantially all of said aluminum is dissolved away, collecting the undissolved particles comprising finely divided Fe_3O_4 in a matrix of oxyferrite, without completely drying the same, and processing said particles including compacting said particles to render them substantially less pyrophoric while retaining their magnetic properties.

7. The method of making a magnetic material which comprises reacting particles of a finely divided aluminum-iron alloy containing between 50% and 60% aluminum by weight with 25% to 35% concentration aqueous caustic alkali solution at a temperature above 100° C. until substantially all of said aluminum is dissolved away, collecting the undissolved particles comprising finely divided Fe_3O_4 in a matrix of oxyferrite, without completely drying the same, and processing said particles including the step of compacting said particles to render them substantially less pyrophoric while retaining their magnetic properties.

8. The method of making a magnetic material which comprises reacting a finely divided aluminum-iron alloy containing between 45% and 75% aluminum by weight with a hot aqueous solution of a caustic alkali containing between 25% and 35% by weight of the caustic alkali to dissolve away the aluminum content of said alloy until not more than about 5% of undissolved aluminum remains combined with the iron of said alloy, washing undissolved particles with cold aqueous caustic alkali solution to partially remove soluble aluminates, collecting the undissolved particles comprising finely divided Fe_3O_4 in a matrix of oxyferrite without completely drying the same, compacting said particles to render them less pyrophoric while retaining their magnetic properties, and magnetizing the compact produced.

9. The method of making magnetic material which comprises adding a finely divided aluminum-iron alloy containing between 45% and 75% aluminum by weight to a hot concentrated aqueous solution of a caustic alkali of from 25% to 35% by weight concentration, maintaining said solution at around its boiling point to dissolve away the aluminum content of said alloy until not more than about 5% of undissolved aluminum remains combined with the iron of said alloy, washing the resulting undissolved particles to partially remove soluble aluminates therefrom, collecting the undissolved particles comprising finely divided Fe_3O_4 in a matrix of oxyferrite without completely drying the same, and compacting said particles to render them substantially less pyrophoric while retaining their magnetic properties.

10. The method of making magnetic material which comprises reacting an aluminum-iron alloy containing between 45% and 75% by weight aluminum with a hot aqueous caustic soda solution of between 10% and 40% concentration until the dissolution of aluminum is substantially com-

plete, washing the undissolved residue first with an aqueous medium and then with acetone containing dissolved $\frac{1}{2}$ to 1% by weight iodine, collecting the washed residue, comprising finely divided Fe_3O_4 in a matrix of oxyferrite, without completely drying the same, and compacting said particles to render them less pyrophoric while retaining their magnetic properties.

11. A magnetizable composition consisting largely of well dispersed finely divided Fe_3O_4 in a matrix of oxyferrite, said composition having been produced by reacting a finely divided aluminum-iron alloy containing between 45% and 75% aluminum by weight with a hot aqueous solution of a caustic alkali of 10% to 40% by weight concentration to dissolve away substantially all of the aluminum, collecting the undissolved particles, and compacting them to render them substantially less pyrophoric while retaining their magnetic properties.

12. A magnetizable composition consisting largely of well dispersed finely divided Fe_3O_4 in a matrix of oxyferrite, said composition having been produced by reacting a finely divided aluminum-iron alloy containing between 50% and 60%

aluminum by weight with a hot aqueous solution of a caustic alkali of 25% to 35% by weight concentration to dissolve away substantially all of the aluminum, collecting the undissolved particles, and compacting the particles to render them substantially less pyrophoric while retaining their magnetic properties.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,669,642	Andrews	May 15, 1928
1,946,964	Cobb	Feb. 13, 1934
1,976,230	Kato et al.	Oct. 9, 1934
2,196,824	Dahl et al.	Apr. 9, 1940
2,254,976	Powell	Sept. 2, 1941
2,273,832	Carney	Feb. 24, 1942
2,402,694	Tanner	June 25, 1946
2,427,018	Nesbitt	Sept. 9, 1947
2,463,413	Neel	Mar. 1, 1949