

SPECIFICATION

(MIN-1567)

BE IT KNOWN, that we, SANAA E. KHALAFALLA and GEORGE W. REIMERS, have invented a new and useful improvement in MAGNETOFLUIDS AND THEIR MANUFACTURE, of which the following is a specification.

Abstract

Magnetofluids, comprising a stable, colloidal suspension of magnetite and elemental iron, are produced by comminuting a nonmagnetic or anti-magnetic precursor compound to colloidal size, dispersing the precursor in a carrier fluid and thereafter converting the precursor to ferromagnetic forms while in stable suspension.

Background of the Invention

Ferromagnetic liquids, commonly known as "ferrofluids" comprise a permanent suspension of ferromagnetic particles in a liquid carrier. Typical compositions consist of submicron-sized magnetite particles suspended in an organic liquid, such as kerosene, with a dispersing agent added to prevent flocculation of the particles. Properties of the fluids are highly dependent upon particle size and upon the concentration of ferromagnetic particles in the liquid. A detailed discussion of ferrofluids, their properties and their uses may be found in an article by R. E. Rosensweig published in International Science and Technology, July 1966, pages 48-56.

Ferromagnetic liquids are conventionally produced by the long-term grinding of magnetite in a carrier liquid. Grinding times required in order to obtain a true colloidal suspension range to 1000 hours or more. Grinding ferromagnetic materials is complicated by interparticle magnetic flocculation arising from the attraction of one particle to another. This magnetic attraction is in addition to the usual interparticle attraction caused by van der Waal's forces. Consequently, the conventional preparation processes are extremely inefficient.

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Summary of the Invention

We have found that the grinding or comminuting time necessary to prepare magnetofluids may be greatly reduced by appropriate use of a non-magnetic precursor compound. The nonmagnetic precursor compound, preferably a suboxide of iron, is comminuted to colloidal size and dispersed in a carrier liquid. It is then converted to ferromagnetic forms while in suspension to form a stable magnetofluid.

A preferred embodiment comprises preparing submicron sized wustite particles by controlled reduction of ferric oxide and further comminuting the wustite particles in the presence of a dispersing agent until colloidal dimensions are obtained. The wustite particles are then converted to ferromagnetic forms by disproportionation to iron and magnetite.

Hence, it is an object of our invention to prepare magnetofluids from nonmagnetic precursor compounds.

Another object of our invention is to reduce the grinding time required in the production of stable magnetofluids.

Yet another object of our invention is to provide a magnetofluid of novel composition.

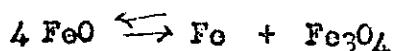
Detailed Description of the Invention

We have discovered that ferromagnetic liquids, hereafter referred to as ferrofluids, may be produced in a simple fashion by comminuting a non-magnetic or antimagnetic precursor compound to produce a stable, colloidal suspension and thereafter converting the precursor compound to ferromagnetic forms. As used herein, the term "nonmagnetic" will be understood to include antimagnetic compounds. This technique reduces grinding time required to produce a stable, submicron sized particulate suspension to as little as 5% of that required by conventional methods.

Substitution of magnetite by a nonmagnetic precursor allows grinding or other comminution techniques to be accomplished without complications arising from interparticle magnetic attraction. Precursor compounds may

comprise the lower or suboxides of iron or ferrous oxides generally. The preferred precursor is wustite which is FeO with a defect structure. Wustite is also commonly represented by formula Fe_{1-x}O wherein x will typically vary from about 0.01 to about 0.20.

Wustite has been the subject of a number of theoretical studies. It is thermodynamically unstable below its eutectoidal temperature of 570°C but the metastable phase can be prepared by rapid quenching from higher temperatures to room temperature. Quenching will preserve or freeze the wustite structure due to extreme sluggishness of solid-solid transformations at ordinary temperatures. Heating the metastable phase to temperatures below the eutectoidal point causes wustite to disproportionate to the thermodynamically stable phases of α -iron and magnetite according to the following general formula:



The kinetics of this reaction were studied by Ilchner and Mitake, who found that Fe_{1-x}O decomposes in the temperature range of 220° to 450°C . They found that the apparent activation energy varied between 17 and 12 KCal per mole magnetite formed as x changed from 0.06 to 0.11, respectively. Growth of Fe_3O_4 particle with a specific orientation relationship with respect to the matrix was controlled by an interfacial reaction. This work was reported in Acta Metallurgica, V. 13, pages 855-867 (1965).

It is also known that wustite has a sodium chloride structure and that the number of metal ion vacancies in Fe_{1-x}O is twice as large as the iron deficiency would indicate. The extra iron is located interstitially in tetrahedral sites while vacancies in the crystal lattice represent extra octahedral sites. As a result the crystal has a local configuration analogous to that of Fe_3O_4 and magnetite resulting from partial decomposition of the wustite phase is oriented identically with and grows epitaxially on the parent substrate.

In practicing our invention, it is highly advantageous to obtain wustite of a very small particle size in order to substantially reduce the

amount of grinding required to reach colloidal dimensions. Hence, we prefer to prepare wustite by the low temperature reduction of finely divided iron oxides such as hematite. It is known that metallic iron produced by low temperature hydrogen reduction of iron oxides is pyrophoric. This form of iron ignites easily, even spontaneously in air and is reoxidized. Presumably when reduction proceeds at relatively low temperatures, only a skeleton framework of iron atoms remain where the iron oxide was before; thermal motion of the atoms being too sluggish to cause crystallization into a denser and more stable form. Pyrophoric iron has been reported at reduction temperatures as high as 600°C.

While nothing is known about pyrophoric iron oxides, it was hypothesized that low temperature reduction of hematite might yield wustite in the pyrophoric state. These predictions were verified by experiments in which reagent grade iron oxide powder (hematite) was reduced at 650°C with 25% CO-75% CO₂ in one case and with 50% CO-50% CO₂ in a second case to yield magnetite and wustite respectively. Both products were found to be pyrophoric in the sense that they reoxidized spontaneously and caught fire when exposed to air. Hence, it was clear that wustite having a very small particle size could be prepared but the product could not be further processed by conventional means because of its pyrophoric nature.

We then found that wustite in the pyrophoric state could be protected from oxidation during further processing by coating or covering it with a dispersing agent. A dispersing agent is a necessary component of any ferrofluid composition. Its purpose is to maintain a coating around each individual ferromagnetic particle of sufficient thickness to prevent agglomeration or flocculation induced by the attractive van der Waals force. Essentially, the dispersing agent acts as an elastic coating around each colloidal particle preventing the close approach of one particle to another. Dispersing agents generally useful in ferrofluid preparation comprise long-chain organic molecules having a reactive end group. Aliphatic monocarboxylic acids having from

about 8 to about 24 carbon atoms are typical of dispersing agents useful in ferrofluid preparation. Oleic acid in particular is commonly used and produces excellent results. Dispersing agents useful in ferrofluid stabilization were found to be completely satisfactory for protecting wustite from pyrophoric oxidation. Hence the dispersing agent performed a dual function; first to prevent pyrophoric oxidation and second to stabilize the ferrofluid product.

Broadly, our process comprises comminuting a non or antimagnetic suboxide of iron to colloidal dimensions, dispersing the oxide in a carrier liquid to form a stable non-settling suspension and thereafter converting the nonmagnetic iron oxide to ferromagnetic forms while maintaining the particles in stable suspension. Our preferred lower iron oxide precursor compound is wustite.

Our most preferred embodiment comprises first subjecting a higher oxide of iron, such as hematite, to low temperature reduction to produce wustite of similar particle size. The wustite is then quenched to a low temperature, ambient or somewhat above, to recover the wustite in a metastable but pyrophoric state. Next the pyrophoric wustite is protected against oxidation by coating it with a dispersing agent such as oleic acid. The mixture is then added to a carrier liquid, typically a hydrocarbon such as kerosene, and subjected to grinding for a time sufficient to reduce the wustite particles to colloidal dimensions. After formation of a stable suspension, the wustite is converted to ferromagnetic forms, comprising metallic iron and magnetite, by refluxing at temperatures above about 200°C. The resulting ferrofluid product displays a strong magnetic response and is stable and non-settling under the influence of gravitational or magnetic fields. It is to be noted that our ferrofluid compositions differ from those of the prior art in that they comprise a mixture of colloidal particles of magnetite and elemental iron. Ferrofluids of conventional manufacture comprise a suspension of ferrite material.

It is not necessary that the precursor compound be prepared or obtained in a finely divided form prior to the comminution step. Large particle, non-pyrophoric wustite could be used with substantial advantage over prior art methods. However, preparation of wustite in a finely divided form substantially decreases comminution or grinding time required to obtain a colloidal suspension. Ferric oxide having a median particle diameter substantially less than 1 micron is commercially available and controlled reduction of such products will give wustite particles of approximately the same size. A stable, colloidal suspension is formed when the maximum particle size is less than about 0.01 microns ($100 \text{ \AA}$), provided of course that flocculation of the particles is avoided. Advantages arising from production of the wustite precursor in a finely divided form are readily apparent.

Reduction of ferric oxides must be carried out at temperatures above the wustite eutectoidal temperature, or 570°C . Temperatures within the general range of about 570° to 800°C produce satisfactory results. A preferred reduction temperature is in the range of 600° to 700°C . Gases are advantageously used as the reducing agents and a gaseous mixture of carbon monoxide and carbon dioxide is preferred. Wustite composition may vary from a nominal $\text{Fe}_{0.99}\text{O}$ to $\text{Fe}_{0.80}\text{O}$ while a preferred composition range is from $\text{Fe}_{0.95}\text{O}$ to $\text{Fe}_{0.85}\text{O}$. Conversion of the wustite precursor to ferromagnetic forms is most conveniently accomplished by refluxing the colloidal suspension at temperatures above about 200°C and below 570°C . Care must also be taken to avoid thermal decomposition of either the carrier liquid or the dispersing agent. Refluxing time required for substantially complete conversion of wustite to metallic iron and magnetite is temperature dependent but will typically range from about $\frac{1}{2}$ to about 10 hours at temperatures ranging from 200 to 300°C .

Carrier liquids useful in our ferrofluid compositions include hydrocarbons, fluorocarbons, silicone oils, or esters. Choice of carrier liquid does not affect the process except that the dispersing agent chosen

must be compatible with the carrier. Magnetic properties of the ferrofluid may be adjusted by varying the concentration of ferromagnetic particles suspended in the carrier liquid. This may readily be accomplished either by simple dilution or by evaporating a portion of the carrier. Concentrations of ferromagnetic particles as high as 40 to 50 g per 100 ml fluid are obtainable while retaining the liquid properties of the composition.

Ferrofluids produced by the method of this invention are useful in a host of different applications. For example, when a ferrofluid is subjected to an applied magnetic field, a magnetic levitation force is created within the ferrofluid thus giving the effect of an apparent increase in specific gravity. Nonmagnetic bodies immersed in the fluid may be levitated by the fluid even if they have substantially greater densities than the fluid. By adjusting the strength of the applied magnetic field, bodies of differing density may be selectively levitated thus providing a separation process based upon differing densities.

Other uses include accelerometers, attitude control devices, oscillation damping devices, rotating shaft seals and bearings. It has also been proposed to use hydrocarbon base or oil soluble ferrofluids for cleaning up oil spills. A relatively concentrated ferrofluid is sprayed on or otherwise mixed with an oil slick thus making the entire mixture magnetic. The oil slick is then skimmed from the water surface using a traveling magnet.

The following examples serve to illustrate specific embodiments of our invention.

Example 1

A 200 g sample of reagent grade ferric oxide powder was reduced at 650°C using a 50% carbon monoxide -50% carbon dioxide mixture. According to the thermodynamic phase diagram of the iron-oxygen system, the resulting product should comprise wustite having a composition of $\text{Fe}_{0.92}\text{O}$. A thermobalance was used to monitor the progress of reduction which was complete in about 1 hour. The resulting wustite, weighing 184 g, was removed from the

furnace crucible and quenched to room temperature using an inert gas atmosphere of helium. One hundred ml of oleic acid, enough to cover the oxide phase, was then added. The resulting mixture was then transferred to a ball mill containing 1 liter of kerosene and 7.3 kg of steel balls. Grinding continued for a total of 40 hours.

At the end of that time, the fluid was separated from the balls, poured into a graduated cylinder and allowed to stand for 48 hours. No solid sedimentation occurred after that time, indicating the fluid to be a true colloidal suspension. The fluid had a specific gravity of 0.806 g/ml and a viscosity of 2.87 cp compared to the carrier fluid (kerosene containing 10% oleic acid) which had a specific gravity of 0.772 g/l and a viscosity of 1.46 cp. A negative magnetic response was exhibited by the fluid when placed near the poles of an electromagnet.

Example 2

The antimagnetic colloidal wustite suspension of Example 1 was converted by disproportionation into magnetite and iron by refluxing at 250°C. Refluxing was continued for 6 hours, resulting in a fluid which exhibited a strong magnetic response. This resulting ferrofluid had the same specific gravity, 0.806 g/ml, as did the wustite suspension but the viscosity decreased to 2.61 cp. The fluid was stable and non-settling thus indicating that no flocculation or agglomeration occurred during the conversion of the wustite particles to ferromagnetic forms.

Example 3

Samples of the ferrofluid of Example 2 were concentrated by evaporation. Nitrogen was bubbled through the fluid at a temperature of 200°C until the volume was reduced to 72.5% of that originally present. At this point the specific gravity (measured at 20°C) was 0.820 g/ml and the viscosity was 3.50 cp. Evaporation was then continued as before until the

volume was reduced to 50% of that originally present. Specific gravity increased at this point to 0.848 g/ml and the viscosity increased to 4.55 cp. The resulting fluid was again concentrated to a volume 25% of that originally present. This fluid, now concentrated 4-fold, had a specific gravity of 0.916 g/ml. Viscosity was not measured.

All of the ferrofluid concentrates retained the properties of a true colloidal suspension displayed by the original fluid. Progressively increasing magnetic response was noted as the concentration increased.

Example 4

A comparative test was performed using the same reagent grade hematite powder as was utilized in Example 1. In this case, 190 grams of the powder was completely converted to magnetite by controlled reduction. Weight of the magnetite product was 184 g. The magnetite was cooled under an inert atmosphere and transferred under 100 ml oleic acid to the ball mill containing 1 liter of kerosene. Small samples of the product were intermittently withdrawn as grinding proceeded. These samples were centrifuged and the supernatant portion was tested for magnetic response. The first positive response was obtained after 300 hours of grinding time. At this point, the specific gravity of the fluid was 0.827 g/ml and its viscosity was 2.86 cp.

Example 5

In another test ferric oxide, in the form of $\text{-Fe}_2\text{O}_3$ or maghemite, was used to prepare magnetite. The finely divided ferric /oxide had an average particle size of 0.02 microns according to the manufacturer and displayed a surface area of $27 \text{ m}^2/\text{g}$. A particle diameter of 0.02 microns is approximately twice the particle diameter which will form a stable ferrofluid. The maghemite was reduced under controlled conditions and relatively low temperature in order to obtain particulate magnetite of approximately the same particle size. After reduction, the magnetite product was treated in a fashion identical to that set out in Examples 1 and 4.

After 56 hours of grinding, the resulting fluid gave a very feeble magnetic response. At this point the fluid had a specific gravity of 0.787 g/ml and a viscosity of 1.77 cp. Magnetite particles in the fluid settled out after 48 hours of standing in a graduated cylinder. Additional grinding was required in order to reach the colloidal state.