Sept. 29, 1970 R. E. ROSENSWEIG 3,531,413

METHOD OF SUBSTITUTING ONE FERROFLUID SOLVENT FOR ANOTHER

Filed Sept. 22, 1967 2 Sheets-Sheet 1

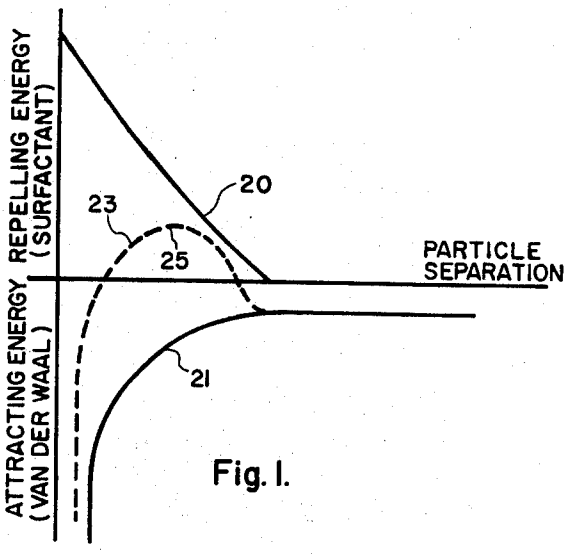


Fig. 1.

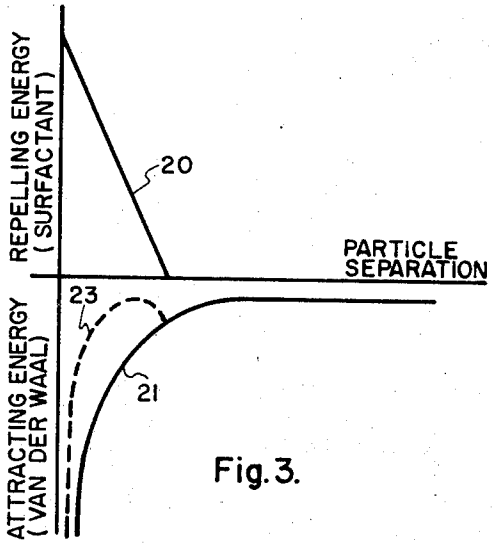


Fig. 3.

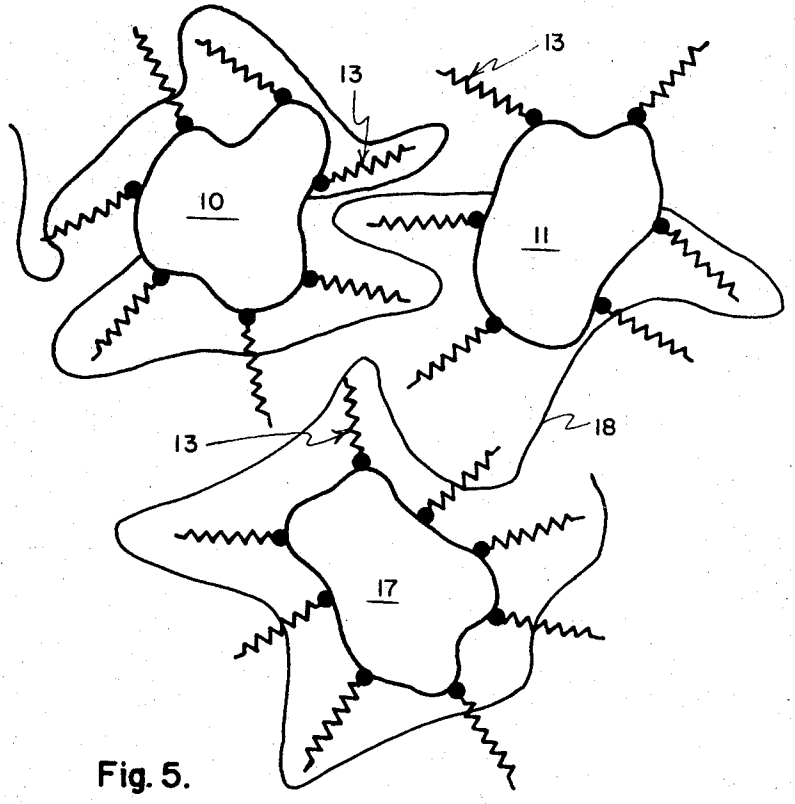


Fig. 5.

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METHOD OF SUBSTITUTING ONE FERROFLUID SOLVENT FOR ANOTHER

Filed Sept. 22, 1967 2 Sheets-Sheet 2

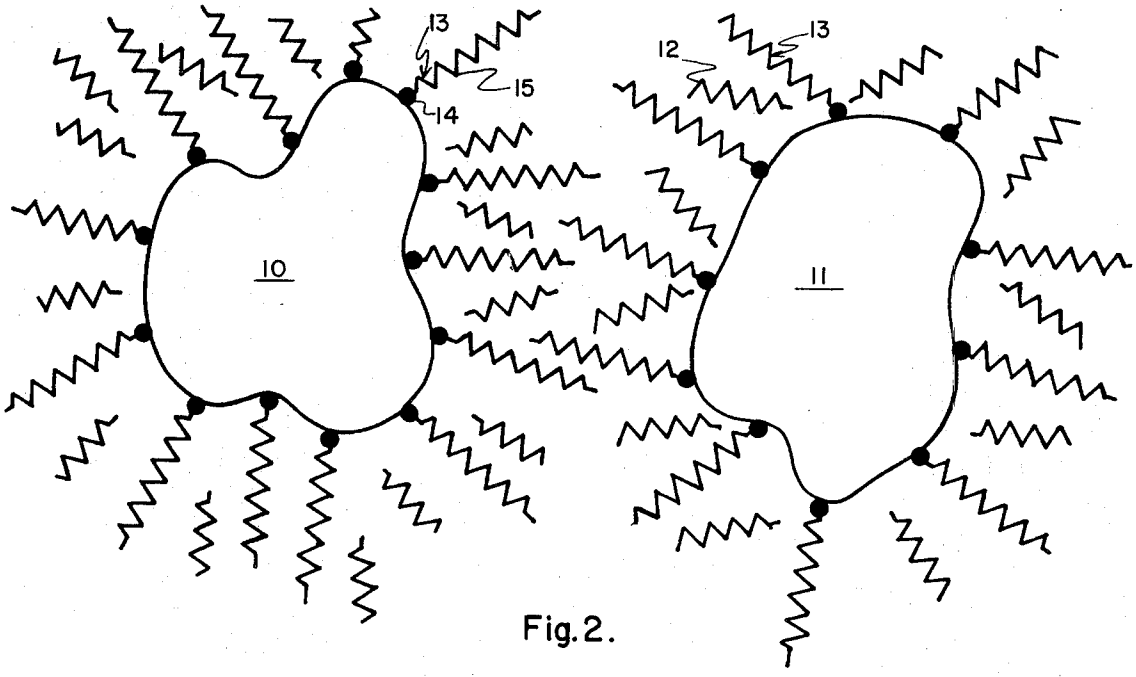


Fig. 2.

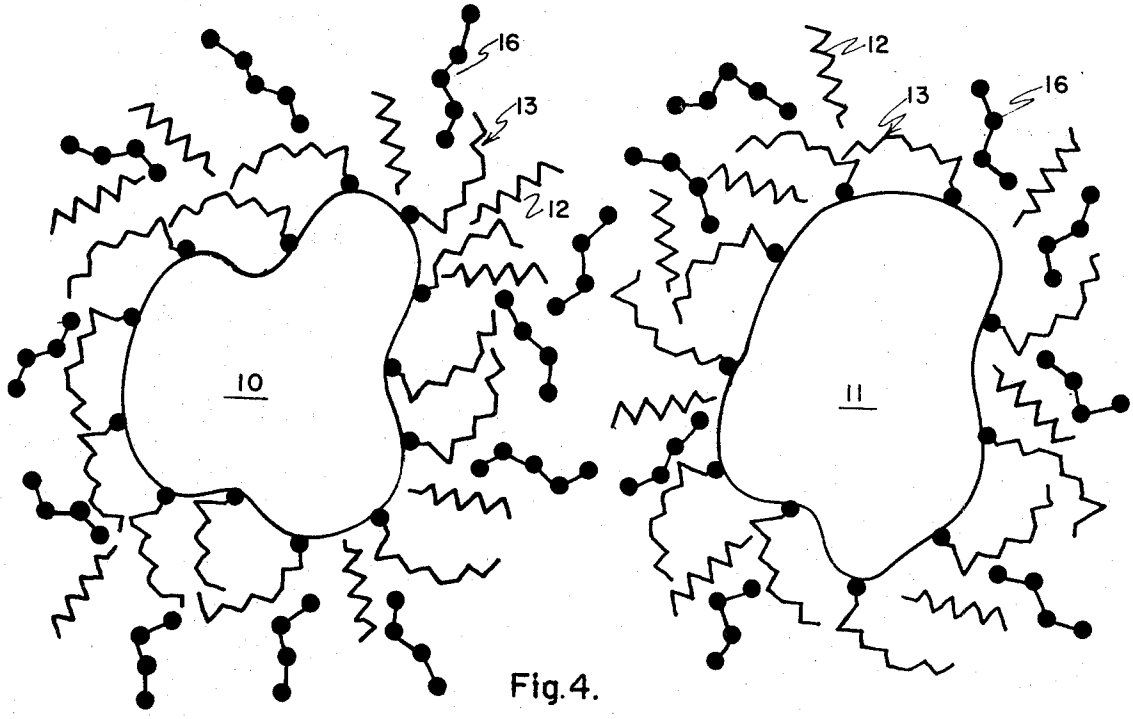


Fig. 4.

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United States Patent Office 3,531,413 Patented Sept. 29, 1970

3,531,413

METHOD OF SUBSTITUTING ONE FERROFLUID SOLVENT FOR ANOTHER

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Filed Sept. 22, 1967, Ser. No. 669,938
Int. Cl. B01d 21/01
U.S. Cl. 252—62.62 6 Claims

ABSTRACT OF THE DISCLOSURE

This invention covers a method of substituting one ferrofluid solvent for another. A typical class of ferrofluid contains magnetic particles with a polar surfactant adsorbed on the surface thereof suspended in a non-polar solvent. To substitute one solvent for another in accordance with the invention, a polar flocculating solvent is introduced into the ferrofluid causing the particles with the adsorbed surfactant to flocculate, and to settle out of solution.

The particles and solvent are separated. The particles are then redistributed within another solvent which may be the same as the original solvent or a different composition.

BACKGROUND OF THE INVENTION

The invention relates to ferrofluid and more particularly to methods of making ferrofluids. Related information may be found in Pat. No. 3,281,403.

In general, ferrofluids contain submicron particles of magnetic material such as magnetite and ferrites. A surfactant or dispersing agent is adsorbed on the surface of these particles and acts as a coupling agent between the particle and a solvent in which the particles are dispersed. Additional information on the structure of typical ferrofluids are found in an article entitled "Magnetic Fluids" by R. E. Rosensweig in the July 1966 issue of International Science and Technology.

Ferrofluids are generally made by grinding magnetic particles together with a surfactant and solvent over a prolonged period of time.

Not all surfactants or solvents are suitable grinding media. At times they are totally unsuitable and other times inefficient.

Examples of magnetic material which are suitable for this purpose are magnetite (FE_3O_4), manganese-zinc ferrite, γ-Fe_2O_3, and any solid magnetic material that can be formed in the proper particle size. Surfactants of the following general nature have been used to make ferrofluids. Carboxylic acids and their metallic salts, amines, succinic acid derivatives, condensation product of an amino ester of a fatty acid. The chain length should usually be eight carbon atoms or greater. Examples of solvents are aliphatic hydrocarbons such as heptane, octane, decane, mineral oil, kerosene etc., halogenated hydrocarbons such as carbon tetrachloride or trichlorethylene and aromatic solvents such as benzene, toluene and their non-polar derivatives. All of these solvents are suitable for grinding and are interchangeable.

Pentane is a suitable solvent but not useful as a grinding aid because it is very volatile.

Flocculation is used herein to denote the aggregation of individual particles into larger masses. These aggregations eventually grow large enough to deposit out of suspension.

It is an object of the invention to provide a method of substituting one solvent of a ferrofluid by another.

It is an object of the invention to provide a method of substituting one solvent of a ferrofluid by another by inducing particle flocculation to cause the magnetic particle to deposit out of solution.

It is another object of the invention to provide a means for formulating ferrofluids containing solvents that are not suitable as grinding or manufacturing aids.

It is yet another object of the invention to provide means for altering the particle concentration in a ferrofluid particularly where a ferrofluid surfactant is more volatile than the solvent.

It is still another object of the invention to induce flocculation for the purpose of substituting solvents by reducing the repelling forces overriding the Van der Waal forces of attraction.

In accordance with the invention a method of substituting one ferrofluid solvent for another ferrofluid comprises the steps of introducing a flocculation agent into the ferrofluid thereby causing the particles with adsorbed surfactant to come out of suspension. The particles are separated from the solvent and this is followed by resuspending them in another solvent.

The novel features that are considered characteristic of the invention are set forth in the appended claims; the invention itself, however, both as to its organization and method of operation, together with additional objects and advantages thereof, will best be understood from the following description of a specific embodiment when read in conjunction with the accompanying drawings, in which:

FIG. 1 shows a curve useful in explaining the forces acting on ferrofluid particles.

FIG. 2 is a schematic representation of a ferrofluid structure.

FIG. 3 shows a second curve useful in explaining the forces acting on ferrofluid particles.

FIG. 4 depicts the relationship of the various components of a ferrofluid in which a flocculation solvent has been added.

FIG. 5 illustrates an alternate method of causing particles to flocculate.

Characteristically, magnetic particles in a ferrofluid remain in suspension without changing the characteristics of the ferrofluid as a homogeneous medium under the influence of applied magnetic fields and magnetic field gradients. There are two contributing factors that maintain the magnetic particles in suspension. The first relates to the size of the particles which typically are in the submicron region so that particle motion is maintained by thermal agitation. Secondly, the surfactant or dispersing agent acts to maintain the particles sufficiently remote from one another to overcome the force of attraction caused by Van der Waal's forces.

The origin of the Van der Waal force is the attraction of a fluctuating electric dipole for a neighboring induced dipole. So long as the surfaces of adjacent particles are about one radius apart, the particles will not be strongly attracted toward each other and flocculation can be avoided. The function of the adsorbed coating or surfactant on the particles is to provide at least the minimum distance required for separation.

In FIG. 1 curve **21** represents the magnitude of Van der Waal energy as a function of distance separating two particles. Curve **20** represents the repelling energy generated by coatings of adsorbed surfactant on the surface of two adjacent particles. Curve **22** represents the algebraic sum of the attracting and repelling energies.

The repulsive force equals the negative rate of change of energy with distance

$$\left(F=-\frac{dE}{dX}\right)$$

(assuming the convention that positive force represents repulsion.) Clearly that repulsion occurs to the right of the apex **25** of curve **23** since the slope of the curve $23dE/dX$ or the rate of change of energy as a function of distance is negative.

Additionally, if the magnitude of energy at the apex exceeds the thermal energy per particle, the thermal fluctuations of the particles will now throw the particles close enough together to come within the attraction region, to the left of the apex.

Referring to FIG. 2 of the drawings, there is a schematic representation of two adjacent particles **10** and **11** suspended within a non-polar solvent **12.** Absorbed on each surface of the particles **10** and **11** are molecules **13** of a polar surfactant. It will be noted that the molecules **13** contain a polar head **14** and a non-polar tail **15.** The surfactant molecules **13** coat the surface of the particles, and in effect, form as an elastic boundary between the particles. When two particles such as **10** and **11** approach each other the coating is compressed and provides an elastic repulsion greater than the attractive forces that would otherwise cause particles to come into contact until flocculation occurs and the solid material settles out.

Referring to FIG. 4 of the drawings, the particles **10** and **11** are depicted in substantially the same environment as shown for FIG. 2, except for the fact that a flocculating solvent depicted by molecules **16** has been added to the ferrofluid. The flocculating solvent is a polar solvent. Its effect on the ferrofluid is to make the surfactant molecules less compatible with its fluid environment comprising the combination of ferrofluid solvent and flocculating solvent. The tail sections **15** of the surfactant molecules are repelled by the combination of solvents and tend to fold back on themselves toward the surface of the particles. Thus, the depth of coating is materially reduced.

The curves in FIG. 3 denote, as before, Van der Waal attraction, surfactant repulsion and the algebraic sum. Energy curve **23** in FIG. 3 reflects the shortened surfactant thickness as shown in FIG. 4. At no point does it go above the abscissa and therefore nowhere does the repulsion energy exceed the Van der Waal attraction energy.

Particles in their random movement through the combined solvent no longer encounter a repelling force in excess of the Van der Waal attraction force. The particles adhere to each other, flocculate and deposit out of the combined solvent.

From this point it is a relatively simple matter to separate the particles from the combined solvent. A little of the flocculating and ferrofluid solvent remains on the particles. These solvents appear as a very small impurity when the particles are resuspended in the new solvent. No problems are encountered by these impurities as they are compatible with the new ferrofluid in these small quantities.

In the event the purpose in flocculating the particles was to increase the concentration, it is now clearly obvious that the one need only add a reduced amount of solvent to the particles. On the other hand, if the purpose in flocculating the particles was to substitute one solvent for another, this step is now clearly possible.

Typical formulations used in practicing the invention are provided in Table No. 1 which follows. The ferrofluid solvents and flocculation solvents are fully interchangeable.

TABLE NO. 1—TYPICAL EXAMPLES

Particle	Surfactant	Ferrofluid solvent	Flocculation solvent
Magnetite	Oleic acid	Kerosene	Acetone.
Do	do	Heptane	Ethyl alcohol.
Do	do	Kerosene	Dioxane.
Do	do	Decane	Ethyl acetate.
Do	Tenlo-70	Kerosene	Acetone.

Another means for causing flocculation, called polymeric flocculation, is shown in FIG. 5. Flocculation is caused by linking of two—or more—particles **10, 11, 17**

by a polymer molecule **18** as shown in FIG. 5. The particles that settle out of solution may be redispersed by supplying excess solvent to the particles to dissolve some of the entangling species.

The amount of flocculating agent that is required differs with each application. It is, however, determinable through routine procedures.

Observed flocculating agents are polyisobutylene which works with aliphatic and chlorinated aliphatic solvents; polystyrene which may be used with aromatic solvents including toluene; and dimethylene siloxane polymers with the aliphatics.

Two important criteria of polymer flocculation agents are: (i) they be miscible in the ferrofluid solvent, and (ii) the molecule length shall be several times in the diameter of a particle since a linking of particles is an important consideration.

CONCLUSION

In its broadest aspect, the invention covers the substitution of one ferrofluid solvent for another by introducing into the ferrofluid a flocculating agent. The agent can reduce the forces acting in opposition to the Van der Waal forces to the extent that the particles can be attracted to one another and deposit out of solution. Alternatively, the flocculating agent can act to link particles causing flocculation and ultimately the separation of particles and solvent.

Secondarily, with respect to the former approach, the invention covers the concept of shrinking the thickness of the surfactant coating thus enabling the Van der Waal forces to bring and maintain adjacent particles together. Another aspect of the invention causes the coating to shrink and reduce its effective thickness by introducing into a ferrofluid containing a polar surfactant and a non-polar solvent, a polar flocculating agent.

The various features and advantages of the invention are thought to be clear from the foregoing description. Various other features and advantages not specifically enumerated will undoubtedly occur to those versed in the art, as likewise will many variations and modifications of the preferred embodiment illustrated, all of which may be achieved without departing from the spirit and scope of the invention as defined by the following claims.

What is claimed is:

1. A method of substituting one ferrofluid solvent for another ferrofluid solvent in a ferrofluid consisting essentially of suspended magnetic particles, a polar surfactant and a non-polar ferrofluid solvent comprising the steps of:

(a) introducing a polar flocculation agent into the ferrofluid causing the particles with adsorbed surfactant to flocculate and settle out of suspension;

(b) separating the original ferrofluid solvent and flocculation agent from the particles with adsorbed surfactant; and

(c) dispersing said flocculated particles in another non-polar ferrofluid solvent.

2. A method as defined in claim **1** in which the surfactant is a long chain molecule having a chain length of at least eight carbon atoms having a polar end group and a non-polar tail, said ferrofluid solvent is a non-polar organic fluid and said flocculating agent is a polar organic fluid soluble in the ferrofluid solvent.

3. A method as defined in claim **1** in which the surfactant is a member of the class consisting of carboxylic acids and their metallic salts, amines, succinic acid derivatives, condensation product of an amino ester of a fatty acid, said ferrofluid solvent is a member of the class consisting of aliphatic hydrocarbons, halogenated aliphatic hydrocarbons and aromatic hydrocarbons, and said flocculating agent is a member of the class consisting of acetone, ethyl alcohol, dioxane, ethyl acetate and acetone.

4. A method of substituting one ferrofluid solvent for another ferrofluid solvent in a ferrofluid consisting essentially of magnetic particles a surfactant adsorbed on said

particles and a non-polar ferrofluid solvent comprising the steps of:

(a) introducing a flocculating agent which is a miscible polymer particle linking agent having a molecular chain length at least twice the diameter of the magnetic particles into the ferrofluid and flocculating said particles causing said particles to settle out of suspension;

(b) separating the ferrofluid solvent and polymer linking agent from the particles with adsorbed surfactant; and

(c) dispersing said flocculated particles in another non-polar ferrofluid solvent.

5. A method as defined in claim **4** in which the ferrofluid solvent is an aliphatic hydrocarbon and the flocculating agent is selected from the group consisting of polyisobutylene and dimethyl siloxane.

6. A method as defined in claim **4** in which the ferrofluid solvent is an aromatic hydrocarbon and the flocculating agent is polystyrene.

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J. COOPER, Assistant Examiner

U.S. Cl. X.R.

252—62.51, 62.56, 309, 327

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,531,413 Dated September 29, 1970

Inventor(s) Ronald E. Rosenweig

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 48, for "(FE_3O_4)" read--(Fe_3O_4)--; Column 2, line 15, after "ferrofluid" read--solvent--; Column 3, line 8, for "now" read-- not--; Column 3, line 39, after "thickness" omit--as--; Column 3, line 57, after "that" omit--the--.

SIGNED AND SEALED
DEC 15 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents