(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 579 229 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
30.09.1998 Bulletin 1998/40

(51) Int Cl.[6]: **C10M 171/00**, H01F 1/00, H01F 1/37

(21) Application number: **93111379.9**

(22) Date of filing: **15.07.1993**

(54) **Fluid having magnetic and electrorheological effects simultaneously**

Flüssigkeit mit gleichzeitig magnetischen und elektrorheologischen Effekten

Huile ayant des effets magnétiques et électrorheologues simultanément

(84) Designated Contracting States:
DE FR GB

(30) Priority: **16.07.1992 JP 210655/92**

(43) Date of publication of application:
19.01.1994 Bulletin 1994/03

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- **DATABASE WPI Section Ch, Week 9244, Derwent Publications Ltd., London, GB; Class G04, AN 92-360957 & JP-A-4 261 496 (TOYOTA JIDOSHA K.K.)**
- **DATABASE WPI Section Ch, Week 8310, Derwent Publications Ltd., London, GB; Class M22, AN 83-24583K & SU-A-925 520 (CHURKIN)**

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Description

BACKGROUND OF THE INVENTION

1) Field of the Invention

The present invention relates to a fluid having a characteristic of a magnetic fluid susceptible to a magnetic field and a characteristic of an electrorheological fluid whose viscosity can increase with an applied electric field at the same time, and particularly to a fluid capable of outputting a large force at a high response speed.

2) Prior Art

A magnetic fluid is a colloidal solution, which is a uniform dispersion of ferromagnetic particles in a solvent, and, when a magnet is provided near the magnetic fluid, the entire fluid is attracted towards the magnet and behaves as if the entire fluid is apparently charged with a magnetism.

Furthermore, the magnetic fluid has such a characteristic that a large force can be induced in the magnetic fluid with an applied magnetic field. By virtue of this characteristic, the magnetic fluid is utilized for rotating shaft sealing, and further application to e.g. dampers, actuators, gravity separation or jet printers can be expected.

A typical process for preparing a magnetic fluid is a chemical coprecipitation process disclosed in JP-A-51-44579, where an aqueous slurry of magnetic particles prepared from an aqueous solution of ferrous sulfate and an aqueous solution of ferric sulfate is admixed with a surfactant, followed by water washing, drying and dispersion into an organic solvent, thereby preparing a magnetic fluid.

An electrorheological fluid, on the other hand, is a suspension of inorganic or polymeric particles in an electrically insulating liquid, whose viscosity can be rapidly and reversibly changed from a liquid state to a plastic state or to a solid state or vice versa upon application of an electric field thereto. A high response speed is one of the characteristics.

As dispersion particles, those whose surfaces are readily depolarizable under an electric field are usually used. For example, as inorganic dispersion particles, silica is disclosed in US-A-3,047,507, GB-A-1,076,754 and JP-A-61-44998, and zeolite is disclosed in JP-A-62-95397. As polymeric dispersion particles, arginic acid, glucose having carboxyl groups and glucose having sulfone groups are disclosed in JP-A-51-33783; polyacrylic acid crosslinked with divinylbenzene is disclosed in JP-A-53-93186; and resol-type phenol resin is disclosed in JP-A-58-179259.

As an electrically insulating liquid, e.g. mineral oil, silicone oil, fluorohydrocarbon-based oil and halogenated aromatic oil are known.

It is preferable from the viewpoint of higher electrorheological effect that water is adsorbed on the surfaces of dispersion particles. In most cases, the electrorheological fluid contains a small amount of water.

Mechanism of increase in the viscosity of an electrorheological fluid with an applied electric field can be clarified on the basis of the electric double layer theory. That is, an electric double layer is formed on the surfaces of dispersion particles of an electrorheological fluid, and when there is no application of an electric field, dispersion particles repulse one another on the surfaces and are never in a particle alignment structure. When an electric field is applied thereto, on the other hand, an electrical deviation occurs in the electrical double layers on the surfaces of dispersion particles, and the dispersion particles are electrostatically aligned to one another, thereby forming bridges of dispersion particles. Thus, the viscosity of the fluid is increased, and sometimes the fluid is solidified. The water contained in the fluid can promote formation of the electrical double layer.

Application of the electrorheological fluid to e.g. engine mounts, shock absorbers or clutches can be expected.

However, the magnetic fluid still has such problems that neither high permeability nor higher response speed as aims to a quick response is obtainable. When it is used as a seal, a low sealability is also one of the problems. These problems are obstacles to practical applications. The electrorheological fluid still has such a problem that the torque induced upon application of an electrical field is so small that no larger force can be obtained.

EP-A-566931 (relevant with respect to Art. 54(3) EPC) discloses a fluid having magnetic and electrorheological effects simultaneously, said fluid containing ferromagnetic particles, dispersion particles in an electrorheological fluid and a solvent.

SU-A-925520 discloses an electrorheological suspension containing quartz powder, glycerol monooleate and refined white oil, and a ferromagnetic suspension containing quartz powder, ferromagnetic powder and mineral oil.

US-A-3385793 discloses an electroviscous fluid composition containing a conventional alternating-field-sensitive electroviscous fluid and a particulate conductive metal in an amount of 1 to 40 wt.%.

US-A-2661596 discloses fluids responsive to both electric and magnetic fields, said fluids containing an oily vehicle and ferrite powders.

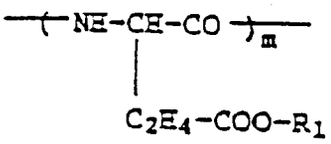
SUMMARY OF THE INVENTION

An object of the present invention is to provide a fluid capable of producing a large torque at a high response speed.

As a result of extensive studies to solve the problems, the present inventors have found that a fluid containing a magnetic field-susceptible component and an electric field-susceptible component together at the same time can solve the problems and have established the present invention.

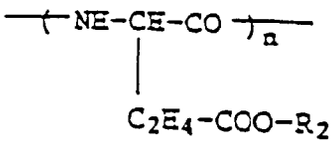
That is, the present invention provides a fluid having magnetic and electrorheological effects simultaneously, which comprises magnetic field-susceptible ferromagnetic particles, an electric field-susceptible component and a solvent, the mixing ratio of the sum total of the magnetic field-susceptible ferromagnetic particles and the electric field-susceptible component to the solvent being 2-70 wt.% to 98-30 wt.%, wherein the electric field-susceptible component is a liquid crystallizable polymer component, said liquid crystallizable polymer component being

(a) poly(γ-glutamate) comprising constituents represented by the following general formulae (1) and (2):



(1)

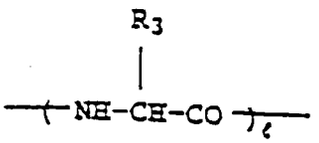
and



(2)

wherein R_1 has 1 to 7 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, R_2 has 8 to 30 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, and a composition ratio of (2) to (1) ranging from 100/0 to 10/90; or

(b) poly(α-aminoacid) represented by the following general formula (3):



(3)

wherein R_3 has 1 to 30 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, and ℓ is a degree of polymerization ranging from 5 to 10,000.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in detail below.

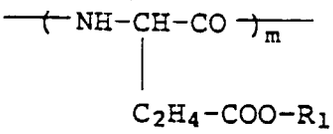
The term "susceptible to a magnetic field" or "a magnetic field-susceptible" used herein means "a property attractive to, for example, a magnet". Magnetic field-susceptible components used in the present invention are ferromagnetic particles, more specifically magnetic particles of oxides such as e.g. magnetite, manganese ferrite or barium ferrite; magnetic particles of metals such as iron, cobalt, nickel or permite; or particles of iron nitride.

Magnetic particles preferably have particle sizes of 0.003 to 200 μm, and particularly hard magnetic particles preferably have particle sizes of 0.003 to 0.5 μm and soft magnetic particles preferably have particle sizes of 0.1 to 200 μm. In case of obtaining a particularly very large force, soft magnetic particles having particle sizes of 1 to 100 μm

are preferable. Below 0.003 μm, the particles fail to show a magnetism, whereas above 200 μm the dispersibility in the fluid is much deteriorated.

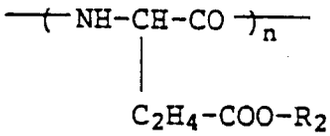
The term "susceptible to an electric field" or "an electric field-susceptible" used herein means "a property to increase the viscosity of a fluid upon application of an electric field". Electric field-susceptible components used in the present invention are the following liquid crystallizable polymer components (a) or (b):

(a) poly(γ-glutamate) comprising constituents represented by the following general formulae (1) and (2):



(1)

and



(2)

wherein R_1 has 1 to 7 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, R_2 has 8 to 30 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, and a composition ratio of (2) to (1) ranging from 100/0 to 10/90.

R_1 includes, for example, alkyls such as methyl, ethyl, propyl, butyl, pentyl, hexyl; aryls such as phenyl; aralkyls such as benzyl; cycloalkyls such as cyclohexyl. It is preferable to use methyl and benzyl as R_1. R_1s are not always the same in polymers.

R_2 includes, for example, alkyls such as octyl, nonyol, decyl, dodecyl, oleyl; aralkyls such as butylbenzyl; aryls such as butylphenyl; cycloalkyls such as butylcyclohexyl. It is preferable to use octyl, decyl, dodecyl, oleyl, and butylphenyl as R_2. It is more preferable to use dodecyl and oleyl as R_2, because they can effectively increase a solubility in hydrocarbon-based oil or ester-based oil, which can be used as preferable solvents. R_2s in polymers are not always the same.

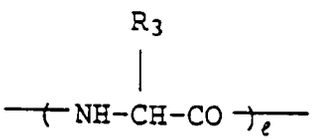
R_2 is important for making the poly(γ-glutamate)s soluble in hydrocarbon-based oil or ester-based oil. When R_2 has less than 8 carbon atoms, solubility in hydrocarbon-based oil or ester-based oil will be not satisfactory, whereas when R_2 has more than 30 carbon atoms, it will be very difficult to synthesize such poly(γ-gutamate)s.

Composition ratio of the general formula (2) to the general formula (1), that is, n/m, is 100:0 to 10:90, preferably 80:20 to 30:70. When n/m is less than 10/90, solubility in hydrocarbon-based oil or ester-based oil will be not satisfactory.

The constituents of general formulae (1) and (2) can be arranged in an alternate, block or random state. Alternater or random arrangement is preferable.

Poly(γ-glutamate)s having constituents of general formulae (1) and (2) can be prepared by polymerizing corresponding γ-glutamates, using phosgene, or by exchanging poly(γ-glutamate) consisting only of R_1-containing units with alcohol or ester corresponding to R_2, or by any other known procedure for producing poly(γ-glutamate)s.

(b) poly(α-aminoacid) represented by the following general formula (3):



(3)

wherein R_3 has 1 to 30 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl,

aryl and cycloalkyl, and ℓ is a degree of polymerization, which is 5 to 10,000, preferably 10 to 5,000, where below 5, the resulting electrorheological effect is not satisfactory, whereas above 10,000 the solubility in a solvent is lowered.

R_3 includes, for example, alkyls such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, tetradodecyl, oleyl; aryls such as phenyl, butylphenyl; aralkyls such as benzyl, butylbenzyl; cycloalkyls such as cyclohexyl, butylcyclohexyl. It is particularly preferable to use alkyl having 6 to 16 carbon atoms, aralkyl, aryl and cycloalkyl as R_3. Furthermore, it is more preferable to use octyl, docyl, dodecyl, tetradecyl and hexadecyl as R_3, because they can effectively increase a solubility in hydrocarbon-based oil or ester-based oil, which can be used as preferable solvents. R_3s in polymers are not always the same.

Poly(α-aminoacid)s represented by the general formula (3) can be prepared by polymerization corresponding α-amino acids through N-carboxy anhydride, using phosgene (NCA polymerization process).

As a liquid crystallizable polymer component, those having a plurality of liquid crystallizable groups bonded to one molecular chain directly or through a spacer can be also used, and include, for example, a side chain type having pendant liquid crystallizable groups bonded to one molecular chain directly or through a spacer as branches; a main chain type having liquid crystallizable groups and the molecular chain on the main chain; and a complex type having a liquid crystallizable chain further bonded to the liquid crystallizable groups or the molecular chain of a main chain type, liquid crystallizable polymer compound.

The liquid crystallizable polymer component has a molecular weight of preferably 500 to 1,000,000, more preferably 2,000 to 500,000. Below 500, the resulting electrorheological effect will be not satisfactory, whereas above 1,000,000 the solubility in a solvent will be lowered.

Integrated form of the magnetic field-susceptible component and the electric field-susceptible component includes dispersion or solution of the respective components separately in a solvent, or particles that integrate these two component, that is, integrated particles, when the electric field-susceptible component is in the form of dispersion particles. Integrated particles are preferable for obtaining higher response speed and torque.

Integrated particles used in the present invention can be prepared, for example, in the following manner:

The first procedure comprises dispersing ferromagnetic particles into an aqueous solution containing a component having an electrorheological effect, then separating the component having an electrorheological effect having ferromagnetic particles dispersed therein by e.g. reprecipitation, followed by drying and pulverization.

The second procedure comprises subjecting a raw material for the component having an electrorheological effect to emulsion or suspension polymerization in the presence of ferromagnetic particles, thereby fixing a layer of the component having an electrorheological effect to the surfaces of ferromagnetic particles.

In the foregoing procedures, raw materials for the ferromagnetic particles, for example, sulfates or carbonyl compounds, can be used in place of the ferromagnetic particles, to form ferromagnetic particles in the course of preparing integrated particles. Integrated particles can be prepared according to any other known procedure than the above-mentioned ones.

In the present invention, the mixing ratio of the magnetic field-susceptible component to the electric field-susceptible component is preferably 99.8 - 3 wt.% to 0.2 - 97 wt.%, more preferably 99 - 30 wt.% to 1 - 70 wt.%. When the electric field-susceptible component is below 0.2 wt.%, no electrorheological effect can be obtained, whereas above 97 wt.% only the electrorheological effect can be obtained.

When the electric field-susceptible component further comprises dispersion particles of, for example, silica, the mixing ratio of the magnetic field-susceptible component to the electric field-susceptible component is preferably 99 - 10 wt.% to 1 - 90 wt.%, more preferably 97 - 30 wt.% to 3 - 70 wt.%. When the electric field-susceptible component is less than 1 wt.%, no electrorheological effect can be obtained, whereas above 90 wt.% only the electrorheological effect can be obtained.

The solvent for use in the present invention includes, for example, polar solvents such as dioxane, tetrahydrofuran, cresol; chlorinated solvents such as methylene chloride, chloroform, chlorobenzene, o-dichlorobenzene; hydrocarbon-based oils such as mineral oil, alkylbenzene, alkylnaphthalene, poly-α-olefin; ester-based oils such as dibutyl phthalate, dioctyl phthalate, dibutyl sebacate; ether-based oils such as oligophenylene oxide; silicone oils; and fluorocarbon-based oils, among which hydrocarbon-based oils and ester-based oils are particularly preferable from the viewpoints of less toxicity and less electric current passage. These oils can be used in mixture.

The boiling point of the solvent is preferably 150°C or higher under the atmospheric pressure, more preferably 150°C to 700°C, most preferably 200 to 650°C. Below 150°C, the solvent is more vaporizable, and thus this is not preferable. The viscosity is preferably 1 to 500 cSt at 40°C, more preferably 5 to 300 cSt at 40°C.

The mixing ratio of the sum total of the magnetic field-susceptible component and the electric field-susceptible component to the solvent is 2 - 70 wt.% to 98 - 30 wt.%, preferably 10 - 50 wt.% to 90 - 50 wt.%. When the sum total is more than 70 wt.%, the viscosity of the fluid will be considerably increased under no application of either magnetic field or electric field or both. This is practically not preferable.

It is not always necessary that the liquid crystallizable component shows a liquid crystal phase in the fluid. An electrorheological effect can be obtained even at such a concentration as not to show a liquid crystal phase.

A fluid having a magnetic effect and an electrorheological effect simultaneously can be prepared by dissolving the liquid crystallizable polymer component in a magnetic fluid prepared in a well known procedure, or by mixing a magnetic fluid prepared in a well known procedure with a solution of the liquid crystallizable polymer component.

In the present invention, addition of a small amount of water can promote an electrorheological effect in some cases. An amount of water to be added is preferably not more than 30 wt.% on the basis of the electric field-susceptible component.

In the present invention it is possible to add additives such as a surfactant to the fluid within such a range as not to deteriorate the effect of the present invention.

In the present invention, both magnetic field and electric field can be applied at the same time with constant intensities, or while changing the intensities in accordance with changes in the necessary torque, or one of the magnetic field and the electric field can be applied continuously with a constant intensity while changing the applied intensity of other field in accordance with changes in the necessary torque. It is particularly preferable to apply a magnetic field with a constant intensity to obtain a torque to some degree, and change applied intensity of an electric field by making fine adjustment of the necessary torque.

The present fluid can be applied to e.g. engine mounts, shock-damping apparatuses such as shock absorbers, clutches, torque converters, brake systems, valves, dampers, suspensions, actuators, vibrators, inject printers, seals, gravity separation, bearings, polishing, control valves or vibration-preventing materials.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be explained in detail below referring to Examples.

Reference Example 1

20 g of sodium polyacrylate having a degree of polymarization of 22,000 to 70,000 was dissolved into 800 g of deionized water, and then 20 g of soft magnetic iron particles having particle sizes of 3 μm was added to the solution, and the soft magnetic iron particles were uniformly dispersed therein by stirring. Then, the resulting aqueous solution of sodium polyacrylate containing the dispersed soft magnetic iron particles was added to 1.5 ℓ of ethanol, and sodium polyacrylate containing soft magnetic iron particles was obtained by reprecipitation, followed by drying at 100°C/2 mmHg for 6 hours and pulverization by a Henschel mixer. Thus, integrated particles (1-1) having an average particle size of 12 μm were obtained. It was found by atomic absorption spectrometry that the integrated particles (1-1) contained 48 wt.% of iron.

Then, 30 g of the integrated particles (1-1) was dispersed into 70 g of silicone oil KF-96 (trademark of a product made by Shinetzu Silicone K.K., Japan) having a viscosity of 20 cSt at 25°C, and 5 wt.% of water was added thereto on the basis of the integrated particles (1-1) to prepare a fluid (1-2). The fluid (1-2) had a saturation magnetization of 390 Gauss and it was found that the fluid (1-2) was attracted to a magnet.

Then, a high voltage-applicable test provided with two electrode each having an area of 400 mm^2 and being faced to each other at a clearance of 1 mm, and with an electromagnet on both electrodes was placed sideways, and then the fluid (1-2) was filled into the cell to determine magnetic and electrorheological characteristics, while determining torques by changing the position of the upper electrode in the horizontal direction. The response speed was determined with an oscillograph by measuring a delay in a torque following application of either magnetic or electric field or both.

The fluid (1-2) had a torque of 26 g·cm under no application of both magnetic and electric fields. When only a magnetic field of 1,500 Oe was applied to the fluid (1-2), the torque was 205 g·cm and the response speed was 0.37 s.

When only an electric field of 3 kV/mm was applied to the fluid (1-2), the torque was 221 g·cm and the response speed was 0.02 s. Thus, it was found that the fluid (1-2) had both magnetic and electrorheological effects.

When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (1-2) at the same time, the torque was 494 g·cm and the response speed was 0.06 s.

Reference Example 2

20 g of soft magnetic ferrite particles having particle sizes of 10 μm, 50 g of an aqueous 15 wt.% sodium acrylate solution and 300 g of xylene were put into a reactor vessel with a stirrer, and 7 ml of an aqueous solution containing 0.3 g of ammonium persulfate was added thereto with stirring at 40°C. Then, 7 ml of an aqueous solution containing 0.1 g of sodium hydrogen sulfite was added thereto. The mixture was subjected to polymerization at 40°C for 4 hours.

After the end of polymerization, the particles were recovered therefrom by filtration, and dried at 100°C/2 mmHg for 6 hours, whereby soft magnetic ferrite particles (2-1) coated with sodium polyacrylate were obtained. The thus

obtained integrated particles (2-1) contained 87 wt.% of soft magnetic ferrite.

Then, a fluid (2-2) was prepared in the same manner as in Reference Example 1. The fluid (2-2) had a saturation magnetization of 260 Gauss, and it was found that the fluid (2-2) was attracted to a magnet.

Then, magnetic and electrorheological characteristics of the fluid (2-2) were investigated in the same manner as in Reference Example 1. Under no application of both magnetic and electric fields the fluid (2-2) had a torque of 23 g·cm. When only a magnetic field of 1,500 Oe was applied to the fluid (2-2), a torque of 193 g·cm and a response speed of 0.31 s were obtained. When only an electric field of 3 kV/mm was applied to the fluid (2-2), a torque of 209 g·cm and a response speed of 0.02 s were obtained. It was found that the fluid (2-2) had both magnetic and electrorheological effects. Furthermore, when a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (2-2) at the same time, a torque of 419 g·cm and a response speed of 0.06 s were obtained.

Reference Example 3

20 g of soft magnetic iron particles having particle sizes of 3 μm was added to a solution consisting of 60 g of tetraethoxysilane, 55 g of ethanol and 20 g of deionized water, and then 8 ml of 20 wt.% ammonia water was further added thereto with stirring. Immediately after the addition, particles were formed, and the reaction was continuously carried out at 80°C for 3 hours thereafter to complete the sol-gel reaction to form silica.

After the end of the reaction, degasification and drying were carried out at 100°C/2 mmHg for 4 hours to obtain integrated particles (3-1) of silica and soft magnetic iron particles. The integrated particles (3-1) contained 54 wt.% of iron.

Then, a fluid (3-2) was prepared in the same manner as in Reference Example 1. The fluid (3-2) had a saturation magnetization of 410 Gauss, and it was found that the fluid (3-2) was attracted to a magnet.

Then, magnetic and electrorheological characteristics of the fluid (3-2) were investigated in the same manner as in Reference Example 1. Under no application of magnetic and electric fields, the fluid (3-2) had a torque of 33 g·cm. When only a magnetic field of 1,500 Oe was applied to the fluid (3-2), a torque of 236 g·cm and a response speed of 0.39 s were obtained. When only an electric field of 3 kV/mm was applied to the fluid (3-2), a torque of 327 g·cm and a response speed of 0.02 s were obtained. It was found that the fluid (3-2) had both magnetic and electrorheological effects. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (3-2) at the same time, a torque of 544 g·cm and a response speed of 0.08 s were obtained.

Reference Example 4

When only a magnetic field of 1,500 Oe was applied to the fluid (1-2) of Reference Example 1, a torque of 205 g·cm was obtained. When an electric field of 3 kV/mm was applied additionally thereto in that state, the torque was increased to 494 g·cm. Upon the torque increase by the additional application of the electric field, a response speed of 0.20 s was obtained.

Reference Example 5

A fluid (4-2) was prepared in the same manner as in Reference Example 1, except that sodium polyacrylate having a degree of polymerization of 22,000 to 70,000 and particle sizes of 20 μm were used in place of the dispersion particles for the fluid used in Reference Example 1.

Then, magnetic and electrorheological characteristics of the fluid (4-2) were investigated in the same manner as in Reference Example 1. Under no application of both magnetic and electric fields, the fluid (4-2) had a torque of 19 g·cm. When only a magnetic filed of 1,500 Oe was applied to the fluid (4-2), the same torque as above, i.e. 19 g·cm was obtained. The fluid was not attracted to a magnet and was not susceptible to a magnetic field at all. When only an electric field of 3 kV/mm was applied to the fluid (4-2), a torque of 298 g·cm and a response speed of 0.02 s were obtained. It was found that the fluid (4-2) had only an electrorheological effect.

When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (4-2) at the same time, the same torque and response speed were obtained (as those obtained when only the electric field was applied thereto.

Reference Example 6

20 g of soft magnetic iron particles having particles sizes of 3 μm was added to a solution containing 20 g of polypropylene having no electrorheological effect in 300 g of xylene, and the mixture was stirred to uniformly disperse the soft magnetic iron particles. Then, the dispersion was added to 1 ℓ of deionized water, and polypropylene containing the soft magnetic iron particles was obtained by reprecipitation. Then, the thus obtained integrated precipitates were

dried at 80°C/2 mmHg for 6 hours, followed by pulverization by a Henschel mixer, and integrated particles (5-1) having an average particle size of 15 μm were obtained thereby. It was found by atomic absorption spectrometry that the integrated particles (5-1) contained 46 wt.% of iron.

Then, a fluid (5-2) was prepared in the same manner as in Reference Example 1. The fluid (5-2) had a saturation magnetization of 400 Gauss and it was found that the fluid (5-2) was attracted to a magnet.

Then, magnetic and electrorheological characteristics of the fluid (5-2) were investigated in the same manner as in Reference Example 1. Under no application of both magnetic and electrical fields, the fluid (5-2) had a torque of 31 g·cm. When only a magnetic field of 1,500 Oe was applied to the fluid (5-2), a torque of 261 g·cm and a response speed of 0.42 s were obtained. When only an electric field of 3 kV/mm was applied the fluid (5-2), there was no change in the torque at all, and it was found that the fluid (5-2) had no electrorheological effect. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (5-2) at the same time, the same torque and response speed were obtained as those obtained when only the electric field was applied thereto.

Synthesis Example 1

One mole of ferrous sulfate in an aqueous solution and 2 moles of ferric sulfate in an aqueous solution were mixed together and an aqueous 6N sodium hydroxide solution was added thereto until a pH of 11.5 was obtained. Then, the mixture was stirred at 60°C for one hour to form magnetite. Then, 200 ml of an aqueous 10 wt.% sodium oleate solution was added thereto, thereby conducting adsorption reaction at 80°C for 30 minutes. Then, the solution was diluted to 5 ℓ, and then 3N hydrochloric acid was added thereto until a pH of 5.5 was obtained, thereby coagulating the magnetite. Supernatant was removed therefrom, and distilled water was added to the residue, followed by settling. This procedure was repeated until the supernatant contained no salt.

Then, the magnetite cake was recovered therefrom by filtration under suction, and washed with water and finally with methanol to remove the residual oleic acid. Then, the magnetite cake was dried in a vacuum drier, whereby magnetite particles with oleic acid adsorbed thereon were obtained.

Then, the magnetite particles were dispersed into hexane, and particles having larger particle sizes were removed therefrom by centrifugal separation under 8,000 G for one hour. Then, the dispersion freed from the particles having larger particle size by the centrifugal separation was admixed with α-methylnaphthalene in an amount 1.2 times as large as the weight of the magnetite particles contained in the dispersion, and then hexane was distilled off, whereby a magnetic fluid (6-1) was obtained. The thus obtained magnetic fluid (6-1) had a saturation magnetization of 180 Gauss and it was found that the magnetic fluid was attracted to a magnet.

Synthesis Example 2

200 ml of dichloroethane and 2 g of paratoluenesulfonic acid were mixed together, and the mixture was refluxed at 115°C for 4 hours to remove water from the mixture. Then, 4 g of poly(γ-benzyl-L-glutamate) (molecular weight: 240,000; a product made by Sigma Chemical) was added to the mixture and completely dissolved therein. Then, 20 g of dodecyl alcohol was added thereto, and ester interchange reaction was carried out under dichloroethane reflux for 24 hours.

After the end of the reaction, the resulting solution was added to a large amount of ethanol to reprecipitate the polymers. The, the polymers were recovered by filtration and thorough washed with ethanol, and then dissolved again into dichloroethane. Three runs of this purification step was carried out, and the ultimately recovered polymers were dried at 80°C/2 mmHg to obtain 4.4 g of purified polymers (1). It was found by NMR analysis that the polymers (1) were poly(γ-benzyl L-glutamate-co-γ-dodecyl L-glutamate), where 71% of benzyl groups were replaced with dodecyl groups.

Synthesis Example 3

4.5 g of purified polymers (2) were obtained in the same manner as in Synthesis Example 2, except that 20 g of dodecyl alcohol of Synthesis Example 2 was replaced with 28.9 g of oleyl alcohol. It was found by NMR analysis that polymers (2) were poly(γ-benzyl L-glutamate-co-γ-oleyl L-glutamate), where 59% of benzyl groups were replaced with oleyl groups.

Example 1

0.5 g of the polymers (1) obtained in Synthesis Example 2 were completely dissolved in 9.5 g of α-methylnaphthalene, and then the resulting solution was mixed with 10 g of the magnetic fluid (6-1) obtained in Synthesis Example 1 to prepare a fluid (7-1). The thus obtained fluid (7-1) had a saturation magnetization of 93 Gauss, and it was found

that the fluid (7-1) was attracted to a magnet.

Then, magnetic and electrorheological characteristics of fluid (7-1) were investigated in the same manner as in Reference Example 1. Under no application of both magnetic and electric fields, the fluid (7-1) had a torque of 67 g·cm. When only a magnetic field of 1,500 Oe was applied to the fluid (7-1), a torque of 187 g·cm and a response speed of 0.21 s were obtained. When only an electric field of 3 kV/mm was applied to the fluid (7-1), a torque of 361 g·cm and a response speed of 0.02 s were obtained. It was found that the fluid (7-1) had both magnetic and electrorheological effects. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (7-1) at the same time, a torque of 538 g·cm and a response speed of 0.02 s were obtained. No precipitation of the particles was observed even after the fluid (7-1) was left standing for one month.

Example 2

A fluid (8-1) was prepared in the same manner as in Example 1, except that the polymers (1) used in Example 1 were replaced with the polymers (2) obtained in Synthesis Example 2. The fluid (8-1) had a saturation magnetization of 89 Gauss, and it was found that the fluid (8-1) was attracted to a magnet.

Magnetic and electrorheological characteristics of the fluid (8-1) were investigated in the same manner as in Reference Example 1. Under no application of both magnetic and electric fields, the fluid had a torque of 71 g·cm. When only a magnetic field of 1,500 Oe was applied to the fluid (8-1), a torque of 171 g.cm and a response speed of 0.24 s were obtained. When only an electric field of 3 kV/mm was applied to the fluid (8-1), a torque of 348 g·cm and a response speed of 0.02 s were obtained. It was found that the fluid (8-1) had both magnetic and electrorheological effects. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (8-1) at the same time, a torque of 497 g·cm and a response speed of 0.2 s were obtained. No precipitation of particles was observed even after the fluid (8-1) was left standing for one month.

Example 3

A fluid (9-1) was prepared in the same manner as in Example 1, except that the polymers (1) used in Example 1 were replaced with poly(L-α-aminolauric acid) having a molecular weight of 300,000, synthesized by polymerization of L-α-aminolauric acid through N-carboxy anhydride, using phosgene (NCA polymerization process). The thus obtained fluid (9-1) had a saturation magnetization of 91 Gauss, and it was found that the fluid (9-1) was attracted to a magnet.

Magnetic and electrorheological characteristics of the fluid (9-1) were investigated in the same manner as in Reference Example 1. Under no application of both magnetic and electric fields, the fluid (9-1) had a torque of 63 g·cm. When only a magnetic field of 1,500 Oe was applied to the fluid (9-1), a torque of 169 g·cm and a response time of 0.28 s were obtained. When only an electric field of 3 kV/mm was applied to the fluid (9-1), a torque of 322 g·cm and a response time of 0.02 s were obtained, and it was found that the fluid (9-1) had both magnetic and electrorheological effects. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the fluid (9-1) at the same time, a torque of 507 g·cm and a response speed of 0.02 s were obtained. No precipitation of particles was observed even after the fluid (9-1) was left standing for one month.

Comparative Example 1

Magnetic and electrorheological characteristics of the magnetic fluid (6-1) prepared in Synthesis Example 1 were investigated in the same manner as in Reference Example 1. Under no application of both magnetic and electric fields, the magnetic fluid (6-1) had a torque of 103 g·cm. When only a magnetic field of 1,500 Oe was applied to the magnetic fluid (6-1), a torque of 225 g·cm and a response speed of 0.33 s were obtained. When only an electric field of 3 kV/mm was applied to the magnetic fluid (6-1), there was no change in the torque at all, and it was found that the magnetic fluid (6-1) had no electrorheological effect. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the magnetic fluid (6-1) at the same time, the same torque and response speed were obtained as those obtained when only the electric field was applied to the magnetic field (6-1).

Comparative Example 2

0.5 g of the polymers (1) obtained in Synthesis Example 2 was completely dissolved in 9.5 g of α-methylnaphthalene to prepare a solution (10-1). Then, magnetic and electrorheological characteristics of the solution (10-1) were investigated. Under no application of both magnetic and electric fields, the solution (10-1) had a torque of 32 g·cm. When only a magnetic field of 1,500 Oe was applied to the solution (10-1), there was no change in the torque, i.e. 32 g·cm, and the solution (10-1) was not attracted to a magnet and thus was not susceptible to a magnetic field at all.

When only an electric field of 3 kV/mm was applied to the solution (10-1), a torque of 359 g·cm and a response time of 0.02 s were obtained, and it was found that the solution (10-1) had only an electrorheological effect. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the solution (10-1) at the same time, the same torque and response time were obtained as those obtained when only the electric field was applied thereto.

Comparative Example 3

0.5 g of poly (L-α-aminolauric acid) used in Example 3 was completely dissolved in 9.5 g of α-methylnaphthalene in the same manner as in Comparative Example 2 to prepare a solution (11-1). Magnetic and electrorheological characteristics of the solution (11-1) were investigated.

Under no application of both magnetic and electric fields, the solution (11-1) had a torque of 31 g·cm. When only a magnetic field of 1,500 Oe was applied to the solution (11-1), there was no change in the torque, i.e. 31 g·cm, and the solution (11-1) was not attracted to a magnet and was not susceptible to a magnetic field at all. When only an electric field of 3 kV/mm was applied to the solution (11-1), a torque of 343 g.cm and a response speed of 0.02 s were obtained, and it was found that the solution (11-1) had only an electrorheological effect. When a magnetic field of 1,500 Oe and an electric field of 3 kV/mm were applied to the solution (11-1) at the same time, the same torque and response speed were obtained as those obtained when only an electric field was applied thereto.

As is apparent from the foregoing Examples and Comparative Examples, the present fluid having magnetic and electrorheological effects simultaneously has a larger torque than that of a fluid having only a magnetic effect or an electrorheological effect, and furthermore has a higher response speed, characteristic of an electrorheological fluid.

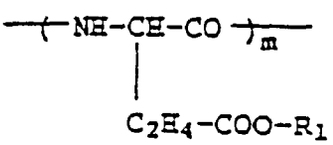
A fluid containing a liquid crystallizable polymer as an electrorheological component has a good dispersion stability for a longer time.

The present fluid has a larger torque, a higher response speed and a good dispersion stability for a longer time, and can be applied to e.g. engine mounts, shock damping apparatuses such as shock absorbers; clutches, torque converters, brake systems, valves, dampers, suspensions, actuators, vibrators, inject printers, seals, gravity separation, bearings, polishing, packings, control valves or vibration-preventing materials.

Claims

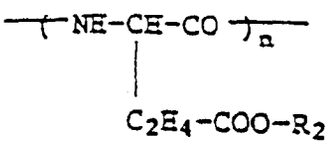
1. A fluid having magnetic and electrorheological effects simultaneously, which comprises magnetic field-susceptible ferromagnetic particles, an electric field-susceptible component and a solvent, the mixing ratio of the sum total of the magnetic field-susceptible ferromagnetic particles and the electric field-susceptible component to the solvent being 2-70 wt.% to 98-30 wt.%, wherein the electric field-susceptible component is a liquid crystallizable polymer component, said liquid crystallizable polymer component being

(a) poly(γ-glutamate) comprising constituents represented by the following general formulae (1) and (2):



(1)

and

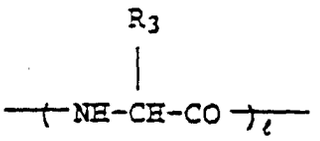


(2)

wherein R_1 has 1 to 7 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, R_2 has 8 to 30 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, and a composition ratio of (2) to (1) ranging from 100/0 to 10/90;

or

(b) poly(α-aminoacid) represented by the following general formula (3):



(3)

wherein R_3 has 1 to 30 carbon atoms and is at least one group selected from the group consisting of alkyl, aralkyl, aryl and cycloalkyl, and ℓ is a degree of polymerization ranging from 5 to 10,000.

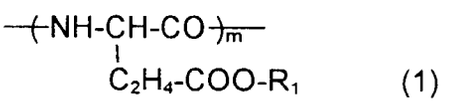
2. The fluid having magnetic and electrorheological effects simultaneously according to Claim 1, wherein the electric field-susceptible component further comprises dispersion particles used in an electrorheological fluid.

3. The fluid having magnetic and electrorheological effects simultaneously according to claim 2, wherein the ferromagnetic particles and the dispersion particles used in an electrorheological fluid are integrated together.

Patentansprüche

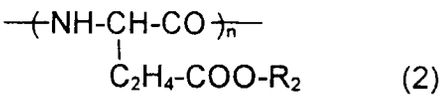
1. Flüssigkeit, die gleichzeitig magnetische und elektrorheologische Effekte aufweist und umfaßt für ein Magnetfeld empfindliche ferromagnetische Teilchen, eine für ein elektrisches Feld empfindliche Komponente und ein Lösungsmittel, wobei das Mischungs-Verhältnis zwischen der Gesamtsumme der für ein Magnetfeld empfindlichen ferromagnetischen Teilchen und der für ein elektrisches Feld empfindlichen Komponente und dem Lösungsmittel 2 bis 70 Gew.-% zu 98 bis 30 Gew.-% beträgt, wobei die für ein elektrisches Feld empfindliche Komponente eine flüssigkristallisierbare Polymer-Komponente ist, bei der es sich handelt um

(a) Poly(γ-glutamat), das Bestandteile der nachstehend angegebenen allgemeinen Formeln (1) und (2) umfaßt:



(1)

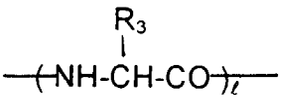
und



(2)

worin R_1 1 bis 7 Kohlenstoffatome aufweist und mindestens eine Gruppe darstellt, die ausgewählt wird aus der Gruppe, die besteht aus Alkyl, Aralkyl, Aryl und Cycloalkyl, R_2 8 bis 30 Kohlenstoffatome aufweist und mindestens eine Gruppe darstellt, die ausgewählt wird aus der Gruppe, die besteht aus Alkyl, Aralkyl, Aryl und Cycloalkyl, und
wobei das Zusammensetzungs-Verhältnis von (2) zu (1) in dem Bereich von 100:0 bis 10:90 liegt; oder

(b) Poly(α-aminosäure), dargestellt durch die folgende allgemeine Formel (3):



(3)

worin R_3 1 bis 30 Kohlenstoffatome aufweist und mindestens eine Gruppe darstellt, die ausgewählt wird aus der Gruppe, die besteht aus Alkyl, Aralkyl, Aryl und Cycloalkyl, und ℓ einen Polymerisationsgrad in dem Bereich von 5 bis 10 000 bedeutet.

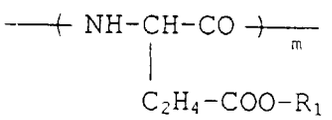
2. Flüssigkeit, die gleichzeitig magnetische und elektrorheologische Effekte aufweist, nach Anspruch 1, in der die für ein elektrisches Feld empfindliche Komponente außerdem Dispersions-Teilchen aufweist, wie sie in einer elektrorheologischen Flüssigkeit verwendet werden.

3. Flüssigkeit, die gleichzeitig magnetische und elektrorheologische Effekte aufweist, nach Anspruch 2, in der die ferromagnetischen Teilchen und die Dispersions-Teilchen, die in einer elektrorheologischen Flüssigkeit verwendet werden, miteinander integriert sind.

Revendications

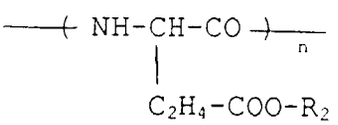
1. Fluide ayant simultanément des effets magnétiques et électrorhéologiques, qui comprend des particules ferromagnétiques ayant une susceptibilité au champ magnétique, un composant ayant une susceptibilité au champ électrique et un solvant, le rapport de mélange de la somme totale des particules ferromagnétiques ayant une susceptibilité magnétique et du composant ayant une susceptibilité électrique au solvant étant de 2:98 à 70:30 en pourcentage pondéral, dans lequel le composant ayant une susceptibilité électrique est un composant polymère liquide cristallisable, ledit composant polymère liquide cristallisable étant:

(a)un poly(γ-glutamate) comprenant des constituants représentés par les formules générales suivantes (1) et (2):



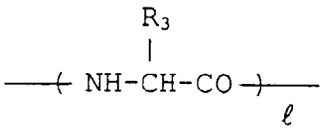
(1)

et



(2)

dans lesquelles R_1 possède 1 à 7 atomes de carbone et représente au moins un groupement choisi dans le groupe formé par les groupements alkyle, aralkyle, aryle et cycloalkyle, R_2 possède 8 à 30 atomes de carbone et représente au moins un groupement choisi dans le groupe formé par les groupements alkyle, aralkyle, aryle et cycloalkyle, et un rapport de composition de (2) à (1) compris entre 100:0 et 10:90; ou
(b) un poly(α-aminoacide) représenté par la formule générale (3) suivante:



(3)

dans laquelle R_3 possède 1 à 30 atomes de carbone et représente au moins un groupement choisi dans le groupe formé par les groupements alkyle, aralkyle, aryle et cycloalkyle, et ℓ est un degré de polymérisation de 5 à 10 000.

2. Fluide ayant simultanément des effets magnétiques et électrorhéologiques selon la revendication 1, dans lequel le composant ayant une susceptibilité électrique comprend en outre des particules de dispersion utilisées dans un fluide électrorhéologique.

3. Fluide ayant simultanément des effets magnétiques et électrorhéologiques selon la revendication 2, dans lequel les particules ferromagnétiques et les particules de dispersion utilisées dans un fluide électrorhéologique sont intégrées ensemble.