

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 636 683 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94304455.2**(51) Int. Cl.⁶: **C10M 171/00, C08F 30/08**(22) Date of filing: **20.06.94**(30) Priority: **30.07.93 JP 189529/93**(43) Date of publication of application:
01.02.95 Bulletin 95/05(84) Designated Contracting States:
DE GB(71) Applicant: **NIPPON SHOKUBAI CO., LTD.**
1-1, Koraibashi, 4-chome
Chuo-ku,
Osaka-shi,
Osaka-fu 541 (JP)(72) Inventor: **Ono, Satoru**
1-6-B-102 Shimotakatsu
Tsuchiura-shi,
Ibaragi-ken (JP)
Inventor: **Aizawa, Ryuji**
4844-304 Ino
Toride-shi,
Ibaragi-ken (JP)
Inventor: **Asako, Yoshinobu**
17-22-610 Bunkyo-cho
Tsuchiura-shi,
Ibaragi-ken (JP)(74) Representative: **Rees, David Christopher et al**
Kilburn & Strode
30 John Street
London WC1N 2DD (GB)(54) **Electrorheological fluid.**

(57) An electrorheological fluid comprising a disperse phase formed of dielectric particles and a dispersion medium formed of an electrical insulating oil and characterized by exhibiting a viscosity of not more than 0.2 Pa·s at a shear rate of 33/s when measured at 25 °C in the absence of supply of an electric field and a structural viscosity satisfying the condition of the formula (1):

$$0.01 \text{ Pa} \cdot \text{s} \leq \eta_1 - \eta_2 \leq 0.5 \text{ Pa} \cdot \text{s} \quad (1)$$

wherein η_1 is the viscosity in at a shear rate of 3.3/s when measured at 25 °C in the absence of supply of an electric field and η_2 is the viscosity in at a shear rate of 33/s when measured at 25 °C in the absence of supply of an electric field. This electrorheological fluid generates a large shear stress, exhibits an excellent current property and an excellent durability, and excels particularly in dispersion stability, redispersibility and fluidity.

EP 0 636 683 A1

The present invention relates to an electrorheological fluid. More specifically, it relates to an electrorheological fluid which has excellent properties in that a large shear stress and low current density can be generated even when a relatively low electrical field is applied to the fluid and the generated shear stress and current density has excellent stability properties with time (durability). The invention also has excellent properties in regard to dispersion stability under the conditions of no electrical field (the ability to uniformly maintain an electrorheological fluid and not settle or float the disperse phase therein), redispersibility (the ability to duplicate a uniform electrorheological fluid by applying a simple external force when the dispersed phase therein has settled and floats in a non-uniform state), and fluidity (having a low viscosity under the conditions of no electrical field).

There are known, as electrorheological fluid generating high shear stress, a fluid in which a powdered ion-exchange resin is dispersed in the higher alkyl ester of an aromatic carboxylic acid (JP-A-50-92278), a composition composed of a crystalline material which conducts current only along one of the three crystalline axes, a dielectrical fluid, and suspension stabilizing agent (JP-A-1-170693), and a fluid using, as a disperse phase, a conductive particle covered with a film layer of insulating material (JP-A-64-6093). However, these electrorheological fluids have the disadvantages of poor dispersion stability under the conditions of no electrical field, poor re-dispersibility after sedimentation and floatation, and poor fluidity when the concentration of the disperse phase is increased.

In order to improve the dispersion stability, there have been proposed the use of modified polysiloxane as an composite polymer (JP-A-3-39560), the use of a polymer having an ester group and an aromatic group structure as the composite polymer (JP-A-4-96997) or the like. However, these composite polymers serve only to prevent the sedimentation of the disperse phase, but have the drawback of a reduction of the re-dispersibility after sedimentation.

Further, in order to improve the re-dispersibility, there have been proposed electrorheological fluids using fine particles as the composite polymer (JP-A-3-160094 and JP-A-3-166295) or the like. However, these electrorheological fluids have problems in that the shear stress obtained when an electrical field is applied, decreases due to the addition of the fine particles, the conditions of use for the electrorheological fluids are defined due to the poor dispersion stability, and it is necessary for the device used to be equipped with an additional re-dispersibility system.

An electrorheological fluid which uses a copolymer obtained by polymerizing a raw-material monomer mixture having as essential components thereof a polymerizable monomer (A) such as (meth)acryloyl group-containing poly(methylene glycol) and at least one polymerizable monomer (B) selected from the group consisting of cross-linking monomers and silicone type polymerizable monomers and optionally containing another polymerizable monomer (C) as an composite polymer capable of improving dispersion stability, redispersibility, and fluidity has been proposed (EP-0 529 166). This electrorheological fluid, however, exhibits poor fluidity because it requires use of the composite polymer in a large amount for the sake of improving the dispersion stability.

The object of this invention, therefore, is to provide an electrorheological fluid which has excellent properties in that a large shear stress and low current density can be generated even when a relatively low electric field is applied to the fluid and the generated shear stress and current density has excellent stability properties with time (durability). The electrorheological fluid of this invention also has excellent properties in regard to dispersion stability under the conditions of no electric field (the ability to uniformly maintain an electrorheological fluid and not settle or float the disperse phase therein), re-dispersibility (the ability to duplicate a uniform electrorheological fluid by applying a simple external force when the disperse phase therein has settled and floats in a non-uniform state), and fluidity (having a low viscosity under the conditions of no electric field).

The object mentioned above is accomplished by an electrorheological fluid which comprises a disperse phase formed of dielectric particles and a dispersive medium formed of an electrical insulating oil and which is characterized by possessing a viscosity of not more than 0.2 Pa·s at a shear rate of 33/s measured at 25°C in the absence of supply of an electrical field and exhibiting a structural viscosity satisfying the condition of the formula (1):

$$0.01 \text{ Pa}\cdot\text{s} \leq \eta_1 - \eta_2 \leq 0.5 \text{ Pa}\cdot\text{s} \quad (1)$$

wherein η_1 is a viscosity at a shear rate of 3.3/s measured at 25°C in the absence of supply of an electric field and η_2 is a viscosity at a shear rate of 33/s measured at 25°C in the absence of supply of an electric field.

The electrorheological fluid of this invention exhibits excellent properties in that a large shear stress and low current density can be generated even when a relatively low electric field is applied to the fluid and the

generated shear stress and current density has excellent stability properties with time (durability).

The electrorheological fluid of this invention also has excellent properties in regard to dispersion stability under the conditions of no electric field (the ability to uniformly maintain an electrorheological fluid and not settle or float the disperse phase therein), redispersibility (the ability to duplicate a uniform electrorheological fluid by applying a simple external force when the disperse phase therein has settled and floats in a non-uniform state), and fluidity (having a low viscosity under the conditions of no electric field). Therefore, the electrorheological fluid of this invention can be effectively used for engine mount, clutch, damper, brakes, shock absorber, actuator, valve, and the like.

In order to develop devices operating by an electrorheological fluid, it is necessary that dispersion stability, redispersibility and fluidity of the fluid are good. It is particularly desirable that an electrorheological fluid has good shear stress property, current property and durability in addition to good dispersion stability, redispersibility and fluidity. We supposed that the properties (dispersion stability, redispersibility and fluidity) were dependent on the state of existence of the disperse phase in the dispersive medium. Then we found that the properties of an electrorheological fluid were ideally improved when the fluid exhibited structural viscosity while it possessed low viscosity in absence of supply of an electric field. The electrorheological fluid of this invention, therefore, is required to manifest the specific viscosity and the structural viscosity which is represented by the specific condition formula, mentioned above.

The expression "structural viscosity manifested by an electrorheological fluid" as used in this invention means the specific viscous form to be caused by a structure which is composed of disperse phase particles and a dispersive medium in consequence of weak aggregation of the disperse phase particles in the dispersive medium. This structural viscosity is controlled by the intensity of an interaction between a disperse phase particle and other disperse phase particle, and it gives suitable dispersion stability and suitable redispersibility to the electrorheological fluid.

The viscosity of the electrorheological fluid of this invention is required to be not more than 0.2 Pa·s at a shear rate of 33/s when measured at 25 °C in the absence of an electric field preferably to be in the range of 0.01 to 0.1 Pa·s. If the viscosity exceeds 0.2 Pa·s, the produced electrorheological fluid is at a disadvantage in exhibiting only poor fluidity and, at the same time, failing to acquire a sufficient electrorheological effect in consequence of the supply of an electric field or presenting difficulties to the design of a device.

The structural viscosity which is manifested by the electrorheological fluid of this invention is required to satisfy the condition of the following formula (1).

$$0.01 \text{ Pa}\cdot\text{s} \leq \eta_1 - \eta_2 \leq 0.5 \text{ Pa}\cdot\text{s} \quad (1)$$

wherein η_1 is the viscosity of at a shear rate of 3.3/s when measured at 25 °C in the absence of supply of an electric field and η_2 is a viscosity at a shear rate of 33/s when measured at 25 °C in the absence of supply of an electric field (hereinafter the difference, $\eta_1 - \eta_2$, will be referred to simply as "Ti").

As indicated by the formula (1), the Ti value of the electrorheological fluid of this invention is required to be in the range from not less than 0.01 Pa·s to not more than 0.5 Pa·s. Preferably, this range is from not less than 0.05 Pa·s to not less than 0.1 Pa·s. When the Ti value is in this range, the electrorheological fluid satisfies the dispersion stability, the redispersibility, and the fluidity at higher levels. If the Ti value is less than 0.1 Pa·s, the structural viscosity is insufficient and the dispersion stability is insufficient. If the Ti value exceeds 0.5 Pa·s, the fluidity is insufficient.

The dielectric particles to be used as disperse phase are preferable to have an average particle diameter of 1-50 μm , more preferably 3-20 μm . If the average particle diameter is not more than 1 mm, the resultant electrorheological fluid is not likely to induce a large shear stress when an electric field is applied. Adversely, if the average particle diameter is not less than 50 mm, it is difficult to obtain an electrorheological fluid with excellent dispersion stability.

The dielectric particles are particles which can be polarized when an electric field is applied. Examples of the dielectric particles are, but not limited to, organic particles having an hydrophilic group such as starch, cellulose, an ion-exchange resin, and a sulphonic acid group-containing polystyrene polymer; hydrophilic inorganic particles such as silica and alumina; a composite particle being a particle having three layers with an organic solid particle for center portion, a conductive film layer covering the organic solid particle, and an electric insulating film layer covering the conductive film layer, a particle in which the surface of a conductive particle such as aluminum is covered with a thin insulating film, a carbonaceous powder, a particle obtained by dispersing a conductive particle such as carbon black into a resin; an organic semiconductive particle such as poly(acene-quinone); strong dielectric particles such as barium titanate, lithium tartrate. In view of the large shear stress small current density when an electric field is

applied and excellent durability, a sulfonic acid group-containing polystyrene polymer is preferred among the mentioned particles.

The dispersive medium to be used for the electrorheological fluid of the present invention is an electrical insulating oil. Examples of the dispersive medium are, but not limited to, silicone oils such as polydimethylsiloxane, a partially octyl replaced polydimethyl-siloxane, a partially phenyl replaced polydimethyl-siloxane; hydrocarbons such as fluid paraffin, decane, methyl naphthalene, decalin, diphenylmethane, and a partially hydrogenated triphenyl; halogenated hydrocarbons such as chlorobenzene, dichlorobenzene, bromobenzene, chlorodiphenyl methane; fluorides of organic compound such as Difloil (a product sold by Daikin Industries Ltd. in Japan), Demnum (a product sold by Daikin Industries Ltd. in Japan); and ester compounds such as dioctyl phthalate, trioctyl trimellitate, and dibutyl sebacate. Of these one or more members may be used. In view of the fluidity, the viscosity of the dispersive medium is preferably not more than 0.05 Pa·s.

The electrical insulating oil is preferable to be a silicon element-containing insulating oil or a fluorine element-containing insulating oil.

The silicon element-containing insulating oil has no particular restriction except for the requirement that it should have a silicone oil as a main component thereof and should be a substantially electrical insulating liquid. The silicone oil possesses siloxane structure and generally finds utilities in brake oil, air insulating oil, saturation oil, lubricating oil, polish, component for cosmetic articles, mold release agent, defoaming agent, and the like. As concrete examples of the silicone oil, those already mentioned above may be cited.

The fluorine element-containing insulating oil has no particular restriction except for the requirement that it should have a fluoride of organic compounds as a main component thereof and should be a substantially electrical insulating liquid. Low polymers of ethylene trifluoride chloride which are generally used for lubricants and mold release agents, perfluoropolyether oils which are generally used as for lubricants, and fluorine-modified silicone oils which are used as for lubricants may be cited as typical examples.

In this invention, the method for enabling an electrorheological fluid to be endowed with the structural viscosity represented by the specific conditional formula while retaining the specific viscosity mentioned above is not particularly limited. Use of a composite polymer in the electrorheological fluid or treatment of the surface of the particles of the disperse phase with a polymeric compound is effective in implementing the endowment mentioned above. As the composite polymer, a composite polymer which is substantially insoluble in an electrical insulating oil and is possessed both of a silicone component-containing structural unit (A) and a disperse phase-adsorbing chain-containing structural unit (B) may be used for example.

When such a composite polymer as is defined above is used as the composite polymer, since this composite polymer has the nature of being adsorbed on the surface of the particle of the disperse phase, an interaction occurs between the composite polymer and the surface of the particle of the disperse phase. Further, since the composite polymer has the nature of exhibiting affinity for the dispersive medium, an interaction likewise occurs between the composite polymer and the dispersive medium. As a result, a ternary structure is formed through the medium of the composite polymer. Since the composite polymer is substantially insoluble in the dispersive medium, it is capable of obstructing mutual contact of the particles of the disperse phase. By using the composite polymer of this description as the composite polymer, the electrorheological fluid can be endowed with the structural viscosity represented by the specific conditional formula while retaining the specific viscosity and, at the same time, can be vested with highly satisfactory dispersion stability, redispersibility, and fluidity.

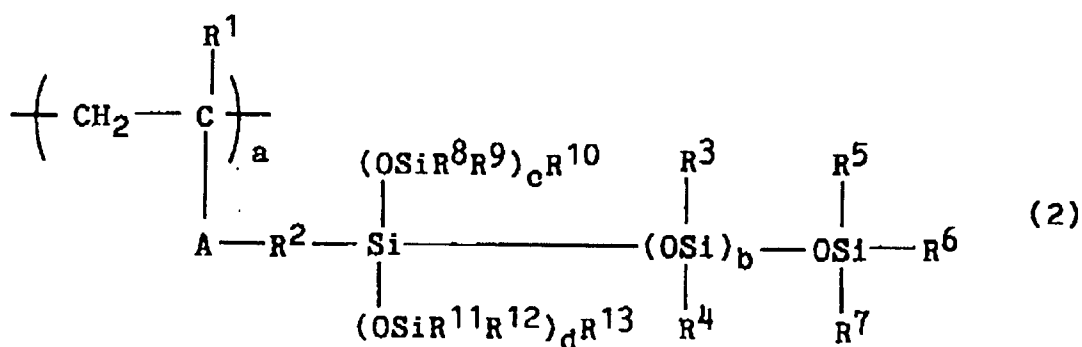
Though the composite polymer is preferable to be substantially insoluble in an electric insulating oil, it may contain not more than 90% by weight of soluble materials. Further, the composite polymer may be partially swelled or wholly swelled by absorbing an electrical insulating oil so long as it avoids being solved in an electrical insulating oil and converted into a homogeneous solution. If the composite polymer dissolves in an electrical insulating oil or instead contains 90% or more by weight of soluble materials, the produced electrorheological fluid will be possibly at a disadvantage in being deficient in redispersibility.

The composite polymer is preferable to possess a silicone component-containing structural unit (A). If the composite polymer does not possess this structural unit (A), the produced electrorheological fluid will be possibly at a disadvantage in being deficient in dispersion stability or fluidity. The term "silicone component" means polysiloxane groups such as, for example, a polydimethylsiloxane group, a partially alkyl group-substituted polydimethylsiloxane group, a partially aryl group-substituted polydimethylsiloxane group, or a tris(trialkylsiloxy)-cyclopropyl group.

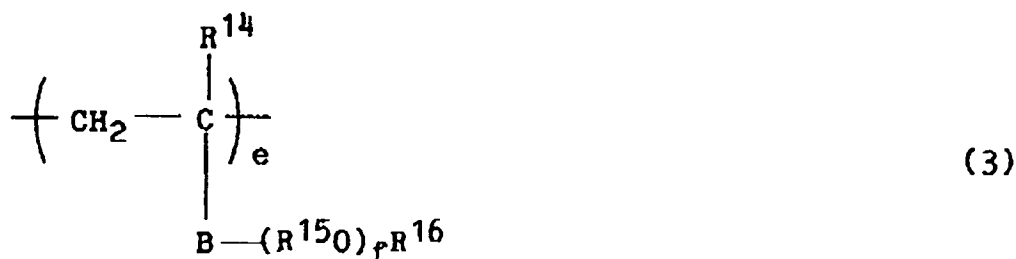
The composite polymer is preferable to possess disperse phase-adsorbing chain-containing structural unit (B). If the composite polymer does not possess the structural unit (B), the produced electrorheological fluid will possibly be at a disadvantage in being deficient in dispersion stability. The adsorption may be in the form of chemical adsorption or physical adsorption. When the interaction between

the composite polymer and the surface of the particles of the disperse phase is unduly intense, it will possibly degrade the redispersibility and the fluidity of the produced electrorheological fluid. Thus, the adsorption is desired to be in the form of physical adsorption or electrostatic chemical adsorption. The term "disperse phase-adsorbing chain" means functional groups such as a hydrocarbon groups, a atomic groups containing oxygen atom which exhibit the Lewis basicity.

As typical examples of the composite polymer for enabling an electrorheological fluid to be endowed with the structural viscosity represented by the specific conditional formula while retaining the specific viscosity, (1) a composite (1) which is obtained by complexing particle (I) substantially insoluble in an electrical insulating oil with a polysiloxane-containing polymer (II), the polymer (II) having as the silicone component-containing structural unit (A) thereof a polysiloxane-containing structural unit (A-1) represented by the general formula (2):



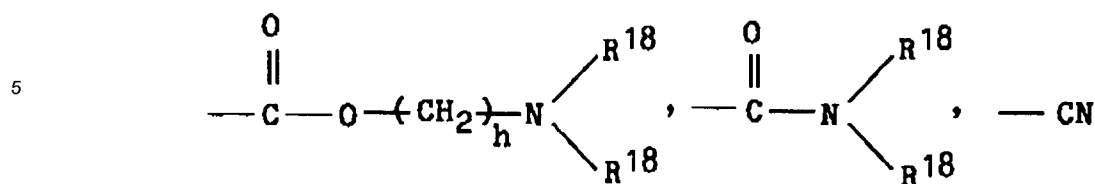
wherein A is -COO- or phenylene group, R¹ is hydrogen atom or methyl group; R² is an alkylene group of 1 to 6 carbon atoms, R³ to R¹³ are independently an aryl group, an alkyl group of 1 to 6 carbon atoms, or an alkoxy group of 1 to 10 carbon atoms, a is an arbitrary integer, c and d are independently an integer in the range or 0 to 10, and b is an integer in the range of 0 to 200, and as the disperse phase-adsorbing chain-containing structural unit (B) thereof at least one member selected from the group consisting of an alkyleneoxide chain-containing structural unit (B-1) represented by the general formula (3):



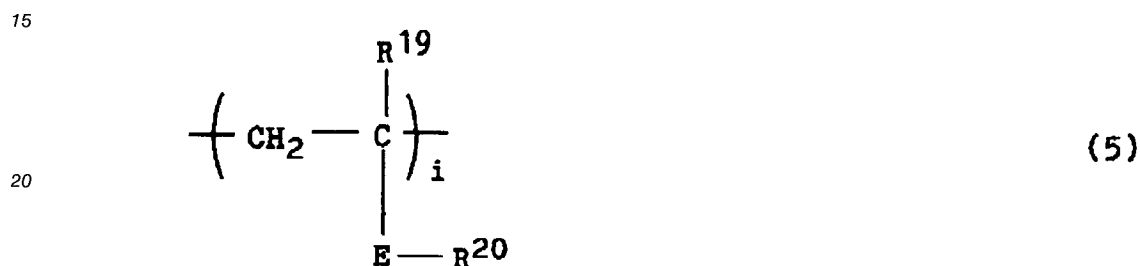
wherein B is -COO- or phenylene group, R¹⁴ is hydrogen atom or methyl group, R¹⁵ is an alkylene group of 2 to 4 carbon atoms, R¹⁶ is hydrogen atom or an alkyl group, e is an arbitrary integer, and f is an integer in the range of 2 to 100, a nitrogen atom-containing chain-containing structural unit (B-2) represented by the general formula (4):



wherein D is



or a nitrogen-containing heterocycle-containing substituent, R^{17} is hydrogen atom or methyl group, R^{18} is hydrogen atom or an alkyl group, g is an arbitrary integer, and h is an integer in the range of 2 to 6, and/or a hydrocarbon chain-containing structural unit (B-3) represented by the general Formula (5):



wherein E is -COO- or phenylene group, R^{19} is hydrogen atom or methyl group, R^{20} is an alkyl group of 1 to 30 carbon atoms, and i is an arbitrary integer; and (2) a composite (2) which is substantially insoluble in an electrical insulating oil and comprises a polysiloxane-containing polymer (III), the polymer (III) having as the silicone component-containing structural unit (A) thereof a polysiloxane-containing structural unit (A-1) represented by the general formula (2) and as the disperse phase-adsorbing chain-containing structural unit (B) thereof a long alkyl chain-containing structural unit (B-4) represented by the general formula (10):



wherein L is -COO- or phenylene group, R^{41} is hydrogen atom or methyl group, R^{42} is an alkyl group of 8 to 30 carbon atoms, and s is an arbitrary integer, may be cited.

When the composite polymer is used, it is preferable to be added in the amount in the range of 0.01 to 6 parts by weight, based on 100 parts by weight of the disperse phase. If the amount of the composite polymer is less than 0.01 part by weight, the produced electrorheological fluid will be possibly at a disadvantage in exhibiting no structural viscosity or acquiring no dispersion stability. If the amount of the composite polymer exceeds 6 parts by weight, the produced electrorheological fluid will be possibly at a disadvantage in having the redispersibility and the fluidity thereof notably degraded. It is particularly preferable to use the composite polymer in the amount falling in the range of 0.1 to 5 parts by weight.

When the composite (1) mentioned above is used as the composite polymer, this composite (1) is obtained by complexing the particle (I) which are substantially insoluble in an electrical insulating oil with a polysiloxane-containing polymer (II) which comprises a polysiloxane-containing structural unit (A-1) and a disperse phase-adsorbing chain-containing structural unit (B) as described above. As the structural unit (B), at least one member selected from the group consisting of an alkyleneoxide chain-containing structural unit (B-1), a nitrogen atom-containing chain-containing structural unit (B-2), and a hydrocarbon chain-containing structural unit (B-3) mentioned above can be used. By causing a suitable interaction between the particles

of the disperse phase and the dispersive medium through the medium of this composite (1), the electrorheological fluid can be endowed with dispersion stability, redispersibility, and fluidity.

The composite (1) to be used in this invention possess a moiety of the particle (I) which are substantially insoluble in an electrical insulating oil. The composite(1) itself, therefore, is substantially insoluble in an insulating oil. Since the composite(1) is substantially insoluble in the oil, the mutual contact of the particles of the disperse phase can be obstructed in the electrorheological fluid and the electrorheological fluid can be endowed with highly satisfactory redispersibility and fluidity. If the composite polymer is soluble substantially in the electrical insulating oil, the produced electrorheological fluid will be possibly at a disadvantage in being incapable of acquiring redispersibility and fluidity.

The particle (I) which is substantially insoluble in an electric insulating oil and which is compositeed with the polysiloxane-containing polymer (II) have no particular restriction except for the requirement that they should be substantially insoluble in an electrical insulating oil. As typical examples of the particle (I), organic particle such as of polystyrene, poly(meth)acrylate, polyacrylonitrile, phenol resin, benzoguanamine resin, and melamine resin; inorganic particles such as of silica and alumina; organic or inorganic particles having such condensation or addition reaction groups as hydroxyl group, amino group, carboxyl group, epoxy group, and isocyanate group; and organic or inorganic particles having such polymerization reaction groups as styryl group and (meth)acryloyl group may be cited.

The composite (1) to be used in this invention possesses a polysiloxane-containing polymer (II) moiety having a polysiloxane-containing structural unit (A-1) and a disperse phase-adsorbing chain-containing structural unit (B) as essential components thereof. By the polysiloxane-containing structural unit (A-1) in the composite (1), a suitable interaction can be caused between the composite (1) and the dispersive medium to endow the electrorheological fluid with dispersion stability and fluidity. If the composite (1) possesses no polysiloxane-containing structural unit (A-1), the electrorheological fluid will be possibly at a disadvantage in encountering degradation of dispersion stability and fluidity. By the disperse phase-adsorbing chain-containing structural unit (B) in the composite (1), a suitable interaction can be caused between the composite (1) and the particles of the disperse phase to impart dispersion stability to the electrorheological fluid. If the composite (1) possesses no disperse phase-adsorbing chain-containing structural unit (B), the electrorheological fluid will be possibly at a disadvantage in encountering degradation of dispersion stability.

The ratio of the polysiloxane-containing polymer (II) to the particle (I) substantially insoluble in an electrical insulating oil in the composite (1) is preferable to be such that the proportion of the polymer (II) is in the range of 0.1 to 100 parts by weight, particularly preferably 1 to 10 parts by weight, based on 100 parts by weight of the particle (I). If the proportion of the polymer (II) is less than 0.1 part by weight, the electrorheological fluid will be possibly at a disadvantage in being endowed with no dispersion stability. If the proportion of the polymer (II) exceeds 100 parts by weight, the electrorheological fluid will be possibly at a disadvantage in being endowed with neither redispersibility nor fluidity.

The composite (1) is obtained by compositeing the particle (I) substantially insoluble in an electric insulating oil with the polysiloxane-containing polymer (II). It is not particularly limited by the form of this compositeing reaction. The composite (1), however, is desired to be such that the polymer (II) has been fixed on the surface of the particle (I) in consequence of the complexing. If the polymer (II) has not been fixed on the surface of the particle (I) by the complexing reaction, the electrorheological fluid will be possibly at a disadvantage in being endowed with no dispersion stability.

The composite (1) is preferable to be such that the particle (I) substantially insoluble in an electrical insulating oil is linked to the polysiloxane-containing polymer (II) by a chemical bonding. The composite (1) which serves as an ideal composite polymer in this invention is easily obtained by linking the particle (I) to the polymer (II) by a chemical bonding. If the particle (I) is not linked to the polymer (II) by a chemical bonding, the composite (1) will possibly fail to serve as an ideal composite polymer in this invention.

The method for obtaining the composite (1) by complexing the particle (I) substantially insoluble in an electrical insulating oil with the polysiloxane-containing polymer (II) has no particular restriction. For example, (i) a method which comprises forming the particle (I) in the presence of the polymer (II) thereby simultaneously effecting formation of the particle (I) and the complexing reaction, (ii) a method which comprises forming the polymer (II) in the presence of the particle (I) thereby simultaneously effecting formation of the polymer (II) and the complexing, and (iii) a method which comprises synthesizing the particle (I) and the polymer (II) independently of each other, mixing or kneading them, and then subjecting the resultant mixture to a treatment with heat or radiation thereby effecting the complexing reaction are available for the production of the composite (1).

When the method of complexing (i) is adopted, the composite (1) is synthesized, for example, by (i-1) a method which comprises polymerization of the monomer mixture (X) thereby forming the polysiloxane-containing polymer(II) and dispersion polymerization of a polymerizable monomer (α) capable of producing

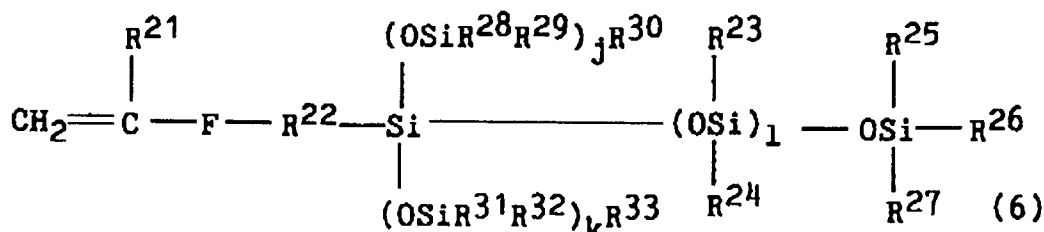
the particle (I) in the presence of the polymer (II), (i-2) a method which comprises polymerization of the monomer mixture (X) thereby forming the polysiloxane-containing polymer (II) and emulsion polymerization of the polymerizable monomer (α) in an aqueous medium in the presence of the polymer (II), (i-3) a method which comprises polymerization of the monomer mixture (X) thereby forming the polysiloxane-containing polymer (II) and solution polymerization of the polymerizable monomer (α) in the presence of the polymer (II). Particularly, the method of (i-1) and the method of (i-2) are used advantageously in respect that the composite (1) having the polymer (II) fixed on the surface of the particle (I) by the complexing is easily obtained with high repeatability. In the operation of the method of (i-1), it is particularly desirable to use the polymer which has an ethylenically unsaturated group therein in advance because this polymer allows the composite(1) having the polymer (II) fixed on the surface of the particle (I) by a chemical bonding to be easily obtained with high repeatability.

When the compositeing method of (ii) is adopted, the composite(1) is synthesized, for example, by (ii-1) a method which adopts a very minute organic or inorganic particle mentioned above as the particle (I) and produces the polysiloxane-containing polymer (II) by polymerizing the monomer mixture (X) in the presence of the very minute organic or inorganic particle, (ii-2) a method which adopts a very minute organic or inorganic particle having the condensation or addition reaction group mentioned above as the particle (I) and produces the polymer (II) by polymerizing the monomer mixture (X) in the presence of the very minute organic or inorganic particle, or (ii-3) a method which adopts a very minute organic or inorganic particles having the polymerization reaction group mentioned above therein as the particle (I) and produces the polymer (II) by polymerising the monomer mixture (X) in the presence of the very minute organic or inorganic particle. It is particularly advantageous to use the method of (ii-2) or the method of (ii-3) because it permits production of the composite (1) having the polymer (II) fixed on the surface of the particle (I) by a chemical bonding. The adoption of the method of (ii-3) proves to be particularly desirable because the composite (1) having the polymer (II) fixed on the surface of the particle (I) by a chemical bonding is easily obtained with high repeatability.

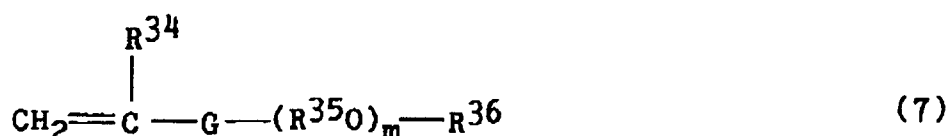
When the compositeing method of (iii) is adopted, the composite(1) is synthesized, for example, by (iii-1) a method which comprises mixing or kneading the particle (I) with the polysiloxane-containing polymer (II) in the presence or absence of a solvent.

The process for synthesizing the composite (1) by the method of (i-1) will be shown below.

The polysiloxane-containing polymer (II) is obtained by polymerizing the monomer mixture (X) containing a silicone-containing macromer (am) represented by the general formula (6):



wherein F is -COO- or phenylene group, R^{21} is hydrogen atom or methyl group, R^{22} is an alkylene group of 1 to 6 carbon atoms, R^{23} to R^{33} are independently an aryl group, an alkyl group of 1 to 6 carbon atoms, or an alkoxy group of 1 to 10 carbon atoms, j and k are independently an integer in the range of 0 to 10, and l for an integer in the range of 0 to 200, and at least one disperse phase-adsorbing chain-containing monomer (b) selected from the group consisting of an alkyleneoxide chain-containing macromer (bm-1) represented by the general formula (7):

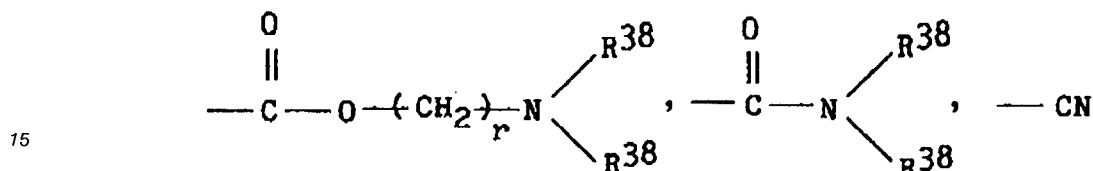


wherein G is -COO- or phenylene group, R^{34} is hydrogen atom or methyl group, R^{35} is an alkylene group of 2 to 4 carbon atoms, R^{36} is hydrogen atom or an alkyl group, and m is an integer in the range of 2 to 100,

a nitrogen-containing chain-containing monomer (b-2) represented by the general formula (8):



wherein J is



or a nitrogen-containing heterocycle-containing substituent, R^{37} is hydrogen atom or methyl group, R^{38} is hydrogen atom or an alkyl group, and r is an integer in the range of 2 to 6, and a hydrocarbon chain-containing monomer (b-3) represented by the general formula (9):



wherein K is $-\text{COO}-$ or phenylene group, R^{39} is hydrogen atom or methyl group and R^{40} is an alkyl group of 1 to 30 carbon atoms, as essential components and an optional monomer (c).

The ratio of a silicone-containing macromer (am) is preferably 10-90%, and more preferably 20-80% by weight, based on the weight of the monomer mixture (X). If the ratio of a silicone-containing macromer (am) is less than 10% by weight or more than 90% by weight, the electrorheological fluid does not have dispersion stability and fluidity. The ratio of a disperse phase adsorbing chain-containing monomer (b) is preferably 10-90%, and more preferably 20-80% by weight, based on the weight of the monomer mixture (X). If the ratio of monomer (b) is less than 10% by weight or more than 90% by weight, the electrorheological fluid does not have full dispersion stability properties.

When the method of (i-1) is adapted, as a silicone-containing macromer (am), there are cited, for instance, (meth)acryloyl group-containing polydimethyl siloxane, styryl group-containing polydimethyl siloxane, (meth)acryloyl group-containing and partially octyl substituted polydimethyl siloxane, styryl group-containing and partially octyl substituted polydimethyl siloxane, (meth)acryloyl group-containing and partially phenyl substituted polydimethyl siloxane, tris(trimethylsiloxy) silylpropyl (meth)acrylate. Of these one or more members may be used.

As an alkylene oxide chain-containing monomer (bm-1), used as the disperse phase-adsorbing chain monomer, there are cited, for instance, a polyalkylene glycol having a double bond such as a (meth)acryloyl group-containing polyethylene glycol, a styryl group-containing polyethylene glycol, a p-isopropenyl benzyl group-containing polyethylene glycol, a (meth)acryloyl group-containing polypropylene glycol, a styryl group-containing polypropylene glycol, a p-isopropenyl benzyl group-containing polypropylene glycol, a (meth)acryloyl group-containing polytetramethylene glycol, a styryl group-containing polytetramethylene glycol, and a p-isopropenyl benzyl group-containing polytetramethylene glycol. Of these one or more members may be used.

As a nitrogen atom-containing monomer (b-2), there are cited monomers including one or more basic nitrogen atoms and an ethylenically unsaturated bond. Examples of nitrogen atom-containing monomer (b-2) are, but not limited to, nitrogen-containing (meth)acrylic acid derivatives, (meth)acrylonitrile, and unsaturated monomers containing a nitrogen heterocyclic ring.

As the nitrogen-containing (meth)acrylic acid derivatives, there are cited, for instance, modified (meth)acrylic esters in which the ester portion includes a substituted or non substituted amino group, and (meth)acrylic acid amide, preferably aminoalkyl (meth)acrylate and (meth)acrylic acid amide. Examples of

aminoalkyl (meth)acrylate are N, N-dimethyl amino ethyl (meth)acrylate, N, N-diethyl amino ethyl (meth)acrylate, N, N-dimethyl amino propyl (meth)acrylate, and N, N-dimethyl amino butyl (meth)acrylate or the like. Examples of (meth)acrylic acid amide are (meth)acrylamide, N-(meth)acrylamide, N-ethyl (meth)acrylamide, N-butyl (meth)acrylamide, N, N-dimethyl (meth)acrylamide, N, N-diethyl (meth)acrylamide, N, N-dimethyl propyl acrylamide or the like. Of these one or more members may be used, and in particular preferably a tertiary amine containing compound.

As the unsaturated monomers containing a nitrogen heterocyclic ring, there are cited, for instance, monomers in which a heterocyclic ring made of a single ring or multiple rings including one to three, preferably one or two nitrogen atoms, bonds to a vinyl group. Examples of these monomers are vinyl pyrrolidones such as 2-vinyl-2-pyrrolidone, and 1-vinyl-3-pyrrolidone; vinyl pyridines such as 2-vinyl pyridine, 4-vinyl pyridine, and 5-methyl-2-vinyl pyridine; vinylimidazoles such as 1-vinyl imidazole, and 1-vinyl-2-methyl imidazole; N-(meth)acryloyl morpholine or N-(meth)acryloyl pyridine or the like. Of these one or more members may be used.

As the hydrocarbon chain-containing monomer (b-3), there are cited, for instance, (meth)acrylic esters such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, dodecyl (meth)acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, 2-methylstearyl (meth)acrylate, and eicosyl (meth)acrylate; or alkyl group substituted styrenes such as methyl styrene, ethyl styrene, butyl styrene, octyl styrene, dodecyl styrene, and stearyl styrene. Of these one or more members may be used.

As the optional monomer (c), there are cited, for instance, polymerizable monomers of olefins such as ethylene, propylene, and cyclohexene; alkyldienes such as butadiene, isoprene, and cyclopentadiene; halogenated olefins such as vinyl fluoride, vinylidene fluoride, vinyl chloride, and vinylidene chloride; aromatic vinyl compounds such as styrene, α -methyl styrene, p-methyl styrene, vinyl naphthalene, vinyl anthracene, chlorostyrene, and chloromethyl styrene; (meth)acrylic alkoxy alkyl esters such as methoxy ethyl (meth)acrylate; (meth)acrylic hydroxyl alkyl esters such as 2-hydroxyl ethyl (meth)acrylate, and hydroxyl butyl (meth)acrylate; esters made from an aromatic alcohol and (meth)acrylate such as benzyl (meth)acrylate; composite polymers of glycidyl (meth)acrylate or (meth)acrylic hydroxy alkyl ester and a monocarboxylic acid having 2-18 carbon atoms such as acetic acid, propionic acid, lauric acid, linoleic acid, and p-tert-benzoic acid; fluorine-containing compounds such as VISCOAT8F, VISCOAT8FM (products, (meth)acrylates containing a fluorine atom, sold by Osaka Yukikagaku Kabushiki Kaisha in Japan), (meth)acrylic perfluoro cyclohexyl, and perfluoro cyclohexyl ethylene; vinyl esters such as vinyl benzoate; polymerizable unsaturated group-containing sulfonic acids such as vinyl sulfonic acid, allyl sulfonic acid, styrene sulfonic acid, 2-acrylamide-2-methyl propane sulfonic acid, 2-sulfoethyl (meth)acrylate, and 3-sulfopropyl (meth)acrylate; or polymerizable unsaturated group-containing carboxylic acid such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, and citraconic acid or salts thereof, the salt being sodium, calcium, ammonium, and pyridinium or the like.

Polysiloxane-containing polymer (II) is produced by a known procedure, e.g. solution polymerization using a radical generating catalyst.

As the radical generating catalyst, there are cited, for instance, conventional catalysts for the polymerization of vinyl monomers. Examples of the radical generating catalyst are, but not limited to, azo compounds such as 2, 2'-azobisisobutyronitrile, and 2, 2'-azobis (2, 4-dimethylvaleronitrile); and per-oxide compounds such as benzoyl peroxide, di-tert-butyl peroxide, tert-butyl peroctate, and tert-butylperoxy-2-ethylhexanoate. The amount of the radical generating catalyst to be added is usually 0.2-10 parts by weight, preferably 0.5-5 parts by weight, based on 100 parts of the monomer used.

The reaction temperature of polymerization is Usually 60 °-100 °C for 1 to 15 hours.

In the polymerization, a solvent may be used. Examples of the solvent are, but not limited to, aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons benzene, toluene, and xylene; alcohols such as isopropyl alcohol, and butanol; ketones such as methyl isobutyl ketone, and methyl ethyl ketone; esters such as ethyl acetate, isobutyl acetate, amyl acetate, 2-ethyl hexyl acetate; and Cellosolve such as methyl cellosolve, and ethyl cellosolve.

After finishing polymerization, a solution of the polymer (II) thus obtained can be used for synthesizing the composite (1) as it is or can be used after separating the polymer (II) by distilling off the solvent.

Polymer (II) preferably has an ethylenically unsaturated group, which is introduced by the reaction of a monomer with an ethylenically unsaturated group.

When polymer (II) having an ethylenically unsaturated group is used for synthesizing the composite (1), due to the formation of chemical bond between polymerizable monomer (α) (particle (I)) and polymer (II), then the electrorheological fluids have improved the dispersion stability during storage and the dispersion stability after the use for a long period time under conditions of high shear stress.

The introduction of an ethylenically unsaturated group into polymer (II) is carried out, for instance, by adopting, as a component of a monomer mixture (X), an acid group-containing monomer such as acrylic acid, methacrylic acid, maleic acid, and vinyl sulfonic acid to form the precursor of polymer (II), and then reacting with the acid group of the precursor a glycidyl group-containing unsaturated monomer such as glycidyl (meth)acrylate or allyl glycidyl ether.

The composite (1) is then produced by dispersion-polymerising polymerizable monomer (α) in the presence of polymer (II) in the method (i-1). The meaning of dispersion polymerization of the method (1-1) is polymerization carried out in the presence of a dispersion stabilizing agent using an organic solvent capable of dissolving polymerizable monomer (α) and not capable of dissolving the resultant polymer. In particular, the organic solvent is capable of dissolving both of polymer (II) and polymerizable monomer (α) and substantially not capable of dissolving the resultant composite. Examples of the organic solvent are, but not limited to, aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons such as benzene, toluene, and xylene; alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and n-butyl alcohol; ethers such as cellosolve, butylcellosolve, and diethylene glycol monobutyl ether; esters such as ethyl acetate, and isobutyl acetate; and ketones and the like. Of these one or more members may be used.

As polymerizable monomer (α) which is polymerized by the method (i-1), there are cited, for instance, aromatic compounds such as styrene, vinyl toluene, vinyl p-chlorotoluene, and vinyl pyridine; and (meth)acrylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and benzyl (meth)acrylate.

The dispersion polymerization for synthesizing the composite (1) to be used in the method (i-1), is carried out usually using a radical generating catalyst. Examples of the radical generating catalyst are, but not limited to, azo compounds such as 2, 2'-azobisisobutyronitrile, and 2, 2'-azobis(2,4-dimethylvaleronitrile); and peroxides such as benzoyl peroxide, and lauroyl peroxide. The amount of the catalyst is usually 0.2-10 parts by weight, preferably 0.5-5 parts by weight, based on 100 parts by weight of polymerizable monomer (α).

The proportion of polymer (II) is preferably 0.1-10 parts by weight, more preferably 1-6 parts by weight, to 100 parts by weight of polymerizable monomer (α) in the method (i-1). If the proportion of polymer (II) is not more than 0.1 part by weight, the polymerization for producing the composite are not reproducible and if obtained, the dispersion stability of electrorheological fluid is poor. Adversely, if the proportion is not less than the 10 parts by weight, the resultant electrorheological fluid is liable to be poor in re-dispersibility and fluidity properties.

The total concentration of polymerizable monomer (α) and polymer (II) in the reaction mixture is usually 5-50% by weight, preferably 10-30% by weight. Further, a conventional surfactant or a dispersion stabilizer such as high polymers may be added.

The dispersion polymerization may be carried out usually at 60°-100°C and for 0.5-30 hours. After polymerization, a post treatment may be carried out for solvent replacement, solvent distillation, drying, and grinding. When the polymerization solvent used is replaced with a silicone insulating oil, the workability of producing electrorheological fluid is improved. Process for synthesizing the composite (10 by the method (i-2) is shown as follows.

The composite (1) used in the method (i-2) is obtained by emulsion-polymerizing the polymerizable monomer (α) in a medium mainly comprising water in the presence of the polymer (III). The emulsion polymerization is preferred using a radical generating catalyst soluble in water. The radical generating catalyst is a conventional one for emulsion polymerization of vinyl monomers. Examples of the radical generating catalyst are, but not limited to, sodium persulfate, potassium persulfate, ammonium persulfate, 4, 4'-azobis-4-cyanovaleric acid, and 2, 2'-azobis-aminopropane hydrochloric acid salt.

In the method (i-2) the proportion of polymer (II) is preferably 0.1-10 parts by weight, more preferably 1-6 parts by weight, based on 100 parts by weight of polymerizable monomer (α) used. If the proportion is not more than 0.1 part by weight, the polymerization for producing the composite is reproducible, and the if obtained electrorheological fluid does not have a sufficient dispersion stability. Adversely, if the proportion is not less than 10 parts by weight, the electrorheological fluid has poor re-dispersibility and fluidity.

The total concentration of polymerizable monomer (α) and polymer (II) is preferably 5-50% by weight, more preferably 10-30% by weight, based on the weight of the aqueous solvent used.

The emulsion-polymerization for synthesizing the composite (1) by the method (i-2) can be carried out in water or in an aqueous medium comprising water and an organic solvent. As the organic solvent, there are an organic solvent having a high affinity to water, e.g. alcohols such as methanol, ethanol, and isopropanol; Cellosolve such as methylcellosolve, and ethylcellosolve; glycols such as ethylene glycol, and diethylene glycol. When the mixture is used as the solvent, it is preferred for polymerizable monomer (α) not to dissolve into the solvent.

The polymerization for synthesizing the composite (I) in the method (i-2) may be carried out at 50 °-100 °C for 2-40 hours.

The procedure of polymerization is carried out by charging water and polymer (II) into a reactor, mixing the resultant mixture to form an uniform dispersion, adding a part or whole of polymerizable monomer (α) into the dispersion, regulating the temperature of the dispersion, and adding a radical generating catalyst into the regulated dispersion to start polymerization. The polymerization is carried out in the emulsified state at a prescribed temperature by adding the residual polymerizable monomer (α), if present. After polymerization, a post treatment may be carried out for solvent replacement, solvent distillation, drying and grinding. Process for synthesizing the composite (1) by the method (ii-3) is shown as follows.

As the particle (I) which is substantially insoluble in the electrical insulating liquid used in the method (ii-3), an organic or inorganic fine particle with (e) a compound having polymerizable reactive group can be used. The fine particle having polymerizable reactive group is, for example, a compound (e) having both functional group capable of reacting with the functional group existed on the surface of the organic or inorganic fine particle and the polymerizable reactive group and can be obtained by treating the organic or inorganic fine particle. Examples of compound (e) are vinyl group-containing silane coupling agents such as γ -(meth)acryloxy propyl trimethoxy silane, vinyl trimethoxy silane, vinyl triethoxy silane, and vinyl trichloro silane; and glycidyl group-containing unsaturated compounds such as glycidyl (meth)acrylate, and allyl glycidyl ether.

The amount of compound (e) is usually 10-100 parts by weight, based on 100 parts by weight of the organic or inorganic fine particle used.

The polymerization of the monomer mixture (X) for producing the composite (I) by the method (ii-3) may be carried out using a polymerization initiator in the presence of particle (I) which has a polymerizable group thereon in an organic solvent.

Examples of the organic solvent are, but not limited to, aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons such as benzene, toluene, and xylene; alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and n-butyl alcohol; ethers such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, diethylene glycol monobutyl ether; esters such as ethyl acetate, and isobutyl acetate; and ketones. Of these one or more members may be used.

The polymerization initiator may be peroxide initiators such as benzoyl peroxide, and lauroyl peroxide; azo initiators such as 2, 2'-azobisisobutyronitrile, 2, 2'-azobis (2, 4'-dimethyl valeronitrile).

The mentioned polymerization may be carried out at 50 °-100 °C for 0.5-15 hours. After polymerization, a post treatment may be carried out for solvent replacement, solvent distillation, drying and grinding.

The other matters and compounds not explained are the same as described in method (ii-1).

As concrete examples of the compound (e) having such twokinds of groups as mentioned above, vinyl group-containing silane type coupling agents such as γ -(meth)acryloxypropyl trimethoxy silane, vinyl trimethoxy silane, vinyl triethoxy silane, and vinyl trichlorosilane and glycidyl group-containing unsaturated compounds such as glycidyl (meth)acrylate and allyl glycidyl ether may be cited.

Though the mount of the compound (e) to be used for the introduction of the polymerization reaction group into the very minute organic or inorganic particles is not particularly limited, the compound (e) is desired to be used in an amount in the range of 10 to 100 parts by weight based on 100 parts by weight of the very minute organic or inorganic particles.

When the composite (1) is obtained by the method of (ii-3), the polymerization of the monomer mixture (Y) is desired to be effected in an organic solvent by use of a polymerization initiator in the presence of the particles (I) which are formed of very minute organic or inorganic particles having the polymerization reaction group incorporated therein.

As typical examples of the organic solvent to be used for the polymerization, aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons such as benzene, toluene, and xylene; alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and n-butyl alcohol; and ether type, ketone type, and ester type organic solvents such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, diethylene glycol monobutyl ether, ethyl acetate, and isobutyl acetate may be cited. One member or a mixture of two or more members selected from the group of organic solvents cited above may be used.

As typical examples of the polymerization initiator for use in the polymerization, peroxide type initiators such as benzoyl peroxide and lauroyl peroxide; and azo type initiators such as 2,2'-azo-bis-isobutyronitrile and 2,2'-azo-bis-2,4'-dimethyl valeronitrile) may be cited.

The polymerization is carried out at a temperature of 50 °-100 °C generally for 0.5-15 hours.

After the polymerization is completed, the produced polymerization solution may be optionally treated by the well-known methods of displacement of solvent, expulsion of solvent by distillation, drying, and pulverization.

When the composite (2) is used as the additive, the composite (2) which contains a polysiloxane-containing polymer (III) is substantially insoluble in the electrical insulating oil and has the above-mentioned polysiloxane structural unit (A-1) and a long alkyl chain containing structural unit (B-4). An appropriate interaction between disperse phase particle and dispersing medium through the composite (2) is generated and it gives dispersion stability, redispersibility and fluidity.

Further, the composite (2) is preferable a composite product of the particle (I) which is substantially insoluble in the electrical insulating oil, the polysiloxane-containing structural unit (A-1) and a long alkyl chain-containing structural unit (B-4).

The composite (2) is substantially insoluble in the electrical insulating oil. Contact between particles of the disperse phase in the electrorheological fluid can be prevented based on substantial insolubility in the composite (2), and it can give good redispersibility and fluidity to the electrorheological fluid. If the composite polymer is substantially soluble in the electrical insulating oil, the problem wherein redispersibility and fluidity cannot be given to the electrorheological fluid sometimes occurs.

The composite (2) has a polysiloxane-containing polymer (III) having both polysiloxane-containing structural unit (A-1) and long alkyl chain-containing structural unit (B-4) as an essential component. An appropriate interaction is generated between the composite (2) and the dispersive medium by the polysiloxane-containing structural unit (A-1), so dispersion stability and fluidity can be given to the electrorheological fluid. If it lacks the polysiloxane-containing structural unit (A-1), there is a problem that both dispersibility and fluidity of the electrorheological fluid decrease. Further an appropriate interaction is generated between the composite (2) and the dispersing phase particle by the long alkyl chain containing structural unit (B-4), so dispersion stability can be given to the electrorheological fluid. If it lacks the long alkyl chain-containing structural unit, the problem that the dispersion stability decreases occurs. It is preferable that the composite (2) is obtained by complexing the particle (I) which is substantially insoluble in the electric insulating oil with the polysiloxane-containing polymer (III). The particle (I) substantially insoluble in electric insulating oil which is complexed with the polysiloxane-containing polymer (III) is not limited. As the particle (I), the same organic and inorganic particles which is explained about the composite (1) can be cited.

In the present invention, a ratio of the polysiloxane-containing polymer (III) to the particle (I) substantially insoluble in the electrical insulating oil is preferably 0.1 to 100 parts by weight, more preferably 1 to 10 parts by weight to 100 parts by weight of the particle (I). If the ratio of the former is less than 0.1 part by weight, dispersion stability cannot sometimes be given to the electrorheological fluid. If the ratio of the former is more than 100 parts by weight, redispersibility and fluidity cannot sometimes be given to the electrorheological fluid.

It is preferable that the composite (2) is obtained by complexing the particle (I) with the polysiloxane-containing polymer (III), but a kind of complexing is not limited. However, the composite (2) is preferable to have the polymer (III) fixed on the surface of the particle (I). If the polymer (III) is not fixed on the surface of the particle (I), dispersion stability cannot sometimes be given to the electrorheological fluid.

Further, it is preferable that the composite (2) has the particle (I) substantially insoluble in the electrical insulating oil linked to the polysiloxane-containing polymer (III) by chemical bonding. If the complexing of the particle (I) with the polymer (III) is not carried out by a chemical bonding, the composite (2) is not sometimes suitable composite polymer.

The method for obtaining the composite (2) by complexing the particle (I) substantially insoluble in an electrical insulating oil with the polysiloxane-containing polymer (III) has no particular restriction. For example, (iv) a method which comprises forming the particle (I) in the presence of the polymer (III) thereby simultaneously effecting formation of the particle (I) and the complexing (v) a method which comprises forming the polymer (III) in the presence of the particle (I) thereby simultaneously effecting formation of the polymer (III) and the complexing and (vi) a method which comprises synthesizing the particle (I) and the polymer (III) independently of each other, mixing or kneading them, and then subjecting the resultant mixture to a treatment with heat or radiation thereby affecting the complexing are available for the production of the composite (2).

When the method of complexing (iv) is adopted, the composite (I) is synthesized, for example, by (iv-1) a method which comprises polymerization of the monomer mixture (Y) thereby forming the polysiloxane-containing polymer (III) and dispersion polymerization of a polymerizable monomer (α) capable of producing the particle (I) in the presence of the polymer (III), (iv-2) a method which comprises polymerization of the monomer mixture (Y) thereby forming the polysiloxane-containing polymer (III) and solution polymerization of the polymerizable monomer (α) in the presence of the polymer (III).

Particularly, the method of (iv-1) is used advantageously in respect that the composite (2) having the polymer (III) fixed on the surface of the particle (I) by the complexing is easily obtained with high

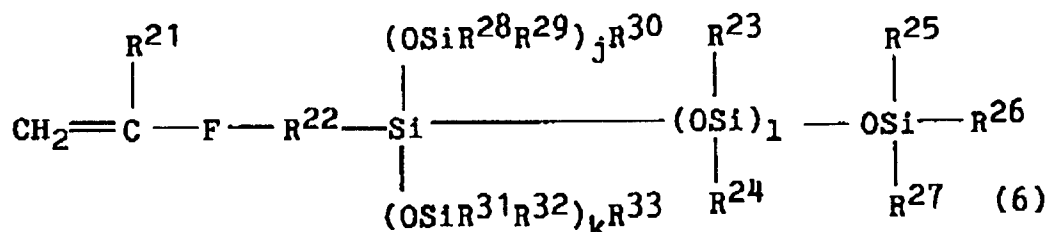
repeatability. In the operation of the method of (iv-1), it is particularly desirable to use the polymer which has an ethylenically unsaturated group therein in advance because this polymer allows the composite (2) having the polymer (III) fixed on the surface of the particle (I) by a chemical bonding to be easily obtained with high repeatability.

When the complexing method of (v) is adopted, the composite (2) is synthesized, for example, by (v-1) a method which adopts a very minute organic or inorganic particle as the particle (I) and produces the polysiloxane-containing polymer (III) by polymerizing the monomer mixture (Y) in the presence of the very minute organic or inorganic particle, (v-2) a method which adopts a very minute organic or inorganic particle having the condensation or addition reaction group mentioned above as the particle (I) and produces the polymer (III) by polymerizing the monomer mixture (Y) in the presence of the very minute organic or inorganic particle, or (v-3) a method which adopts a very minute organic or inorganic particles having the polymerization reaction group mentioned above as the particle (I) and produces the polymer (III) by polymerizing the monomer mixture (Y) in the presence of the very minute organic or inorganic particle. It is particularly advantageous to use the method of (v-2) or the method of (v-3) because it permits production of the composite (2) having the polymer (III) fixed on the surface of the particle (I) by a chemical bonding. The adoption of the method of (v-3) proves to be particularly desirable because the composite (2) having the polymer (III) fixed on the surface of the particle (I) by a chemical bonding is easily obtained with high repeatability.

When the complexing method of (vi) is adopted, the composite(2) is synthesized, for example, by (vi-1) a method which comprises mixing or kneading the particle (I) with the polysiloxane-containing polymer (III) in the presence or absence of a solvent.

A process for synthesizing the composite (2) by a method of (iv-1) will be explained as follows:

The polysiloxane-containing polymer (III) is obtained by polymerizing the monomer mixture (Y) containing a silicone-containing macromer (am) represented by the general formula (6):



wherein F is -COO- or phenylene group, R²¹ is hydrogen atom or methyl group, R²² is an alkylene group of 1 to 6 carbon atoms, R²³ to R³³ are independently an aryl group, an alkyl group of 1 to 6 carbon atoms, or an alkoxy group of 1 to 10 carbon atoms, j and k are independently an integer in the range of 0 to 10, and l is an integer in the range of 0 to 200, and a chain alkyl group-containing monomer (b-4) represented by the general formula (11):



wherein M is -COO- or phenylene group, R⁴³ is hydrogen atom or methyl group, and R⁴⁴ is an alkyl group of 8 to 30 carbon atoms, as essential components thereof and an optional monomer (d).

The ratio of a silicone-containing macromer (am) is preferably 10-90%, and more preferably 20-80% by weight, based on the weight of monomer mixture (Y). If the proportion of a silicone-containing macromer (am) is less 10% by weight or more than 90% by weight, the electrorheological fluid does not have dispersion stability and fluidity. The ratio of the long chain-containing monomer (b-4) is preferably 10-90%, and more preferably 20-80% by weight, based on the weight of the monomer mixture (Y). If the proportion of the long alkyl chain-containing monomer (b-4) is less than 10% by weight or more than 90% by weight, the electrorheological fluid does not have full dispersion stability.

As the silicone-containing macromer (am), for example, the macromer explained in the explanation about the composite (1) can be cited.

As a long alkyl chain-containing monomer (b-4), there can be cited, for example, long alkyl chain (meth)acrylates such as octyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate dodecyl (meth)acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, 2-methyl stearyl (meth)acrylate, eicosyl (meth)acrylate and hexacosyl (meth)acrylate; a long alkyl chain substituted styrene such as octyl styrene, dodecyl styrene and stearyl styrene and of these one or more can be used.

Among the monomer mixture (Y), if necessary, an optional monomer (d) can be used in addition to the silicone-containing macromer (am) and the long alkyl chain-containing monomer (b-4), and it can be used in the amount of less than 80% by weight or the monomer mixture (Y) (total of the monomers (a), (b) and (d) is 100% by weight).

As the optional monomer (d), for example, there can be cited polymerizable monomers of olefins such as ethylene, propylene, and cyclohexene; alkyldienes such as butadiene, isoprene, and cyclopentadiene; halogenated olefins such as vinyl fluoride, vinylidene fluoride, vinyl chloride, and vinylidene chloride; aromatic vinyl compounds such as styrene, α -methyl styrene, p-methyl styrene, vinyl naphthalene, vinyl anthracene, chlorostyrene, and chloromethyl styrene; (meth)acrylic esters such as methyl (meth)acrylate, and ethyl (meth)acrylate; (meth)acrylic alkoxy alkyl esters such as methoxy ethyl (meth)acrylate; (meth)acrylic hydroxyl alkyl esters such as 2-hydroxyl ethyl (meth)acrylate, and hydroxyl butyl (meth)acrylate; esters made from an aromatic alcohol and (meth)acrylate such as benzyl (meth)acrylate; Composite Polymers of glycidyl (meth)acrylate or (meth)acrylic hydroxy alkyl ester and a monocarboxylic acid having 2-18 carbon atoms such as acetic acid, propionic acid, lauric acid, linoleic acid, and p-tert-benzoic acid; fluorine-containing compounds such as VISCOAT8F, VISCOAT8FM (products, (meth)acrylates containing a fluorine atom, sold by Osaka Yukikagaku Kabushiki Kaisha in Japan), (meth)acrylic perfluoro cyclohexyl, and perfluoro cyclohexyl ethylene; vinyl esters such as vinyl acetate and vinyl benzoate; aminoalkyl (meth)acrylates such as (meth)acrylonitrile, N,N-dimethyl aminoethyl (meth)acrylate, N,N-diethyl aminoethyl (meth)acrylate, N,N-dimethyl aminopropyl (meth)acrylate and N,N-dimethyl aminobutyl (meth)acrylate, and salts thereof such as hydrochlorides and hydrobromides; (meth)acrylamides such as (meth)acrylamide, N-methyl (meth)acrylamide, N-ethyl (meth)acrylamide, N-butyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, N,N-diethyl(meth)acrylamide and N,N-methyl propyl (meth)acrylamide; vinyl pyrrolidones such as 1-vinyl-2-pyrrolidone and 1-vinyl-3-pyrrolidone; vinyl pyridines such as 2-vinyl pyridine, 4-vinyl pyridine and 5-methyl-2-vinyl pyridine; vinyl imidazoles such as 1-vinyl imidazole and 1-vinyl-2-methyl imidazole; and nitrogen-containing heterocyclic compounds such as N-(meth)acryloyl morpholine and N-(meth)acryloyl pyrrolidine.

The polymer (III) is produced by a known procedure, e.g. solution polymerization using a radical generating catalyst.

As the radical generating catalyst, there are cited, for instance, conventional catalysts for the polymerization of vinyl monomers. Examples of the radical generating catalyst are, but not limited to, azo compounds such as 2,2'-azobisisobutyronitrile, and 2, 2'-azobis (2, 4-dimethylvaleronitrile); and per-oxide compounds such as benzoyl peroxide, di-tert-butyl peroxide, tert-butyl peroxide, and tert-butylperoxy-2-ethylhexanoate. The amount of the radical generating catalyst to be added is usually 0.2-10 parts by weight, preferably 0.5-5 parts by weight, based on 100 parts of the monomer used.

The reaction temperature of polymerization is usually 60-100 °C for 1 to 15 hours.

In the polymerization, a solvent may be used. Examples of the solvent are, but not limited to aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons benzene, toluene, and xylene; alcohols such as isopropyl alcohol, and butanol; ketones such as methyl isobutyl ketone, and methyl ethyl ketone; esters such as ethyl acetate, isobutyl acetate, amyl acetate, 2-ethyl hexyl acetate; and Cellosolve such as methyl cellosolve, and ethyl cellosolve.

After finishing the polymerization, a solution of the polymer (III) thus obtained may be used for dispersion polymerization when the polymer which is an Composite Polymer is synthesized as it is or may be used after separating the polymer (III) by distilling off the solvent.

Polymer (III) preferably has an ethylenically unsaturated group, which is introduced by the reaction of a monomer with an ethylenically unsaturated group.

When polymer (III) having an ethylenically unsaturated group is used, due to the formation of chemical bond between polymerizable monomer (α) (particle (I)) and polymer (III), then the electroheological fluids have improved the dispersion stability during storage and the dispersion stability after the use for a long period time under conditions of high shear stress.

The introduction of an ethylenically unsaturated group into polymer (III) is carried out, for instance, by adopting, as a component of a monomer mixture (Y), an acid group-containing monomer such as acrylic

acid, methacrylic acid, maleic acid, and vinyl sulfonic acid to form the precursor of polymer (III), and then reacting with the acid group of the precursor a glycidyl group-containing unsaturated monomer such as glycidyl (meth)acrylate or allyl glycidyl ether.

According to the method of (iv-1), the composite (2) is then produced by dispersion-polymerizing polymerizable monomer (α) in the presence of polymer (III). The meaning of dispersion polymerization of method (iv-1) is polymerization carried out in the presence of a dispersion stabilizing agent using an organic solvent capable of dissolving polymerizable monomer (α) and not capable of dissolving the resultant polymer. In particular, the organic solvent is capable of dissolving both of polymer (III) and polymerizable monomer (α) and substantially not capable of dissolving the resultant composite. Examples of the organic solvent are, but not limited to, aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons such as benzene, toluene, and xylene; alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and n-butyl alcohol; ethers such as cellosolve, butylcellosolve, and diethylene glycol monobutyl ether; esters such as ethyl acetate, and isobutyl acetate; and ketones and the like. Of these one or more members may be used.

As polymerizable monomer (α) polymerized in the presence of the polymer (III), there are cited, for instance, aromatic compounds such as styrene, vinyl toluene, vinyl p-chlorotoluene, and vinyl pyridine; and (meth)acrylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and benzyl (meth)acrylate.

The dispersion polymerization for synthesizing the composite (2) in the method of (iv-1) is carried out usually using a radical generating catalyst. Examples of the radical generating catalyst are, but not limited to, azo compounds such as 2, 2'-azobisisobutyronitrile, and 2, 2'-azobis(2,4-dimethylvaleronitrile); and peroxides such as benzoyl peroxide, and lauroyl peroxide. The amount of the catalyst is usually 0.2-10 parts by weight, preferably 0.5-5 parts by weight, based on 100 parts by weight of polymerizable monomer (α).

The proportion of polymer (III) is preferably 0.1-10 parts by weight, more preferably 1-6 parts by weight, to 100 parts by weight of polymerizable monomer (α). If the proportion of polymer (III) is not more than 0.1 part by weight, the polymerization for producing the composite are not reproducible and if obtained, the dispersion stability of electrorheological fluid is poor. Adversely, if the proportion is not less than the 10 parts by weight, the resultant electrorheological fluid is liable to be poor in re-dispersibility and fluidity properties.

The total concentration of polymerizable monomer (α) and polymer (III) in the reaction mixture is usually 5-50% by weight, preferably 10-30% by weight. Further, a conventional surfactant or a dispersion stabilizer such as high polymers may be added.

The dispersion polymerization may be carried out usually at 60°-100°C and for 0.5-30 hours. After polymerization, a post treatment may be carried out for solvent replacement, solvent distillation, drying, and grinding. When the polymerization solvent used is replaced with a silicone insulating oil, the workability of producing electrorheological fluid is improved. Process of synthesizing the composite (2) by a method (v-3) is shown as follows.

When the method of (v-3) is adopted, the particle (I) may be an organic or inorganic fine particle with a polymerizable group. The fine particle is produced, for instance, by treating an organic or inorganic fine particle with (e) a compound having both polymerizable group and reactive group capable of reacting with the functional group present in the surface of the organic or inorganic fine particle. Examples of compound (e) are, but not limited to, vinyl group-containing silane coupling agents such as γ -(meth)acryloxy propyl trimethoxy silane, vinyl trimethoxy silane, vinyl triethoxy silane, and vinyl trichloro silane; and glycidyl group-containing unsaturated compounds such as glycidyl (meth)acrylate, and allyl glycidyl ether.

The amount of compound (e) is usually 10-100 parts by weight, based on 100 parts by weight of the organic or inorganic fine particle used. If the compound is less than 10 parts by weight, introduction of the polymerizable reactive group is sometimes insufficient, and if it is more than 100 parts by weight, sufficient effect equivalent to the addition is not sometimes obtained.

The polymerization of monomer mixture (Y) for producing the composite (2) by the method of (v-3) may be carried out using a polymerization initiator in the presence of particle (I) which has a polymerizable group thereon in an organic solvent.

Examples of the organic solvent are, but not limited to, aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons such as benzene, toluene, and xylene; alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and n-butyl alcohol; ethers such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, diethylene glycol monobutyl ether; esters such as ethyl acetate, and isobutyl acetate; and ketones. Of these one or more members may be used.

The polymerization initiator may be peroxide initiators such as benzoyl peroxide, and lauroyl peroxide; azo initiators such as 2, 2'-azobisisobutyronitrile, 2, 2'-azobis (2, 4'-dimethyl valeronitrile).

The mentioned polymerization may be carried out at 50°-100°C, preferably 60°-90°C for 0.5-15 hours, preferably 4-10 hours. After polymerization, a post treatment may be carried out for solvent replacement, solvent distillation, drying and grinding.

Now, this invention will be described more specifically below with reference to working examples. It should be noted that this invention is not limited to these working examples.

Referential Example 1

10

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 150 g of toluene, 1 g of azo-bis-isobutyronitrile, 50 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721"), and 50 g of cetyl methacrylate were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 75°C for three hours to be polymerized. After the reaction was completed, the reaction solution was heated in an evaporator under a reduced pressure to expel the solvent and obtain an oily macromolecular polymer (1).

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2 g of the macromolecular polymer (1), 2 g of azo-bis-isobutyronitrile, and 50 g of styrene were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70°C for 24 hours to be polymerized. The reaction solution, with 200 g of silicone oil of 20 cs (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under a reduced pressure to expel a volatile component by distillation and obtain a silicone oil dispersion of a composite polymer (1) of a styrene type graft polymer having a composite polymer (1) content of 20% by weight (hereinafter referred to as "composite polymer dispersion (1)").

Referential Example 2

30

In a flask having an inner volume of 300 ml, 200 ml of methanol and 100 ml of deionized water were mixed and 100 g of truly spherical fine particles of silica gel having an average particle diameter of 1.5 μ m (produced by Nippon Shokubai Co., Ltd.) were dispersed in the resultant mixture. Further 7 g of γ -methacryloxypropyl trimethoxy silane was added thereto, the reaction was carried out at 70°C for one hour. The resultant reaction mixture was heated to expel the solvent. The reaction product consequently obtained was dried under a reduced pressure at 60°C.

In a flask having an inner volume of 500 ml, 300 ml of toluene was placed and 100 g of the reaction product obtained after the drying mentioned above was dispersed. The dispersion and 1 g of azo-bis-isobutyronitrile, 5 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 and a silicon content of 36% (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721"), and 3 g of hexyl methacrylate dissolved therein were left reacting at 70°C for 5 hours. After the reaction was completed, the resultant reaction solution was heated under a reduced pressure to expel the solvent by distillation and obtain a composite polymer (2) formed of minute surface-treated particles of silica gel.

45

Referential Example 3

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 200 g of deionized water, 1 g of polyoxyethylene alkylstyryl ether (a reactive emulsifier produced by Dai-ichi Kogyo Seiyaku Co., Ltd. and marketed under trademark designation of "Acharon RN-20"), 1 g of dodecyl methacrylate, and 1 g of sodium persulfate were placed and dissolved. In the resultant solution, the monomer mixture consisting of 50 g of methyl methacrylate and 5 g of industrial grade divinyl benzene (a mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.) was stirred at 20,000 r.p.m. by use of a dispersing device for two minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70°C for 3 hours and further heated at 90°C for 3 hours to be polymerized. After the polymerization was completed, the reaction solution was subjected to azeotropic distillation to displace water with isopropyl alcohol as the dispersive medium. The distillate, with a mineral type electrical

insulating oil (produced by Cosmo Oil Co., Ltd. and marketed under trademark designation of "a high-tension insulating oil") added thereto, was distilled under a reduced pressure to expel isopropyl alcohol and obtain a mineral type electrical insulating oil dispersion of a composite polymer (3) formed of microgel of a methyl methacrylate type cross-linked polymer having a composite polymer (3) content of 20% by weight (hereinafter referred to as "composite polymer dispersion (3)").

Referential Example 4

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 150 g of toluene, 1.5 g of azo-bis-isobutyronitrile, 80 g of styrene, and 20 g of dodecyl methacrylate were placed and stirred for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70 °C For 20 hours and heated and stirred at 85 °C For 4 hours to be polymerized. After the reaction was completed, the resultant reaction solution was distilled under a reduced pressure to expel a volatile component and obtain a composite polymer (1) for comparison formed of a styrene-dodecyl methacrylate copolymer.

Example 1

In a four-neck separable flask having an inner volume of 3 liters and provided with a stirrer, a reflux condenser, and a thermometer, 1.2 liters of water was placed, 16.0 g of polyvinyl alcohol (produced by Kuraray Co., Ltd. and marketed under trademark designation of "Kuraray Poval PVA-205") was dissolved in the water, and then a mixture consisting of 270 g of styrene, 30 g of industrial grade divinyl benzene (a mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.), and 8 g of azo-bis-isobutyronitrile was added to the aqueous solution. Then, the contents of the flask were dispersed by stirring at a rate of 7,000 rpm and heated at 80 °C for 8 hours to be polymerized. The solid product consequently obtained was separated by filtration, thoroughly washed with water, and dried at 80 °C for 12 hours by use of a hot air drier to obtain 289 g of a cross-linked polymer in the shape of beads (hereinafter referred to as "cross-linked polymer (1)").

Then, in a four-neck separable flask having an inner volume of 2 liters and provided with a stirrer, a thermometer, and a dropping funnel, 100 g of the cross-linked polymer (1) and 700 g of concentrated sulfuric acid with an assay of 98% by weight were stirred until they formed a homogeneous dispersion. The reaction mixture was heated to 80 °C and then heated and stirred at the same temperature for 24 hours to undergo sulfonation. The reaction mixture was poured into water at 0 °C, separated by filtration, and washed with water. The solid product which was consequently obtained was neutralized with 500 ml of an aqueous 10 wt% sodium hydroxide solution and thoroughly washed with water. The product was then dried at 80 °C for 10 hours by use of a vacuum drier to obtain 298 g of sulfonic acid group-containing polystyrene polymer particles having an average particle diameter of 6 μm (hereinafter referred to as "disperse particles (1)"). The disperse particles (1) were found to have an anion dissociating group density of 4.2 mg equivalent/g.

The amount 30 g of the disperse particles (1) was dried at 150 °C for 3 hours, left absorbing the moisture in the air until the water content thereof reached 2.0% by weight, and uniformly dispersed in a dispersive medium prepared by adding 1 g of the composite polymer dispersion (1) obtained in Referential Example 1 to 69 g of silicone oil of 0.02Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs"), to produce an electrorheological fluid (1) of this invention.

Example 2

An electrorheological fluid (2) of this invention was obtained by following the procedure of Example 1 while using 0.5 g of the composite polymer (2) obtained in Referential Example 2 in the place of the composite polymer dispersion (1) and a mixture of 19.5 g of a silicone oil of 0.02Pa·s (produced by Shin-etsu Chemical Industry Co. Ltd. and marketed under product code of KF96-20cs) and 50 g of a fluorine element-containing oil (produced by Daikin Industries Co., Ltd. and market under product code of Daifloil #1) in the place of the silicone oil of 0.02Pa·s.

Example 3

An electrorheological fluid (3) of this invention was obtained by following the procedure of Example 1 while using 0.5 g of the composite polymer dispersion (3) obtained in Referential Example 3 in the place of the composite polymer dispersion (1) and 69.5 g of a mineral type electric insulating oil of 0.01Pa·s (a

high-tension insulating oil produced by Cosmo Oil Co., Ltd.) in the place of the silicone oil of 0.02Pa·s.

Control 1

5 An electrorheological fluid for comparison (hereinafter referred to as "fluid (1) for comparison") was obtained by drying 30 g of the disperse particles (1) obtained in Example 1 at 150 °C for 3 hours, allowing the dried particles to absorb the moisture in the air until the water content thereof reached 2.0% by weight, and dispersing the wet particles by stirring in 70 g of a silicone oil of 0.02Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of KF96-20cs").

10

Control 2

15 An electrorheological fluid for comparison (hereinafter referred to as "fluid (2) for comparison") was obtained by drying 30 g of the disperse particles (1) obtained in Example 1 at 150 °C for 3 hours, allowing the dry particles to absorb the moisture in the air until the water content thereof reached 2.0% by weight, and dispersing the particles by stirring in 70 g of a mineral electrical insulating oil of 0.01Pa·s (a high-tension insulating oil; produced by Cosmo Oil Co., Ltd.).

Control 3

20

25 An electrorheological fluid for comparison (hereinafter referred to as "fluid (3) for comparison") was obtained by drying 30 g of the disperse particles (1) obtained in Example 1 at 150 °C for 3 hours, allowing the dry particles to absorb the moisture in the air until the water content thereof reached 2.0% by weight, and dispersing the particles uniformly by stirring in a dispersive medium prepared by adding 1.2 g of a powdery silica having an average particle diameter of 0.007 μm (produced by Japan Aerosil Ltd. and marketed under trademark designation of "AEROSIL 380") to 68.8 g of a silicone oil of 0.02Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs").

Control 4

30

35 An electrorheological fluid for comparison (hereinafter referred to as "fluid (4) for comparison") was obtained by drying 30 g of the disperse particles (1) obtained in Example 1 at 150 °C for 3 hours, allowing the dry particles to absorb the moisture in the air until the water content thereof reached 2.0% by weight, and dispersing the particles by stirring in 68 g of a mineral electrical insulating oil (a high-tension insulating oil; produced by Cosmo Oil Co., Ltd.) having dissolved in advance therein 2.0 g of the composite polymer (1) for comparison obtained in Referential Example 4.

Example 4

40 The electrorheological fluids (1) to (3) of this invention and the fluids (1) to (4) for comparison obtained respectively in Examples 1 to 3 and Controls 1 to 4 were severally tested for viscosity at 25 °C in the absence of supply of an electric field under the conditions of shear rates respectively of 3.3/s and 33/s to determine the T_i values thereof in accordance with the Formula (1) mentioned above. Then, the electrorheological fluids were severally placed in test tubes 150 mm in height and 15 mm in diameter to a height of 100 mm from the bottom, tightly sealed therein, and left standing at room temperature to allow observation of the condition of gradual sedimentation of the disperse particles in the test tubes. The electrorheological fluids were evaluated for the dispersion stability by measuring the heights of sediment layers formed in the test tubes in consequence of the sedimentation of disperse particles of the electrorheological fluids after one day and one week. Then, 50 ml of each of the electrorheological fluids were severally placed in containers having an inner volume of 100 ml, tightly stoppered, and left standing for a month. The containers were rotated at a rate of 30 r.p.m. to find the total numbers of revolutions required for the electrorheological fluids to resume the former homogeneous state and evaluate the redispersibility thereof. The results are shown in Table 1.

55

Table 1

		Viscosity during absence of supply of electric field		Ti value ($\eta_1 - \eta_2$)	Dispersion stability (mm)		Redispersibility (number of revolutions)
		η_1 (Pa·s)	η_2 (Pa·s)		After one day's standing	After one week's standing	
5							
10	Electrorheological fluid of this invention (1)	0.13	0.073	0.057	93	90	5
	Electrorheological fluid of this invention (2)	0.11	0.052	0.058	98	98	4
15	Electrorheological fluid of this invention (3)	0.18	0.11	0.07	85	81	12
	Electrorheological fluid for comparison (1)	0.047	0.045	0.002	35	35	60
20	Electrorheological fluid for comparison (2)	0.032	0.030	0.002	35	35	60
	Electrorheological fluid for comparison (3)	0.82	0.29	0.53	91	91	>100
25	Electrorheological fluid for comparison (4)	0.69	0.22	0.54	83	83	>100

The electrorheological fluids were measured for the values of shear stress (initial value) and the current density (initial value) using coaxial rotational viscometer with electrical fields when an AC external electric field of 4,000 V/mm (frequency: 50 Hz) was applied under the conditions of an inner/outer cylinder gap of 1.0 mm, a shear rate of 33/s, and a temperature of 25 °C to the electrorheological fluids were continuously treated using the external electric field of 4,000 V/mm at 25 °C for 3 days and then measured for the values of shear stress (the value after the three days' operation) and the current density (the value after the three days' operation) to evaluate the durability. The results are shown in Table 2.

Table 2

		Value of shear stress (g/cm ²)		Current density (μ A/cm ²)	
		Initial	After 3 days	Initial	After 3 days
40	Electrorheological fluid of this invention (1)	21	21	18	18
	Electrorheological fluid of this invention (2)	17	16	16	16
45	Electrorheological fluid of this invention (3)	15	15	14	14
	Electrorheological fluid for comparison (1)	18	18	17	18
	Electrorheological fluid for comparison (2)	16	16	16	16
50	Electrorheological fluid for comparison (3)	19	19	18	17
	Electrorheological fluid for comparison (4)	4	4	8	9

It is clearly noted from Table 1 that the electrorheological fluids (1) to (3) of this invention were endowed with structural viscosity and therefore were excellent in dispersion stability and redispersibility as evinced by the fact that the values of η_2 were not more than 0.2Pa·s and the Ti values were in the range of satisfying the condition of the formula (1). The fluids (1) and (2) for comparison were not endowed with structural viscosity and were deficient in dispersion stability and redispersibility notwithstanding the values

of η_2 were not more than 0.2Pa•s. In contrast thereto, the fluids (3) and (4) for comparison were deficient in redispersibility because the values of η_2 exceeded 0.2Pa•s and the Ti values exceeded 0.5Pa•s. From Table 2, it is clearly noted that the electrorheological fluids (1) to (3) of this invention retained as satisfactory shear stress property and current property as the fluids (1) and (2) for comparison.

5

Referential Example 5

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 150 g of toluene, 1 g of benzoyl peroxide, 40 g of methacryloyl group-containing methoxy poly(ethylene glycol) having an average molecular weight of about 1,100 (produced by Shinnakamura Kagaku Kogyo K.K. and marketed under trademark designation of NK Ester M230G, and 60 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721") were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 75 °C for three hours to be polymerized. After the reaction was completed, the resultant reaction solution was heated in an evaporator under reduced pressure to expel the solvent by distillation and obtain an oily macromolecular polymer (2) having an average molecular weight of 70,000.

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2 g of the polymer (2), 2 g of benzoyl peroxide, and 50 g of styrene were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70 °C for 24 hours to be polymerized. The reaction solution, with 200 g of a silicone oil of 0.02Pa•s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel the volatile component by distillation and obtain a silicone oil dispersion of a composite polymer (4) having the polymer (2) joined.

Referential Example 6

In a flask having an inner volume of 300 ml, 200 ml of methanol and 100 ml of deionized water were mixed and 100 g of fine truly spherical silica gel particles having an average particle diameter of 1.5 μ m (produced by Nippon Shokubai Co., Ltd.) were dispersed in the resultant mixture. The dispersion and 7 g of γ -methacryloxypropyl trimethoxy silane added thereto were left reacting at 70 °C for one hour. The reaction solution were heated to expel the solvent by distillation. The reaction product consequently obtained was dried at 60 °C under reduced pressure.

In a flask having an inner volume of 500 ml, 300 ml of toluene was placed and 100 g of the reaction product obtained in a dry state was dispersed in the toluene. The resultant dispersion and 1 g of azo-bis-isobutyronitrile, 5 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721"), and 5 g of butyl methacrylate dissolved therein were left reacting at 70 °C for 5 hours. After the reaction was completed, the reaction solution was heated under a reduced pressure to expel the solvent by distillation and obtain a composite polymer (5) having a polymer of an average molecular weight of 25,000 fixed on the surface of minute silica gel particles.

Referential Example 7

In a flask having an inner volume of 300 ml, 200 ml of methanol and 100 ml of deionized water were mixed and 100 g of fine truly spherical silica gel particles having an average particle diameter of 1.5 μ m (produced by Nippon Shokubai Co., Ltd.) were dispersed in the resultant mixture. The dispersion and 7 g of γ -methacryloxypropyl trimethoxy silane added thereto were left reacting at 70 °C for one hour. The reaction solution were heated to expel the solvent by distillation. The reaction product consequently obtained was dried at 60 °C under reduced pressure.

In a flask having an inner volume of 500 ml, 300 ml of toluene was placed and 100 g of the reaction product obtained in a dry state was dispersed in the toluene. The resultant dispersion and 1 g of azo-bis-isobutyronitrile, 5 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721"), and 5 g of dimethyl aminoethyl methacrylate dissolved therein were left reacting at 70 °C for 5 hours. After the reaction was completed, the reaction solution was heated under a reduced

pressure to expel the solvent by distillation and obtain a composite polymer (6) having a polymer of an average molecular weight of 25,000 fixed on the surface of minute silica gel particles.

Example 5

5

In a four-neck separable flask having an inner volume of 3 Oliters and provided with a stirrer, a reflux condenser, and a thermometer, 1.2 liters of water was placed, 8.0 g of polyvinyl alcohol (produced by Kuraray Co., Ltd. and marketed under trademark designation of "Kuraray Poval PVA-205") was dissolved in the water, and then a mixture consisting of 270 g of styrene, 30 g of industrial grade divinyl benzene (mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.), and 8 g of azo-bis-isobutyronitrile was added to the aqueous solution. Then, the contents of the flask were dispersed by stirring at a rate of 8,000 rpm and left polymerizing at 80 °C for 8 hours. The solid product consequently obtained was separated by filtration, thoroughly washed with water, and dried at 80 °C for 12 hours by use of a hot air drier, to obtain 291 g of a cross-linked polymer of the shape of beads (hereinafter referred to as "cross-linked polymer (2)").

Then, in a four-neck separable flask having an inner volume of 2 liters and provided with a stirrer, a thermometer, and a dropping funnel, 100 g of the cross-linked polymer (2) was placed and the polymer (2) and 700 g of concentrated sulfuric acid with an assay of 98% by weight added thereto were stirred until they formed a homogeneous dispersion. The resultant reaction mixture was heated to 80 °C and then heated and stirred at the same temperature to undergo sulfonation. Then, the reaction mixture was poured into water at 0 °C, separated by filtration, and washed with water. The solid product consequently obtained was neutralized with 500 ml of an aqueous 10 wt% sodium hydroxide solution and then thoroughly washed with water. Then, the wet solid product was dried at 80 °C for 10 hours by use of a vacuum drier to obtain 180 g of sulfonic acid group-containing polystyrene type polymer particles having an average particle diameter of 5 μm (hereinafter referred to as "disperse particles (2)"). The disperse particles (2) were found to have an anion dissociating group density of 4.3 mg equivalent/g.

Thirty (30) g of the disperse particles (2) was dried at 150 °C for 3 hours and left absorbing the moisture in the air until the water content thereof reached 2.0% by weight. An electrorheological fluid (4) of this invention was obtained by uniformly dispersing the disperse particles (2) of the adjusted water content in the dispersive medium prepared by adding 4 g of the composite polymer dispersion (4) to a mixture consisting of 16 g of a silicone oil of 0.2 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") and 50 g of a fluorine element-containing oil (produced by Daikin Industries Co., Ltd. and marketed under trademark designation of "Daifloil #1").

Example 6

An electrorheological fluid (5) of this invention was obtained by following the procedure of Example 5 while using 0.5 g of the composite polymer (5) obtained in Referential Example 6 in the place of the composite polymer dispersion (4) and changing the amount of the silicone oil of 20 cs (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96--20cs") to be used to 69.5 g.

Example 7

An electrorheological fluid (6) of this invention was obtained by following the procedure of Example 5 while using 0.5 g of the composite polymer (6) obtained in Referential Example 7 in the place of the composite polymer dispersion (4) and changing the mount of the silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF9-20cs") to be used to 69.5 g.

Control 5

Thirty (30) g of the disperse particles (2) obtained in Example 5 was dried at 150 °C for three hours and then left absorbing the moisture in the air until the water content thereof reached 2.0% by weight. An electrorheological fluid for comparison (hereinafter referred to as "fluid (5) for comparison") was obtained by dispersing the disperse particles in 70 g of a silicone oil of 20 Cs (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of KF96-20cs").

Control 6

Thirty (30) g of the disperse particles (2) obtained in Example 5 was dried at 150 °C for 3 hours and then left absorbing the moisture in the air until the water content thereof reached 2.0% by weight. An electrorheological fluid for comparison (hereinafter referred to as "fluid (6) for comparison") was obtained by uniformly dispersing the disperse particles in a dispersive medium prepared by adding 1.5 g of a powdery silica having an average particle diameter of 0.007 μm (produced by Japan Aerosil Co., Ltd. and marketed under trademark designation of "AEROSIL380") to 68.5 g of silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of KF96-20cs).

Example 8

The electrorheological fluids (4) to (6) of this invention and the fluids (5) and (6) for comparison obtained respectively in Examples 5 to 7 and Controls 5 and 6 were severally measured for viscosity at 25 °C in the absence of supply of an electric field under the conditions of a shear rate of 3.3/s and a share rate of 33/s to find the viscosities, η_1 and η_2 , and determine the Ti values thereof in accordance with the formula (1) mentioned above. Then, the electrorheological fluids were severally placed in test tubes 150 mm in height and 15 mm in diameter to a height of 100 mm from the bottom, tightly sealed therein, and left standing at room temperature to allow observation of the condition of gradual sedimentation of the disperse particles in the test tubes. The electrorheological fluids were evaluated for dispersion stability of by measuring the heights of sediment layers formed in the test tubes in consequence of the sedimentation of disperse particles of the electrorheological fluids after one day and one week. Then, 50 ml of each of the electrorheological fluids were severally placed in containers having an inner volume of 100 ml, tightly stoppered, and left standing for a month. The containers were rotated at a rate of 30 r.p.m. to find the total numbers of revolutions required for the electrorheological fluids to resume the former homogeneous state and evaluate the redispersibility thereof. The electrorheological fluids were measured for the values of shear stress (initial value) and the current density (initial value) using coaxial field rotational viscometer with electric fields when an AC external electric field of 4,000 V/mm (frequency: 50 Hz) was applied under the conditions of an inner/outer cylinder gap of 1.0 mm, a shear rate of 400/s, and a temperature of 25 °C. The electrorheological fluids were continuously treated using the external electric field of 4,000 V/mm at 25 °C for 3 days and then measured for the values of shear stress (the value after the 3 days' operation) and the current density (the value after the 3 days' operation) to evaluate the durability. The results are shown in Table 3.

Table 3

	Viscosity (Pa•s)	Ti value	Disposition stability(mm)		Redispersibility (Number of revolutions)	Values of shear stress (g/cm ²)		Current density (μ A/cm ²)	
			After 1 day	After 1 week		Initial	After 3 days	Initial	After 3 days
5									
10	Electrorheological fluid of this invention (4) $\eta_1 = 0.18$ $\eta_2 = 0.095$	0.085	93	92	4	22	22	19	20
15	Electrorheological fluid of this invention (5) $\eta_1 = 0.2$ $\eta_2 = 0.11$	0.09	85	81	8	21	20	20	21
20	Electrorheological fluid of this invention(6) $\eta_1 = 0.24$ $\eta_2 = 0.195$	0.045	70	68	20	22	22	21	22
25	Electrorheological fluid for comparison (5) $\eta_1 = 0.04$ $\eta_2 = 0.038$	0.002	34	34	60	24	23	22	21
30	Electrorheological fluid for comparison (6) $\eta_1 = 0.4$ $\eta_2 = 0.24$	0.160	76	73	15	3	3	13	14

It is clearly noted from Table 3 that the electrorheological fluids (4) to (6) of this invention were endowed with structural viscosity and were consequently excellent in dispersion stability of and redispersibility as evinced by the fact that the magnitudes of η_2 were not more than 0.2 Pa•s and the Ti values were in the range of satisfying the condition of the formula (1). The fluid (5) for control was deficient in dispersion stability of because the Ti value thereof was small. The fluid (6) for comparison was deficient in redispersibility because the value of η_2 exceeded 0.2 Pa•s. The electrorheological fluids (4) to (6) of this invention invariably maintained excellent shear property and electric property.

Referential Example 8

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 150 g of toluene, 1 g of azo-bis-isobutyronitrile, 50 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "FMO721") as a silicone-containing macromer (am), and 50 g of stearyl methacrylate as a long-chain alkyl group-containing monomer (b-4) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 80 °C for 2 hours to be polymerized. After the reaction was completed, the reaction solution consequently obtained was heated in an evaporator under reduced pressure to expel the solvent by distillation and obtain an oily polymer (3).

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2.5 g of the polymer (3), 1.5 g of azo-bis-isobutyronitrile, and 50 g of styrene as a polymerizable monomer (α) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70 °C for 24 hours to be polymerized. The reaction solution, with 200 g of a silicone oil of 0.02 Pa•s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs")

added dropwise thereto, was dried in an evaporator under a reduced pressure to expel a volatile component by distillation and obtain a silicone oil dispersion of a composite (1) (composite (1) content 20% by weight; hereinafter referred to as "composite polymer dispersion (7)").

5 Referential Example 9

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 150 g of toluene, 1 g of azo-bis-isobutyronitrile, 40 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000
 10 (produced by Chisso Corporation and marketed under trademark designation of "FMO721") as a silicone-containing macromer (am), and 60 g of dodecyl methacrylate as a long-chain alkyl group-containing monomer (b-4) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 75 °C for 3 hours to be polymerized. After the reaction was completed, the reaction solution consequently obtained was heated in an evaporator under a reduced
 15 pressure to expel the solvent by distillation and obtain an oily polymer (4).

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2 g of the polymer (4), 1 g of azo-bis-isobutyronitrile, and 50 g of styrene as a polymerizable monomer (α) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at
 20 70 °C for 14 hours to be polymerized. The reaction solution, with 200 g of a silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel a volatile component by distillation and obtain a silicone oil dispersion of a composite (2) (composite (2) content 20% by weight; hereinafter referred to as "composite polymer dispersion (8)").

25

Referential Example 10

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 200 g of toluene, 1 g of benzoyl peroxide, 60 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 10,000 (produced by
 30 Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO725") as a silicone-containing macromer (am), and 40 g of dodecyl styrene as a long-chain alkyl group-containing monomer (b-4) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 75 °C for 20 hours to be polymerized. After the reaction was
 35 completed, the reaction solution consequently obtained was heated in an evaporator under reduced pressure to expel the solvent by distillation and obtain an oily polymer (5).

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 1.5 g of the polymer (5), 2 g of benzoyl peroxide, and 50 g of styrene as a polymerizable monomer (α) were placed and stirred at room temperature
 40 for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 75 °C for 20 hours to be polymerized. The reaction solution, with 200 g of a silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel the volatile component by distillation and obtain a silicone oil dispersion of a composite (3) (composite (3) content 20% by weight; hereinafter
 45 referred to as "composite polymer dispersion (9)").

Referential Example 11

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 200 g of toluene, 1 g of benzoyl peroxide, 65 g of tris(trimethyl siloxy)silylpropyl methacrylate having an average molecular weight of about 422 (produced by Shin-etsu
 50 Chemical Industry Co., Ltd. and marketed under product code of "X-22-5002"), as a silicone-containing monomer (am), 25 g of dodecyl acrylate as a long-chain alkyl group-containing monomer (b-4), and 10 g of acrylonitrile as an optional monomer (d) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70 °C for 24 hours to be
 55 polymerized. After the reaction was completed, the reaction solution consequently obtained was heated in an evaporator under a reduced pressure to expel the solvent by distillation and obtain an oily polymer (6).

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of hexane, 2.5 g of the polymer (6), 1 g of azo-bis-isobutyronitrile, 40 g of methyl methacrylate as a polymerizable monomer (α), and 10 g of benzyl methacrylate were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70 °C for 20 hours to be polymerized. The reaction solution, with 200 g of a silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel the volatile component by distillation and obtain a silicone oil dispersion of a composite (4) (composite (4) content 20% by weight; hereinafter referred to as "composite polymer dispersion (10)").

Referential Example 12

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 150 g of toluene, 1 g of azo-bis-isobutyronitrile, 50 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721") as a silicone-containing macromer (am), 45 g of dodecyl methacrylate as a long-chain alkyl group-containing monomer (b-4), and 5 g of methacrylic acid as an optional monomer (d) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 80 °C for 2 hours to be polymerized. It was further left reacting with 5 g of glycidyl methacrylate and 1 g of dimethyl amino ethanol at 100 °C For 5 hours. After the reaction was completed, the reaction solution consequently obtained was heated in an evaporator under reduced pressure to expel the solvent by distillation and obtain an oily polymer (7).

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2.5 g of the polymer (7), 1.5 g of azo-bis-isobutyronitrile, and 50 g of styrene as a polymerizable monomer (α) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70 °C For 24 hours to be polymerized. The reaction solution, with 200 g of a silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel the volatile component by distillation and obtain a silicone oil dispersion of a composite (5) (composite (5) content 20% by weight; hereinafter referred to as "composite polymer dispersion (11)").

Referential Example 13

In a flask having an inner volume of 300 ml, 150 ml of methanol and 50 ml of deionized water were placed and 10 g of truly spherical silica particles having an average particle diameter of 1 μ m (produced by Nippon Shokubai Co., Ltd.) were dispersed in the aqueous methanol solution. The dispersion and 5 g of γ -(methacryloxypropyl)trimethoxy silane added thereto were left reacting at 40 °C for two hours to introduce the methacryloyl group to the surface of the spherical silica particles. Then, the solvent was distilled off in vacuo in an evaporator and it was dried at 50 °C by using a vacuum drier to obtain the reaction product. Then, in a flask having an inner volume of 200 ml, 150 ml of toluene was placed and 15 g of the reaction product obtained as described above was dispersed. The dispersion and 0.1 g of azo-bis-isobutyronitrile, 0.6 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 and a silicon content of 36% (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721") as a silicone-containing macromer (am), and 0.9 g of dodecyl methacrylate as a long-chain alkyl group-containing monomer (b-4) solved in the dispersion were left reacting at 70 °C for five hours. The resultant reaction solution, with 66 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was heated in an evaporator under reduced pressure to expel a volatile component by distillation and obtain a silicone oil dispersion of a composite (6) (composite (6) content 20% by weight; hereinafter referred to as "composite polymer dispersion (12)").

Referential Example 14

In a four-neck separable flask having an inner volume of 1 liter and provided with a stirrer, a reflux condenser, and a thermometer, 480 ml of water was placed, 6.4 g of polyvinyl alcohol (produced by

Kuraray Co., Ltd. and marketed under trademark designation of "Kuraray Poval PVA-205") was dissolved in the water, and a mixture consisting of, 110 g of methyl methacrylate, 10 g of industrial grade divinyl benzene (mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.), and 3 g of azo-bis-isobutyronitrile was added to the aqueous solution.

5 Then, the contents of the flask were dispersed by stirring at a rate of 20,000 rpm by use of a dispeising device and left polymerizing at 70 °C for 8 hours. The solid product consequently obtained was separated by filtration, thoroughly washed with water, and then dried at 80 °C for 12 hours by use of a hot air drier, to obtain 115 g of minute spherical cross-linked polymer particles.

10 Then, in a three-neck separable flask having an inner volume of 1 liter and provided with a stirrer and a thermometer, 100 g of the minute cross-linked polymer particles were placed and the particles and 400 g of a methanol 10 wt% sodium hydroxide solution added thereto were stirred until they were uniformly dispersed. The resultant mixture was heated to 70 °C and then stirred at this temperature for 24 hours to be saponified. Then, the reaction mixture was separated by filtration and washed with water. The solid product consequently obtained was dispersed in 500 ml of 2N hydrochloric acid and then washed thoroughly with
15 water. The wet solid product was dried at 80 °C For 10 hours by use of a vacuum drier to obtain 95g of carboxylic acid group-containing polymer particles having an average particle diameter of 2 μ m and insoluble in a silicone-containing insulating oil.

In a flask having an inner volume of 300 ml, 150 ml of toluene was placed and 10 g of the carboxylic acid group-containing polymer particles synthesized above were dispersed. The resultant dispersion and 5
20 g of glycidyl methacrylate and 0.75 g of dimethylaminoethyl methacrylate added thereto were left reacting at 40 °C for 5 hours to introduce the methacryloyl group to the surface of the polymer particles. The resultant mixture and 0.1 g of azo-bis-isobutyronitrile, 0.75 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "Silaplain FMO721") as a silicone-containing macromer (am), and 0.5 g of
25 stearyl methacrylate as a long-chain alkyl group-containing monomer (b-4) dissolved therein were left reacting at 70 °C for 5 hours. The resultant reaction solution, with 68 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under a reduced pressure to expel the volatile component and obtain a silicone oil dispersion of a composite (7) (composite (7) content 20% by weight;
30 hereinafter referred to as "composite polymer dispersion (13)").

Reference Example 15

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a
35 thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2.5 g of polyvinyl pyrrolidone, 1 g of azo-bis-isobutyronitrile, and 50 g of styrene as a polymerizing monomer (α) were placed and then stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The stirred mixture wail heated at 70 °C for 24 hours to be polymerized. The resultant reaction solution, with 200 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-
40 20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel the volatile component and obtain a silicone oil dispersion of polystyrene particles (polystyrene particles content 20% by weight; hereinafter referred to as "composite polymer dispersion (2) for comparison").

Referential Example 16

45 In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 200 g of toluene, 3 g of azo-bis-isobutyronitrile, 50 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721") as
50 a silicone-containing macromer (am), and 50 g of methyl methacrylate as an optional monomer (d) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The stirred mixture was heated at 70 °C for 3 hours to be polymerized. After the reaction was completed; the reaction solution was heated in an evaporator under reduced pressure to expel the solvent and obtain an oily polymer (8).

55 In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2 g of the polymer (8), 2 g of azo-bis-isobutyronitrile, and 50 g of styrene as a polymerizing monomer (α) were placed and then stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The stirred mixture was heated at

70 °C for 24 hours to be polymerized. The resultant reaction solution, with 200 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel the volatile component and obtain a silicone oil dispersion of an composite polymer (3) for comparison (comparison composite polymer (3) content 20% by weight; hereinafter referred to as "composite polymer dispersion (3) for comparison").

Referential Example 17

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 200 g of toluene, 1 g of azo-bis-isobutyronitrile, 5 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000 (produced by Chisso Corporation and marketed under product code of "Sairapurehn FMO721"), and 95 g of dodecyl methacrylate as a long-chain alkyl group-containing monomer (b-4) were placed and then stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The resultant mixture was heated at 70 °C for 24 hours to be polymerized. After the reaction was completed, the reaction solution was heated in an evaporator under a reduced pressure to expel the solvent and obtain an oily polymer (9).

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 350 g of isopropyl alcohol, 2.0 g of the polymer (9), 1 g of azo-bis-isobutyronitrile, and 50g of styrene as the polymerizable monomer (α) were placed and then stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The stirred mixture was heated at 70 °C for 24 hours to be polymerized. The reaction product thus obtained, with 200 g of silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was dried in an evaporator under reduced pressure to expel the volatile component by distillation and obtain a silicone oil dispersion of an composite polymer (4) for comparison (comparison composite polymer (4) content 20% by weight; hereinafter referred to as "composite polymer dispersion (4)for comparison").

Referential Example 18

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 200 g of deionized water, 2 g of sodium dodecylsulfonate, and 1 g of sodium persulfate were mutually dissolved. The solution and a monomer component consisting of 35 g of styrene and 15 g of industrial divinyl benzene (mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.) were emulsified by stirring at a rate of 20,000 r.p.m. for 2 minutes by use of a dispersing device as kept swept meanwhile with nitrogen gas. The emulsified mixture was heated at 70 °C for 3 hours and then further heated at 90 °C for 4 hours to be polymerized. The resultant reaction solution was heated in an evaporator under a reduced pressure to expel the water and then dried in an air oven at 80 °C to obtain cross-linked polymer particles (hereinafter referred to as "composite polymer (5) for comparison").

Referential Example 19

An composite polymer dispersion (6) for comparison was obtained by adding 0.2 g of the polymer (3) synthesized in Referential Example 8 to 20 g of the composite polymer dispersion (2) for comparison prepared in Referential Example 15 and stirring them for dispersion.

Referential Example 20

In a flask having an inner volume of 300 ml, 150 ml of methanol and 50 ml of deionized water were placed and 10 g of truly spherical silica particles having an average particle diameter of 1 μ m (produced by Nippon Shokubai Co., Ltd.) were dispersed in the aqueous methanol solution. The resultant dispersion and 5 g of methacryloxypropyl trimethoxy silane added thereto were left reacting at 40 °C for 2 hours to introduce the methacryloyl group to the surface of the spherical silica particles. Then, the dispersion was heated in an evaporator under reduced pressure to expel the solvent and dried at 50 °C in a vacuum drier to obtain a reactant. Then 150 ml of toluene was charged into a flask having inner volume of 200 ml and 15 g of the reactant was dispersed. The dispersed reactant and 0.1 g of azo-bis-isobutyronitrile, 0.1 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 5,000

(produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO721") as a silicone-containing macromer (am), and 1.4 g of dodecyl methacrylate as a long-chain alkyl group-containing monomer (b-4) solved therein were left reacting at 70 °C for 5 hours. The reaction solution, with 66 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was distilled in an evaporator under reduced pressure to expel the volatile component and obtain a silicone oil dispersion of an composite polymer (7) for comparison (comparison composite polymer (7) content 20% by weight; hereinafter referred to as "composite polymer dispersion (7) for comparison").

10 Referential Example 21

In a four-neck flask having an inner volume of 1,000 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 567 g of isopropyl alcohol, 5 g of azo-bis-isobutyronitrile, 35 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 10,000 and a silicon content of 37% (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO725"), 40 g of methacryloyl group-containing polyethylene glycol tetraethylene glycol having a polyethylene glycol polymerization degree of 10, a polytetramethylene glycol polymerization degree of 5, an average molecular weight of about 900, and an oxygen content of 31% (produced by Nippon Oils & Fats Co., Ltd. and marketed under trademark designation of "Blemmer 55PET-800") and 25 g of industrial grade divinyl benzene (mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The stirred mixture was heated at 65 °C for 20 hours and then further heated at 83 °C for 4 hours to be polymerized. When the solid component in the reaction solution was assayed, the conversion of monomer was found to be 98%. The reaction solution, with 392 g of a silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was heated in an evaporator under reduced pressure to expel the volatile component and obtain a silicone oil dispersion of an composite polymer (8) for comparison (comparison composite polymer (8) content 20% by weight; hereinafter referred to as "composite polymer dispersion (8) for comparison").

30

Referential Example 22

In a four-neck flask having an inner volume of 1,000 ml and provided with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, 567 g of isopropyl alcohol, 5 g of azo-bis-isobutyronitrile, 60 g of methacryloyl group-containing polydimethyl siloxane having an average molecular weight of about 10,000 and a silicon content of 37% (produced by Chisso Corporation and marketed under trademark designation of "Sairapurehn FMO725"), 30 g of methacryloyl group-containing polyethylene glycol tetraethylene glycol having a polyethylene glycol polymerization degree of 10, a polytetramethylene glycol polymerization degree of 5, an average molecular weight of about 900, and an oxygen content of 31% (produced by Nippon Oils & Fats Co., Ltd. and marketed under trademark designation of "Blemmer 55PET-800") and 10 g of industrial grade divinyl benzene (mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.) were placed and stirred at room temperature for 30 minutes as kept swept meanwhile with nitrogen gas. The stirred mixture was heated at 65 °C for 20 hours and then further heated at 83 °C for four hours to be polymerized. When the solid component in the reaction solution was assayed, the conversion of monomer was found to be 98%. The reaction solution, with 392 g of silicone oil of 0.2 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") added dropwise thereto, was heated in an evaporator under a reduced pressure to expel the volatile component and obtain a silicone oil dispersion of an composite polymer (9) for comparison (comparison composite polymer (9) content 20% by weight; hereinafter referred to as "composite polymer dispersion (9) for comparison").

Example 9

In a four-neck separable flask having an inner volume of 3 liters and provided with a stirrer, a reflux condenser, and a thermometer, 1.2 liters of water was placed, 16.0 g of polyvinyl alcohol (produced by Kuraray Co., Ltd. and marketed under trademark designation of "Kuraray Poval PVA-205") was solved in the water, and then a mixture consisting of 270 g of styrene, 30 g of industrial grade divinyl benzene (a mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure

Chemical Industries, Ltd.), and 8 g of azo-bis-isobutyronitrile was added to the aqueous solution. Then, the contents of the flask were dispersed by stirring at a rate of 7,000 rpm and heated at 80 °C for 8 hours to be polymerized. The solid product consequently obtained was separated by filtration, thoroughly washed with water, and dried at 80 °C for 12 hours by use of a hot air drier to obtain 289 g of a cross-linked polymer in the shape of beads (hereinafter referred to as "cross-linked polymer (3)").

Then, in a four-neck separable flask having an inner volume of 2 liters and provided with a stirrer, a thermometer, and a dropping funnel, 200 g of the cross-linked polymer (3) and 1,400 g of concentrated sulfuric acid with an assay of 98% by weight were stirred until they formed a homogeneous dispersion. The reaction mixture was heated to 80 °C and then heated and stirred at the same temperature for 24 hours to undergo sulfonation. The reaction mixture was poured into water at 0 °C, separated by filtration, and washed with water. The solid product which was consequently obtained was neutralized with 1,000 ml of an aqueous 10 wt% sodium hydroxide solution and thoroughly washed with water. The product was then dried at 80 °C for 10 hours by use of a vacuum drier to obtain 372 g of sulfonic acid group-containing polystyrene polymer particles having an average particle diameter of 6 μm (hereinafter referred to as "disperse particles (3)"). The disperse particles (3) were found to have an anion dissociating group density of 4.2 mg equivalent/g.

The amount 30 g of the disperse particles (3) was dried at 150 °C for 3 hours, left absorbing the moisture in the air until the water content thereof reached 2.0% by weight, and uniformly dispersed in a dispersive medium prepared by adding 4 g of the composite polymer dispersion (7) obtained in Referential Example 8 to 66 g of silicone oil of 0.2 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs"), to produce an electrorheological fluid (7) of this invention.

Example 10

An electrorheological fluid (8) of this invention was obtained by following the procedure of Example 9 while using 3 g of the composite polymer dispersion (8) obtained in Referential Example 9 in the place of the composite polymer dispersion (7) and 67 g of silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-10cs") in the place of the silicone oil of 0.02 Pa·s.

Example 11

An electrorheological fluid (9) of this invention was obtained by following the procedure of Example 9 while using 5 g of the composite polymer dispersion (9) obtained in Referential Example 10 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 65 g.

Example 12

An electrorheological fluid (10) of this invention was obtained by following the procedure of Example 9 while using 5 g of the composite polymer dispersion (10) obtained in Referential Example 11 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 65 g.

Example 13

An electrorheological fluid (11) of this invention was obtained by following the procedure of Example 9 while using 5 g of the composite polymer dispersion (12) obtained in Referential Example 12 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 65 g.

Example 14

In a four-neck separable flask having an inner volume of 3 liters and provided with a stirrer, a reflux condenser, and a thermometer, 1.2 liters of water was placed, 16.0 g of polyvinyl alcohol (produced by Kuraray Co., Ltd. and marketed under trademark designation of "Kuraray Poval PVA-205") was solved in the water, and then a mixture comprising 270 g of styrene, 30 g of industrial grade divinyl benzene (a mixture of 55% by weight of divinyl benzene, 35% by weight of ethyl styrene, etc.; produced by Wako Pure Chemical Industries, Ltd.), and 8 g of azo-bis-isobutyronitrile was added to the aqueous solution. Then, the

contents of the flask were dispersed by stirring at a rate of 20,000 rpm and heated at 80 °C for 8 hours to be polymerized. The solid product consequently obtained was separated by filtration, thoroughly washed with water, and dried at 80 °C for 12 hours by use of a hot air drier to obtain 293 g of a cross-linked polymer in the shape of beads (hereinafter referred to as "cross-linked polymer (3)").

5 Than, in a four-neck separable flask having an inner volume of 2 liters and provided with a stirrer, a thermometer, and a dropping funnel, 100 g of the cross-linked polymer (4) and 700 g of concentrated sulfuric acid with an assay of 98% by weight were stirred until they formed a homogeneous dispersion. The reaction mixture was heated to 80 °C and then stirred at the same temperature for 24 hours to undergo sulfonation. The reaction mixture was poured into water at 0 °C, separated by filtration, and washed with
10 water. The solid product which was consequently obtained was neutralized with 500 ml of an aqueous 10 wt% sodium hydroxide solution and thoroughly washed with water. The product was then dried at 80 °C for 10 hours by use of a vacuum drier to obtain 173 g of sulfonic acid group-containing polystyrene polymer particles having an average particle diameter of 2.5 μm (hereinafter referred to as "disperse particles (4)"). The disperse particles (4) were found to have an anion dissociating group density of 4.1 mg equivalent/g.

15 The amount 30 g of the disperse particles (4) was dried at 150 °C for 3 hours, left absorbing the moisture in the air until the water content thereof reached 2.0% by weight, and uniformly dispersed in a dispersive medium prepared by adding 7 g of the composite polymer dispersion (12) obtained in Referential Example 13 to 63 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs"), to produce an electrorheological fluid (12) of this
20 invention.

Example 15

An electrorheological fluid (13) of this invention was obtained by following the procedure of Example 14
25 while using 4 g of the composite polymer dispersion (13) obtained in Referential Example 14 in the place of the composite polymer dispersion (12).

Example 16

30 An electrorheological fluid (14) of this invention was obtained by drying 30 g of zeolite particles having an average particle diameter of 3 μm (produced by Sigma Corp. and marketed under trademark designation of "Zeolite"; hereinafter referred to as "disperse particles (5)") at 150 °C for 3 hours, allowing the dried zeolite particles to absorb the moisture in the air until the water content thereof reached 10.0%, and uniformly dispersing the zeolite particles in a dispersive medium prepared by adding 4 g of the composite
35 polymer dispersion (7) obtained in Referential Example 8 to 66 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs").

Control 7

40 An electrorheological fluid for comparison (hereinafter referred to as "fluid (7) for comparison") was obtained by drying 30 g of the disperse particles (3) obtained in Example 9 at 150 °C for 3 hours, then allowing the dry disperse particles to absorb the moisture in the air until the water content thereof reached 2.0% by weight, and dispersing wet disperse particles in 70 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs").
45

Control 8

An electrorheological fluid for comparison (hereinafter referred to as "fluid (8) for comparison") was obtained by drying 30 g of the disperse particles (3) obtained in Example 9 at 150 °C for 3 hours, then
50 allowing the dry disperse particles to absorb the moisture in the air until the water content thereof reached 2.0% by weight, and dispersing the wet disperse particles in 70 g of silicone oil of 0.01 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-10cs").

Control 9

55 An electrorheological fluid for comparison (hereinafter referred to as "fluid (9) for comparison") was obtained by drying 30 g of the disperse particles (4) obtained in Example 14 at 150 °C for 3 hours, then allowing the dry disperse particles to absorb the moisture in the air until the water content thereof reached

2.0% by weight, and dispersing the wet disperse particles in 70 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs").

Control 10

5

An electrorheological fluid for comparison (hereinafter referred to as "fluid (10) for comparison") was obtained by following the procedure of Example 9 while using 4 g of the composite polymer dispersion (2) for comparison obtained in Referential Example 15 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 66 g.

Control 11

15 An electrorheological fluid for comparison (hereinafter referred to as "fluid (11) for comparison") was obtained by following the procedure of Example 9 while using 4 g of the composite polymer dispersion (3) for comparison obtained in Referential Example 16 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 66 g.

20 Control 12

An electrorheological fluid for comparison (hereinafter referred to as "fluid (12) for comparison") was obtained by following the procedure of Example 9 while using 5 g of the composite polymer dispersion (4) for comparison obtained in Referential Example 17 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 65 g.

Control 13

30 An electrorheological fluid for comparison (hereinafter referred to as "fluid (13) for comparison") was obtained by following the procedure of Example 9 while using 1 g of the composite polymer dispersion (5) for comparison obtained in Referential Example 18 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 69 g.

35

Control 14

40 An electrorheological fluid for comparison (hereinafter referred to as "fluid (14) for comparison") was obtained by following the procedure of Example 9 while using 5 g of the composite polymer dispersion (6) for comparison obtained in Referential Example 19 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 65 g.

Control 15

45

An electrorheological fluid for comparison (hereinafter referred to as "fluid (15) for comparison") was obtained by following the procedure of Example 14 while using 5 g of the composite polymer dispersion (7) for comparison obtained in Referential Example 20 in the place of the composite polymer dispersion (12) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 65 g.

Control 16

55 An electrorheological fluid for comparison (hereinafter referred to as "fluid (16) for comparison") was obtained by drying 30 g of the disperse particles (5) obtained in Example 16 at 150 °C for 3 hours, then allowing the dry disperse particles to absorb the moisture in the air until the water content thereof reached 10.0% by weight, and dispersing the disperse particles in 70 g of silicone oil of 0.02 Pa·s (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs").

Control 17

An electrorheological fluid for comparison (hereinafter referred to as "fluid (17) for comparison") was obtained by following the procedure of Example 9 while using 20 g of the composite polymer dispersion (8) for comparison obtained in Referential Example 21 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 50 g.

Control 18

An electrorheological fluid for comparison (hereinafter referred to as "fluid (18) for comparison") was obtained by following the procedure of Example 9 while using 2.5 g of the composite polymer dispersion (9) for comparison obtained in Referential Example 22 in the place of the composite polymer dispersion (7) and changing the amount of the silicone oil (produced by Shin-etsu Chemical Industry Co., Ltd. and marketed under product code of "KF96-20cs") to 67.5 g.

Example 17

The electrorheological fluids (7) to (14) of this invention and the fluids (7) and (18) for comparison obtained respectively in Examples 9 to 16 and Controls 7 to 18 were severally tested for viscosity at 25 °C in the absence of supply of an electric field under the conditions of a shear rates of 3.3/s and 33/s to find the viscosities, η_1 and η_2 , and determine the T_i values thereof in accordance with the formula (1) mentioned above. Then, the electrorheological fluids were severally placed in test tubes 150 mm in height and 15 mm in diameter to a height of 100 mm from the bottom, tightly sealed therein, and left standing at room temperature to allow observation of the condition of gradual sedimentation of the disperse particles in the test tubes. The electrorheological fluids were evaluated for dispersion stability by measuring the heights of sediment layers formed in the test tubes in consequence of the sedimentation of disperse particles of the electrorheological fluids after one day and one week. Then, 50 ml of each of the electrorheological fluids were severally placed in containers having an inner volume of 100 ml, tightly stoppered, and left standing for a month. The containers were rotated at a rate of 30 r.p.m to find the total numbers of revolutions required for the electrorheological fluids to resume the former homogeneous state and evaluate the redispersibility thereof. The results are shown in Table 4.

The electrorheological fluids were measured for the values of shear stress (initial value) and the current density (initial value) using coaxial rotational viscometer with electric filed. When an AC external electric field of 4,000 V/mm (frequency: 50 Hz) was applied under the conditions of an inner/outer cylinder gap of 1.0 mm, a shear rate of 400/s, and a temperature of 25 °C. The electrorheological fluids were continuously treated using the external electric field of 4,000 V/mm at 25 °C for 3 days and then the sample was tested for the value of shear stress (the value after the three days' operation) and the current density (the value after the three days' operation) to evaluate the durability. The results are shown in Table 4.

It is clearly noted from Table 4 that the electrorheological fluids (7) to (14) of this invention were endowed with structural viscosity and therefore were excellent in dispersion stability, redispersibility, and fluidity as evinced by the fact that the values of η_2 were not more than 0.2 Pa·s and the T_i values were in the range of satisfying the condition of the formula (1). In contrast thereto, the fluids (7) to (9), (11) and (16) to (18) for comparison were deficient in dispersion stability because of small T_i values. Then, the fluids (10), (12) to (15), and (17) were deficient in redispersibility and fluidity because their values of η_2 exceeded 0.2 Pa·s.

Table 4

	Viscosity (Pa·s)	Ti value	Dispersion stability (mm)		Redispersibility (Number of revolutions)	Value of shear stress (g/cm ²)		Current density (μ A/cm ²)	
			After 1 day	After 1 week		Initial	After 3 days	Initial	After 3 days
Electrorheological fluid of this invention (7)	$\eta_1=0.093$ $\eta_2=0.08$	0.013	92	86	7	21	22	20	21
Electrorheological fluid of this invention (8)	$\eta_1=0.085$ $\eta_2=0.062$	0.023	88	83	5	22	22	20	21
Electrorheological fluid of this invention (9)	$\eta_1=0.109$ $\eta_2=0.075$	0.034	83	80	10	22	23	21	22
Electrorheological fluid of this invention (10)	$\eta_1=0.14$ $\eta_2=0.09$	0.05	90	83	12	21	21	20	21
Electrorheological fluid of this invention (11)	$\eta_1=0.08$ $\eta_2=0.061$	0.019	83	81	7	20	19	19	19
Electrorheological fluid of this invention (12)	$\eta_1=0.19$ $\eta_2=0.10$	0.09	87	86	9	10	11	20	21
Electrorheological fluid of this invention (13)	$\eta_1=0.104$ $\eta_2=0.073$	0.031	83	81	8	9	10	19	20
Electrorheological fluid of this invention (14)	$\eta_1=0.26$ $\eta_2=0.18$	0.08	93	91	15	5	4	30	31

Table 4 (continue)

	Viscosity (Pa·s)	Ti value	Dispersion stability (mm)		Redispersibility (Number of revolutions)	Value of shear stress (g/cm ²)		Current density (μ A/cm ²)	
			After 1 day	After 1 week		Initial	After 3 days	Initial	After 3 days
Electrorheological fluid for comparison (7)	$\eta_1=0.047$ $\eta_2=0.045$	0.002	35	35	60	24	23	22	21
Electrorheological fluid for comparison (8)	$\eta_1=0.036$ $\eta_2=0.034$	0.002	35	35	60	22	22	20	20
Electrorheological fluid for comparison (9)	$\eta_1=0.048$ $\eta_2=0.038$	0.004	35	35	60	10	11	19	20
Electrorheological fluid for comparison (10)	$\eta_1=0.610$ $\eta_2=0.505$	0.105	71	70	>100	23	22	20	20
Electrorheological fluid for comparison (11)	$\eta_1=0.105$ $\eta_2=0.1$	0.005	50	45	15	23	22	20	20
Electrorheological fluid for comparison (12)	$\eta_1=0.286$ $\eta_2=0.33$	0.006	88	87	>100	24	23	22	21
Electrorheological fluid for comparison (13)	$\eta_1=0.36$ $\eta_2=0.25$	0.11	65	60	>100	6	6	10	11
Electrorheological fluid for comparison (14)	$\eta_1=0.32$ $\eta_2=0.21$	0.11	75	70	>100	20	19	17	17
Electrorheological fluid for comparison (15)	$\eta_1=0.4$ $\eta_2=0.32$	0.08	89	84	>100	7	8	18	19
Electrorheological fluid for comparison (16)	$\eta_1=0.058$ $\eta_2=0.052$	0.006	40	40	65	4	4	32	32
Electrorheological fluid for comparison (17)	$\eta_1=0.4$ $\eta_2=0.28$	0.006	95	90	>60	21	21	20	19
Electrorheological fluid for comparison (18)	$\eta_1=0.15$ $\eta_2=0.142$	0.008	95	75	20	22	23	21	22

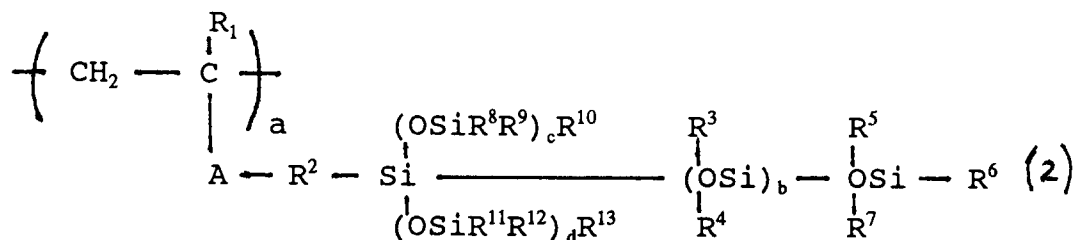
Claims

1. An electrorheological fluid comprising a disperse phase formed of dielectric particles and a dispersive medium formed of an electrical insulating oil, characterised by exhibiting a viscosity of not more than 0.2 Pa.s at a shear rate of 33/s when measured at 25°C in the absence of the supply of an electric field and a structural viscosity satisfying the condition of the formula (1):

$$0.01 \text{ Pa.s} \leq \eta_1 - \eta_2 \leq 0.5 \text{ Pa.s} \quad (1)$$

wherein η_1 is the viscosity at a shear rate of 3.3/s when measured at 25°C in the absence of the supply of an electric field and η_2 is the viscosity at a shear rate of 33/s when measured at 25°C in the absence of the supply of an electric field.

2. An electrorheological fluid as claimed in Claim 1, characterised in that the dielectric particles have an average particle diameter in the range of 1 to 50 μm .
3. An electrorheological fluid as claimed in Claim 1 or Claim 2, characterised in that the amount of the dispersive medium is in the range of 50 to 500 parts by weight based on 100 parts by weight of the disperse phase.
4. An electrorheological fluid as claimed in any preceding Claim, characterised in that the electrical insulating oil is a silicon element containing insulating oil or a fluorine element containing insulating oil.
5. An electrorheological fluid as claimed in any preceding Claim, characterised in that it further comprises a composite polymer exhibiting substantial insolubility in the electrical insulating oil and concurrently comprising a silicone component-containing structural unit (A) and a disperse phase-absorbing chain-containing structural unit (B).
6. An electrorheological fluid as claimed in Claim 5, characterised in that the composite polymer is added in an amount in the range of 0.01 to 6 parts by weight based on 100 parts by weight of the disperse phase.
7. An electrorheological fluid as claimed in Claim 5 or Claim 6, characterised in that the composite polymer is a composite (1) obtained by compositing particles (I) substantially insoluble in the electrical insulating oil with a polysiloxane-containing polymer (II), and the polymer (II) having: as its silicone component-containing structural unit (A), a polysiloxane-containing structural unit (A-1) represented by the general formula (2):



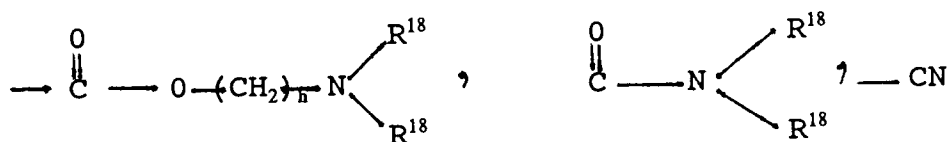
wherein A is -000- or phenylene group, R¹ is hydrogen atom or methyl group. R² is an alkylene group of 1 to 6 carbon atoms, R³ to R¹³ independently for an aryl group, an alkyl group of 1 to 6 carbon atoms, or an alkoxy group of 1 to 10 carbon atoms is an arbitrary integer, c and d are independently an integer in the range of 0 to 10, and b is an integer in the range of 0 to 200; and as its disperse phase-absorbing chain-containing structural unit (B), at least one member selected from an alkyleneoxide chain-containing structural unit (B-1) represented by the general formula (3):



wherein B is -COO- or phenylene group, R¹⁴ is hydrogen atom or methyl group, R¹⁵ is an alkylene group of 2 to 4 carbon atoms, R¹⁶ is hydrogen atom or an alkyl group, e is an arbitrary integer, and f is an integer in the range of 2 to 100; a nitrogen atom-containing chain-containing structural unit (B-2) represented by the general formula (4):



wherein D is

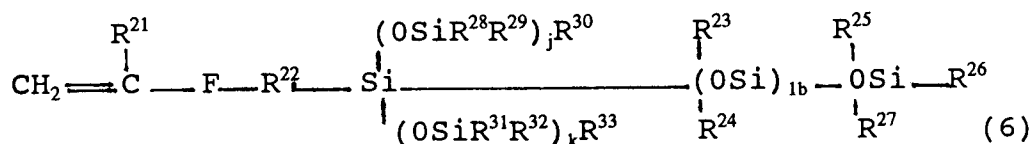


or an nitrogen-containing heterocycle-containing substituent, R^{17} is hydrogen atom or methyl group, R^{18} is a hydrogen atom or an alkyl group, g is an arbitrary integer, and h is an integer in the range of 2 to 6; and/or a hydrocarbon chain-containing structural unit (B-3) represented by the general formula (5):

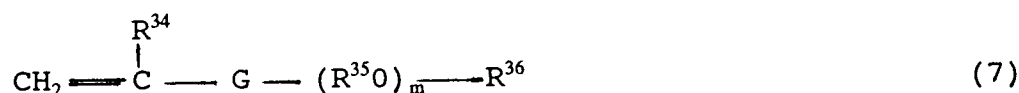


wherein E is -C(=O)- or a phenylene group, R^{19} is hydrogen atom or methyl group, R^{20} is an alkyl group of 1 to 30 carbon atoms, and i is an arbitrary integer.

8. An electrorheological fluid as claimed Claim 7, characterised in that the ratio of the particles (I) the polysiloxane-containing polymer (II) is 100: 0.1 - 100 parts by weight.
9. An electrorheological fluid as claimed in Claim 7 or Claim 8, characterised in that the composite (1) has the polysiloxane-containing polymer (II) fixed on the surface of the particles (I).
10. An electrorheological fluid as claimed in any of Claims 7 to 9, characterised in that the particles (I) are linked to the polysiloxane-containing polymer (II) by a chemical bonding.
11. An electrorheological fluid according to any of Claims 4 to 7, wherein said polysiloxane-containing polymer (II) is obtained by polymerising a monomer mixture (X) which comprises a silicone containing macromer (am) represented by the general formula (6):



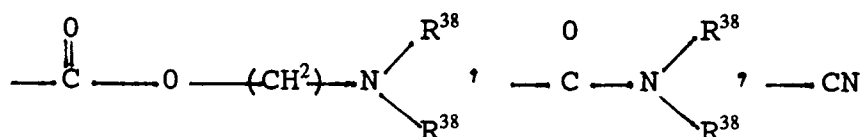
wherein F is -C(=O)- or phenylene group, R^{21} is hydrogen atom or methyl group, R^{22} is an alkylene group of 1 to 6 carbon atoms, R^{23} to R^{33} are independently an aryl group, an alkyl group of 1 to 6 carbon atoms, or an alkoxy group of 1 to 10 carbon atoms, j and k are independently an integer in the range of 0 to 10, and $1b$ for an integer in the range of 0 to 200, and at least one disperse phase-absorbing chain-containing monomer (b) selected from an alkyleneoxide chain-containing macromer (bm-1) represented by the general formula (7):



wherein G is -C000- or phenylene group, R³⁴ is hydrogen atom or methyl group, R³⁵ is an alkylene group of 2 to 4 carbon atoms, R³⁶ is hydrogen atom or an alkyl group, and m is an integer in the range of 2 to 100, a nitrogen-containing chain-containing monomer (b-2) represented by the general formula (8):



wherein J is



or nitrogen-containing heterocycle-containing substituent, R³⁷ is hydrogen atom or methyl group, R³⁸ is hydrogen atom or an alkyl group, and r is an integer in the range of 2 to 6, and a hydrocarbon chain-containing monomer (b-3) represented by the general formula (9):



wherein K is -C000- or phenylene group, R³⁹ is hydrogen atom or methyl group and R⁴⁰ is an alkyl group of 1 to 30 carbon atoms, as essential components and an optional monomer (c).

12. An electrorheological fluid as claimed in Claim 11, characterised in that the monomer mixture (X) contains 10 to 90% by weight of the silicone-containing monomer (am), 10 to 90% by weight of the disperse phase-absorbing chain-containing monomer (b) and 0 to 80% by weight of the optional monomer (c), provided the sum of the monomers used is 100% by weight.

13. An electrorheological fluid as claimed in any of Claims 7 to 12, characterised in that the composite (1) is obtained by the dispersion polymerisation of a polymerisable monomer (α) in the presence of the polysiloxane-containing polymer (II) to produce the particles (I) substantially insoluble in an electrical insulating oil.

14. An electrorheological fluid as claimed in any of Claims 7 to 12, characterised in that the composite (1) is obtained by the emulsion polymerisation of a polymerisable monomer (α) in an aqueous medium in the presence of the polysiloxane-containing polymer (II) to produce the particles (I).

15. An electrorheological fluid as claimed in Claim 11 or Claim 12, characterised in that the composite (1) is obtained by polymerising the monomer mixture (X) in the presence of very minute organic or inorganic particles having a polymerising group as the particles (I) to produce the polysiloxane-containing polymer (II).

16. An electrorheological fluid as claimed in any of Claims 1 to 6, characterised in that the composite polymer is a composite (2) substantially exhibiting insolubility in an electrical insulating oil and comprising a polysiloxane-containing polymer (III), the polymer (III) having a polysiloxane-containing structural unit (A-1) represented by the general formula (2) as the silicone component-containing

structural unit (A) and a long alkyl chain-containing structural unit (B-4) represented by the general formula (10):



wherein L is -C000- or phenylene group, R⁴¹ is hydrogen atom or methyl group, R⁴² is an alkyl group of 8 to 30 carbon atoms, and s is an arbitrary integer, as the disperse phase-absorbing chain-containing structural unit (B).

17. An electrorheological fluid as claimed in Claim 16, characterised in that the composite (2) is composed of the particle (I) and the polysiloxane-containing polymer (III), the polymer (III) having a polysiloxane-containing structural unit (A-1) represented by the general formula (2) as the silicone component-containing structural unit (A) and a long alkyl chain-containing structural unit (B-4) represented by said general formula (10) as the disperse phase-absorbing chain-containing structural unit (B).

18. An electrorheological fluid as claimed in Claim 16, characterised in that the ratio of the particles (I) to the polysiloxane-containing polymer (III) is 100:0.1 - 100 parts by weight.

19. An electrorheological fluid as claimed in any of Claims 16 to 18, characterised in that the composite (2) has the polysiloxane-containing polymer (III) fixed on the surface of the particles (I).

20. An electrorheological fluid as claimed in any of Claims 16 to 18, characterised in that the particles (I) are linked to the polysiloxane-containing polymer (III) by a chemical bonding.

21. An electrorheological fluid as claimed in any of Claims 16 to 20, characterised in that the polysiloxane-containing polymer (III) is obtained by polymerising a monomer mixture (Y) having a silicone containing macromer (am) represented by the general formula (6) and a long alkyl group-containing monomer (b-4) represented by the general formula (11):



wherein M is -C000- or phenylene group, R⁴³ is hydrogen atom or methyl group, and R⁴⁴ is an alkyl group of 8 to 30 carbon atoms, as essential components thereof and an optional monomer (d).

22. An electrorheological fluid as claimed in Claim 21, characterised in that the monomer mixture (Y) contains 10 to 90% by weight of the long alkyl group-containing monomer (b-4) and 0 to 80% by weight of the optional monomer (d), provided the sum of the monomers used is 100% by weight.

23. An electrorheological fluid as claimed in any of Claims 16 to 22, characterised in that the composite (2) is obtained by the dispersion polymerisation of a polymerisable monomer (α) in the presence of the polysiloxane-containing polymer (III) to produce the particles (I).

24. An electrorheological fluid as claimed in any of Claims 16 to 22, characterised in that the composite (2) is obtained by polymerising the monomer mixture (Y) in the presence of a very minute organic or inorganic particles having a polymerising group as the particles (I), to produce the polysiloxane-containing polymer (III).



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 4455

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	EP-A-0 529 166 (NIPPON SHOKUBAI)	1-9, 11, 12, 16-19, 21, 22	C10M171/00 C08F30/08
Y	* the whole document *	10, 13-15, 20, 23, 24	
Y	WO-A-93 06199 (BAYER) * page 18, line 29 - line 38 *	10, 15, 20, 24	
Y	WO-A-92 22623 (BAYER) * the whole document *	13, 14, 23	
Y	EP-A-0 432 601 (BAYER) * the whole document *	13, 14, 23	
A	EP-A-0 453 614 (HERCULES) * page 5, line 30 - line 43 *	1-24	
A	EP-A-0 201 827 (BAYER ET AL.) * the whole document *	1-24	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C10M C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 November 1994	Examiner De La Morinerie, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			