⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 394 049 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **90304228.1**

㉒ Date of filing: **19.04.90**

㉚ Priority: **20.04.89 US 340959**

㊸ Date of publication of application:
24.10.90 Bulletin 90/43

Designated Contracting States:
DE ES FR GB IT SE

(51) Int. Cl.^{5}: **C10M 171/00**

㉛ Applicant: **LORD CORPORATION**
2000 West Grandview Boulevard P.O. Box 10038
Erie Pennsylvania 16514-0038(US)

㉜ Inventor: **Troughton, Barritt E., Jr.**
110 Carmichael Court
Cary, North Carolina 27511(US)
Inventor: **Duclos, Theodore G.**
3100 K, Walnut Creek Parkway
Raleigh, North Carolina 27606(US)
Inventor: **Thuer, Anna Marie**
1811 Treetop Drive, No. 13B
Erie, Pa. 16519(US)
Inventor: **Carlson, J.David**
429 Oakridge Road
Cary, North Carolina 27511(US)
Inventor: **Bares, Joseph E.**
1604 Glengarry Drive
Cary, North Carolina 27511(US)
Inventor: **Yanyo, Lynn C.**
100 W. Kirkfield Drive
Cary, North Carolina 27511(US)
Inventor: **Farley, Stephen Randall Holmes**
301 Brooke Avenue
Raleigh, North Carolina 27607(US)
Inventor: **Acker, Debra Nell**
245 Ocean Shore Blvd.
Ormond Beach, FL 32074(US)

㉞ Representative: **Dunlop, Brian Kenneth Charles et al**
c/o Wynne-Jones, Lainé & James 22 Rodney Road
Cheltenham Gloucestershire GL50 1JJ(GB)

(54) Electrorheological fluids and preparation of particles useful therein.

(57) An electrorheological fluid having one or more of the following characteristics: low D.C. conductivity at room temperature, a low increase in conductivity in response to increasing temperature, electrorheological response over a relatively wide temperature range, and a substantial absence of phase separation. The fluid has a carrier liquid phase and a dispersed particulate phase in which the particulate phase includes a plurality of composite particulate bodies (P), each having a core (4) with an electrically conductive surface (2) coated with a layer of electrically relatively non-conductive material (1), and with the composite particulate body (P) having a density substantially the same as the density of the carrier liquid.

EP 0 394 049 A1

ELECTRORHEOLOGICAL FLUIDS AND PREPARATION OF PARTICLES USEFUL THEREIN

The present invention relates to fluid compositions which demonstrate significant changes in their rheological properties in the presence of an electric field. More particularly, the present invention relates to a composite particle having properties rendering it particularly suited for use in so-called ER fluids and to methods of preparing such fluids and particles used therein.

Fluids which exhibit significant changes in their properties of flow, or rheology, in the presence of an electric field have been known for several decades. Early studies of such fluids were performed by W.M. Winslow, some of which are reported in U.S. Patents Nos. 2,417,850 and 3,047,507. Today, such fluids are commonly referred to as "electrorheological" ("ER") fluids.

Winslow demonstrated that certain suspensions of solids (the "discrete", "particulate", "dispersed" or "discontinuous" phase) in liquids (the "continuous" phase) show large, reversible electrorheological effects. These ER effects are generally as follows: In the absence of an electric field, electrorheological fluids exhibit nearly Newtonian behavior; specifically, their shear stress (applied force per unit area) is directly proportional to the shear rate (relative velocity per unit thickness). When an electric field is applied, a yield stress phenomenon appears and no shearing takes place until the shear stress exceeds a yield value which rises with increasing electric field strength. This phenomenon can appear as an increase in apparent viscosity of several, and indeed, many, orders of magnitude. Thus, it may be said that an ER fluid initially appears as a liquid which, when an electric field is applied, acts almost as if it had become a solid.

ER fluids change their characteristics very rapidly when electric fields are either applied or released, with typical response times being short, eg. on the order of one millisecond. The ability of ER fluids to respond rapidly to electrical signals gives them unique characteristics enabling them to be substituted in mechanical systems in which response time is limited by the inertia of moving mechanical parts. Therefore, electrorheological mechanical systems, particularly those which require a rapid response, can interface between electronic controls and mechanical devices.

A variety of devices have been proposed to take advantage of the electrorheological fluid effect because of its potential for providing a rapid response interface between electronic controls and mechanical devices. Thus, ER fluids have been suggested for a variety of mechanical systems such as electromechanical clutches, fluid filled engine mounts, high speed valves having no moving parts, and active dampers for vibration control, among others. Examples of mechanical devices which are designed to operate with an ER fluid include the mounts disclosed in U.S. Patent Nos. 4,720,087; and 4,733,758, owned by the assignee of the present application.

A rather wide variety of combinations of liquids and suspended solids can demonstrate electrorheological effects. Examples are disclosed in U.S. Patents : 3,397,147 issued August 13, 1968 to T. W. Martinek; 4,502,973 issued March 5, 1985 to J.E. Stangroom; 4,668,417 issued May 26, 1987 to J. Gossens; 4,687,589 issued August 18, 1987 to H. Block et al.; 4,774,914 issued May 17, 1988 to F.F. Filisko; and 4,772,407 issued Sept. 20, 1988 to J.D. Carlson. Also pertinent is the work of Tadashi Sasada, Tustomo Kishi and Kenjiro Kamijo entitled, "On The Electroviscous Effect on Colloidal Liquids", 17th Japan Congress on Materials Research Non-Metallic Mat., March 1974, pp. 229-231. Japanese patent application by Akio Inoue; S.N. 61-241,929, filed October 14, 1986 and published April 28, 1988 entitled "Electroconductive Viscous Liquid" is also pertinent.

Present ER fluids possess one or more disadvantages. For instance, many of them exhibit high D.C. conductivity even at room temperature. This conductivity normally increases rapidly with an increase in temperature, seriously limiting temperatures at which the fluids may be employed. Also, many possess relatively low dielectric strengths, resulting in sparking. In many ER fluids the particulate phase settles out quickly into a thick, mud-like sediment which renders the fluid useless for many applications.

With the foregoing in mind, it is the principal object of the present invention to provide an improved ER fluid.

It is another object of the present invention to provide a method for preparing particles useful in an improved ER fluid.

From one aspect the present invention provides an ER fluid which possesses at least one, and preferably all, of the following characteristics: low D.C. conductivity at room temperature; low to no substantial increase in conductivity with increase in operating temperature; the ability to exhibit an ER effect over a relatively wide temperature range; and substantial lack of particle settling.

More specifically, the novel ER fluid of the present invention is characterized by a continuous liquid phase and a dispersed particulate phase, wherein the dispersed particulate phase is prepared by coating, with an electrically insulative control material, a particle body having at least an electrically conductive surface, and with the particle body and its electrical insulative control coating being selected to provide a composite particle having an average density essentially the same as that of the liquid phase.

The foregoing and other objects, features and advantages of the invention will become apparent from the following description when taken in conjunction with the accompanying drawings in which:

FIG. 1 is a greatly enlarged, schematic, cross sectional view of a composite particle constructed according to one embodiment of the invention;

FIG. 2 is a greatly enlarged, schematic, cross sectional view, of a composite particle constructed according to another embodiment of the invention;

FIG.3 is a greatly enlarged, schematic cross sectional view of a composite particle construction according to yet another embodiment of the invention;

FIG.4 illustrates a simple system showing composite particules as shown in FIG.1 positioned between two electrodes;

FIG.5 illustrates the system of FIG.4 when a potential difference is applied between the electrodes;

FIG.6 illustrates the equipotential lines induced in the system of FIG.5;

FIG.7 illustrates the equipotential lines in the control coating of the particles in the system depicted in FIGS. 5 and 6; and

FIG.8 illustrates the surface used to illustrate the integral of Maxwell's stress tensor in the system of FIGS. 5, 6 and 7.

Referring now to the drawings, FIG.1 illustrates a composite particle P particularly suited for use in an ER fluid. The illustrated composite P particule has four distinct regions, although as will become apparent hereinafter, a lesser number of regions may suffice. In FIG.1, reference numeral 1 designates the outermost region which, as will be discussed, provides an electrical control layer. Preferably, it is provided by a thin, electrically relatively non-conductive, or insulating, coating. Reference numeral 2 designates an electrically conductive layer underneath the control coating 1. Reference numeral 3 designates a shell enveloping a core 4. The core 4 is surrounded by the overlying layers 1, 2 and 3.

As will be discussed in greater detail, each region performs a particular function. In brief, the core 4 (or the shell 3 when the core 4 is hollow) provides the body of the composite particle and controls the buoyancy of the composite particle P. The conductive layer 2 enables the composite particle to be polarized quickly. The control layer 1 insulates the conductive layers of adjacent particles P from one another while permitting rapid polarization of the particle P by an applied electric field.

The core 4 may be of any material, such as, for example a gas, such as air; a liquid such as a parafinic oil or a low density oil of other origin; a solid such as plastic or rubber, or even a vacuum. The core 4 should have a low-density, i.e. less than that of the continuous phase carrier liquid in which the composite particle is to be suspended. This is desirable so that the buoyancy of the core 4 can balance the weight of the other components of the particle to render the composite particle essentially neutrally buoyant in the continuous liquid phase to be described. The core should be small, having maximum dimensions in a range of about 0.001 to about 10 microns; and preferably it is spherical.

The shell 3 in the embodiment of FIG. 1 forms the container for the core 4 and imparts most of the composite particle's structural strength. The shell 3 provides a means for defining the core 4 when the core 4 is hollow, and it provides a substrate for the rest of the layers. The shell 3 may be made from a wide variety of materials such as either glass or polymers in the case of microballoons, and either ceramics or metals or polystyrene in the case of solid or hollow microspheres. When the core 4 is a hollow microsphere, a metal is preferable to a ceramic because of the proclivity of ceramic microspheres to break when the ER fluid is used for purposes other than studying ER fluid rheology.

Electrically conductive layer 2 allows the composite particle P to polarize electrically. It may be composed of a wide variety of conductive materials, which are preferably metals such as copper, silver, aluminum, nickel, and the like. It could be composed of semi-metals, eg. graphite, or semiconductors, eg. silicon or germanium. The layer 2 may be provided on the shell 3 by a variety of means, such as electroless plating. The layer 2 is denser than the core 4, but is relatively thin so that when combined with the other layers, the core 4 can provide a buoyant counterbalance. The conductive layer 2 also adds to the mechanical strength of the composite particle P.

The principal function of the outer control layer 1 is to control the electrical interaction between the conductive layer 2 of one composite particle P_1 and another adjacent composite particle P_2 (FIG. 4). The outer control layer 1 also functions to control the electrical interaction between the shell 3 and the liquid phase of the ER fluid. The control layer 1 conducts electricity relative to the carrier fluid, but insulates relative to the conductive layers of adjacent particles P. The control layer 1 should possess high resistivity and high electrical breakdown strength, and it should be hydrophobic. It should also be as thin as possible.

The outer control layer 1 may be composed of a wide variety of materials, depending on the nature of conductive layer 2. Preferably, the outer control layer 1 is as conductive as the carrier liquid, but may be more conductive. Both are electrically relatively non-conductive. For example, when the conductive layer 2 is aluminum, the outer control layer 1 may be aluminum oxide prepared by oxidizing the surface of the aluminum layer as by boiling in water. On the other hand, the outer control layer 1 may be provided by deposition from a properties. A preferred coating material for the control layer 1 is applied by a solution of tetraethylorthosilicate (TEOS) such as in the manner described in the accompanying examples. Other silane group coating materials may include: tetramethylorthosilicate and tetrabutylorthosilicate. Other metal alkoxide group coating materials may include: titanates, chromates and aluminum zirconates. These groups may be regarded as hydrolyzable metal complexes.

The four regions 1-4 of the composite particle cooperate to provide a composite particle P that solves major problems associated with ER fluids.

A major problem with conventional ER fluids is particle settling due to a density mismatch between the particles and the dielectric liquid in which the particles are intended to remain in suspension. The present invention overcomes the mismatch by enabling the materials composing the various discrete regions, and the amounts thereof, to be selected to provide a composite particle P having an overall average density essentially the same as that of the liquid in which it is to be suspended. This is generally achieved by providing a core region 4 which is substantially lighter, i.e. less dense, than the density of the continuous phase suspending liquid medium.

Previous attempts to achieve density matching have been made by selecting a different suspending liquid for each different type particle. This is difficult to accomplish, and at the very least, inconvenient. The difficulty arises from the fact that the particles exhibiting the best combination of properties are more dense than the least expensive, and most easily used, suspending liquids, like hydrocarbon and silicone oils. Suspending liquids or greater density have been used, but these suffer from problems such as extremely high cost, toxicity (the PCB's and brominated liquids) and incompatibility with other materials normally present in ER fluid containing devices.

The present invention overcomes these problems by enabling the materials and the quantities thereof to be selected for each region in accordance with a desired goal. Thus, for the core 4, and the conductive layer 2 (which tends to be the most dense component of the composite particle), the amount composing each is preselected, as by controlling the size and density of the core 4, and the thicknesses of the various layers, to cause the density of the composite particle P to match the density of the suspending liquid.

Another major problem commonly associated with conventional ER fluids is that they generally perform best within a narrow temperature range, usually centered near 25° C because the discovery of an ER effect in a system is almost always made by testing it at room temperature. As the ER phenomenon is presently understood, conventional ER fluids fail differently at high and low temperature extremes, but the underlying mechanism is the same at the extremes. At low temperatures, conventional ER fluids become very slow to react to an electric field, and they fail because they are not fast enough to react. At high temperatures, conventional ER fluids fail because they become very conductive; they are more easily, and sometimes they entirely lose their ER effect.

The underlying mechanism behind the failures of conventional ER fluids at these temperature extremes is thought to be the temperature dependent changes in charge carrier conductance within the particles and the suspending or carrier liquid. At low temperatures, the conductances are believed to decrease, causing the particles to polarize slowly, and, therefore, exhibit the ER effect slowly. At high temperatures two things happen. First, the conductances become very high, leading to high overall fluid conductivity and ready arcing. Second, if the particles require an activating agent, such as water, the agent can sometimes be driven off at higher temperatures rendering the fluid inactive from an ER perspective.

The present invention solves these temperature-related problems as a result of the composition and thickness of the control layer 1 and the conducting layer, or conductor, 2. For example, the conductor 2 may be made much more conductive than is needed simply to make the composite particles polarize quickly. Therefore, temperature dependent changes in the conductivity of the conductor will not affect the reaction speed of the ER fluid. The control layer 1 can be made highly insulating, thus preventing the large number of charge carriers in the conductive layer 2 from hopping from composite particle to composite particle. Preferably, the insulating or control layer 1 has a high electrical breakdown strength in view of the high electric field drop across it. A high electrical breakdown strength for ER fluid purposes may be regarded to be at least about 4.0 kv/mm.

The strength of the ER effect in an ER fluid utilizing these composite particles will be directly proportional to the breakdown strength of the outer insulating control layer 1. Tests have shown that the dielectric breakdown strength of an ER fluid containing silicate or traethylorthosilicates (TEOS) based coated particles increases with the number of TEOS-based coatings, from a level of 1.5 kv/mm with one coating of 500 Å thickness to a level of 4.0 kv/mm with five coats each of 500 Å thickness on metal coated hollow spheres. Such particles can be prepared in accordance with EXAMPLES I-VI.

Another embodiment of a particle useful in an ER fluid is illustrated in FIG. 2. As shown, reference numeral 11 refers to the control region or relative insulating layer; reference numeral 12 refers to the conducting layer; and reference numeral 14 refers to the core. In this embodiment, regions 11, 12 and 14 are as described above in connection with regions 1, 2 and 4 of FIG. 1. In the embodiment shown in Figure 2, however, conductive layer 12 forms the shell or container for the core 14 which may be gaseous, liquid or solid. The various coatings may be applied in the manner described in Examples 1-6.

In another embodiment illustrated in FIG. 3, reference numeral 21 refers to the control region or relative insulating layer, and reference numeral 22 refers to the conductive region which also form the core of the composite particle. Composite particles embodying the structure shown in FIG. 3 may be prepared by encapsulating fine droplets of high ionic conductors, like water, in an electrically insulating skin or shell, or by coating zeolite particles with an electrically insulating layer. Such a composite particle may be made by applying a silicate coating on an aluminum particle, such as in the manner described in EXAMPLE VII. The silicate coating may be applied either from silicon or metal alkoxides under either acid or base conditions. There exist the possibility of including organic substituents from multifunctional alkoxides in the coatings. The coatings are applied from a solvent such as ethanol.

The theoretical underpinnings of the composite particles of the present invention are straightforward to explain. First, the particles should have high intraparticle conduction, because this allows them to achieve the maximum amount of induced polarization very quickly. At the same time interparticle conduction should be limited because this leads to an overall current flow and undesirable power consumption. The present invention solves these problems by providing composite particles that are highly conductive internally while particle-to-particle conduction is limited by interposing electrical insulating barriers between the particles, i.e. coating each with an electrical insulating layer. Such an insulating layer is necessary to achieve the attractive forces between particles that lead to an electric field induced yield stress in an ER fluid, and it is desirable to make the insulating layer spherical composite particle.

To overcome the particle settling problem, it is desirable to provide the composite particles with a buoyancy as close to neutral as possible in the carrier fluid. This is achieved by separating the roles of various parts of the particle , i.e. letting one region of the particle control density or buoyancy, another region control intraparticle conductivity, and a further region control interparticle insulation. By separating these functions, the regions providing each can be controlled and optimized independently without compromise. Thus, the core region, which makes up the bulk of the particle volume, controls density, and other structural aspects such as shape and mechanical strength without concern as to its electrical properties. Likewise, the region of the particle which controls intraparticle conductivity need only perform that function, since any excess mass it may impart due to a high density must be balanced by providing a lighter core. The region which controls interparticle conduction need only insulate the particles electrically from one another.

The physics of an ER fluid produced in accordance with the present invention can perhaps best be observed from the simple system depicted schematically in FIGS. 4 through 6 in which the composite particle of the present invention as illustrated in FIG. 1 is depicted. In FIGS. 4 through 6, 1a represents the electrical insulating or control layer; 2a represents the conducting layer; 3a represents the shell defining core 4a. Reference numerals 6 and 7 are each an electrode. The system consists of two of the composite particles surrounded by the dielectric suspending liquid 8 and positioned between two electrides, 6 and 7, respectively.

As shown in FIG. 5, when a potential difference is applied across electrodes 6 and 7, the free charge within the conductor layer 2a of each composite particle is redistributed. This redistribution occurs until the electrical potential within each conductor layer 2a reaches equilibrium. When this occurs, equipotential lines can be drawn as shown in FIG. 6. The equipotential lines have been drawn assuming that insulation coating 1a of each composite particle and suspending liquid 8 have electrical conductivities equal to zero and relative electrical permittivities equal to one. The consequences of allowing these parameters to vary from the assumed values will be discussed below. Since the local field is proportional to the gradient of electrical potential, the electric field distribution around the composite particles can be determined from the equipotential lines. In other words, the electric field shown in FIG. 6 will be higher where the equipotential lines are closely spaced as opposed to where the lines are far apart. As shown in FIGS. 6 and 7, the equipotential lines are closest together where the composite particles contact each other and the electrides. Therefore, the electric field is highest near these contact points.

Once the electric field distribution is known, the electric force acting on a particle boundary is found by integrating Maxwell's stress tensor ($F = 0.5 \int_s \epsilon_f E^2 ds$) around the closed surface shown in FIG. 8. In the configuration shown, the forces on the composite particles in each direction are in equilibrium; there is no net force on the composite particles; and the particles do not move when the field is applied.

The yield stress observed in an ER fluid occurs after a field has been applied and the fluid is either sheared perpendicular to the electric field or pulled parallel to the field. The origin of the yield stress can be visualized from FIGS. 4 through 8 and the preceding discussion. If the electrodes are sheared relative to one another, or pulled apart, the highest force, whether it is between the composite particles or between the composite particles and the electrodes, must be overcome before the electrodes will move. Once the force is overcome, the electrodes move and the force required to keep the plates moving will not increase. In actual ER fluid formulations, the composite particle chains are many composite particles long and there are many chains. The yield stress observed in actual ER fluid formulations is the measured result of many chains breaking and reforming. It should be noted that since the suspending liquid will have a viscosity, as the electrodes are moved faster, the force required to move them will actually get higher because the viscous drag will add to the electrical force.

The thickness of the control coating 1a determined the magnitude of the force acting on the composite particles and the electrides. If the coating is very thin, the equipotential lines between the composite particles will get very close together. The electric field will be very high. Taken to the limit, for very high forces, the coating should be infinitesimally thin. However, for a given potential applied to the electrodes, there is a lower limit on the control coating thickness determined by the breakdown strength of the coating material. Thus, composite particles having thin control coatings at low applied potential should exhibit the same yield stress as composite particles with thick coatings at a high applied potential. It is believed there is an optimal control coating thickness determined by the electrical breakdown strength of the coating and possibly by composite particle radius, the dielectric constant of the insulating coating, the dielectric constant of the suspending liquid and the wear characteristics of the insulating coating. The dielectric constant of the control coating should be at least as high as that of the suspending or carrier liquid.

Generally the composite particles will be spherical and have a diameter of between about 0.1 and about 100 microns, preferably between about 0.1 and about 2.0 microns. Although the composite particles have been described in terms of spheres, they can assume other shapes like spindles. The preparation of metal-coated microspheres is disclosed, for example, in European Patent Application, Publication No. 0,167,834, published January 15, 1986, and the preparation of metal-coated particles having various shapes is disclosed in "Preparation and Properties of Uniformly Coated Inorganic Colloidal Particles" by Garg et al. in Langmuir, 1988, Vol. 4, No. 1, pp. 38-44.

The insulating layer should have a thickness of less than about 1 percent of the overall diameter of a spherical composite particle. When the insulating layer is formed by a silicate or TEOS-based coating procedure such as described in EXAMPLE I, the thickness can be in a range of 0.001 to 1.0 microns. The thickness can be controlled by adjusting the number of coats, or by adjusting the concentration of TEOS in the coating solution. The insulating coating should be continuous.

The continuous phase liquid may be any fluid used or usable in electrorheological fluids. Such fluids should have a dielectric constant which is relatively high, a preferred range being between about 2.0 and about 9.0, and a specific gravity of between about 0.7 and about 2.0. The most common light liquids of this type are hydrocarbon oils and silicone oils, although there are other heavy liquids like perfluorinated polyethers, such as sold by Montedison under the trade designation GALDEN D-10. The liquid disclosed in ER fluid U.S. Patent 4,772,407, owned by the assignee of the present application may be used. Because the presence of water in the dielectric carrier liquid is not required in the present invention, the dielectric carrier liquid can be, and preferably is, essentially anhydrous.

The dielectric liquid forming the continuous phase provides an insulating function between the composite particles; however, this function is to be contrasted with the insulating function provided by the insulating layer on the composite particle. In other words, the insulating layer on the particle is distinct from any film or coating that may be present on the particle as a result of its being immersed in the dielectric carrier fluid. Thus, the insulating value of the insulating layer of the composite particle may be different from the corresponding value of the carrier fluid.

The evaluation of a prepared fluid for an ER response is often done in a two-step procedure. In the first step, the fluid is tested to determine whether or not an ER effect is present. If an ER effect is observed, the fluid is subjected to the second-step test procedure which provides a better standard for comparison of ER effects in fluids.

In the first step, a hand-held probe comprising a pair of parallel rods spaced apart about 3 mm and extending from a handle is inserted into a quantity of prepared ER fluid. A voltage in a range of about 2500-3000 D.C. volts is applied across the rods. The probe has a power rating of about 6 watts. An ER effect is regarded as being present when the ER fluid forms a gel-like mass between and around the rods when the probe is removed from the surrounding ER fluid with voltage applied, and when the gel-like mass flows from the rods when the voltage is discontinued.

In the second step, which is disclosed more fully in U.S. Patent 4,772,407, owned by the assignee of the present application, an ER fluid is directed through a defined channel, the sides of which form parallel electrodes with definite spacing therebetween. A pressure transducer measures the pressure drop between the entry and exit ends of the flow channel as a function applied voltage. By keeping flow rates low, the viscous contribution to the pressure drop is kept negligible. Induced yeild stress is calculated according to the formula set forth in the patent, the disclosure of which at Col. 12, lines 13-36, is incorporated by reference herein. The calculated yield stress can be used as a basis for comparison of the ER effect in various fluids.

The invention will be more readily understood from a consideration of the following specific examples which are given for the purpose of illustration only and are not to be considered as limiting the scope of the invention in any way.

EXAMPLE I

Preparation of nickel microspheres and coating them with electrically insulating silicate layer.

Fifty grams of hollow aluminum silicate microspheres are stirred in 900 ml of an activating palladium solution at 25° C for 1 hour.

The activating palladium solution is prepared by combining 18.9 ml palladium chloride in hydrochloric acid, 100 ml 37% hydrochloric acid and 200 ml water. To this is added 2.38 g tin(II) chloride dihydrate, and the resulting solution is stirred for 12 minutes. To the above solution is added another solution of 57.1 g tin(II) chloride dihydrate, 7.0 g sodium stannate and 200 ml 37% hydrochloric acid. The combined solutions are heated to 120 - 150° F for 3 hours, and are subsequently diluted with water in a ratio of 1:1 by volume. The resulting activating solution is acidic, having a pH of less than 1.0.

The treated microspheres are filtered and rinsed with fluoroboric acid. The microspheres are then added to a electroless nickel plating solution at 25° C with stirring. After 10 minutes, a solution of 25 g. of sodium hypophosphite dissolved in 100 ml. of distilled water is added to increase the plating rate. The particles are filtered and rinsed with distilled water. Purification of the nickel-coated microspheres is accomplished in distilled water where broken microspheres and metallic nickel settle out and floating nickel microspheres are collected by filtration. Drying provides pale green particles. Examination of the particles by electron microscopy indicates that the metallic nickel layer applied by electroless deposition is about 2 microns in thickness. The particles have a diameter of about 150 mm.

Coating of the nickel microspheres with an insulating silicate layer is accomplished by first stirring the microspheres in a primer solution consisting of 3 ml of diethylphosphatoethyltriethoxysilane in 210 ml of ethanol, 71 ml of distilled water and 9 ml of concentrated NH_4OH at 25° C for 1 hour. This primer coating insures satisfactory adhesion between the nickel and subsequent silicate layer. The particles are then stirred for 1 hour in a solution of 12 ml tetraethylorthosilicate, 140 ml ethanol, 54 ml distilled water and 6 ml concentrated NH_4OH. The latter procedure is repeated to provide a second silicate coating. The composite particles are then filtered, rinsed with ethanol, filtered, dried in an oven at 120° C for 1-1/2 hour. The composite particles are free flowing. The thickness of the silicate coating is about 2000 Angstroms.

A 33%, by weight, suspension of the composite particles is prepared in 50 centistoke silicone oil. This suspension exhibits an ER response with low electrical conductivity. In control tests, uncoated nickel microspheres exhibit no ER response and are highly conductive as indicated by electrical sparks generated during testing at the same voltage range.

EXAMPLE II

Nickel microspheres are prepared as in EXAMPLE I. Following the procedure of EXAMPLE I, four silicate coats instead of two are provided on the nickel microspheres. The total thickness of the silicate coatings is 1000-40000 Å. A 33%, by weight, suspension of these more heavily coated composite particles in the same silicone oil exhibits an ER effect over a wider voltage range than the silicate-coated microspheres of EXAMPLE I.

EXAMPLE III

Nickel microspheres coated with carboxylated polyethylene.

Ten grams of nickel microspheres prepared as in EXAMPLE I are added to a stirred solution consisting of 1-5 g. of oxidized carboxylated polyethylene in 100 ml of toluene at 80° C. After 1 hour of stirring the composite particles are collected by filtration, rinsed with toluene and dried in air. A 10% suspension of the composite particles in 10 centistoke silicone oil is found to exhibit an ER effect with no electrical sparking.

EXAMPLE IV

Aluminum-coated hollow microspheres coated with an electrically insulating silicate layer

Ten grams of aluminum-coated hollow microspheres are stirred for 1 hour in a solution of 12 ml tetraethylorthosilicate in 140 ml of ethanol, 54 ml of distilled water and 6 ml of concentrated NH_4OH. The resulting composite particles are filtered, rinsed in ethanol, filtered and dried in an oven for 1 hour to remove ethanol. The composite particles are free flowing.

A portion of the composite particles is given a second silicate coating by following the foregoing coating procedure. Another portion of the composite particles is given four more coats using the same coating procedure.

Suspensions comprising 33%, by weight, of the aluminum-coated hollow-microspheres having been treated with 1, 2 and 5 coats of tetraethylorthosilicate to form a silicate coating in 10 centistoke silicone oil exhibit an ER effect. Suspensions of aluminum coated microspheres with 5 coating treatments of TEOS exhibit the ER effect over a wider voltage range than did the aluminum microspheres with fewer coatings. Control tests with untreated aluminum coated microspheres do not exhibit an ER response and are highly conductive as indicated by electrical sparks generated at the same voltage range.

The thickness of the silicate coatings is about 500-1000 Å, per coating.

EXAMPLE V

Hollow aluminum microspheres coated with an insulating aluminum oxide layer

Hollow aluminum microspheres are boiled in distilled water for 1 hour to provide an aluminum oxide coating. A 10%, by weight, suspension of composite particles in 10 centistoke silicone oil gives an ER response with no evidence of electrical sparking. In control tests, untreated aluminum microspheres do not reveal an ER response and are highly conductive as indicated by electrical sparks generated during testing at the same voltage range.

EXAMPLE VI

Silver coated hollow microspheres with an insulating silicate layer.

Twelve ml of mercaptopropyltrimethoxysilane are stirred into 280 ml of ethanol for 15 minutes. Distilled water (108 ml) and 12 ml concentrated NH_4OH are added with stirring until the solution is clear. Ten grams of silver-coated hollow microspheres are added to the solution and stirred for 1 hour.

The microspheres are then treated twice using tetraethylorthosilicate (TEOS) as in EXAMPLE I. The thus-treated particles are filtered, rinsed in ethanol, filtered and dried in an oven at 120° C overnight. The resulting composite particles are free flowing.

A suspension of 8.8 g. of the composite particles in 17.4 g. of 10 centistoke silicone oil exhibits an ER response with low conductivity below the breakdown voltage of the coating. In control tests, untreated silver-coated hollow-microspheres do not exhibit an ER response and are highly conductive as indicated by electrical sparks generated during testing at the same voltage range.

EXAMPLE VII

Solid aluminum particles coated with an electrical insulating control layer.

Aluminum particles (325 mesh) 40 microns in diameter are coated with a silicate coating to a thickness of 0.05 to 0.25 micron by means of the following process.

To 60 g. of aluminum particles is added 280 ml of ethanol. To this mixture is added 108 ml of water, 12 ml of concentrated ammonium hydroxide and 24 ml of tetraethylorthosilicate. The mixture is shaken for 5 seconds after the addition of each ingredient, and then after all the ingredients are added, the mixture is agitated for

1 h. The particles are filtered off and rinsed in water 5 times. The particles are then dried in a vacuum oven at 150° C for 1-3 days. The particles are subsequently allowed to cool to ambient temperature and are later mixed, 30% by weight, with 10 centistoke GALDEN fluid to form an ER fluid. The procedure was repeated so that two coatings were applied. The total thickness of the two coatings was estimated to be between 500 and 2500 Angstroms (0.05-0.25 microns).

The resulting ER fluid was found to exhibit an ER response while being relatively non-conductive. The ER fluid is rendered essentially anhydrous as a result of the prolonged high temperature drying. A similar effect was obtained using silicon particles of the same size treated in the same manner.

Certain advantages accrue from applying the electrical control coating from a solution of tetraethylorthosilicate (TEOS). A significant advantage resides in the controllability of the thickness of application of the coating. Another advantage is the possibility of applying, with the TEOS, a hydrophobic substance to prevent the particle from taking up moisture, and to provide an additional electrical control layer, a desirable attribute of an ER fluid. For example, a desirable hydrophobic agent includes a member of the organo-metal alkyl silane group of compounds, eg. octadecyltrialkoxysilane.

In view of the foregoing it should be apparent that the present invention provides an improved electrorheological fluid which does not have the limitations of known ER fluids, and the invention provides novel composite particles for much fluids and methods for producing such composite particles and fluids. While preferred embodiments and methods of fabricating the same have been described in detail, various modifications, alterations and changes may be made without departing from the spirit and scope of the invention as defined in the appended claims.

Claims

1. In an electrorheological fluid comprising a continuous phase of a carrier liquid and a dispersed particulate phase, the improvement wherein said particulate phase includes means defining a particle body having at least an electrically conductive surface affording rapid intraparticle polarization, an electrical control coating on said surface for permitting said polarization while substantially preventing interparticle conduction, said particle body, exclusive of said conductive surface and control coating, having a density lower than the density of said carrier liquid, and the thickness and density of said conductive surface and said control coating being selected to provide a composite particulate body having an average density essentially the same as the density of said carrier liquid.

2. The electrorheological fluid of Claim 1 wherein said particle body is hollow and is encapsulated by said electrical control coating.

3. The electrorheological fluid of Claim 1 wherein said particle body includes a core structure, a shell on said core structure, and at least one layer of electrically conductive material on said shell.

4. The electrorheological fluid of Claim 1 wherein said particle defining means includes a hollow microsphere having a conductive shell providing said conductive surface.

5. The electrorheological fluid of any of the preceding claims wherein said carrier liquid is electrically relatively non-conductive, and said control layer is similarly electrically relatively non-conductive.

6. The electrorheological fluid of Claim 5 wherein said control coating conducts electricity relative to said carrier liquid, but insulates said shell electrically from said carrier liquid.

7. The electrorheological fluid of Claim 1 wherein said control coating is deposited from a solution of hydrolyzable metal complexes.

8. The electrorheological fluid of Claim 1 wherein said electrically conductive surface is provided by a metal.

9. The electrorheological fluid of any one of the preceding claims wherein said particle body contains a gas.

10. In an electrorheological fluid in which a discontinuous particulate phase is suspended in a continuous liquid carrier phase, the improvement wherein the particulate phase is prepared by coating a particle having a density less than that of the continuous phase liquid and at least an electrically conductive surface with at least one layer of an electrical insulating material, the nature and amount of the electrical insulating material being selected with respect to the electrically conductive surface of the particle to provide a composite particle having an average density essentially the same as the

density of the carrier liquid.

11. The electrorheological fluid according to Claim 10 wherein said electrical insulating layer is formed on said shell by coating from a solution of hydrolyzable metal complexes.

12. The electrorheological fluid according to Claim 11 wherein said hydrolyzable metal complexes are selected from the group consisting of: silane group coating materials and metal alkoxide group coating materials.

13. The electrorheological fluid according to Claim 12 wherein said silane group coating materials are selected from the group consisting of: tetraethylorthosilicate, tetramethylorthosilicate, and tetrabutylorthosilicate, or other silicone alkoxides.

14. The electrorheological fluid according to Claim 12 wherein said metal alkoxide group coating material is selected from the group consisting of: titanates, chromates and aluminum zirconates.

15. The electrorheological fluid according to any one of Claims 10 to 14 wherein said particle is spherical and hollow and said control coating has a thickness of less than about 1% of the diameter of said coated particle.

16. The electrorheological fluid according to any one of Claims 10 to 14 wherein said electrical insulating layer has a thickness of less than about 10,000 Angstroms.

17. The electrorheological fluid according to any one of Claims 10 to 16 wherein said particle has a maximum dimension of less than about 100 microns.

18. In an electrorheological fluid in which a discontinuous particulate phase is suspended in a continuous dielectric liquid phase, the improvement wherein the particulate phase includes a hollow particle body coated with an electrically conductive material and an electrical insulating material on said coated body, the nature and amounts of the electrically conductive material and electrically insulating materials being selected with respect to each other and to the particle body to provide a composite particle having an average density essentially the same as that of the dielectric liquid.

19. The electrorheological fluid according to Claim 18 wherein said hollow particle body is formed of either a ceramic, metallic or polymeric material.

20. The electrorheological fluid according to Claim 18 or Claim 19 wherein said hollow particle body is spherical and has an overall dimension of less than about 100 microns.

21. The electrorheological fluid according to any one of Claims 18 to 20 wherein the density of the hollow body, exclusive of the conductive and insulating coatings, is less than the density of said dielectric liquid phase.

22. An electrorheological fluid in which a discontinuous particulate phase is suspended in a continuous dielectric liquid phase, comprising a particulate phase which includes a particle having a hollow core and a shell with an electrically conductive surface and a coating on the conductive surface of the particle of an electrical insulating material, the electrically conductive material and electrically insulating material and amounts thereof being selected with respect to the density of the follow core to provide a composite particle having an overall density essentially the same as that of the dielectric liquid, said electrical insulating coating having been coated on said electrically conductive layer by deposition from a solution of hydrolyzable metals, and said electrically conductive layer being provided by a metallic material.

23. A particle useful in an electrorheological fluid, comprising a core having a metal shell and a layer of electrical insulating material coated on said shell by deposition from a solution of a hydrolyzable metal complex.

24. The particle according to Claim 23 wherein said hydrolyzable metal complex is selected from the group consisting of silanes and metal alkoxides.

25. The particle according to Claim 23 or Claim 24 wherein said core is hollow.

26. The particle according to any one of Claims 23 to 25 having a maximum dimension of less than about 100 microns and an insulating coating thickness of less than about 10,000 Angstroms.

27. The particle according to Claim 23 wherein said core is hollow, said shell is spherical, said electrically conductive layer is of metal, and said electrical insulating coating is applied by deposition from a solution of tetraethylorthosilicate.

28. The particle according to any one of Claims 23 to 27 further including a hydrophobic coating on said insulating coating.

29. The particle according to Claim 28 wherein said hydrophobic coating is provided by an organmetal alkyl silane group of compounds.

30. The particle according to any one of Claims 23 to 29 in combination with a dielectric liquid carrier.

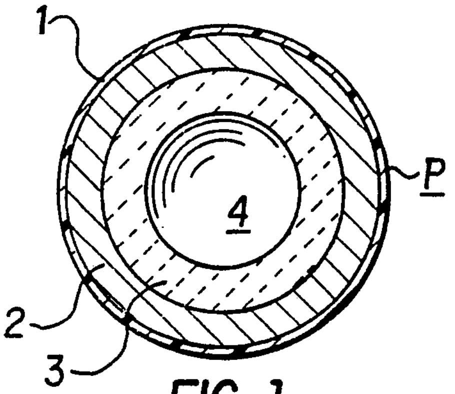

FIG. 1

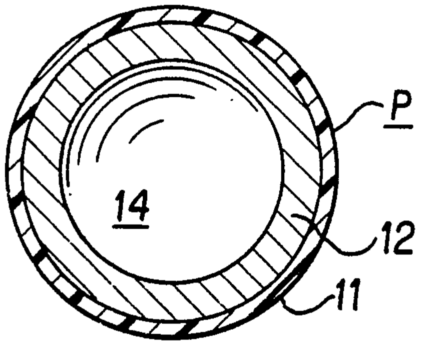

FIG. 2

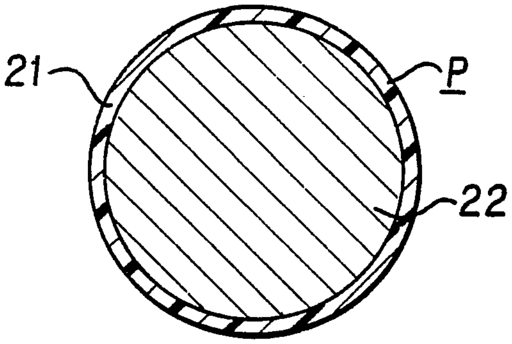

FIG. 3

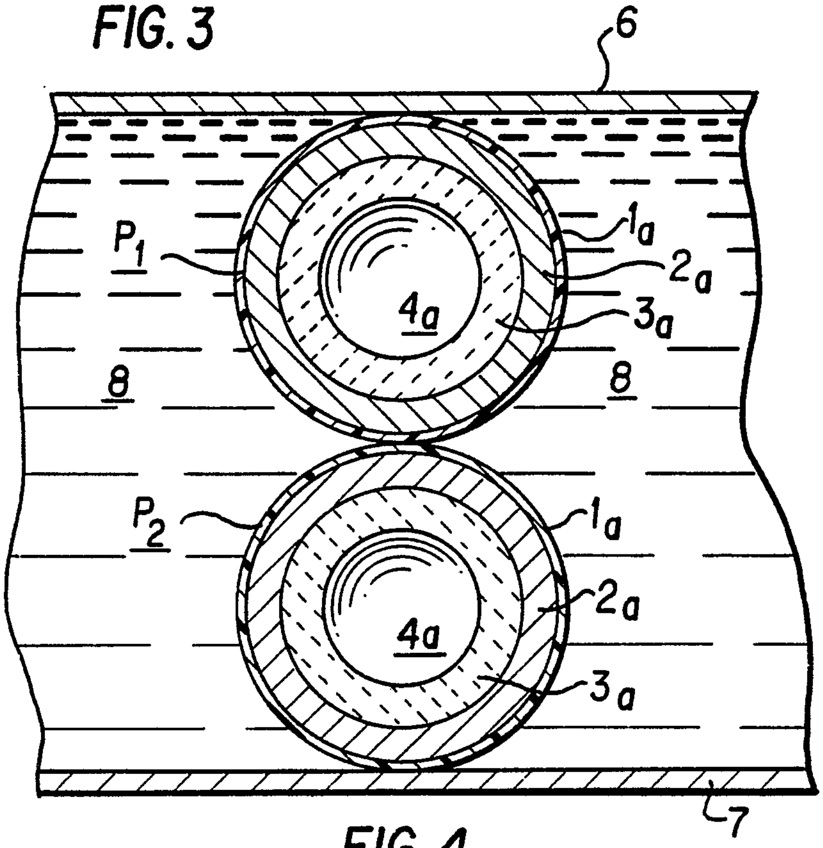

FIG. 4

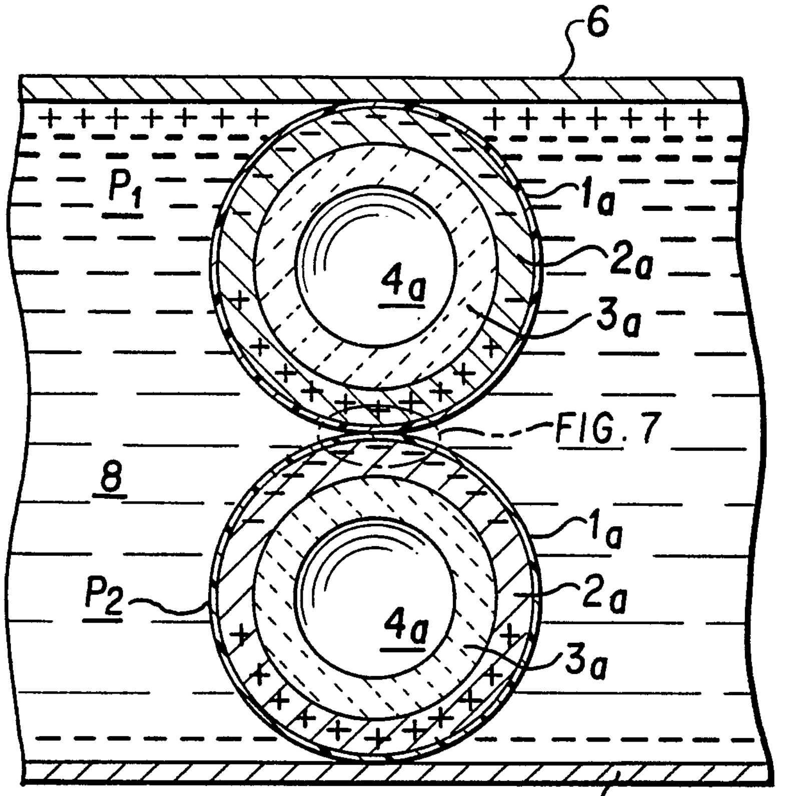
6
P1
1a
2a
4a
3a
FIG. 7
8
1a
2a
P2
4a
3a
7

FIG. 5

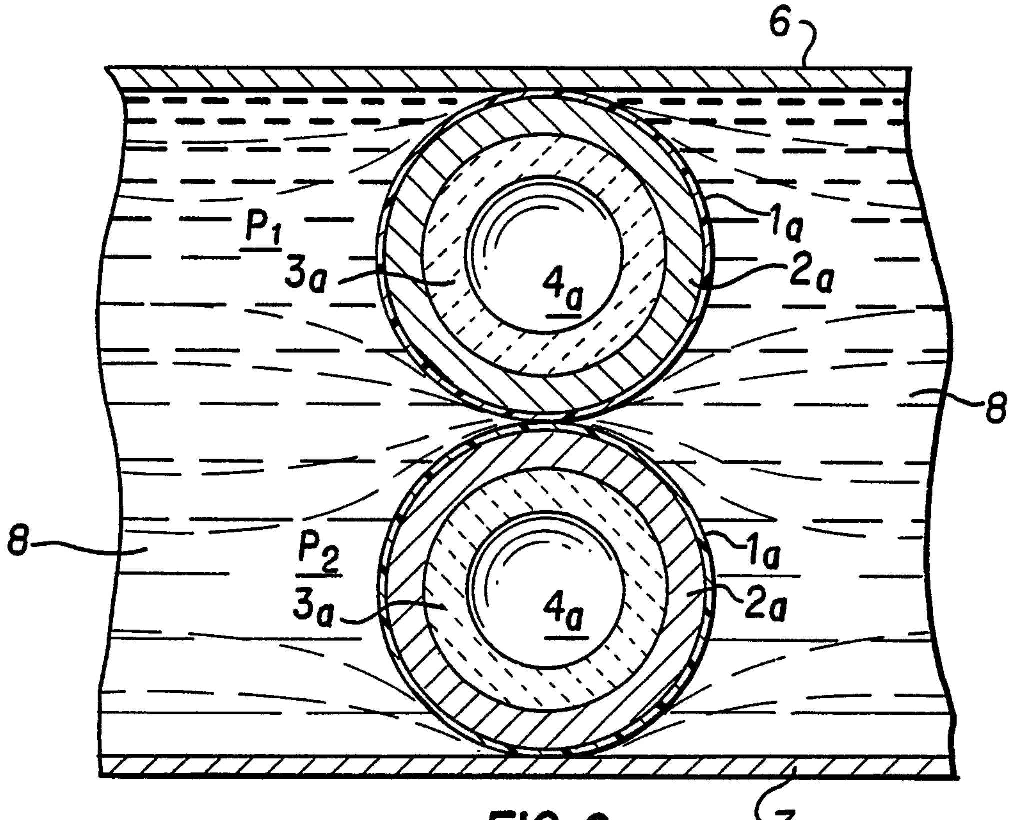
6
P1
3a
1a
4a
2a
8
8
P2
1a
3a
4a
2a
7

FIG. 6

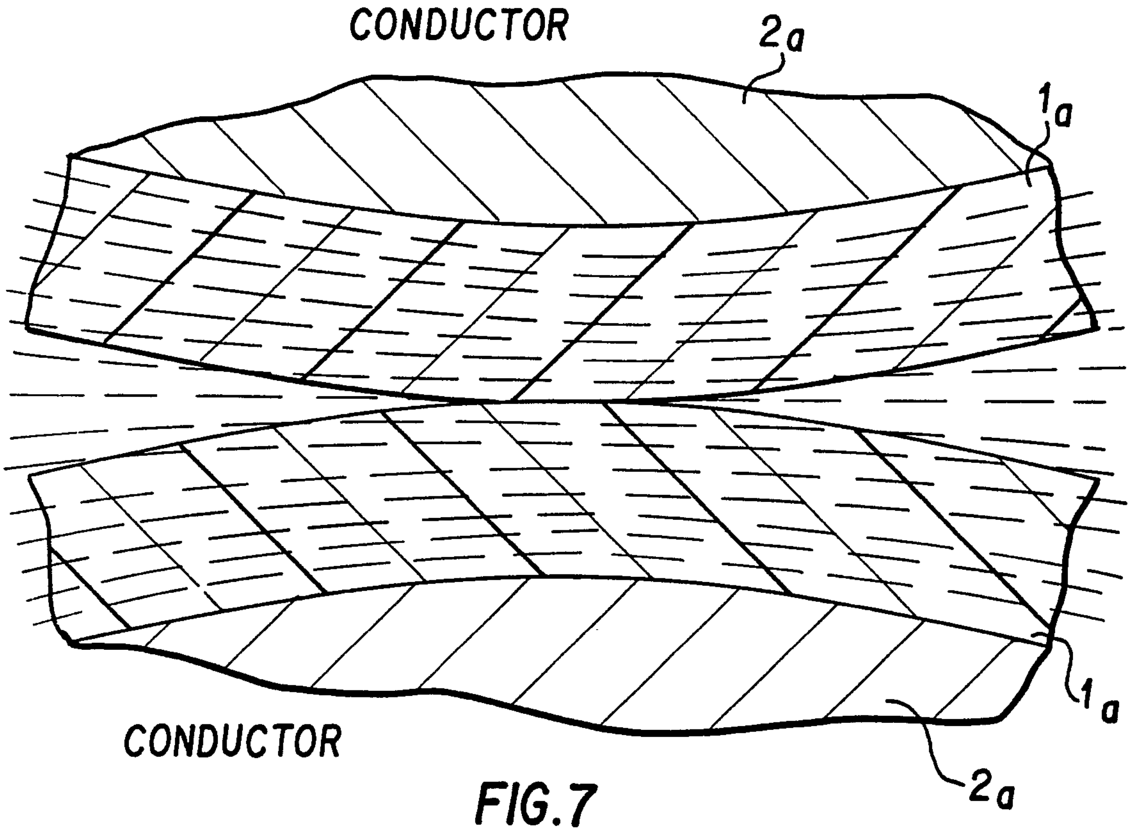
CONDUCTOR
2a
1a
1a
CONDUCTOR
2a

FIG.7

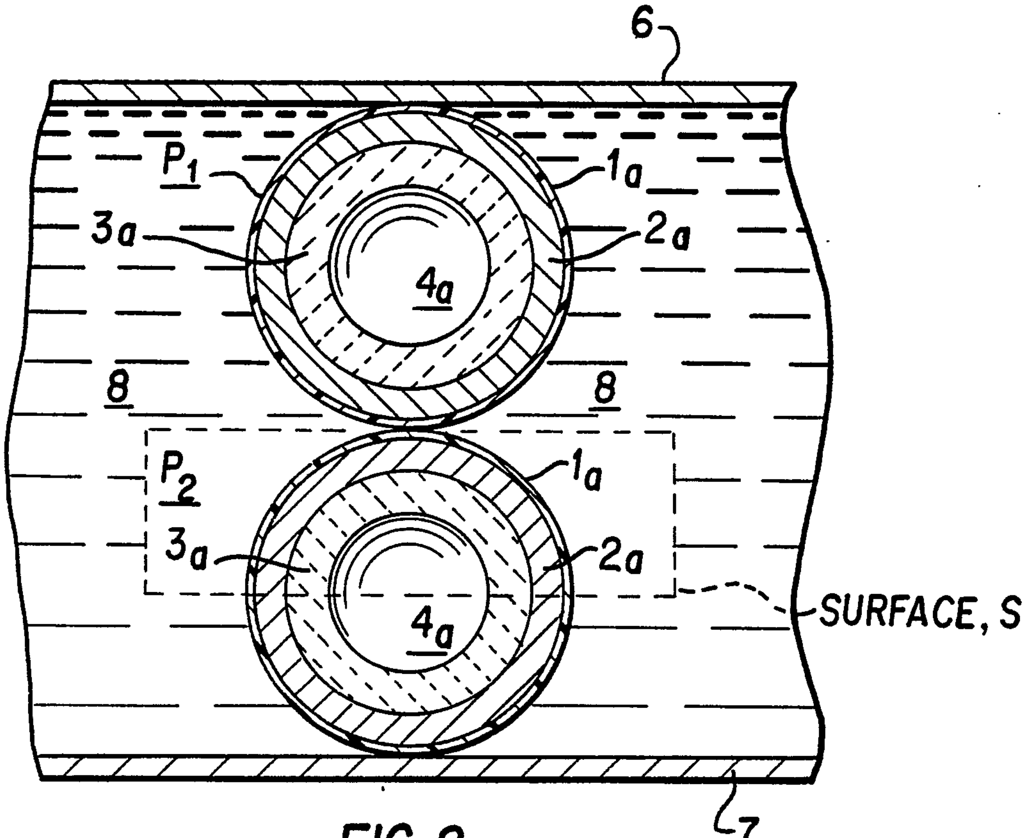
6
P1
1a
3a
2a
4a
8
8
P2
1a
3a
2a
SURFACE, S
4a
7

FIG. 8

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 4228

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.5)
X	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 179 (C-590)[3527], 26th April 1989; & JP-A-1 6093 (ASAHi CHEM. IND. CO., LTD) 10-01-1989 ---	1-6,8, 10,16, 17-21	C 10 M 171/00
Y	IDEM ---	7,11-15 ,22-27	
D,X	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 338 (C-527)[3185], 12th September 1988, page 82 C 527; & JP-A-63 97 694 (ASAHI CHEM. IND., CO., LTD) 28-04-1988 ---	1-6,8, 10,16, 17-21	
Y	IDEM ---	7,11-15 ,22-27	
D,Y	LANGMUIR, vol. 4, no. 1, 1988, pages 38-44, American Chemical Society; A. GARG et al.: "Preparation and properties of uniformly coated inorganic colloidal particles. 2. Chromium hydrous oxide on hematite" * Abstract * ---	7	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
Y	EP-A-0 234 816 (CATALYST & CHEMICALS) * Claim 1 * ---	11-15, 22-27	C 10 M
A	GB-A-2 189 803 (GEC AVIONICS LTD) * Claims 4,5 * -----	9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-06-1990	ROTSAERT L.D.C.

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