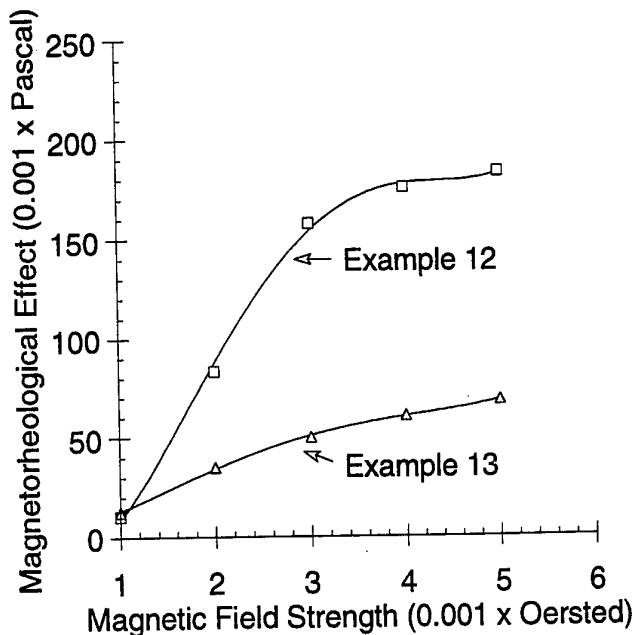




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(54) Title: MAGNETORHEOLOGICAL MATERIALS UTILIZING SURFACE-MODIFIED PARTICLES



(57) Abstract

A magnetorheological material containing a carrier fluid and a magnetically active particle. The particle has been modified so that the surface of the particle is substantially free of contamination products. The contamination products are removed from the surface of the particle by abrader processing, chemical treatment or a combination thereof. Magnetorheological materials prepared using the particles from which contamination products have been removed exhibit significantly enhanced magnetorheological effects.

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Magnetorheological fluids exhibit higher yield strengths than electrorheological materials and are, therefore, capable of generating greater damping forces. Furthermore, magnetorheological materials are activated by magnetic fields which are easily produced by simple, 5 low voltage electromagnetic coils as compared to the expensive high voltage power supplies required to effectively operate electrorheological materials. A more specific description of the type of devices in which magnetorheological materials can be effectively utilized is provided in co-pending U.S. Patent Application Serial Nos. 07/900,571 and 10 07/900,567 entitled "Magnetorheological Fluid Dampers" and "Magnetorheological Fluid Devices," respectively, both filed on June 18, 1992, the entire contents of which are incorporated herein by reference.

Magnetorheological or Bingham magnetic fluids are distinguishable from colloidal magnetic fluids or ferrofluids. In colloidal 15 magnetic fluids the particles are typically 5 to 10 nanometers in diameter. Upon the application of a magnetic field, a colloidal ferrofluid does not exhibit particle structuring or the development of a resistance to flow. Instead, colloidal magnetic fluids experience a 20 body force on the entire material that is proportional to the magnetic field gradient. This force causes the entire colloidal ferrofluid to be attracted to regions of high magnetic field strength.

Magnetorheological fluids and corresponding devices have been discussed in various patents and publications. For example, U.S. 25 Pat. No. 2,575,360 provides a description of an electromechanically controllable torque-applying device that uses a magnetorheological material to provide a drive connection between two independently rotating components, such as those found in clutches and brakes. A fluid composition satisfactory for this application is stated to consist of 30 50% by volume of a soft iron dust, commonly referred to as "carbonyl iron powder", dispersed in a suitable liquid medium such as a light lubricating oil.

Another apparatus capable of controlling the slippage between moving parts through the use of magnetic or electric fields is disclosed 35 in U.S. Pat. No. 2,661,825. The space between the moveable parts is

filled with a field responsive medium. The development of a magnetic or electric field flux through this medium results in control of resulting slippage. A fluid responsive to the application of a magnetic field is described to contain carbonyl iron powder and light weight
5 mineral oil.

U.S. Pat. No. 2,886,151 describes force transmitting devices, such as clutches and brakes, that utilize a fluid film coupling responsive to either electric or magnetic fields. An example of a magnetic field responsive fluid is disclosed to contain reduced iron
10 oxide powder and a lubricant grade oil having a viscosity of from 2 to 20 centipoises at 25°C.

The construction of valves useful for controlling the flow of magnetorheological fluids is described in U.S. Pat. Nos. 2,670,749 and 3,010,471. The magnetic fluids applicable for utilization in the
15 disclosed valve designs include ferromagnetic, paramagnetic and diamagnetic materials. A specific magnetic fluid composition specified in U.S. Pat. No. 3,010,471 consists of a suspension of carbonyl iron in a light weight hydrocarbon oil. Magnetic fluid mixtures useful in U.S. Pat. No. 2,670,749 are described to consist of a carbonyl iron
20 powder dispersed in either a silicone oil or a chlorinated or fluorinated suspension fluid.

Various magnetorheological material mixtures are disclosed in U.S. Patent No. 2,667,237. The mixture is defined as a dispersion of small paramagnetic or ferromagnetic particles in either a liquid,
25 coolant, antioxidant gas or a semi-solid grease. A preferred composition for a magnetorheological material consists of iron powder and light machine oil. A specifically preferred magnetic powder is stated to be carbonyl iron powder with an average particle size of 8 micrometers. Other possible carrier components include kerosene,
30 grease, and silicone oil.

U.S. Pat. No. 4,992,190 discloses a rheological material that is responsive to a magnetic field. The composition of this material is disclosed to be magnetizable particles and silica gel dispersed in a liquid carrier vehicle. The magnetizable particles can be powdered

magnetite or carbonyl iron powders with insulated reduced carbonyl iron powder, such as that manufactured by GAF Corporation, being specifically preferred. The liquid carrier vehicle is described as having a viscosity in the range of 1 to 1000 centipoises at 100°F. 5 Specific examples of suitable vehicles include Conoco LVT oil, kerosene, light paraffin oil, mineral oil, and silicone oil. A preferred carrier vehicle is silicone oil having a viscosity in the range of about 10 to 1000 centipoise at 100°F.

In many demanding applications for magnetorheological 10 materials, such as dampers or brakes for automobiles or trucks, it is desirable for the magnetorheological material to exhibit a high yield stress so as to be capable of tolerating the large forces experienced in these types of applications. It has been found that only a nominal increase in yield stress of a given magnetorheological material can be 15 obtained by selecting among the different iron particles traditionally utilized in magnetorheological materials. In order to increase the yield stress of a given magnetorheological material, it is typically necessary to increase the volume fraction of magnetorheological particles or to increase the strength of the applied magnetic field. 20 Neither of these techniques is desirable since a high volume fraction of the particle component can add significant weight to a magnetorheological device, as well as increase the overall off-state viscosity of the material, thereby restricting the size and geometry of a magnetorheological device capable of utilizing that material, and high 25 magnetic fields significantly increase the power requirements of a magnetorheological device.

A need therefore exists for a magnetorheological particle component that will independently increase the yield stress of a magnetorheological material without the need for an increased 30 particle volume fraction or increased magnetic field.

Disclosure of Invention

The present invention is a magnetorheological material comprising a carrier fluid and a magnetically active particle wherein the particle has been modified so that the surface of the particle is

substantially free of contamination products such as corrosion products. The formation of corrosion products on the surface of a magnetically active particle results from both chemical and electrochemical reactions of the particle's surface with water and atmospheric gases, as well as with electrolytes and particulates or contaminants that are either present in the atmosphere or left as a residue during particle preparation or processing. Corrosion products can either be compact and strongly adherent to the surface of the metal or loosely bound to the surface of the metal and can be in the form of a powder, film, flake or scale. The most common types of corrosion products include various forms of a metallic oxide layer, which are sometimes referred to as rust, scale or mill scale.

It has presently been discovered that the yield stress exhibited by a magnetorheological material can be significantly enhanced by the removal of contamination products from the surface of the magnetically active particles. Contamination products can be efficiently removed from the surface of metallic particles through abrader processing, chemical treatment or a combination thereof. In order to be effective, these techniques must be employed during the preparation of the magnetorheological material (in situ) or immediately prior to either the preparation of the magnetorheological material or the application of a protective coating. Abrader processing involves the physical or mechanical removal of the contamination products by impacting the surface of the magnetically active particles at a high velocity with an abrasive media. This abrasive media can either be an abrasive additive to the magnetorheological material or a form of grinding media used as a processing aid.

Chemical treatment methods or techniques applicable to the removal of contamination products during the preparation of the magnetorheological material include acid etching, cleaning or pickling; alkaline cleaning; electrolytic cleaning; ultrasonic cleaning and combinations thereof. Additional chemical treatment methods applicable to the removal of the contamination products prior to preparing the magnetorheological material include metal reduction

or reactive gas processes, plasma cleaning, ion etching, sputter cleaning and combinations thereof.

The types of barrier coatings that are effective in protecting the surface of the particles can be comprised of nonmagnetic metals, ceramics, high performance thermoplastics, thermosetting polymers and combinations thereof. In order to effectively protect the surface of the particle from recontamination by a contamination product, it is necessary that this coating or layer substantially encase or encapsulate the particle.

10 **Brief Description of the Drawing**

Figure 1 is a plot of magnetorheological effect at 25°C as a function of magnetic field strength for magnetorheological materials prepared in accordance with Example 12 and comparative Example 13.

15 **Best Mode for Carrying Out the Invention**

The present invention relates to a magnetorheological material comprising a carrier fluid and a particle component wherein the particle component has been modified so that the surface of the particle component is substantially free of contamination products.

20 The contamination products can essentially be any foreign material present on the surface of the particle and the contamination products are typically corrosion products. As stated above, the formation of corrosion products on the surface of a magnetically active particle results from both chemical and electrochemical reactions of the particle's surface with water and atmospheric gases, as well as with electrolytes and particulates or contaminants that are either present in the atmosphere or left as a residue during particle preparation or processing. Examples of atmospheric gases commonly
25 involved in this surface degradation process include O₂, SO₂, H₂S, NH₃, NO₂, NO, CS₂, CH₃SCH₃, and COS. Although a metal may resist attack by one or more of these atmospheric gases, the surface of a metal is typically reactive towards several of these gases. Examples of chemical elements contaminating the surface of metal particles
30

resulting from known powder processing techniques and methods include carbon, sulfur, oxygen, phosphorous, silicon and manganese. Examples of atmospheric particulates or contaminants involved in the formation of corrosion products on various metals include dust, water
5 or moisture, dirt, carbon and carbon compounds or soot, metal oxides, (NH₄)SO₄, various salts (i.e., NaCl, etc.) and corrosive acids, such as hydrochloric acid, sulfuric acid, nitric acid and chromic acid. It is normal that metallic corrosion takes place in the presence of a combination of several of these atmospheric gases and contaminants.
10 The presence of solid particulates, such as dust, dirt or soot on the surface of a metal increases the rate of degradation because of their ability to retain corrosive reactants, such as moisture, salts and acids. A more detailed discussion of the atmospheric corrosion of iron and other metals is provided by H. Uhlig and R. Revie in "Corrosion and
15 Corrosion Control," (John Wiley & Sons, New York, 1985), the entire content of which is incorporated herein by reference.

The inherent degradation of the surface of a metal exposed to the atmosphere typically continues until either the corrosion product completely encompasses or encapsulates the particle or the entire bulk
20 of the particle has reacted with the contaminants. Corrosion products can either be compact and strongly adherent to the surface of the metal or loosely bound to the surface of the metal as a powder, film, flake or scale. The most common types of corrosion products include various forms of a metallic oxide layer, which are sometimes referred
25 to as rust, scale or mill scale.

The present invention is based on the discovery that the removal of contamination products from the surface of a magnetically polarizable particle causes the particle to be particularly effective in creating a magnetorheological material which is capable of exhibiting
30 high yield stresses. Contamination products can be efficiently removed from the surface of metallic particles through abrader processing, chemical treatment or a combination thereof. In order to be effective, these techniques must be employed during the preparation of the magnetorheological material (in situ) or immediately prior to

either the preparation of the magnetorheological material or the application of a particle barrier layer or coating.

Abrader processing involves the physical or mechanical removal of the contamination products resulting from impacting the surface of the magnetically active particles at a high velocity with an abrasive media. This abrasive media can either be an abrasive additive to the magnetorheological material or a form of grinding media used only as a processing aid.

The abrasive additive of the invention must be a material capable of sufficiently abrading a magnetorheological particle so as to substantially remove the contamination products from the surface of the particle. The abrasive additive must, therefore, possess a substantial degree of hardness or roughness so as to effectively abrade the surface of the magnetorheological particle. Various types of abrasive materials capable of removing contamination products from the surface of a metal are well known to those skilled in the art of tribology or superabrasives and can be utilized as abrasive additives in the invention. The abrasive additives of the invention are typically in the form of a powder and can be comprised of various materials such as the oxides of aluminum, chromium, zirconium, hafnium, titanium, silicon, and magnesium; the carbides, nitrides and borides of aluminum, silicon and boron; and cermets, such as WC-Co and Ni-Cr-Al₂O₃, as well as combinations thereof. Specific examples of abrasive additives include diamond dust, garnet, corundum, alumina, black mineral slag, Cr₂O₃, HfO₂, TiO₂, MgO, glass, sand, silica, aluminum silicates, pumice, rouge, emery, feldspar, SiC, B₄C, BN, Si₃N₄, AlN, cerium oxide, and fused alumina, as well as other refractory or ceramic abrasives.

Iron oxides have also been found to be effective as abrasive additives for purposes of the present invention. Specifically, it has been found that the relatively hard iron oxides can be utilized in combination with relatively soft iron powders such that the contamination products are removed from the surface of the iron by the iron oxides. It should be noted that although used in relatively minor amounts in the overall magnetorheological material, the iron

oxides are magnetically active and also function as an additional magnetorheological particle in combination with the iron. The iron oxide includes all known pure iron oxides, such as Fe_2O_3 and Fe_3O_4 , as well as those containing small amounts of other elements, such as 5 manganese, zinc or barium. Specific examples of iron oxide include ferrites and magnetites with ferrites being preferred.

The silica useful as an abrasive additive in the invention must be hydrophobic. In other words, the surface of the silica must be treated so as to contain a minimal amount of hydroxyl functionality and 10 the silica must be relatively free of adsorbed moisture. It is important that the surface of the silica be chemically treated to be hydrophobic since it has been found that conventional drying of otherwise hydrophilic silica (e.g., silica gel such as that supplied by PPG Industries under the trade name HI-SIL 233) is not sufficient to 15 render the silica hydrophobic for purposes of the invention. Although not completely understood, it is believed that an excess of adsorbed moisture and/or hydroxyl functionality prevents the hydrophilic silica from sufficiently abrading the surface of the particle component.

The hydrophobic silica of the invention can be prepared by 20 reacting the hydroxyl groups on the surface of the silica with various organofunctional monomeric silanes or silane coupling agents, such as hydroxysilanes, acyloxysilanes, epoxysilanes, oximesilanes, alkoxysilanes, chlorosilanes and aminosilanes as is known in the art. The hydroxyl groups on the surface of the silica may also be reacted 25 with polymeric compounds such as silicone oils, mineral oils and paraffin oils. The modification of the surface of silica with various materials to render the silica hydrophobic is described by W. Noll in "Chemistry and Technology of Silicones," Academic Press, Inc., New York, 1968 and by E. P. Plueddemann in "Silane Coupling Agents," 30 Plenum Press, New York, 1982, both the entire disclosures of which are incorporated herein by reference. Specific examples of hydrophobic silicas include those commercially obtainable under the trade names AEROSIL and CABOSIL from Degussa Corporation and Cabot Corporation, respectively.

The preferred abrasive additives of the present invention include hydrophobic silica, iron oxides, and alumina because of their potential to contribute to the formation of a thixotropic network as described hereinafter. Iron oxides are specifically preferred due to
5 their magnetorheological activity and relatively high specific gravity.

The diameter of the abrasive additives utilized herein can range from about 0.001 to 50.0 μm , preferably from about 0.001 to 20.0 μm with about 0.001 to 5.0 μm being specifically preferred. These abrasive additives are typically utilized in an amount ranging from
10 about 0.05 to about 10.0, preferably from about 0.1 to about 5.0, with about 0.2 to about 3.0 percent by volume of the total magnetorheological material being especially preferred.

In order to be effective, the abrasive additive must be caused to impact the surface of a magnetorheological particle with a kinetic
15 energy high enough to efficiently remove contamination products from the surface of the particle. This can be carried out during the preparation of the magnetorheological material (*in situ*), immediately prior to the preparation of the magnetorheological material or immediately prior to the application of a protective coating to the
20 particle. If carried out during the preparation of the magnetorheological material, the abrasive additive is combined with the magnetorheological particle component, carrier fluid and any optional ingredients, and the resulting combination of ingredients is initially mixed by hand with a spatula or the like and then more thoroughly
25 mixed with a homogenizer, mechanical mixer, mechanical shaker, or an appropriate milling device such as a ball mill, sand mill, attritor mill, colloid mill, paint mill, pebble mill, shot mill, vibration mill, roll mill, horizontal small media mill, or the like (all hereinafter collectively referred to as "mixing devices").

30 It is the mass of the abrasive additive, as well as the velocity achieved by this additive during the mixing or dispersing process that determines the magnitude of kinetic energy available for the removal of contamination products from the magnetorheological particles. The velocity of the abrasive additive is dependent upon the viscosity of
35 the magnetorheological material and the speed at which the mixing

device is operated. For a typical magnetorheological material with a viscosity less than about 1000 centipoise at 25°C, sufficient velocity is achieved by the abrasive additive to effectively remove contamination products from the magnetorheological particles when the mixing
5 device is operated with a minimum tip speed of about 50 ft/min. The ingredients must be mixed together or dispersed for a sufficient length of time to substantially remove contamination products from the surface of the magnetorheological particle. An increase in the velocity of the abrasive additive will usually result in a decrease in the
10 required mixing or dispersion time. In general, the ingredients should be mixed for a period of time typically ranging from about 1 minute to 24 hours, preferably ranging from about 5 minutes to 18 hours. A certain amount of experimentation may be required to determine the optimum parameters that will allow for efficient
15 removal of contamination products from a particular magnetorheological particle.

Confirmation of the substantial removal of contamination products from the surface of a magnetorheological particle may be obtained by utilizing various material characterization techniques
20 known to those skilled in the art of analytical chemistry and surface analysis. Examples of several known techniques for the quantitative/qualitative detection of atomic and/or molecular species include neutron activation analysis; scanning ion mass spectrometry (SIMS); x-ray methods, such as x-ray powder diffraction, x-ray fluorescence
25 spectroscopy (XRF), x-ray photoelectron spectroscopy (XPS) and electron spectroscopy for chemical analysis (ESCA); and microscopy methods, such as scanning tunneling microscopy (STM), scanning electron microscopy (SEM), scanning auger microanalysis (SAM), and electron probe microanalysis (EPMA). Microscopy of powder
30 samples are typically performed using an ultramicrotomy procedure well known to those skilled in the art.

If the contamination products are to be removed from the surface of the magnetorheological particle immediately prior to either the preparation of the magnetorheological material or the application
35 of a protective coating, the above mixing procedure is followed except

that only the magnetorheological particle and abrasive additive are utilized. After the mixing procedure, the abraded particle may be immediately combined with the other ingredients to prepare a magnetorheological material or immediately coated with a protective
5 coating to prevent the reformation of corrosion products. By "immediately," it is typically meant that the abraded particle is combined with the other ingredients of the magnetorheological material or coated with a protective coating within no more than about 60 minutes, preferably within no more than about 30 minutes, after completion of
10 the mixing procedure, unless the particles are stored for a longer time period under a contaminant-free atmosphere.

Contamination products can also be removed from the particle component through abrader processing using various grinding media as a processing aid. This form of abrader processing can also be
15 performed during the preparation of the magnetorheological material or immediately prior to either preparing the magnetorheological material or applying a protective coating to the particles. The type of grinding media and the nature of the corresponding equipment needed to perform this abrading process are described as those capable
20 of reducing or changing the diameter or size of the particle component. Specific types of appropriate media and equipment are well known to those skilled in the art of manufacturing paints and coatings. Devices such as homogenizers, mechanical mixers and shakers that do not utilize a milling-type process, and are therefore
25 not capable of reducing particle size, provide inadequate removal of contamination products from the surface of magnetorheological particles for purposes of the present invention, unless an abrasive additive as previously described is utilized in combination with the device.

30 Examples of common grinding media appropriate for use as a processing aid include balls, beads, pellets, pebbles, grit or shot comprised of various materials including stainless steel, ceramic, porcelain, flint, high carbon steel, high manganese steel, cast nickel alloy, low carbon forged steel, tungsten carbide, glass, zirconium
35 silicate, zirconium oxide, and aluminum oxide. Examples of common

media milling devices or mills that utilize these types of grinding media include sand mills, ball mills, attritor mills, pebble mills, shot mills, vibration mills and horizontal small media mills. In addition, the grinding media may be in the form of a wheel, disc or blade, such as that typically used in roll mills. A more complete description of media mills is provided by G. Tank and T. Patten in "Industrial Paint Finishing Techniques and Processes" (Ellis Horwood Limited, West Sussex, England, 1991) and "Paint Flow and Pigment Dispersion" (2nd edition, John Wiley & Sons, New York, 1979), respectively, the entire contents of which are incorporated herein by reference.

As is the case with the abrasive additive described above, the grinding media must be caused to impact the surface of a magnetorheological particle with a kinetic energy high enough to sufficiently remove contamination products from the surface of the particle. It is the mass of the grinding media, as well as the velocity achieved by this media during the milling process that determines the magnitude of kinetic energy available for the removal of contamination products from the magnetorheological particles. The velocity of the grinding media is dependent upon the viscosity of the magnetorheological material and the speed at which the milling device is operated. For a typical magnetorheological material with a viscosity less than about 1000 centipoise at 25°C, sufficient velocity is achieved by the grinding media to effectively remove contamination products from the magnetorheological particles when the milling device is operated with a minimum tip speed of about 300 ft/min. The ingredients must be mixed together or dispersed for a sufficient length of time to substantially remove contamination products from the surface of the magnetorheological particle. An increase in the velocity of the grinding media will usually result in a decrease in the required milling time. In general, the ingredients should be mixed for a period of time typically ranging from about 1 hour to 48 hours, preferably ranging from about 2 hours to 24 hours. A certain amount of experimentation may be required to determine the optimum parameters that will allow for efficient removal of contamination products from a particular magnetorheological particle.

It should be noted that abrasive additives can be utilized in combination with grinding media and, in this case, the efficiency of the corresponding milling device may be increased resulting in a lesser amount of both time and speed of the milling device needed to
5 remove the contamination products from the surface of the magnetorheological particle.

Removal of contamination products from the surface of the magnetorheological particle can also be accomplished through chemical treatment techniques. The chemical treatment can be
10 carried out during the preparation of the magnetorheological material (in situ), immediately prior to the preparation of the magnetorheological material or immediately prior to the application of a protective coating to the particle. Chemical treatment methods or techniques applicable to the removal of contamination products during the
15 preparation of the magnetorheological material include acid cleaning, alkaline cleaning, electrolytic cleaning, ultrasonic cleaning and combinations thereof, such as the combination of electrolytic cleaning and alkaline cleaning commonly utilized in the electroplating industry. Examples of alkaline cleaners useful in the invention
20 include alkali metal orthophosphates, condensed phosphates, hydroxides, carbonates, bicarbonates, silicates and borates. Alkaline cleaners are typically utilized in combination with a surfactant as is known in the art.

Examples of common acid cleaners useful in the invention
25 include organic acids, such as citric, tartaric, acetic, oxalic and gluconic acid, acid salts, such as sodium phosphate, ammonium persulfate, sodium acid sulfate and bifluoride salts, and inorganic acids, such as sulfuric acid, phosphoric acid and hydrochloric acid.

Acid and alkaline cleaning during the preparation of the
30 magnetorheological material can be carried out by adding an acid or alkaline cleaner to the ingredients utilized to prepare the magnetorheological material and then thoroughly mixing the ingredients first by hand with a spatula or the like and then with a mechanical mixing device. The acid or alkaline cleaner is typically utilized in an amount

ranging from 0.1 to 5.0, preferably from about 0.5 to 3.0, percent by weight of the particle component.

Electrolytic cleaning or electrocleaning during the preparation of the magnetorheological material is typically carried out by applying
5 an electric current to the material in order to produce vigorous gassing on the surface of the particles and promote the release of contaminants. Electrocleaning can be either cathodic or anodic in nature. This technique is generally used in conjunction with acid or alkaline cleaning as previously described.

10 Ultrasonic cleaning during the preparation of the magnetorheological material is typically carried out by passing sound waves at high frequencies through the material. These ultrasonic waves create tiny gas bubbles throughout the carrier component, which vigorously cleans the surface of the particles. This technique is often used in
15 conjunction with acid or alkaline cleaning as previously described.

The chemical treatment methods that are applicable to the removal of contamination products immediately prior to either preparing the magnetorheological material or applying a protective coating include the techniques described above for in situ treatment,
20 as well as metal reduction; plasma cleaning; ion etching; sputter cleaning and combinations thereof. Metal reduction typically involves the reduction of the metal particle's surface through a reaction with a gaseous molecule, such as hydrogen, at elevated temperatures. Due to their ability to provide very clean surfaces and control contaminant
25 removal, the preferred methods of removing contamination products from the surface of the particles prior to preparing a magnetorheological material or applying a protective coating are metal reduction and plasma cleaning.

A thorough description of the chemical treatment techniques
30 described above is provided by B. Bhushan and B. Gupta in "Handbook of Tribology," McGraw-Hill, Inc., New York, 1991 (hereinafter referred to as Bhushan), the entire contents of which are incorporated herein by reference.

As stated above, immediately after removing the contamination products from the particle's surface through either abrader processing, chemical treatment or a combination thereof, a protective coating can be applied to the surface of the particle. In order to
5 effectively protect the surface of the particle from recontamination by a contamination product, it is necessary that the protective coating substantially, preferably entirely, encase or encapsulate the particle. Protective coatings that substantially encapsulate the particle are to be distinguished from insulation coatings, such as those presently found
10 on carbonyl iron powder such as the insulated reduced carbonyl iron powder supplied by GAF Corporation under the designations "GQ-4" and "GS-6."

The insulation coatings found on insulated reduced carbonyl iron are intended to prevent particle-to-particle contact and are simply
15 formed by dusting the particles with silica gel particulates. Insulation coatings therefore do not substantially encapsulate the particle so as to prevent the formation of contamination products. The sporadic coverage of a particle's surface by an insulation coating can be seen in the scanning electron micrographs presented in the article by J.
20 Japka entitled "Iron Powder for Metal Injection Molding" (International Journal of Powder Metallurgy, 27(2), 107-114), the entire contents of which are incorporated herein by reference. Incomplete coverage of the particle's surface by a coating typically will result in the accelerated formation of contamination products through the
25 process described above for solid atmospheric particles, such as dust and soot. Iron oxide, previously described in the literature as being useful as an insulation coating, cannot be used as a protective coating for purposes of the present invention because iron oxide itself is a corrosion product.

30 The protective coatings of the invention that are effective in preventing the formation of contamination products on the surface of magnetorheological particles can be derived from a variety of materials including nonmagnetic metals, ceramics, high performance thermoplastics, thermosetting polymers and combinations
35 thereof. Examples of thermosetting polymers useful for forming a

protective coating include polyesters, polyimides, phenolics, epoxies, urethanes, rubbers and silicones, while thermoplastic polymeric materials include acrylics, cellulose, polyphenylene sulfides, polyquinoxilines, polyetherimides and polybenzimidazoles. Typical
5 nonferrous metals useful for forming a protective coating include refractory transition metals, such as titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, copper, silver, gold, and lead, tin, zinc, cadmium, cobalt-based intermetallic alloys, such as Co-Cr-W-C and Co-Cr-Mo-Si, and nickel-
10 based intermetallic alloys, such as Ni-Cu, Ni-Al, Ni-Cr, Ni-Mo-C, Ni-Cr-Mo-C, Ni-Cr-B-Si-C, and Ni-Mo-Cr-Si. Examples of ceramic materials useful for forming a protective coating include the carbides, nitrides, borides, and silicides of the refractory transition metals described above; nonmetallic oxides, such as Al₂O₃, Cr₂O₃, ZrO₃,
15 HfO₂, TiO₂, SiO₂, BeO, MgO, and ThO₂; nonmetallic nonoxides, such as B₄C, SiC, BN, Si₃N₄, AlN, and diamond; and various cermets.

A thorough description of the various materials typically utilized to protect metal surfaces from the growth of corrosion products is provided by C. Munger in "Corrosion Prevention by
20 Protective Coatings" (National Association of Corrosion Engineers, Houston, Texas, 1984), the entire content of which is incorporated herein by reference. A commercially available iron powder that is encapsulated with a polyetherimide coating is manufactured under the trade name ANCOR by Hoeganaes.

25 The protective coatings of the invention can be applied by techniques or methods well known to those skilled in the art of tribology. Examples of common coating techniques include both physical deposition and chemical vapor deposition methods. Physical deposition techniques include both physical vapor deposition and
30 liquid or wetting methods. Physical vapor deposition methodology includes direct, reactive, activated reactive and ion-beam assisted evaporation; DC/RF diode, alternating, triode, hollow cathode discharge, sputter ion, and cathodic arc glow discharge ion plating; direct, cluster ion and ion beam plating; DC/RF diode, triode and
35 magnetron glow discharge sputtering; and single and dual ion beam

sputtering. Common physical liquid or wetting methodology includes air/airless spray, dip, spin-on, electrostatic spray, spray pyrolysis, spray fusion, fluidized bed, electrochemical deposition, chemical deposition such as chemical conversion (e.g., phosphating, chromating, metallizing, etc.), electroless deposition and chemical reduction; intermetallic compounding, and colloidal dispersion or sol-gel coating application techniques. Chemical vapor deposition methodology includes conventional, low pressure, laser-induced, electron-assisted, plasma-enhanced and reactive-pulsed chemical vapor deposition, as well as chemical vapor polymerization. A thorough discussion of these various coating processes is provided in Bhushan.

Due to the additional production costs associated with removing the corrosion products from the surface of the particles prior to preparing a magnetorheological material, the preferred abrader processing and chemical treatment methods of the invention include those performed during the preparation of the magnetorheological material. In this regard, abrader processing is generally preferable over chemical treatment.

The magnetically active particle component to be modified according to the present invention can be comprised of essentially any solid which is known to exhibit magnetorheological activity and which can inherently form a contamination product on its surface. Typical particle components useful in the present invention are comprised of, for example, paramagnetic, superparamagnetic, or ferromagnetic compounds. Specific examples of particle components useful in the present invention include particles comprised of materials such as iron, iron nitride, iron carbide, carbonyl iron, chromium dioxide, low carbon steel, silicon steel, nickel, cobalt, and mixtures thereof. In addition, the particle component can be comprised of any of the known alloys of iron, such as those containing aluminum, silicon, cobalt, nickel, vanadium, molybdenum, chromium, tungsten, manganese and/or copper. The particle component can also be comprised of the specific iron-cobalt and iron-nickel alloys described in the U.S. patent application entitled "Magnetorheological Materials Based on Alloy Particles" filed concurrently herewith by Applicants J. D. Carlson and

K. D. Weiss and also assigned to the present assignee, the entire disclosure of which is incorporated herein by reference.

The particle component is typically in the form of a metal powder which can be prepared by processes well known to those skilled in the art. Typical methods for the preparation of metal powders include the reduction of metal oxides, grinding or attrition, electrolytic deposition, metal carbonyl decomposition, rapid solidification, or smelt processing. Various metal powders that are commercially available include straight iron powders, reduced iron powders, insulated reduced iron powders, and cobalt powders. The diameter of the particles utilized herein can range from about 0.1 to 500 μm and preferably range from about 1.0 to 50 μm .

The preferred particles of the present invention are straight iron powders, reduced iron powders, iron-cobalt alloy powders and iron-nickel alloy powders.

The particle component typically comprises from about 5 to 50, preferably about 15 to 40, percent by volume of the total composition depending on the desired magnetic activity and viscosity of the overall material.

The carrier fluid of the magnetorheological material of the present invention can be any carrier fluid or vehicle previously disclosed for use in magnetorheological materials, such as the mineral oils, silicone oils and paraffin oils described in the patents set forth above. Additional carrier fluids appropriate to the invention include silicone copolymers white oils, hydraulic oils, chlorinated hydrocarbons, transformer oils, halogenated aromatic liquids, halogenated paraffins, diesters, polyoxyalkylenes, perfluorinated polyethers, fluorinated hydrocarbons, fluorinated silicones, and mixtures thereof. As known to those familiar with such compounds, transformer oils refer to those liquids having characteristic properties of both electrical and thermal insulation. Naturally occurring transformer oils include refined mineral oils that have low viscosity and high chemical stability. Synthetic transformer oils generally comprise chlorinated aromatics (chlorinated biphenyls and

trichlorobenzene), which are known collectively as "askarels", silicone oils, and esteric liquids such as dibutyl sebacates.

Additional carrier fluids suitable for use in the present invention include the silicone copolymers, hindered ester compounds
5 and cyanoalkylsiloxane homopolymers disclosed in co-pending U.S. Patent Application Serial No. 07/942,549 filed September 9, 1992, and entitled "High Strength, Low Conductivity Electrorheological Materials," the entire disclosure of which is incorporated herein by reference. The carrier fluid of the invention may also be a modified
10 carrier fluid which has been modified by extensive purification or by the formation of a miscible solution with a low conductivity carrier fluid so as to cause the modified carrier fluid to have a conductivity less than about 1×10^{-7} S/m. A detailed description of these modified carrier fluids can be found in the U.S. Patent Application entitled
15 "Modified Electrorheological Materials Having Minimum Conductivity," filed October 16, 1992, by Applicants B. C. Muñoz, S. R. Wasserman, J. D. Carlson, and K. D. Weiss, and also assigned to the present assignee, the entire disclosure of which is incorporated herein by reference.

20 Polysiloxanes and perfluorinated polyethers having a viscosity between about 3 and 200 centipoise at 25°C are also appropriate for utilization in the magnetorheological material of the present invention. A detailed description of these low viscosity polysiloxanes and perfluorinated polyethers is given in the U.S. patent application
25 entitled "Low Viscosity Magnetorheological Materials," filed concurrently herewith by Applicants K. D. Weiss, J. D. Carlson, and T. G. Duclos, and also assigned to the present assignee, the entire disclosure of which is incorporated herein by reference. The preferred carrier fluids of the present invention include mineral oils, paraffin
30 oils, silicone oils, silicone copolymers and perfluorinated polyethers, with silicone oils and mineral oils being especially preferred.

The carrier fluid of the magnetorheological material of the present invention should have a viscosity at 25°C that is between about 2 and 1000 centipoise, preferably between about 3 and 200 centipoise,
35 with a viscosity between about 5 and 100 centipoise being especially

preferred. The carrier fluid of the present invention is typically utilized in an amount ranging from about 50 to 95, preferably from about 60 to 85, percent by volume of the total magnetorheological material.

5 Particle settling may be minimized in the magnetorheological materials of the invention by forming a thixotropic network. A thixotropic network is defined as a suspension of particles that at low shear rates form a loose network or structure, sometimes referred to as clusters or flocculates. The presence of this three-dimensional
10 structure imparts a small degree of rigidity to the magnetorheological material, thereby, reducing particle settling. However, when a shearing force is applied through mild agitation, this structure is easily disrupted or dispersed. When the shearing force is removed, this loose network is reformed over a period of time.

15 A thixotropic network or structure is formed through the utilization a hydrogen-bonding thixotropic agent and/or a polymer-modified metal oxide. Colloidal additives may also be utilized to assist in the formation of the thixotropic network. The formation of a thixotropic network utilizing hydrogen-bonding thixotropic agents,
20 polymer-modified metal oxides and colloidal additives is further described in the U.S. Patent Application entitled "Thixotropic Magnetorheological Materials," filed concurrently herewith by applicants K. D. Weiss, D. A. Nixon, J. D. Carlson and A. J. Margida and also assigned to the present assignee, the entire disclosure of
25 which is incorporated herein by reference.

The formation of a thixotropic network in the invention can be assisted by the addition of low molecular weight hydrogen-bonding molecules, such as water and other molecules containing hydroxyl, carboxyl or amine functionality. Typical low molecular weight
30 hydrogen-bonding molecules other than water include methyl, ethyl, propyl, isopropyl, butyl and hexyl alcohols; ethylene glycol; diethylene glycol; propylene glycol; glycerol; aliphatic, aromatic and heterocyclic amines, including primary, secondary and tertiary amino alcohols and amino esters that have from 1-16 atoms of carbon in the molecule;
35 methyl, butyl, octyl, dodecyl, hexadecyl, diethyl, diisopropyl and

dibutyl amines; ethanolamine; propanolamine; ethoxyethylamine; dioctylamine; triethylamine; trimethylamine; tributylamine; ethylene-diamine; propylene-diamine; triethanolamine; triethylenetetramine; pyridine; morpholine; imidazole; and mixtures thereof. The low
5 molecular weight hydrogen-bonding molecules, if utilized, are typically employed in an amount ranging from about 0.1 to 10.0, preferably from about 0.5 to 5.0, percent by weight relative to the weight of the particle component.

An additional surfactant to more adequately disperse the
10 particle component may be optionally utilized in the present invention. Such surfactants include known surfactants or dispersing agents such as ferrous oleate and naphthenate, sulfonates, phosphate esters, glycerol monooleate, sorbitan sesquioleate, stearates, laurates, fatty acids, fatty alcohols, and the other surface active agents discussed in
15 U.S. Pat. No. 3,047,507 (incorporated herein by reference). Alkaline soaps, such as lithium stearate and sodium stearate, and metallic soaps, such as aluminum tristearate and aluminum distearate can also be presently utilized as a surfactant. In addition, the optional surfactants may be comprised of steric stabilizing molecules,
20 including fluoroaliphatic polymeric esters, such as FC-430 (3M Corporation), and titanate, aluminate or zirconate coupling agents, such as KEN-REACT® (Kenrich Petrochemicals, Inc.) coupling agents. Finally, a precipitated silica gel, such as that disclosed in U.S. Patent No. 4,992,190 (incorporated herein by reference), can be used to
25 disperse the particle component. In order to reduce the presence of moisture in the magnetorheological material, it is preferred that the precipitated silica gel, if utilized, be dried in a convection oven at a temperature of from about 110°C to 150°C for a period of time from about 3 to 24 hours.

30 The surfactant, if utilized, is preferably a "dried" precipitated silica gel, a fluoroaliphatic polymeric ester, a phosphate ester, or a coupling agent. The optional surfactant may be employed in an amount ranging from about 0.1 to 20 percent by weight relative to the weight of the particle component.

The preparation of magnetorheological materials according to the invention where contamination products are removed from the surface of the magnetorheological particle in situ has previously been described. If contamination products are removed from the particle
5 immediately prior to either the preparation of the magnetorheological material or the application of a protective coating, the magnetorheological materials of the present invention can be prepared by simply mixing together the carrier fluid, the pre-treated particle component, and any optional ingredients.

10 The ingredients of the magnetorheological materials may be initially mixed together by hand with a spatula or the like and then subsequently more thoroughly mixed with a homogenizer, mechanical mixer, mechanical shaker, or an appropriate milling device such as a ball mill, sand mill, attritor mill, colloid mill, paint mill, pebble
15 mill, shot mill, vibration mill, roll mill, horizontal small media mill or the like, in order to create a more stable suspension. The mixing conditions for the preparation of a magnetorheological material utilizing a magnetorheological particle that has had contamination products previously removed can be somewhat less rigorous than the
20 conditions required for the preparation and in situ removal of contamination products.

Evaluation of the mechanical properties and characteristics of the magnetorheological materials of the present invention, as well as other magnetorheological materials, can be obtained through the use
25 of parallel plate and/or concentric cylinder couette rheometry. The theories which provide the basis for these techniques are adequately described by S. Oka in *Rheology, Theory and Applications* (volume 3, F. R. Eirich, ed., Academic Press: New York, 1960) the entire contents of which are incorporated herein by reference. The information that
30 can be obtained from a rheometer includes data relating mechanical shear stress as a function of shear strain rate. For magnetorheological materials, the shear stress versus shear strain rate data can be modeled after a Bingham plastic in order to determine the dynamic yield stress and viscosity. Within the confines of this model
35 the dynamic yield stress for the magnetorheological material corres-

ponds to the zero-rate intercept of a linear regression curve fit to the measured data. The magnetorheological effect at a particular magnetic field can be further defined as the difference between the dynamic yield stress measured at that magnetic field and the dynamic
5 yield stress measured when no magnetic field is present. The viscosity for the magnetorheological material corresponds to the slope of a linear regression curve fit to the measured data.

In a concentric cylinder cell configuration, the magnetorheological material is placed in the annular gap formed between an inner
10 cylinder of radius R_1 and an outer cylinder of radius R_2 , while in a simple parallel plate configuration the material is placed in the planar gap formed between upper and lower plates both with a radius, R_3 . In these techniques either one of the plates or cylinders is then rotated with an angular velocity ω while the other plate or cylinder is
15 held motionless. A magnetic field can be applied to these cell configurations across the fluid-filled gap, either radially for the concentric cylinder configuration, or axially for the parallel plate configuration. The relationship between the shear stress and the shear strain rate is then derived from this angular velocity and the torque, T , applied to
20 maintain or resist it.

The following examples are given to illustrate the invention and should not be construed to limit the scope of the invention.

Examples 1 and 2

In Example 1, a magnetorheological material is prepared by
25 slowly adding a total of 117.9 g of carbonyl iron powder (Sigma Chemical Company) to a mixture of 3.54 g of an 11 N phosphoric acid solution, which is prepared using phosphoric acid (99%, Aldrich Chemical Company) and distilled water, and 28.29 g of 20 cstk mineral oil (DRAKEOL 10, Pennzoil Products Company). The temperature of
30 the magnetorheological material is maintained during this initial mixing procedure within the temperature range of about 30 to 45°C. The fluid is initially mixed by hand with a spatula (low shear) and then more thoroughly dispersed into a homogeneous mixture through the use of a high speed disperserator (high shear) equipped with a 16-

tooth rotary head. The weight amount of the chemically treated iron particles in the magnetorheological material is equivalent to a volume fraction of about 0.30. The magnetorheological material is stored in a polyethylene container.

5 In Example 2, a magnetorheological material is prepared according to the procedure described in Example 1. However, in this example the phosphoric acid solution is replaced with 3.54 g of an 11 N sulfuric acid solution, which is prepared using sulfuric acid (95-98%, Aldrich Chemical Company) and distilled water. The amount of
10 mineral oil is adjusted to maintain the particle volume fraction in the magnetorheological material at 0.30. The magnetorheological material is stored in a polyethylene container.

Comparative Example 3

In Example 3, a magnetorheological material is prepared
15 according to the procedure described in Example 1. However, in this example a total of 117.9 g of carbonyl iron powder (Sigma Chemical Company), 2.35 g of stearic acid (Aldrich Chemical Company) as a dispersant and 28.67 g of 20 cstc mineral oil (DRAKEOL 10, Pennzoil Products Company) are mixed together. The weight amount of
20 untreated iron particles in the magnetorheological material is equivalent to a volume fraction of about 0.30. The conventional magnetorheological material is stored in a polyethylene container.

Magnetorheological Activity for Examples 1-3

The magnetorheological materials prepared in Examples 1, 2
25 and 3 are evaluated through the use of parallel plate rheometry. A summary of the magnetorheological effect observed for these magnetorheological materials at various magnetic field strengths and 25°C is provided in Table 1. A significantly higher magnetorheological effect is observed for the magnetorheological materials utilizing
30 particles wherein contamination products have been removed by chemical treatment (Examples 1 and 2) as compared to a magnetorheological material containing conventional untreated particles (Example 3). At a magnetic field strength of 5000 Oersted the mag-

netorheological effect exhibited by the magnetorheological materials containing the chemically treated particles is about 71% greater than that exhibited by a conventional magnetorheological material.

Table 1

		Magnetic Field Strength (Oersted)				
		1000	2000	3000	4000	5000
Magneto- rheological Effect (kPa)	Example 1	32.4	46.2	72.5	91.7	100.7
	Example 2	10.0	38.0	65.4	80.3	94.5
	Comparative Example 3	8.9	25.1	43.3	53.5	55.3

5

Example 4

A magnetorheological material is prepared by mixing together a total of 123.2 g of carbonyl iron powder (Sigma Chemical Company), 2.46 g of stearic acid (Aldrich Chemical Company) as a dispersant and 34.20 g of 200 cstc silicone oil (Dow Corning Corporation). This weight
 10 amount of iron particles is equivalent to a volume fraction in the magnetorheological material of about 0.30. The fluid is made into a homogeneous mixture using an Union Process 01HD attritor mill equipped with a 110 cm³ tank. The grinding media used in this attritor mill is in the form of stainless steel balls. This mill has the
 15 capability to reduce the mean size and distribution of the particle component when the impacting grinding media has high kinetic energy. This grinding media imparts sufficient kinetic energy to remove the contamination products from the particle component when the agitator shaft and arms of this mill are rotated at tip speed of about
 20 300 ft./min. The maximum tip speed of this mill is measured to be about 600 ft./min. The magnetorheological material is aggressively milled in this abrader process over a 48-hour period with a tip speed of

about 445 ft./min. The magnetorheological material is separated from the grinding media and stored in a polyethylene container.

Comparative Example 5

A magnetorheological material is prepared according to the procedure described in Example 4. However, in this example the mill is operated with a tip speed of about 250 ft./min. over a 96-hour period. The rotation of the agitator shaft and arms at this angular speed does not impart sufficient kinetic energy to the stainless steel grinding media to remove the contamination products from the surface of particle component. The conventional magnetorheological material is separated from the grinding media and stored in a polyethylene container.

Magnetorheological Activity for Examples 4 & 5

The magnetorheological materials prepared in Examples 4 and 5 are evaluated through the use of parallel plate rheometry. A summary of the magnetorheological effect for these magnetorheological materials at various magnetic field strengths and 25°C is provided in Table 2. A significantly higher magnetorheological effect is observed for the magnetorheological material utilizing particles wherein contamination products have been removed by stainless steel grinding media in an abrader process (Example 4) as compared to a magnetorheological material containing conventional particles (Example 5). At a magnetic field strength of 3000 Oersted the magnetorheological effect exhibited by the magnetorheological material containing the abrader process modified particles is about 69% greater than that exhibited by a conventional magnetorheological material.

Table 2

		Magnetic Field Strength (Oersted)		
		1000	2000	3000
Magneto- rheological Effect (kPa)	Example 4	19.1	43.0	84.3
	Comparative Example 5	8.0	31.9	50.0

Example 6

A magnetorheological material is prepared by adding together a total of 117.9 g of reduced iron powder (ATOMET 95G, Quebec Metal Powders Limited), 8.75 g of Mn/Zn ferrite powder (#73302-0, D. M. Steward Manufacturing Company) as an abrasive additive, 2.53 g polyoxyethylene/silicone graft copolymer (SILWET L7500, Union Carbide Chemicals and Plastics Company, Inc.) as a thixotropic agent and 29.13 g of 10 cstk silicone oil (L-45, Union Carbide Chemicals and Plastics Company, Inc.). The fluid is initially mixed by hand with a spatula (low shear) and then more thoroughly dispersed into a homogeneous mixture through the use of a high speed disperser (high shear) equipped with a 16-tooth rotary head and operated at a tip speed of about 400 ft./min. for about 5 minutes. The weight amount of the iron particles in the magnetorheological material is equivalent to a volume fraction of about 0.30. The presence of the abrasive ferrite powder in this magnetorheological material efficiently removes the contamination products from the surface of the iron particles. The magnetorheological material whose particle component has been modified by abrader processing is stored in a polyethylene container.

Comparative Example 7

A magnetorheological material is prepared according to the procedure described in Example 6 with the exception that the abrasive ferrite powder is excluded. The weight amount of the oil component is

modified to maintain an iron particle volume fraction in the magnetorheological material of 0.30. This conventional magnetorheological material is stored in a polyethylene container.

Magnetorheological Activity for Examples 6 & 7

5 The magnetorheological materials prepared in Examples 6 and 7 are evaluated through the use of parallel plate rheometry. A summary of the magnetorheological effect observed for these magnetorheological materials at various magnetic field strengths and 25°C is provided in Table 3. A significantly higher magnetorheological effect
10 is observed for the magnetorheological material utilizing particles wherein contamination products have been removed by the presence of an abrasive additive in an abrader process (Example 6) as compared to a magnetorheological material containing conventional particles (Example 7). At a magnetic field strength of 5000 Oersted the mag-
15 netorheological effect exhibited by the magnetorheological material containing the abrader process modified particles is about 147% greater than that exhibited by a conventional magnetorheological material.

Table 3

		Magnetic Field Strength (Oersted)				
		1000	2000	3000	4000	5000
Magnetorheological Effect (kPa)	Example 6	11.2	31.4	62.5	93.1	122.4
	Comparative Example 7	7.74	31.8	43.5	46.6	49.5

20

Examples 8-10

In Example 8, a magnetorheological material is prepared by adding together a total of 117.9 g of straight carbonyl iron powder (MICROPOWDER S-1640, GAF Chemicals Corporation), 1.18 g of Boron Carbide (99%, Johnson Matthey Company) as an abrasive

additive, 2.36 g organomodified polydimethylsiloxane copolymer (SILWET L7500, Union Carbide Chemicals and Plastics, Company, Inc.) as a hydrogen-bonding thixotropic agent and 27.55 g of 10 cstc silicone oil (L-45, Union Carbide Chemicals and Plastics Company, Inc.). The fluid is initially mixed by hand with a spatula (low shear) and then more thoroughly dispersed into a homogeneous mixture through the use of a high speed disperser (high shear) equipped with a 16-tooth rotary head and operated at a tip speed of about 400 ft./min. for about 5 minutes. The weight amount of the iron particles in the magnetorheological material is equivalent to a volume fraction of about 0.32. The presence of the abrasive additive in this magnetorheological material efficiently removes the contamination products from the surface of the iron particles. The magnetorheological material whose particle component has been modified by abrader processing is stored in a polyethylene container.

Magnetorheological materials are prepared in Examples 9 and 10 according to the procedure described for Example 8. However, in Example 9 the boron carbide powder is replaced with 1.51 g silicon carbide powder (alpha, 99.8%, Johnson Matthey Company) as an abrasive additive. In Example 10, the abrasive additive is replaced with 2.43 g iron (II, III) oxide powder (97%, Johnson Matthey Company). The weight amount of the iron particles in each of the magnetorheological materials is equivalent to a volume fraction of about 0.32. The magnetorheological materials whose particle component has been modified by abrader processing is stored in a polyethylene container.

Comparative Example 11

A magnetorheological material is prepared according to the procedure described in Example 8. However, in this case no abrasive additive is incorporated into the magnetorheological material. The amount of the carrier oil component is appropriately increased to insure that the volume fraction of iron particles in the magnetorheological material is about 0.32. The conventional magnetorheological material is stored in a polyethylene container.

Magnetorheological Activity for Examples 8-11

The magnetorheological materials prepared in Examples 8, 9, 10 and 11 are evaluated through the use of parallel plate rheometry. A summary of the magnetorheological effect observed for these 5 magnetorheological materials at various magnetic field strengths and 25°C is provided in Table 4. A significantly higher magnetorheological effect is observed for the magnetorheological materials utilizing particles wherein contamination products have been removed by the presence of an abrasive additive or iron oxide particles in an abrader 10 process (Examples 8-10) as compared to a magnetorheological material containing conventional particles (Example 11). At a magnetic field strength of 3000 Oersted the magnetorheological effect exhibited by the magnetorheological material containing the abrader process modified particles is about 74% greater than that exhibited by a 15 conventional magnetorheological material.

Table 4

		Magnetic Field Strength (Oersted)		
		1000	2000	3000
Magnetorheological Effect (kPa)	Example 8	18.8	74.3	131.0
	Example 9	26.2	73.8	129.5
	Example 10	10.8	62.4	120.6
	Comparative Example 11	22.5	46.5	69.4

Example 12

A magnetorheological material is prepared by adding together a total of 117.9 g of reduced carbonyl iron powder (MICROPOWDER R-1430, GAF Chemicals Corporation), 1.90 g of hydrophobic fumed silica (CABOSIL TS-720, Cabot Corporation) and 29.95 g of 10 cstc silicone oil (L-45, Union Carbide Chemicals and Plastics Company, Inc.). The fluid is initially mixed by hand with a spatula (low shear) and then more thoroughly dispersed into a homogeneous mixture through the use of a high speed disperser (high shear) equipped with a 16-tooth rotary head and operated at a tip speed of about 400 ft./min. for about 5 minutes. The weight amount of the iron particles in the magnetorheological material is equivalent to a volume fraction of about 0.32. The presence of the abrasive hydrophobic silica powder in this magnetorheological material efficiently removes the contamination products from the surface of the iron particles. The magnetorheological material whose particle component has been modified by abrader processing is stored in a polyethylene container.

Comparative Example 13

A magnetorheological material is prepared according to the procedure described in Example 12 with the exception that the hydrophobic silica powder is replaced with an identical amount of a hydrophilic silica gel dispersant (HI-SIL 233, PPG Industries). This silica gel dispersant, which has previously been disclosed as a dispersant in U.S. Patent No. 4,992,190, is dried in a convection oven at 130°C for 24 hours prior to use. This magnetorheological material contains a particle volume fraction of 0.32. This conventional magnetorheological material is stored in a polyethylene container.

Magnetorheological Activity for Examples 12 & 13

The magnetorheological materials prepared in Examples 12 and 13 are evaluated through the use of parallel plate rheometry. A summary of the magnetorheological effect observed for these magnetorheological materials at various magnetic field strengths and 25°C is provided in Figure 1. A significantly higher magnetorheo-

logical effect is obtained for the magnetorheological material utilizing particles wherein contamination products have been removed by the presence of an abrasive hydrophobic silica additive in an abrader process (Example 12) as compared to a magnetorheological material
5 containing conventional particles (Example 13). At a magnetic field strength of 5000 Oersted the magnetorheological effect exhibited by the magnetorheological material containing the abrader process modified particles is about 167% greater than that exhibited by a conventional magnetorheological material.

10 As can be seen from the above examples, magnetorheological materials that contain a particle component that has been modified by the removal of inherent contamination products through chemical treatment or abrader processing exhibit a significantly higher magnetorheological effect than conventional magnetorheological
15 materials.

Claims

1. A magnetorheological material comprising a carrier fluid and a magnetically active particle wherein the particle has been modified so that the surface of the particle is substantially free of
5 contamination products.
2. A magnetorheological material according to Claim 1 wherein the contamination products have been removed from the surface of the particle through abrader processing, chemical treatment, or a combination thereof.
- 10 3. A magnetorheological material according to Claim 2 wherein the abrader processing involves the physical removal of the contamination products by impacting the surface of the particle at a high velocity with an abrasive media.
4. A magnetorheological material according to Claim 3
15 wherein the abrasive media is an abrasive additive.
5. A magnetorheological material according to Claim 4 wherein the abrasive additive is selected from the group consisting of the oxides of aluminum, iron, chromium, zirconium, hafnium, titanium, silicon, and magnesium; the carbides, nitrides and borides
20 of aluminum, silicon and boron; cermets; or combinations thereof.
6. A magnetorheological material according to Claim 4 wherein the abrasive additive is selected from the group consisting of diamond dust, garnet, corundum, alumina, black mineral slag, Cr_2O_3 , HfO_2 , TiO_2 , MgO , glass, sand, hydrophobic silica, aluminum
25 silicates, pumice, rouge, emery, feldspar, SiC , B_4C , BN , Si_3N_4 , AlN , cerium oxide, ferrite, magnetite and fused alumina.
7. A magnetorheological material according to Claim 6 wherein the abrasive additive is hydrophobic silica, ferrite, or alumina.
- 30 8. A magnetorheological material according to Claim 4 wherein the high velocity is imparted by combining the magnetically

active particle, carrier fluid, and any optional ingredients, and thoroughly mixing with a spatula or the like and then more thoroughly mixing with a homogenizer, mechanical mixer, mechanical shaker, or an appropriate milling device such as a ball mill, sand mill, attritor mill, colloid mill, paint mill, pebble mill, shot mill, vibration mill, roll mill, horizontal small media mill, or the like.

9. A magnetorheological material according to Claim 3 wherein the abrasive media is a grinding media.

10. A magnetorheological material according to Claim 9 wherein the grinding media comprises balls, beads, pellets, pebbles, grit or shot comprised of various materials including stainless steel, ceramic, porcelain, flint, high carbon steel, high manganese steel, cast nickel alloy, low carbon forged steel, tungsten carbide, glass, zirconium silicate, zirconium oxide, and aluminum oxide.

15 11. A magnetorheological material according to Claim 9 wherein the velocity is imparted by a milling device selected from the group consisting of sand mills, ball mills, attritor mills, pebble mills, shot mills, vibration mills and horizontal small media mills.

20 12. A magnetorheological material according to Claim 9 wherein the grinding media is a wheel, disc, or blade, and the velocity is imparted by a roll mill.

25 13. A magnetorheological material according to Claim 2 wherein the chemical treatment is carried out by acid cleaning, alkaline cleaning, electrolytic cleaning, ultrasonic cleaning, or combinations thereof.

30 14. A magnetorheological material according to Claim 2 wherein the chemical treatment is carried out prior to either preparing the magnetorheological material or applying a protective coating to the surface of the particle and wherein the chemical treatment is selected from the group consisting of acid cleaning, alkaline cleaning, electrolytic cleaning, ultrasonic cleaning, metal reduction, plasma cleaning, ion etching, sputter cleaning, and combinations thereof.

15. A magnetorheological material according to Claim 2 wherein the contamination products are removed immediately prior to applying a protection coating to the surface of the particle.

16. A magnetorheological material according to Claim 15 wherein the protective coating is derived from nonmagnetic metals, ceramics, high performance thermoplastics, thermosetting polymers or combinations thereof.

17. A magnetorheological material according to Claim 16 wherein the protective coating is applied by physical deposition or by 10 chemical vapor deposition.

18. A magnetorheological material according to Claim 1 wherein the particle is comprised of a paramagnetic, superparamagnetic or ferromagnetic compound.

19. A magnetorheological material according to Claim 18 15 wherein the particle is comprised of a material selected from the group consisting of iron, iron alloys, iron nitride, iron carbide, carbonyl iron, chromium dioxide, low carbon steel, silicon steel, nickel, cobalt, and mixtures thereof.

20. A magnetorheological material according to Claim 1 20 wherein the particle is a metal powder selected from the group consisting of straight iron powders, reduced iron powders, insulated reduced iron powders, and cobalt powders.

21. A magnetorheological material according to Claim 1 wherein the particle is a straight iron powder, a reduced iron powder, 25 an iron-cobalt alloy powder or an iron-nickel alloy powder.

22. A magnetorheological material according to Claim 1 wherein the carrier fluid is selected from the group consisting of mineral oils, silicone oils, silicone copolymers white oils, paraffin oils, hydraulic oils, chlorinated hydrocarbons, transformer oils, halo- 30 genated aromatic liquids, halogenated paraffins, diesters, polyoxyalkylenes, perfluorinated polyethers, fluorinated hydrocarbons, fluorinated silicones, hindered ester compounds, cyanoalkylsiloxane homo-

polymers, modified carrier fluids having a conductivity less than about 1×10^{-7} S/m, polysiloxanes, and mixtures thereof.

23. A magnetorheological material according to Claim 22 wherein the carrier fluid is selected from the group consisting of 5 mineral oils, paraffin oils, silicone oils, silicone copolymers and perfluorinated polyethers.

24. A magnetorheological material according to Claim 23 wherein the carrier fluid is a silicone oil or a mineral oil.

25. A magnetorheological material according to Claim 1 10 wherein particle settling is minimized by the formation of a thixotropic network.

26. A magnetorheological material according to Claim 25 wherein the formation of the thixotropic network is assisted by the addition of a low molecular weight hydrogen-bonding molecule con- 15 taining hydroxyl, carboxyl, or amine functionality.

27. A magnetorheological material according to Claim 26 wherein the low molecular weight hydrogen-bonding molecule is selected from the group consisting of water; methyl, ethyl, propyl, isopropyl, butyl and hexyl alcohols; ethylene glycol; diethylene glycol; 20 propylene glycol; glycerol; aliphatic, aromatic and heterocyclic amines, including primary, secondary and tertiary amino alcohols and amino esters that have from 1-16 atoms of carbon in the molecule; methyl, butyl, octyl, dodecyl, hexadecyl, diethyl, diisopropyl and dibutyl amines; ethanolamine; propanolamine; ethoxyethylamine; 25 dioctylamine; triethylamine; trimethylamine; tributylamine; ethylene-diamine; propylene-diamine; triethanolamine; triethylenetetramine; pyridine; morpholine; imidazole; and mixtures thereof.

28. A magnetorheological material according to Claim 1 further comprising a surfactant.

29. A magnetorheological material according to Claim 28 30 wherein the surfactant is selected from the group consisting of ferrous oleate and naphthenate, sulfonates, phosphate esters, glycerol mono--

oleate, sorbitan sesquioleate, laurates, fatty acids, fatty alcohols, lithium stearate, sodium stearate, aluminum tristearate, precipitated silica gel, aluminum distearate, fluoroaliphatic polymeric esters and titanate, aluminate and zirconate coupling agents.

5 30. A magnetorheological material according to Claim 29 wherein the surfactant is a precipitated silica gel, a fluoroaliphatic polymeric ester, a phosphate ester, or a coupling agent.

31. A magnetorheological material according to Claim 30
10 wherein the precipitated silica gel is dried in a convection oven at a temperature of from about 110°C to 150°C for a period of time from about 3 hours to about 24 hours.

32. A magnetorheological material according to Claim 1
15 wherein the particle is present in an amount from about 5 to 50 percent by volume and the carrier fluid is present in an amount from about 40 to 95 percent by volume of the total magnetorheological material.

33. A magnetorheological material according to Claim 32
20 wherein the particle is present in an amount from about 15 to 40 percent by volume and the carrier fluid is present in an amount from about 60 to 85 percent by volume of the total magnetorheological material.

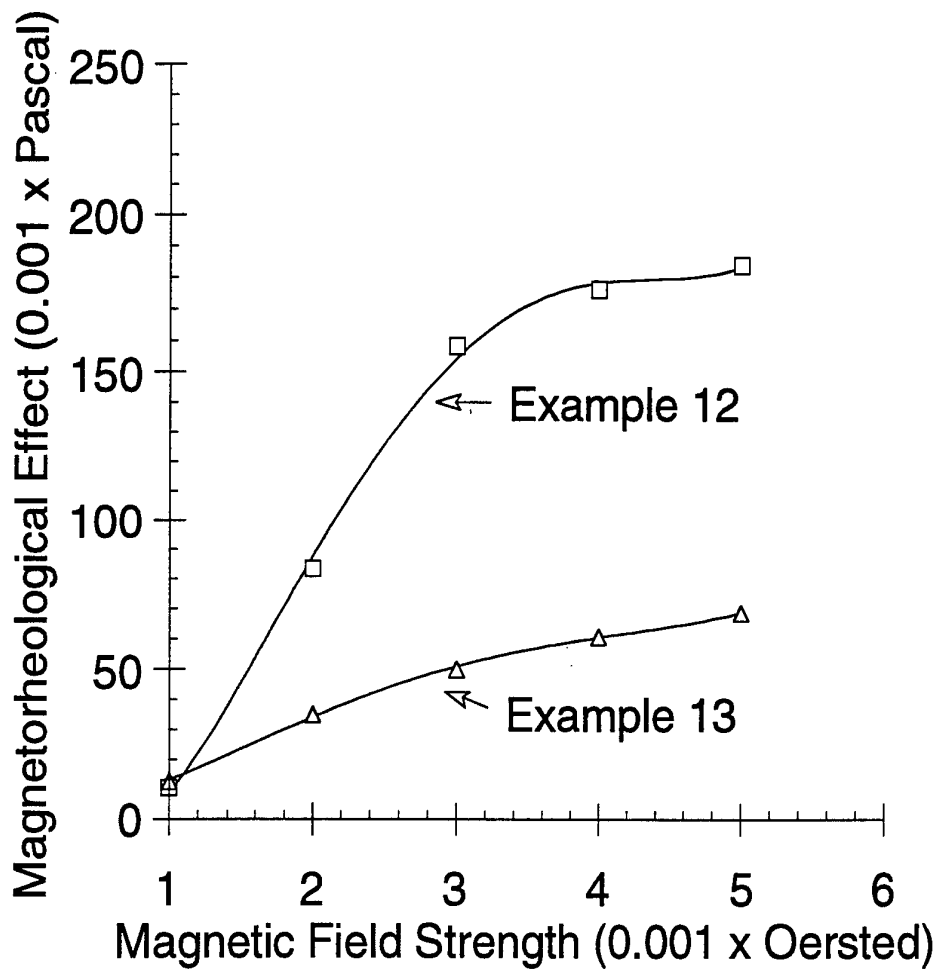


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10285

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(5) :H01F 1/28
 US CL :252/62.52, 62.54, 62.55, 62.56
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 U.S. : 252/62.52, 62.54, 62.55, 62.56; 51/281R, 313, 317, 318, 289R, 289S

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 none


C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU, A, 162,371 (Bataafsche) 23 October 1952. See page 2, line 28 - page 3, line 20; page 5, lines 11-29 and 33-39; and Composition N at page 7.	1-3, 8-14, 18-33
X	US, A, 3,764,540 (Khalafalla et al.) 9 October 1973. See abstract; col. 3, lines 6-28; and col. 4, lines 30-41.	1-6, 8-15, 18-25, 28-29, 32-33
X	US, A, Re. 32,573 (Furumura et al.) 5 January 1988. See col. 3, lines 43-55; col. 4, lines 15-21 and 61-68.	1-14, 18-22, 25, 28-29, 32-33
X	EP, A, 406,692 (Shtarkman) 9 January 1991. See page 3, lines 25-34; page 3, line 55 - page 4, line 44; page 5, lines 28-43; Table 2 at page 5; and claim 5 at page 7.	1-3, 8-20, 22-25, 28-33

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* & * document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 08 DECEMBER 1993	Date of mailing of the international search report 14 JAN 1994
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Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer  PRINCE WILLIS Telephone No. (703) 308-0661
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10285

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 2,661,596 (Winslow)08 December 1953.	1-33
A	US, A, 3,917,538 (Rosenweig)04 November 1975.	1-33
A	US, A, 4,992,190 (Shtarkman) 12 February 1991.	1-33