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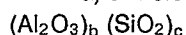
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Electrorheological fluids.

An electrorheological fluid composition comprising a dispersion of an aluminosilicate in an electrically highly resistive fluid vehicle, characterised in that the aluminosilicate comprises

a) a moiety of empirical formula



where b and c are any numerical values provided that the ratio of b/c lies in the range of 1:1 to 1:9,

b) mono- or divalent main group metal cations, hydrogen ions or optionally substituted ammonium ions, and

c) a non-aqueous polar adsorbate. eg a crystalline zeolite comprising a non-aqueous polar adsorbate, a particulate material for use as the disperse phase of an electrorheological fluid, which comprises such an aluminosilicate, and a process for the preparation of such a material.

COMPOSITIONS

The present invention relates to electroviscous (EV) fluid compositions (also known as electrorheological (ER) fluids), to a process for their preparation, and to their use in electrorheological fluid apparatus (ER apparatus), that is, apparatus which relies for its operation on the virtual solidification of the electrorheological (ER) fluid under an applied electric field against a shear stress.

5 Examples of ER apparatus include devices for the transmission of force by the solidified fluid, such as the transmission of torque in an ER clutch against shear stress between driving and driven surfaces, and apparatus in which valves are closed by the solidified fluid against the shear stress of hydrodynamic pressure on the solid plug, such as an ER damper using ER fluid valves.

10 ER apparatus is generally known, and the electric field applied in use of such apparatus is typically a d.c. field.

EV fluid compositions comprising a dispersion of a salified acid group containing organic polymer in a high electrical resistance fluid are known, for e.g. hydraulic clutches and dampers.

In conventional d.c. ER apparatus the static yield stress of a conventional ER fluid increases with increasing applied electric field intensity, and the ER fluid is useful in applications where the fluid is used in a static 'locked-on', 'solid' state, eg as a torque transmitter in a clutch.

However, ER fluids appear to require some d.c. conductivity to work; above a breakdown value for such a fluid, that d.c. conductivity increases markedly and there is arcing through the fluid.

Conventional ER fluids generally have a relatively low yield stress to applied field intensity ratio, a relatively high d.c. conductivity, and a relatively low electrical breakdown voltage.

20 The above low ratio means that a relatively high potential gradient must be applied to the fluid in use, and the electrodes must be of high opposed surface area and be close together. Together with the relatively high d.c. conductivity, this results in practice in undesirably high electrical power consumption, and consequent excessive heating of the apparatus (the electrical energy being converted to heat).

ER apparatus, eg ER clutches and dampers, may often have a moderately high operational temperature (eg in excess of 50° C), owing to electrical heating, and in the case of dampers to the conversion of absorbed mechanical energy to heat.

The electrical d.c. conductivity of ER fluids increases markedly and even exponentially with temperature, leading in practical use to a continuing cycle of further power consumption and increased apparatus temperature. Typically, such fluids in a d.c. apparatus exhibit a so called doubling temperature (ie the operating temperature increment which causes the conductivity to double) of about 6° C.

An equilibrium temperature below the long-term degradation temperature of the fluid may not be reached at an acceptable level of power consumption.

35 If this does not occur below breakdown conditions for the fluid, d.c. conductivity and power consumption increases until the capacity of the power source is exceeded and/or the apparatus and/or the fluid fails electrically.

It would be desirable to provide an ER fluid for use in 'static' d.c. applications which has a relatively high yield stress to applied field intensity ratio, a relatively low d.c. conductivity, and a relatively high electrical breakdown voltage.

40 Such a fluid is clearly of use in applications such as 'locked-on' ER clutches where good static performance is required.

Notwithstanding the foregoing, in a steady d.c. field, a conventional ER fluid in a d.c. apparatus often has poor dynamic performance, in that the dynamic shear stress of the fluid decreases markedly with the shear rate, and may even decrease exponentially with the shear rate (somewhat resembling the plastic behaviour of a solid past its yield point).

45 Such ER fluids in such an apparatus are clearly of limited use in applications such as ER dampers, where good dynamic performance of the fluid when already in shear is required.

It would be desirable to provide an ER fluid for use in 'dynamic' applications which has a relatively high shear stress to applied field intensity ratio which does not decrease markedly with shear rate, a relatively low conductivity, and a relatively high electrical breakdown voltage.

50 We have found that certain ER fluids used with an a.c. applied potential have these desirable properties, in particular if at least one of the electrodes by which the potential is applied is insulated from the fluid. Thus, eg the fluid in such an application tends to have good dynamic performance, in that the shear stress increases slightly, and possibly even significantly with increasing shear rate.

Such a fluid is clearly of use in applications such as ER dampers, requiring good dynamic performance.

The present invention provides ER fluids which may be used in

- a) static and/or d.c. applications and/or
- b) dynamic and/or a.c. applications, and avoid the foregoing disadvantages.

Accordingly, the present invention provides an ER fluid composition comprising a dispersion of a high alumina exchanger aluminosilicate comprising a non-aqueous polar adsorbate in an electrically highly resistive fluid vehicle.

The term 'adsorbate' herein comprises any material which is adsorbed, coordinated and/or absorbed onto/into the aluminosilicate structure.

The term 'exchanger aluminosilicate' herein means any inorganic material comprising

- a) a moiety of empirical formula

(Al_2O_3)_b (SiO_2)_c

where b and c are any numerical values provided that the ratio of b/c never exceeds 1, and

- b) mono- or divalent main group metal cations, hydrogen ions or optionally substituted ammonium ions.

In some of these materials the ions are exchangeable. The term embraces for example zeolites, micas and vermiculites, which may be natural or synthetic and commercially available or derivable from such materials e.g. by ion exchange, and extends to materials in which the cations are an infinitely variable mixture of two or more such species.

'High alumina' herein means any exchanger aluminosilicate in which the ratio of b:c lies in the range of 1:1 to 1:9. Crystalline materials are preferred. Examples of high alumina exchanger aluminosilicates are given hereinafter.

The particulate disperse phase, or the exchanger aluminosilicate comprised therein, which is used within the EV fluids of the present invention, forms an aspect of the invention. Zeolites within the scope of the aluminosilicates of the present invention include crystalline inorganic materials of which the empirical formula is

$\text{MaO}(\text{Al}_2\text{O}_3)_b' (\text{SiO}_2)_c' \text{Q}_d$ (I)

where

M is a mono or divalent main group metal cation or hydrogen or ammonium ion,

Q is a non-aqueous polar adsorbate,

a is 1 where M is divalent and 2 where M is monovalent, and

b', c', d are any numerical values, save that the ratio of b'/c' can never exceed 1:1 and c' is never less than 1.

They thus include natural and commercially available zeolites and materials derivable therefrom by ion exchange of M_a or by indirect exchange of water with Q. (Zeolites are known ion exchange and hygroscopic minerals with a labile water content).

The definition extends to materials in which M_aO is an infinitely variable mixture of two or more species falling within the definition of M_aO .

ER fluids of the present invention tend to have good ER properties, including for example a good static yield stress to applied potential ratio for a d.c. applied potential and/or a good dynamic shear stress to applied potential ratio for an a.c. applied potential.

When used herein in relation to the applied potential 'd.c.' means any essentially steady applied potential.

When used herein in relation to the applied potential 'a.c.' means any essentially cyclically variable applied potential (whether symmetrical about zero or not).

Suitable high alumina exchanger aluminosilicate in the present fluids include those wherein the or one cationic species is a Group IA or IIA metal, for example lithium, sodium, potassium, magnesium or calcium, and mixtures thereof, in particular potassium or calcium.

Suitable high alumina exchanger aluminosilicates also include those wherein the or one cationic species is a Group IIB metal. Examples of such cations include those of zinc and mixtures thereof with other suitable cations.

In the materials of the present invention the cations generally form 1 to 50% w/w of the disperse phase.

In one group of exchanger aluminosilicates of interest the ratio of b:c lies in the range of 1:1 to 1:5, in particular 1:1 to 1:3.

The adsorbate content of the present aluminosilicates may be any polar non-aqueous adsorbate capable of adsorption onto, coordination to and/or absorption into the structure of the exchanger aluminosilicate, and may be a pure gas or liquid or mixtures thereof or a solution, eg of a gas or polar solid, and may be inorganic or organic.

Typically the non-aqueous adsorbate is pure, but it may also be a non-aqueous solution of inorganic salts.

Examples of such salts include salts of any of the cations listed above with sulphuric or hydrochloric acids or with organic carboxylic or sulphonic acids.

The precise physical state of polar adsorbates which are adsorbed, coordinated and/or adsorbed into the aluminosilicate structure is not always clear.

5 However, suitable polar adsorbates which are capable of such binding include gases such as ammonia and alkylene oxides such as ethylene and propylene oxides, and liquids such as polar organic liquids e.g. cyclic ethers such as tetrahydrofuran and dioxan, acyclic amines such as ethylamine, ethylenediamine and aniline, and cyclic amines such as pyrrolidine, piperidine, piperazine and morpholine.

10 The terms 'gas' and 'liquid' used herein in relation to the normal state of the adsorbate at room temperature and atmospheric pressure' thus extend to all physical states of the relevant adsorbate in the present aluminosilicates, as is conventional e.g. for zeolites with a water content.

The adsorbate comprised in the aluminosilicate will generally be 1 to 10% w/w of the disperse phase, and preferably 1 to 5 % where the polar adsorbate is water, although it may vary widely up to larger values, e.g. up to 30% w/w.

15 However, we have found that above a certain polar adsorbate content the d.c. conductivity of corresponding ER fluids tends to increase disadvantageously.

Consequently the power consumption and tendency to electrical breakdown at lower applied d.c. voltages in commercial use also tend to increase disadvantageously, eg by more than 50% in the case of power consumption. This militates against such higher polar adsorbate contents for (generally static) d.c. applications, even though good values of static yield stress to applied d.c. potential ratio tend to be retained in the corresponding ER fluids.

For use with d.c. applied potentials, preferred fluids thus have a low d.c. conductivity, and thus often a low polar adsorbate content.

25 However, each suitable or the optimum polar adsorbate content may vary widely with the desired characteristics of the fluid, the particular disperse phase and the specific EV fluid vehicle.

Each such content may however be determined routinely.

For, example, preferred ER fluids for dynamic applications have a fast dynamic energisation response time. Such a desirable fast response time may often be associated with higher d.c. conductivities, which may be conferred eg by a higher polar adsorbate content of the ER fluid disperse phase.

30 Higher polar adsorbate contents (and hence higher d.c. conductivities) may be permissible even for use with d.c. applied potentials, where the polar adsorbate and/or each relevant disperse phase particle and/or exchanger aluminosilicate component of the phase or particle is encapsulated from the rest of the EV fluid e.g. by a hydrophobic fluid, gel or wax which is insoluble in the vehicle of the corresponding EV fluid of the present invention or by a surface layer of coke.

35 As noted hereinbefore, it is often favourable to use a.c. applied potentials for dynamic applications.

In such applications, the d.c. conductivity of the fluid and associated power losses have less effect.

This is especially the case if at least one of the electrodes by which the potential is applied is insulated from the fluid. If any of the present fluids is used in this way with a steady applied (d.c.) potential between the electrodes, no ER effect is observed, since the resistance of the insulating layer on at least one electrode is the current-limiting factor, and the negligible conduction through the fluid is insufficient to produce the ER effect.

When a cyclically varying ('a.c.') potential is applied between the mutually insulated electrodes, the current induced in the ER fluid is sufficient to give rise to an ER effect.

45 This ER effect is comparable to that achieved with the same d.c. potential. However, although an apparent current flows through the fluid in use, its magnitude is limited by the impedance of the apparatus rather than by the d.c. resistance of the fluid.

Power consumption for an equivalent shear stress will therefore generally tend to be reduced, so that the effect of the d.c. conductivity of the fluid on power consumption is controlled.

50 Higher polar adsorbate contents may be permissible, and even desirable with such a.c. applied potentials, especially where the disperse phase of the ER fluid is insulated from the rest of the relevant electrical circuit by an insulator on at least one of the electrodes.

It is still in general preferred that the total polar adsorbate contents of the disperse phase exchanger aluminosilicate is less than 10% w/w, .

55 In all the present exchanger aluminosilicates the polar adsorbate content is often exchangeable, and may be adjusted by equilibration of an adsorbate-free material (including water-free materials)

i) with a relevant polar adsorbate as a gas or a liquid or with air at a desired non-aqueous polar adsorbate partial vapour pressure, or

ii) as the disperse phase or a component thereof of an ER fluid, with the vehicle of the fluid which

has a controlled non-aqueous polar adsorbate content.

Generally, the adsorbate-free material is prepared by full desiccation of a corresponding water-containing (eg an at least partially hydrated) material.

Such dessication is usually carried out with heat and/or reduced pressure, optionally in the presence of a desiccant such as P_2O_5 .

As discussed further hereinafter, the present particles may be of 0.1 to 20 micron mean cross-dimension, eg less than 2 micron. Such particular particles of the present invention are preferred inter alia for their shorter desiccation equilibration times compared with larger particles.

Particular high alumina exchanger aluminosilicates thus include zeolites such as materials for the fluids of the present invention derivable from Zeolites A and X (Union Carbide) and Y (Strem), for example by indirect exchange of water content with non-polar aqueous adsorbate Q as in formula (I) and optionally conventional ion exchange of M_a . Thus for example in derivatives of the A series M_a may be inter alia potassium, K_2 (from Zeolite 3A), sodium, Na_2 Zeolite 4A), or calcium, Ca (from Zeolite 5A). Similarly, the Na_2 in Zeolite X derivatives may be optionally exchanged with the same cations. M_a may of course be exchanged with two or more ions to give a 'mixed' zeolite within the scope of present invention. These zeolites have cubic particle morphology.

Favoured exchanger aluminosilicate as, or as a component of, the disperse phases of an ER fluid include those with a low d.c. conductivity. These tend to give rise to fluids with reproducible and controllable operational parameters, and good static yield and/or dynamic shear stress to applied d.c. or a.c. voltage ratio, with low power consumption.

Such materials are particularly suitable for static and/or d.c. operation. This is especially the case in view of the high breakdown voltage in the corresponding EV fluids in d.c. operation.

In addition to those with a low non-aqueous adsorbate content generally (which is similar to that indicated hereinbefore as desirable), these include in particular those zeolites of formula (I) wherein M_aO is CaO especially Zeolite 5A derivatives.

Another group of favoured exchanger aluminosilicates disperse phases or exchanger aluminosilicate components of such phases include those giving rise to fluids with good static yield and/or dynamic shear stress to applied d.c. or a.c. voltage ratio at elevated temperatures.

Such temperatures may be for example over $40^\circ C$, such as 50 to $100^\circ C$ or 50 to $150^\circ C$.

Such ER fluid disperse phases or components are favoured for use in some typical working environments where the fluid itself (owing to heat generated in the fluid in use, eg as a clutch fluid) or the environment generally have such elevated temperatures.

Such present materials include those zeolites of formula (I) wherein M_aO is K_2O , especially Zeolite 3A (potassium) derivatives, having a low polar adsorbate content similar to that indicated hereinbefore as desirable.

As noted hereinbefore, the conductivity of ER fluid disperse phases (and particularly the d.c. conductivity) tends to increase with temperature, leading to higher power consumption, and in d.c. operation to a lower breakdown voltage.

There is thus a preferred group of materials within those with a good static yield and/or dynamic shear stress to applied d.c. or a.c. voltage ratio.

These are such materials which also have a low d.c. conductivity at elevated temperatures. Such materials are again particularly suitable for static and/or d.c. operation.

Such materials again include those of the present invention wherein M_aO is K_2O , especially Zeolite 3A derivatives.

Another group of favoured exchanger aluminosilicates disperse phases or components of disperse phases include those with a good static yield and/or dynamic shear stress to applied d.c. or a.c. voltage ratio over a wide temperature range. Such a range may be eg 0 to $100^\circ C$ or 0 to $150^\circ C$, for use in a wide variety of working environments.

Such materials include those single zeolite materials of formula (I) wherein M_aO is a mixture of two or more species within the definition of M_aO .

Such materials also include mixtures of two or more such single materials in each of which M_aO is a single species.

Where the different M_aO species are present in different zeolite exchanger aluminosilicates in the present EV fluid disperse phases, they may each be present in each particle of the EV fluid disperse phase, either in mutual admixture and/or as a coating of at least one on at least one other, that is, concentrated at and/or near the core surface.

Alternatively, the disperse phase may consist of a mixture of sets of particles, the particles in each set being essentially homogenous and of one zeolite exchanger aluminosilicate species.

In either type of mixture, two species of M_aO will often be used, chosen such that one has a good performance towards the lower end of the desired temperature range and the other towards the upper end.

The choice will also be dependent at the upper end of the range, however, on the thermal stability of both materials.

5 Such materials will be determined by the particular application profile required but include single and two species in which M_aO is CaO and K_2O , for example a Zeolite A derivative containing both CaO and K_2O , or a mixture of derivatives of Zeolites 5A and 3A.

In either case of such materials containing two M_aO species, the two may each be present as 1 to 99% and 99 to 1% w/w respectively of the total M_aO content.

10 The specific percentages will of course depend on the exact performance against temperature profile desired and the specific ions or materials used.

In all such species, the total polar adsorbate content of the disperse phase is desirably similar to those values indicated as favoured or preferred for an aluminosilicate hereinbefore.

15 As noted above, the d.c. conductivity of most ER fluids increases with their operating temperature, to the extent that many cannot be put to practical use under every-day working conditions. These include fluids which may have other desirable characteristics such as a fast energisation response time.

We have found that by using the present fluids in an a.c. ER apparatus, the typical doubling temperature of many such fluids is increased markedly.

The increase is typically from about 6 to about 25° C.

20 This increases the practical operating temperature range which is accessible by many such fluids without excessive power consumption.

Such materials thus include those wherein the or one cationic species within M_aO as hereinbefore defined is Ca.

25 Any of the foregoing disperse phase materials may advantageously consist of at least one exchanger aluminosilicate and at least one other material.

Again, the components may be either in mutual admixture and/or as a coating of at least one component on at least one other, that is, concentrated at and/or near the core surface. In the latter case the exchanger aluminosilicate will often be the surface component.

30 The other material may be any material compatible with the exchanger aluminosilicate(s) and such that the resultant disperse phase is compatible with the properties of the vehicle and desired properties of the corresponding EV fluid.

In the latter regard it may often be desirable that the alumina content and any polar adsorbate content of the total disperse phase are similar to those indicated hereinbefore as suitable, favoured or preferred for the exchanger aluminosilicate itself.

35 Where an exchanger aluminosilicate is in mutual admixture with, or present as a coating on or core for, another material in the disperse phase or particles, the exchanger aluminosilicate content will thus generally be much greater than that of other components. Its content may be for example 80 to 100% w/w of the disperse phase.

40 However, the optimum aluminosilicate (e.g. zeolite) proportion may vary widely from this figure with the specific ER fluid. The optimum aluminosilicate proportion may also vary widely from this figure with the specific desired EV effect. Either optimum may be readily ascertained by routine trial.

In all such species, the total polar adsorbate content of the disperse phase is desirably similar to those values indicated as favoured or preferred hereinbefore.

45 Among suitable other materials in the disperse phase particles of the EV fluids of the present invention are conductors and conventional inert coating and core materials.

Conductors include eg carbon, such as a coating of coke produced in situ upon a core of the present aluminosilicate (which materials are however much less preferred, as they tend to make the corresponding EV fluid more conducting to a disadvantageous extent).

Inert materials include materials such as cellulose derivatives, alumina and silica.

50 Again, the disperse phase may consist of a mixture of any of the foregoing particles with other particles, the other particles preferably being also capable of imparting ER properties to the fluid.

Such other particle species may of course also comprise polar adsorbate or a different polar adsorbate. Any such adsorbate is preferably polar adsorbate.

55 A total polar adsorbate content in the disperse phase which is similar to that described hereinbefore will be desirable.

Where all the particles of a disperse phase comprise a labile polar adsorbate content, it is desirable that the polar adsorbate content of the disperse phase is essentially homogeneous for operational stability of the corresponding EV fluid.

Suitable materials in the other particle species include organic ion-exchange resins.

The proportion of disperse phase in any ER fluid composition of the present invention is determined by the particular application of the composition, and the vehicle used, since these will determine the desired or acceptable viscosity. The desired proportion of the ER fluid which is disperse phase may thus be
 5 determined by routine optimisation.

However, in general a weight fraction of the total composition of 15 to 65% will be pumpable in use.

Depending on the vehicle, 25 to 60% by weight will be suitable for most applications.

For some applications, higher or lower viscosities and hence higher or lower fractions respectively may be tolerable or necessary.

10 Higher fractions may be used if the disperse phase is surface treated, or the vehicle has a fairly low viscosity, or if high temperature operation is envisaged, provided that the (solids content-related) no-field and/or room-temperature viscosity of the fluid is not thereby increased to a disadvantageous or impractical extent.

Where high static yield and/or dynamic shear stresses at relatively low d.c. or a.c. voltage gradients
 15 and/or current densities can be achieved, lower weight fractions, eg a weight fraction of 15 to 25% may be suitable.

Such a weight fraction may be suitable for the preferred fluids of the present invention in their most suitable (static, dynamic, d.c. or a.c.) application.

The disperse phase particles of the composition of the present invention may suitably have a mean
 20 cross-dimension of 0.1 to 50 micron, preferably 0.1 to 20 microns, and in particular less than 2 micron.

This is dependent at the upper end of the size range, however, on the minimum in-use field gap.

This gap should be at least 10 times the largest particle cross-dimension.

Conversely, particle cross-dimensions below 0.1 micron are best avoided, because of

- a) the undesirable effect thereof on the physical properties of the corresponding EV fluids, and
- 25 b) the generally higher potential toxicity of the dry disperse phase compared with that of larger particles.

For reproducible and controllable operational parameters of the corresponding EV fluids of the present invention, a narrow size distribution is advantageous.

Within the present fluids, suitable vehicles or components therefor include halogenated higher aliphatics
 30 such as chlorinated C₁₀₋₃₀ paraffins. These typically will be hydrocarbon cuts such as C₁₀₋₃₀, C₁₄₋₁₇, C₁₈₋₂₃ and C₂₄₋₃₀. Typically these will have a chlorine content of 25 to 60% w/w, for example 29 to 33% and 49 to 53%. Examples include the Cereclor series (registered trade mark, ICI). Suitable materials also include halogenated vinylic polymers, eg poly(trifluorovinylchloride) (eg Fluorolube FS-5; Hooker) and perfluoro polyethers such as Fomblin (Montedison).

35 Lower aliphatic derivatives such as cyclohexane, carbon tetrachloride and chloroform are also suitable as vehicle components.

Other suitable vehicles or components therefor include optionally substituted aromatic hydrocarbons, such as toluene and xylene.

Some aromatic vehicles which are less preferred, as they are more conducting than the earlier-named
 40 suitable components, include nitrobenzene, chlorobenzene, bromobenzene and o-dichlorobenzene,

Aromatic vehicles also include p-chlorotoluene and polychlorinated biphenyl fractions such as Aroclor 1242 (registered trade mark, Monsanto).

Silicones, especially polydialkylsiloxanes and substituted aromatic silicones such as bis(chlorinated phenyl) silicones are particularly favoured as vehicles or vehicle components. Examples include silicone oil
 45 C111/50 (ICI).

It will be appreciated that the first-named halogenated higher aliphatics and in particular the silicones are also favoured because of their generally lower toxicity than that of other vehicles/components.

All the foregoing may be used alone or (to the extent that they are miscible) in mutual admixture.

It is desirable to optimise the ER fluid dispersion, and to ensure that the (density-related) vehicle
 50 viscosity does not unduly increase composition viscosity.

To achieve this, it is advantageous that the vehicle does not differ in density too greatly from the disperse phase and they are preferably density matched. To achieve this in turn, the vehicle may be a mixture of at least two components, one denser, and the other less dense, than the disperse phase.

Since densities and viscosities vary widely with temperature any match should be at the desired
 55 operating temperature.

The preferred zeolite materials of the present invention have relative densities in the range of 1.5 to 2.2, and the preferred vehicles relative densities in the range of 0.8 to 1.3, both at 25°C.

The dispersion may also be optimised by using a surface-treated (e.g. surfactant-treated) disperse

phase and including a gellant in the vehicle such that the ER fluid composition has a rest viscosity which works against settling out of the disperse phase yet has a sufficiently low dynamic viscosity to be of use as an ER fluid.

The composition may also comprise a fluidiser such as sorbitan mono- or sesqui-oleate, although it is preferred to adjust the ER fluid viscosity as hereinbefore described.

The present invention also provides the use of a composition of the present invention as an EV fluid (for example in an applied electric field in hydraulic clutches or dampers).

The preparation and use of such compositions as EV fluids is conventional.

The exchanger aluminosilicate of the present invention may be prepared as in the following Example 1; the compositions of the present invention as in the following Example 2.

In general in the Examples the aluminosilicates are prepared by

a) equilibrating a essentially adsorbate-free (eg anhydrous) aluminosilicate at ambient temperature and pressure with a non-aqueous polar fluid,

b) optionally followed by partial removal of the resulting polar adsorbate from the product.

The starting aluminosilicate may be prepared from a commercially available ion-exchange aluminosilicate by conventional ion exchange followed by washing, and by dessication with heat and/or reduced pressure.

The operational potential gradient applied to the ER fluid of the present invention may conveniently be in the range of 1 to 20, eg 2 to 10 kV mm⁻¹.

For dynamic applications, the applied potential may suitably be a.c. as hereinbefore defined.

Such an a.c. potential may be varied in any manner which is cyclical. Thus it may be a potential varying about earth potential in any wave-form, including sinusoidal, square or saw-tooth (triangular).

It may also be a positive or negative similarly varying potential with respect to earth, eg pulsed d.c. at any mean potential with respect to earth.

No difference in the ER behaviour of a given ER fluid is observed whether the applied varying potential is a.c. or pulsed d.c. of the same magnitude and wave-form at any mean potential with respect to earth.

As might be expected, the observed ER effect increases with the applied a.c. potential gradient. It also increases with the power put in at a given maximum input potential. Thus, for a given maximum applied potential, the observed ER effect increases as the wave form is changed from triangular to sinusoidal to square.

Suitable frequencies for the cyclically variable potential will depend greatly on the type of ER device in which the present fluid is to be used.

Thus, at medium and higher frequencies problems associated with the skin effect, inductance, pick up and transmission, interference increase greatly. The consequent need for rigorous screening of all electrical parts consequently also greatly increases. These engineering problems may be acceptable eg in some specialist dampers (eg for aerospace applications), but not in automotive applications.

In general, the frequency may suitably be in the range of 1 to 6,000 Hz, for example 1 to 2,000 Hz.

Generally applicable frequencies are often in the range of 1 to 600, eg 1 to 200 Hz, favourably 3 to 150, and preferably 5 to 100 Hz.

We have found that with an a.c. applied potential, eg in a dynamic application, the present fluids exhibit a marked maximum shear stress at a specific frequency.

That frequency of maximum shear stress may well be another factor determining the desired operating frequency of the present ER fluids.

Such a frequency may indeed be used in controlling the response of the ER apparatus in which it is used.

As noted above, in a particular use embodiment, the present fluid may be subjected to an applied a.c. potential between electrodes, where at least one electrode comprises an electrically insulating surface coating.

By 'insulating surface coating' herein is meant any coating on such an electrode which gives an apparent d.c. conductivity of an ER fluid in the apparatus of less than 5×10^{-10} ohm⁻¹.cm⁻¹ at 25° C.

At the practical field frequencies used (as discussed above) the ER effect is comparable to that achieved with the same d.c. potential under the same conditions.

Suitable apparatus for applying a.c. potentials as hereinbefore defined to the present ER fluids in general is described in GB 89 , from which this application claims priority and which is incorporated herein by way of reference.

The varying potential may be applied by any suitable means which is capable of generating the necessary potentials, frequencies and wave-forms.

In general the impedance is relatively high, taking into account the factors mentioned above, so that a

large power source is not generally crucial in most practical ER applications which can be envisaged.

An industrial high-voltage signal generator will often be suitable.

The present invention is illustrated by the following Examples.

5

EXAMPLE 1

Preparation of aluminosilicates for EV fluids of the present invention is described in the following Table I. The following Zeolites are denoted by the Union Carbide reference numbers.

10

TABLE I

For Composition	Zeolite	Treatment
1	5A(Calcium)	450°C for 4 hr, then vacuum cool, treated with ultra high purity ammonia gas (BDH) to give ammonia saturated zeolite (RTP) then heat treated (+vacuum) at 255°C
2	5A(Calcium)	450°C for 2.5 hr, vacuum cooled in dessicator at < 1mbar, and the anhydrous product treated with high purity ethylene diamine, ED (BDH) vapour from 1 mbar to RTP, giving an ED-saturated zeolite, then heat treated (+vacuum) at 250°C, twice

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EXAMPLE 2

The following compositions were prepared by conventional dispersion of the zeolite in the vehicle.

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TABLE II

Composition	Percent w/w	
	Zeolite	Silicone Oil C111/50
1	50	50
2	46	54

EXAMPLE 3

The yield stress and current density at yield stress of the foregoing composition against applied voltage across a 0.5 mm gap was determined.

This was carried out on a rig and in the manner described in GB 1,501,635, giving the following results

TABLE III

VOLTAGE	COMPOSITION NUMBER	MEAN CURRENT DENSITY	MEAN YIELD STRESS
KV		$\mu\text{A cm}^{-2}$	kPa
1.5	1	1.111	2.15
2.0		2.531	3.23
2.5		4.753	4.05
3.0		7.438	4.90
3.5		11.728	6.24
4.0		16.358	7.13
4.5	2	20.370	7.30
3.0		0.036	2.16
3.5		0.053	3.01
4.0		0.070	3.32

EXAMPLE 4

The performance of an ER fluid of the present invention may also be dynamically tested. The apparatus is in the form of an ER clutch, comprising a pair of coaxially mounted cylindrical electrode clutch members, the outer stationary, the inner rotated.

The inner member is a solid copper cylinder, optionally covered with an insulating coating, and housed within the outer member, which is a hollow steel cylinder axially coterminous with the inner.

The dimensions of the clutch may vary, but for example the inner member may be 25.64mm long and 49.64mm in diameter, and optionally covered with an insulating coating of self-adhesive PVC tape 0.12mm thick.

The outer member may be of such diameter that the radial gap between the two is 1.20mm without the tape and 1.08mm with the tape on the inner member.

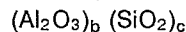
The ER fluid between the two electrodes may be one selected from those of the foregoing examples.

The inner member is rotated with a variable speed motor with feedback control, the transmitted torque being measured with a rotary torque transducer.

Claims

1. An electrorheological fluid composition comprising a dispersion of an aluminosilicate in an electrically highly resistive fluid vehicle, characterised in that the aluminosilicate comprises

5 a) a moiety of empirical formula



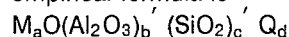
where b and c are any numerical values provided that the ratio of b/c lies in the range of 1:1 to 1:9,

b) mono- or divalent main group metal cations, hydrogen ions or optionally substituted ammonium ions, and

10 c) a non-aqueous polar adsorbate.

2. A composition according to claim 1, wherein the aluminosilicate is crystalline. (I)

3. A composition according to claim 1, wherein the aluminosilicate is a crystalline zeolite of which the empirical formula is



15 where

M is a mono or divalent main group metal cation or hydrogen or ammonium ion,

Q is a non-aqueous polar adsorbate,

a is 1 where M is divalent and 2 where M is monovalent, and

b', c', d are any numerical values, save that the ratio of b'/c' can never exceed 1:1 and c' is never less than

20 1,

4. A composition according to claim 3, wherein the cations comprise a Group IA or IIA metal.

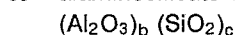
5. A composition according to claim 4, wherein the cations are lithium, sodium, potassium, magnesium or calcium, or a mixture thereof.

6. A composition according to claim 3, wherein the cations comprise a Group IIB metal.

25 7. A composition according to claim 6, wherein the cations are zinc, or a mixture thereof with other cations.

8. A composition according to claim 1, wherein the aluminosilicate within the disperse phase comprises ammonia or ethylenediamine as 0.05 to 10% w/w of the disperse phase.

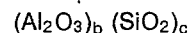
9. A particulate material for use as the disperse phase of an electrorheological fluid, which comprises an aluminosilicate which comprises a moiety of empirical formula



as defined in claim 1.

10. A process for the preparation of a material according to claim 9, characterised by ion exchange of and optional removal of water from an aluminosilicate, to give an aluminosilicate which comprises a moiety

35 of empirical formula



as defined in claim 1.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 2712

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	US-A-3 367 872 (T.W. MARTINEK) * Claims 1,2,6,10; column 2, line 72 - column 3, line 7; column 5, lines 37-63; column 5, line 74 - column 6, line 16 *	1,2	C 10 M 171/00 C 10 M 129/26 // (C 10 N 40/06 C 10 N 40:14 C 10 N 50:00)
A	EP-A-0 265 252 (THE BOARD OF REGENTS ACTING FOR AND ON BEHALF OF THE UNIVERSITY OF MICHIGAN) * Whole document *	1-10	
A	EP-A-0 219 751 (BAYER AG) * Claim 1; page 18, table 1; page 19, table 2; page 8, line 18 - page 9, line 31 *	1-10	
X	US-A-2 882 244 (R.M. MILTON) * Column 6, lines 40-73 *	10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-06-1990	Examiner RO TSAERT 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			