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(54) Electroviscous fluid.

(57) The electroviscous fluid is a suspension composed of a finely divided dielectric solid dispersed in an electrically nonconductive oil. The viscosity of the fluid increases swiftly and reversibly under an influence of electric field applied thereto and the fluid turns to a state of plastic or solid when the influence is sufficiently strong.

The electroviscous fluid of the present invention comprises

(A) 1-60% by weight of a dispersed phase composed of crystalline zeolite having the following properties (1), (2), (3) and (4).

(1) a general formula $M_{(x/n)}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$,
wherein, M is a hydrogen ion, a metallic cation or a mixture of metallic cations having an average electron value n; x and y are integers; w is a mole number of crystallization water,
(2) Si/Al atomic ratio (y/x) of 10-200,
(3) a water content of 0.05-10% by weight and
(4) an average particle size of 0.01-20 micrometer,
and

(B) 99-40% by weight of a liquid phase of an electric insulating oil having a viscosity of 0.65-500 centistokes at room temperature.

The electroviscous fluid exhibits an excellent electroviscous effect with a low electric power consumption together with a quick response at the application and cancellation of an electric potential difference.

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Electroviscous Fluid

FIELD OF THE INVENTION

The present invention relates to an electroviscous fluid which increases its viscosity when an electric potential difference is applied thereto.

DESCRIPTION OF THE PRIOR ART

The electroviscous fluid is a suspension composed of a finely divided hydrophilic solid dispersed in an electrically nonconductive oil. The viscosity of the fluid increases swiftly and reversibly under influence of an electric field applied thereto and the fluid turns to a state of plastic or solid when the influence of the electric field is sufficiently strong.

The electric field to be applied for changing the viscosity of the fluid can be not only that of a direct current but also that of an alternating current, and the electric power requirement is very small to make it possible to give a wide range of viscosity variation from liquid state to almost solid state with a small consumption of electric power.

The electroviscous fluid has been studied with an expectation that it can be a system component to control such apparatus or parts as a crutch, a hydraulic valve, a shock absorber, a vibrator, a vibration-isolating rubber, an actuator, a robot arm, a damper, for example.

USP 3,047,507 proposed various kinds of materials as the dispersed phase of an electroviscous fluid, and silica gel was mentioned as a preferable material among them. As the liquid medium for dispersion, an electrically nonconductive oil such as silicone oil was used. However, the electroviscous fluid using silica gel as the dispersed phase showed small electroviscous effect which is unsatisfactory for practical usages.

To improve the electroviscous effect, Japanese Patent Provisional Publication Tokkaisho 53-93186 proposed lithium polyacrylate particles as the dispersed phase. However, the electroviscous fluid using lithium polyacrylate particles as the dispersed phase has a disadvantage of large electric power consumption, because the lithium polyacrylate dispersed phase requires to contain a large amount of water to exhibit the electroviscous effect and the water induces an excessive electric conductivity.

Japanese Patent Provisional Publication Tokkaisho 62-95397 proposed electroviscous fluids using alumino-silicates having Al/Si atomic ratio of 0.15-0.80 at the surface and water content of 1-25% by weight as the dispersed phase, and mentioned electroviscous fluids using various kinds of crystalline zeolite as the dispersed phase in its examples.

In general, crystalline zeolites are expressed with following general formula:

$M_{(x/n)}\,[(AlO_2)_x(SiO_2)_y]\cdot wH_2O,$

wherein, M is a hydrogen ion, a metallic cation or a mixture of metallic cations having an average electron value n; x and y are integers; w is a mole number of crystallization water.

It is known that the crystalline zeolite becomes more hydrophilic when the Si/Al atomic ratio (y/x) becomes smaller.

In general, Al content of a crystalline zeolite as a whole particle is larger than Al content at the surface of it. In the case of the crystalline zeolite mentioned in Tokkaisho 62-95397, Al content of the crystalline zeolite as a whole particle is larger than Al content at the surface of it. Thus the Al/Si atomic ratio of 0.15-0.80 (which is equivalent to Si/Al atomic ratio of 1.25-6.67) at the surface is thought to correspond Si/Al atomic ratio of from about 1 to about 6.7 as a whole particle.

As mentioned above, the crystalline zeolite of such composition is hydrophilic and contains much water in its crystal. Accordingly, an electroviscous fluid using such crystalline zeolite as the dispersed phase shows an excessive electric conductivity to have a disadvantage of much electric power consumption.

In order to solve the problem caused by contained water, USP 4,744,914 proposed an electroviscous fluid using crystalline zeolite having the following general formula and containing substantially no adsorbed water as the dispersed phase;

$M_{(x/n)}\,[(AlO_2)_x(SiO_2)_y]\cdot wH_2O,$

wherein, M is a hydrogen ion, a metallic cation or a mixture of metallic cations having an average electron value n; x and y are integers; y/x of from about 1 to about 5; w is an indefinite number.

In order to eliminate the adsorbed water, USP 4,744,914 proposed a treatment wherein the electric insulating oil and the crystalline zeolite particles were treated under a temperature higher than temperatures expected to be employed at the usage of the electroviscous fluid for enough time required to attain necessary degree of degassing and elimination of water.

The characteristics of the electroviscous fluid disclosed in USP 4,744,914 is that, by using crystalline zeolite particles containing substantially no adsorbed water as the dispersed phase, the electroviscous fluid shows a reversible increase of viscosity under a high electrical potential difference without discharging undesirable water even at temperatures higher than 100°C. However, by the dehydration treatment of hydrophilic crystalline zeolite which contains much water originally, the surface of the zeolite becomes very active and tends to cause secondary coagulation.

Mechanism of the electroviscous effect is that the application of an electric potential difference to the electroviscous fluid induces formation of bridges among the particles dispersed therein due to polarization and elevation of viscosity of the fluid.

When the second coagulation of the dispersed particles accompanies at the same time, rearrangement of the dispersed particles occurs and takes a few minutes to reach a stabilized value of viscosity when an electric potential difference is applied thereto and a rapid response required to the electroviscous fluid cannot be expected. This phenomenon is conspicuous at low temperature zone where the movement of ions is slow, though it is not a serious problem at high temperature zone where the movement of ions is rapid. Accordingly, the electroviscous fluid disclosed in USP 4,744,914 has disadvantages such as the requirement of an additional step of drying and a slow response in the usage at room temperature where many applications are expected.

SUMMARY OF THE INVENTION

The object of the present invention is to provide an electroviscous fluid which requires no drying step at preparation and shows a quick responses at the application and cancellation of an electric potential difference and can exhibit a greater electroviscous effect with less electric power consumption.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1A is a graph showing the response behavior of the electroviscous fluid of Example 1 and

Fig.1B is a graph showing the response behavior of the electroviscous fluid of Comparative Example 5 at the application and cancellation of electric potential difference of 2 KV/mm at 25°C.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electroviscous fluid of the present invention comprises;

(A) 1-60% by weight of a dispersed phase composed of crystalline zeolite having the following properties (1), (2), (3) and (4).

(1) a general formula $M_{(x/n)}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$, wherein, M is a hydrogen ion, a metallic cation or a mixture of metallic cations having an average electron value n; x and y are integers; w is a mole number of crystallization water,

(2) Si/Al atomic ratio (y/x) of 10-200,

(3) a water content of 0.05-10% by weight,

(4) and an average particle size of 0.01-20 micrometer,

and

(B) 99-40% by weight of a liquid phase of an electric insulating oil having a viscosity of 0.65-500 centistokes at room temperature.

The crystalline zeolite having the above-mentioned general formula and Si/Al atomic ratio (y/x) of 10-200, preferably of 30-120 is hydrophobic and contains 0.05-10% by weight of water, especially 1-5% by weight of water at the preferable atomic ratio without any treatment. It shows a large electroviscous effect with less electric conductivity without drying. Accordingly the problem of secondary coagulation can be avoided.

When the Si/Al atomic ratio (y/x) is smaller than 10, electric conductivity due to water becomes larger and the drying step is required. When the Si/Al atomic ratio (y/x) is larger than 200, the electroviscous effect becomes smaller due to insufficient water content.

As an example of the crystalline zeolite having the Si/Al atomic ratio (y/x) of 10-200, ZSM-5 type zeolite is well known.

The particle size and shape of the crystalline zeolite to be used in the present invention can be easily controlled by adopting an appropriate manufacturing method to improve the sedimenting property of the particles which is an important property in an electroviscous fluid.

The particle size of the crystalline zeolite suitable for the dispersed phase of the electroviscous fluid is in the range of 0.01-20 micrometer, preferably in the range of 0.3-5 micrometer. When the size is smaller than 0.01 micrometer, initial viscosity of the fluid under no application of electric field becomes extremely large and the change in viscosity due to the electroviscous effect is small. When the size is over 20 micrometer, the dispersed phase can not be held sufficiently stable in the liquid.

As the electric insulating oil to constitute the liquid phase of an electroviscous fluid, hydrocarbon oils, ester oils, aromatic oils, halogenated hydrocarbon oils such as perfluoropolyether and polytrifluoromonochloroethylene, phosphazene oils and silicone oils are mentioned. They may be used alone or in a combination of more than two kinds. Among these oils, such silicone oils as polydimethylsiloxane, polymethylphenylsiloxane and polymethyltrifluropropylsiloxane are preferred, since they can be used in direct contact with materials such as rubber and various kinds of polymers.

The desirable viscosity of the electric insulating oil is in the range of 0.65-500 centistokes (cSt), preferably in the range of 5-200 cSt, and more preferably in the range of 10-50 cSt at 25°C. When the viscosity of the oil is too small, stability of the liquid phase becomes inferior due to an increased content of volatile components, and a too high viscosity of the oil brings about an heightened initial viscosity under no application of electric field to result in a decreased changing range of viscosity by the electroviscous effect. When an electric insulating oil having an appropriate low viscosity is employed as the liquid phase, the liquid phase can suspend a dispersed phase efficiently.

With regard to the ratio of the dispersed phase to the liquid phase constituting the electroviscous fluid according to the present invention, the content of the dispersed phase composed of the aforementioned crystalline zeolite particles is 1-60% by weight, preferably 20-50% by weight, and the content of the liquid phase composed of the aforementioned electrical insulating oils is 99-40% by weight, preferably 80-50% by weight. When the dispersed phase is less than 1% by weight, the electroviscous effect is too small, and when the content is over 60% by weight an extremely large initial viscosity under no application of electric field appears.

It may be possible to incorporate or compound other additives including surface active agents, dispersing agents, antioxidant and stabilizing agent into the electroviscous fluid of the present invention, as far as being within a range of not deteriorating the effects of the present invention.

The present invention will be illustrated with Examples hereinafter.

Example 1

40 parts by weight of H-ZSM-5 type crystalline zeolite particles (manufactured by Catalysts & Chemicals Industries Co.) having an average particle size of 3 micrometer, Si/Al atomic ratio of 100 and water content of 3.1% by weight were dispersed in a liquid phase component being 60 parts by weight of a silicone oil (Toshiba-Silicone Co.: TSF 451-20 ®) having 20 cSt viscosity at 25°C to prepare an electroviscous fluid in a suspension form.

Example 2

40 parts by weight of H-ZSM-5 type crystalline zeolite particles (manufactured by Catalysts & Chemicals Industries Co.) having an average particle size of 1 micrometer, Si/Al atomic ratio of 35.5 and water content of 4.0% by weight were dispersed in a liquid phase component being 60 parts by weight of a silicone oil (Toshiba-Silicone Co.: TSF 451-20 ®) having 20 cSt viscosity at 25°C to prepare an electroviscous fluid in a suspension form.

Example 3

40 parts by weight of H-ZSM-5 type crystalline zeolite particles (manufactured by Catalysts & Chemicals Industries Co.) having an average particle size of 2 micrometer, Si/Al atomic ratio of 13 and water content of 4.5% by weight were dispersed in a liquid phase component being 60 parts by weight of a silicone oil (Toshiba-Silicone Co.: TSF 451-20 ®) having 20 cSt viscosity at 25 °C to prepare an electroviscous fluid in a suspension form.

Comparative Example 1

A silica-gel (Nippon Silica Co.: NIPSIL VN-3 ®) was treated to make the water content to 6% by weight, and 13 parts by weight thereof were dispersed in a liquid phase component being 87 parts by weight of a silicone oil (Toshiba-Silicone Co.: TSF 451-20 ®) having 20 cSt viscosity at 25 °C to prepare an electroviscous fluid in a suspension form.

Comparative Example 2

40 parts by weight of Na-moldenite type crystalline zeolite particles (manufactured by Catalysts & Chemicals Industries Co.) having an average particle size of 1 micrometer, Si/Al atomic ratio of 5.5 and water content of 13% by weight were dispersed in a liquid phase component being 60 parts by weight of a silicone oil (Toshiba-Silicone Co.: TSF 451-20 ®) having 20 cSt viscosity at 25 °C to prepare an electroviscous fluid in a suspension form.

Comparative Example 3

30 parts by weight of Na-Y type crystalline zeolite particles (manufactured by Catalysts & Chemicals Industries Co.) having an average particle size of 1 micrometer, Si/Al atomic ratio of 2.5 and water content of 20% by weight were dispersed in a liquid phase component being 70 parts by weight of a silicone oil (Toshiba-Silicone Co.: TSF 451-20 ®) having 20 cSt viscosity at 25 °C to prepare an electroviscous fluid in a suspension form.

Comparative Example 4

The same Na-Y type crystalline zeolite particles (manufactured by Catalysts & Chemicals Industries Co.) having an average particle size of 1 micrometer, Si/Al atomic ratio of 2.5 and water content of 20% by weight as used in comparative example 3 were dried at 275 °C for 5 hours under vacuum, then cooled for 15 hours under vacuum to room temperature. 30 parts by weight of the dried particles were dispersed in a liquid phase component being 70 parts by weight of a silicone oil (Toshiba-Silicone Co.: TSF 451-20 ®) having 20 cSt viscosity at 25 °C to prepare an electroviscous fluid in a suspension form.

Each of the electroviscous fluids prepared in Examples 1-3 and Comparative Examples 1-4 were subjected to measurements of the electroviscous effect. The results are shown in Table 1. The electroviscous effect was measured with a double-cylinder type rotary viscometer to which a direct current was applied with an electric potential difference of 0-2 KV/mm between the outer and inner cylinder, and the effect was evaluated with shearing force under the same shearing speed (366 sec^{-1}) at 25 °, together with measurement of electric current density between the inner and outer cylinders. (radius of inner cylinder: 34mm, radius of outer cylinder: 36mm, height of inner cylinder: 20mm)

In Table 1, To is the shearing force under no application of electric potential difference, T is the shearing force under application of electric potential difference of 2 KV/mm, T-To is the difference of T and To and the current density is the value under application of electric potential difference of 2KV/mm.

The value of T-To indicates the magnitude of electroviscous effect of the fluid. That is, a fluid showing a larger T-To in Table 1 exhibits a larger electroviscous effect. And the value of the current density ($\mu A/cm^2$) concerns an electric power required to apply the electric potential difference (2KV/mm).

Table 1

	To (g•cm)	T (g•cm)	T-To (g•cm)	Current Density ($\mu A/cm^2$)
Example 1	77	1190	1113	19
Example 2	69	695	626	10
Example 3	99	1450	1351	210
Comparative Example 1	255	540	285	21
Comparative Example 2	142	1230	1088	over 1000
Comparative Example 3	47	635	588	over 1000
Comparative Example 4	121	1120	999	24
To: Shearing force under no application of electric potential difference				
T: Shearing force under application of electric potential difference (2KV/mm)				

The electroviscous fluids of Examples 1-3 showed large electroviscous effects with little electric power consumptions.

On the other hand, the electroviscous fluids of Comparative Example 1 using silica gel as the dispersed phase showed an inferior electroviscous effect though the electric power consumption was small. The electroviscous fluids of Comparative Example 2 and 3 using high water content crystalline zeolite as the dispersed phase showed enormous electric power consumption.

The electroviscous fluids of Example 4, which used the same crystalline zeolite particles as the dispersed phase after drying, showed a large electroviscous effect with less electric power consumption. However, as can be observed in attached Fig.1B, the electroviscous fluid of Comparative Example 4 showed unstable behavior at the application of the electric potential difference E (2 KV/mm) and delayed response at the cancellation of the electric potential difference. The reason of this phenomenon is supposed to be caused by secondary coagulation of zeolite particles.

On the other hand, as can be observed in Fig. 1A, the electroviscous fluid of Example 1 showed a rapid and sharp response at the application and cancellation of electric potential difference (2 KV/mm).

In Fig. 1A and Fig.1B, E in abscissa shows the period of the application of electric field 2 KV/mm at 25 °C and ordinate shows the shearing force observed.

Claims

1. An electroviscous fluid comprising;

(A) 1-60% by weight of a dispersed phase composed of crystalline zeolite having the following properties (1), (2), (3) and (4).

(1) a general formula $M_{(x/n)}\,[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$,
wherein, M is a hydrogen ion, a metallic cation or a mixture of metallic cations having an average electron value n; x and y are integers; w is a mole number of crystallization water,
(2) Si/Al atomic ratio (y/x) of 10-200,
(3) a water content of 0.05-10% by weight and
(4) an average particle size of 0.01-20 micrometer,
and

(B) 99-40% by weight of a liquid phase of an electric insulating oil having a viscosity of 0.65-500 centistokes at room temperature.

2. An electroviscous fluid according to claim 1 wherein the Si/Al atomic ratio (y/x) of the crystalline zeolite is 30-120.

3. An electroviscous fluid according to claim 1 wherein the electric insulating oil is a silicone oil.

4. An electroviscous fluid according to claim 1 wherein the water content of the crystalline zeolite is 1-5% by weight.

5. An electroviscous fluid according to claim 1 wherein the average particle size of the crystalline zeolite is 0.3-5 micrometer.

6. An electroviscous fluid according to claim 3 wherein the silicone oil has a viscosity of 5-50 centistokes at room temperature.

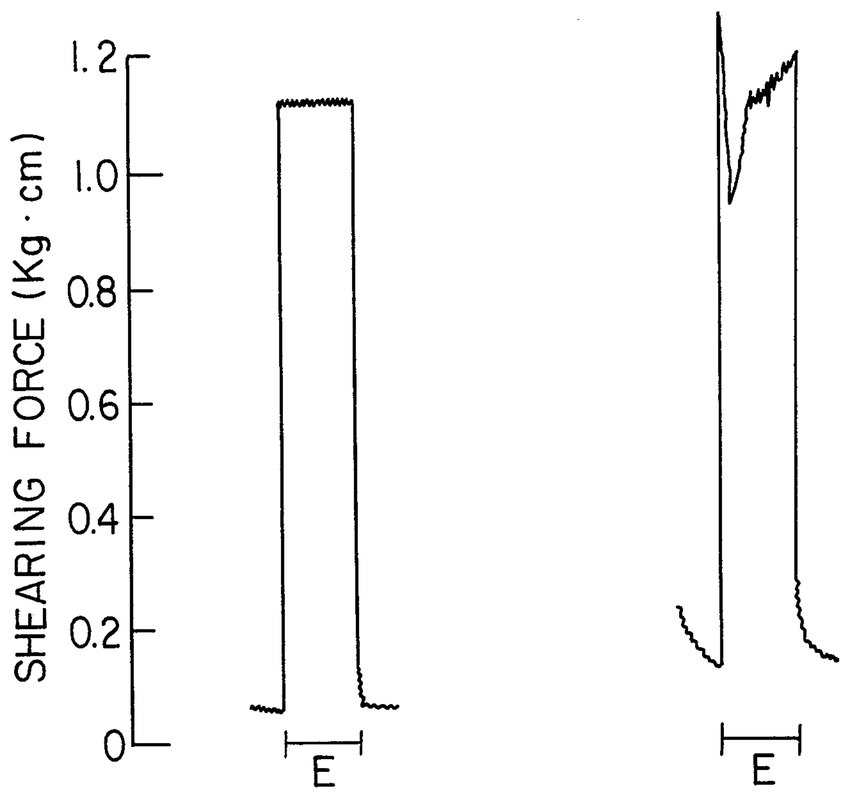
7. An electroviscous fluid according to claim 1 wherein the dispersed phase is 20-50% by weight and the liquid phase is 50-80% by weight.

8. An electroviscous fluid according to anyone of claims 1-7
additionally containing additives including surface active agents, dispersing agents, antioxidants and/or stabilizing agents.

9. A method for preparing an electroviscous fluid according to anyone of claims 1-8,
characterized in that
the component (A) of claim 1 is dispersed in component (B) of claim 1.

10. Use of the electroviscous fluid according to anyone of claims 1-8 as a system component to control such apparatus or parts as a crutch, a hydraulic valve, a shock absorber, a vibrator, a vibration-isolating rubber, an actuator, a robot arm or a damper.

FIG. 1A FIG. 1B



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EUROPEAN SEARCH REPORT

Application Number

EP 89 12 2000

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	FR-A-2 612 910 (MIZUSAWA INDUSTRIAL CHEMICALS) * Claims 1,9,20; page 16, paragraph 1; page 9, paragraphs 2,3; page 11, paragraphe 2; page 12, paragraphs 1,2; pages 29-38; example 9 *	1-7,9	C 10 M 171/00 C 10 M 125/26 // C 10 N 40:00 C 10 N 40:14 C 10 N 60:00
Y	---	8,10	
Y	EP-A-0 170 939 (BAYER) * Claims 1,2; page 1, paragraph 1; page 7, paragraph 3 - page 8 * ---	8,10	
D,Y	US-A-3 047 507 (W.M. WINSLOW) * Claim 1 * -----	8,10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08-03-1990	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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