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(54) **Electroviscous electrically insulating fluids.**

(57) In an electrically insulating liquid medium there are mixed (a) 0.1 - 50 wt% of dispersed solid particles of size 10 nm - 200 µm (e.g. silica gel), (b) 0.1 - 5 wt% of an acid, base or salt, (c) a polyhydric alcohol (e.g. ethylene glycol) and (d) an antioxidant (e.g. 0.01 - 10 wt% of a phenol or amine) which prevents oxidation of the liquid and the alcohol and/or a corrosion inhibitor (e.g. 0.001 - 10 wt% of a benzotriazole derivative or imidazole) which prevents corrosion of the electrode and generation of metallic ions. Optionally an agent to assist dispersing of the solid particles is included (e.g. a sulphonate or phosphonate).

The resultant electroviscous fluid can have good effects, including responsiveness and reproducibility and durability when used at temperatures up to 100°C and can be used in electrical control of mechanical devices by utilizing its viscosity change.

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ELECTROVISCOUS ELECTRICALLY INSULATING FLUIDS

The present invention relates to an electroviscous fluid, the viscosity of which can be controlled by applying voltage, and in particular to an electroviscous fluid, in which the viscosity is changed rapidly and reversibly from low temperature range to high temperature range when voltage is applied and a long and stable electroviscous effect is obtained and which can be used for electrical control of mechanical devices such as a clutch, valve or shock absorber.

An electro-rheological fluid or electroviscous fluid, in which the viscosity of the fluid is changeable by the application of voltage, has been known for many years (Duff, A.W., Physical Review, Vol. 4, No. 1 (1896) 23). Early studies on electroviscous fluids were concentrated on the system containing liquid only, and the effect was not strong enough. Later, studies have been made on the electroviscous fluid of a solid disperse system, where a considerable electroviscous effect could be obtained.

For example, Winslow proposed an electroviscous fluid, using paraffin, silica gel powder and adding water to make the system slightly electroconductive (Winslow, W.M., J. of Applied Physics, Vol. 20 (1949) 1137). From this study by Winslow, the electroviscous (electro-rheological) effect of the electroviscous fluid is called the ER effect or Winslow effect.

On the other hand, study has also been made of the mechanism of the electroviscous effect (ER effect) in the electroviscous fluid. For example, Klass reported that each particle, i.e. the dispersed phase in an electroviscous fluid, generates the induced polarization of the double layer in an electrical field and this was the primary cause of such effect (Klass, D.L. et al., J. of Applied Physics, Vol. 38, No. 1 (1967) 67). If this is explained from the principle of the electric double layer, the ions absorbed on the dispersed solids (such as silica gel) are evenly arranged on the outer surface of dispersed solids when E (electrical field) = 0, while polarization occurs in the ion distribution when E (electrical field) = finite value and each particle exerts an electrostatic action on each other in the electric field. Thus, each particle forms a bridge (cross-linkage) between electrodes and the shear-resistant force to the external stress, i.e., ER effect.

With full consideration given on the mechanism of the ER effect in the electroviscous fluid of this solid dispersing system, various proposals have been made to increase and to stabilize the viscosity of an electroviscous fluid. For example, a proposal was made to use silicon dioxide type fine particles, on which ferroelectric powder and a small quantity of water are absorbed (Japanese Provisional Patent Publication 53-17585), whereas this is disadvantageous and unsatisfactory in various points such as the response, the reproducibility of ER effect, low electroviscous effect, and the stability of ER effect for a long time. Particularly, the conventional electroviscous fluid containing moisture is disadvantageous in that water is evaporated at high temperature of more than 80°C. Further, even at less than 80°C, there are also problems such as unstability due to the migration of moisture on the surface of the particles, the problem of durability by elution of electrode metal (such copper) when high electric field is applied, the enhancement of ionization by increase in temperature and increase of electric current, or unstable temperature property, and other problems caused by the presence of moisture.

It is an object of this invention to provide an electroviscous fluid, by which it is possible to maintain the ER effect stably up to high temperature of 100°C and to achieve high durability.

The electroviscous fluid according to this invention consists of electrically insulating fluid , dispersed porous solid particles, at least one acid, salt or base, at least one polyhydric alcohol and/or water, and an antioxidant and/or corrosion inhibitor.

When a polyhydric alcohol and an acid, salt or base is added to the electroviscous fluid containing electrically insulating fluid and porous solid particles, the electroviscous effect is stabilized in a wide temperature range up to high temperature, and a high electroviscous effect is obtained. However, there is a problem as to durability because of the oxidation of electrically insulating fluid, porous solid particles or polyhydric alcohol, or the increase of electrically conductive substance caused by the corrosion of electrode under high voltage.

In the present invention, an antioxidant and/or corrosion inhibitor are added to such electroviscous fluid to obtain better effects in the responsiveness of viscosity change in a wide temperature range up to high temperature, reproducibility, electroviscous effect and, especially, durability.

Description is now given of each component of the electroviscous fluid according to the present invention.

First, as the electrically insulating fluid, which is the dispersion medium in the electroviscous fluid, a mineral oil or synthetic lubricant oil can for example be used. More specifically, there are oils such as a paraffinic oil, naphthenic oil, poly-α-olefin, polyalkylene glycol, silicone oil, diester, polyolester, phosphoric acid ester, silicon compound, fluorine compound or polyphenylether. An electroviscous fluid having the viscosity of 5 - 300 cP at 40° C can be used.

As the porous solid particles, for example, silica gel, moisture-containing resin, diatomaceous earth, alumina, silica-alumina, zeolite, ion exchange resin or cellulose, can be used. The porous solid particles having a particle size of 10 nm - 200 µm are used in the ratio of 0.1 - 50 wt%. If it is less than 0.1 wt%. the ER effect is too low, and it exceeds 50 wt%, the dispersing property is decreased.

A dispersing agent may optionally be used in the electroviscous fluid of this invention in order to disperse the porous solid particles evenly and stably.

Suitable dispersing agents are sulphonates , phenates, phosphonates, succinic acid imides, amines or non-ionic dispersing agents, e. g., magnesium sulphonate, calcium sulphonate, calcium phosphonate, polybutenyl succinic acid imide, sorbitan mono-oleate or sorbitan sesqui-oleate. These are normally used at the ratio of 0.1 - 10 wt%, while they need not be used if the porous solid particles are easily dispersed.

Polyhydric alcohol components, and acid, salt or base components may be used alone to obtain the higher ER effect. Polyhydric alcohol components keep the ER effect at high temperature, while acid, salt or base components can increase the polarization effect. By using these components simultaneously, it is possible to increase the ER effect at high temperature.

As the polyhydric alcohol, dihydric alcohol and trihydric alcohol are effective. It is preferable to use ethylene glycol, glycerin, propanediol, butanediol or hexanediol, and to use these substance at the ratio of 1 - 30 wt% to porous solid particles, and more preferably at 2 - 15 wt%. If it is less than 1 wt%, the ER effect is too low. If it exceeds 30 wt%, it is undesirable because electric current then flows too easily.

As the acid components, inorganic acids such as sulfuric acid, hydrochloric acid, nitric acid, perchloric acid, chromic acid, phosphoric acid or boric acid, or inorganic acids such as acetic acid, formic acid, propionic acid, lactic acid, isolactic acid, valeric acid, oxalic acid or malonic acid can be used.

As the salts, any compound consisting of a metal or base radical (such as NH_4^+, $N_2H_5^+$) and acid radical can be used. In particular, it is preferable to use a substance which dissolves in a polyhydric alcohol or mixture of polyhydric alcohol and water and is dissociated, or typical ionic crystal such as a halogenated compound of an alkali metal or alkali earth metal, or the alkali salt of an organic acid; e.g., LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, LiBr, NaBr, KBr, $MgBr_2$, LiI, NaI, KI, $AgNO_3$, $Ca(NO_3)_2$, $NaNO_2$, NH_4NO_3, K_2SO_4, Na_2SO_4, $NaHSO_4$, $(NH_4)_2SO_4$ or an alkali salt of an acid such as formic acid, acetic acid, oxalic acid or succinic acid.

A base to be used can be a hydroxide of an alkali earth metal, carbonate of an alkali metal or amine . It is preferable to use a substance which is dissolved in polyhydric alcohol or in the mixture of polyhydric alcohol and water and is dissociates, e. g., NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$, K_3PO_4, Na_3PO_4, aniline, an alkylamine or ethanolamine. The salt and the base as described above may be used simultaneously.

The acid, salt or base may be used in the ratio of 0.01 - 5 wt% to the entire electroviscous fluid. If it is less than 0.01 wt%, the ER effect is too low; and if it exceeds 5 wt%, it is not desirable because electric current flows more easily and the electric power consumption increase.

The present invention is characterized in that an antioxidant and/or corrosion inhibitor is added to the electroviscous fluid.

Antioxidant is added to prevent the oxidation of the electrically insulating liquid and polyhydric alcohol and also to stop the increase of electric conductivity due to oxidation products. Corrosion inhibitor is added to prevent the increase of electrical conductivity caused by the generation of metallic ions due to the corrosion of the electrode (such as copper) under high voltage.

Antioxidants inactive to polarizing agent and porous solid particles may be used. Phenol type or amine type antioxidants can be used. Suitable phenoltype antioxidants, are 2,6-di-t-butylparacresol, 4,4′-methylenebis (2,6-di-t-butylphenol) and 2,6-di-t-butylphenol, As amine type antioxidants, there are dioctyldiphenylamine, phenyl-α-naphthylamine, alkyldiphenylamine or N-nitrodiphenylamine. Preferably, 2,6-di-t-butylparacresol or dioctyldiphenylamine are used. These substances can be used in the ratio of 0.01 - 10 wt% to the entire electroviscous fluid, and more preferably at 0.1 - 2.0 wt%. If it is less than 0.01 wt%, antioxidant effect is too low. If it exceeds 10 wt%, problems occur such as color tone deterioration, increased turbidity, generation of sludge and increase of viscosity.

It is preferable to use a corrosion inhibitor, which is inactive to the polarizing agent and porous solid parti cles, e. g., nitrogen compounds such as benzotriazole and its derivatives, imidazoline, pyrimidine derivative, and compounds containing sulfur and nitrogen, such as 1,3,4-thiadiazolepolysulfide, 1,3,4-thiadiazolil-2,5-bisdialkyldithiocarbamate, 2-(alkyldithio)-benzoimidazole or β -(o-carboxybenzylthio) propionitrile or propionic acid; more preferably, benzotriazole or its derivatives can be used. It is preferable to use these substances in the ratio of 0.001 - 10 wt% to the entire electroviscous fluid, and more preferably at 0.01 - 1.0 wt%. If it is less than 0.001 wt%, there is no corrosion inhibition effect. If it exceeds 10 wt%, problems occur such as color tone deterioration, increased turbidity, generation of sludge, and increase in the consistency of the fluid.

It is naturally possible to also include water in such a proportion as not to reduce the ER effect in the electroviscous fluid.

The invention is now illustrated by the following examples and comparative example

Preparation of electroviscous fluid	
Mineral oil	89.1% by wt
Silica gel	6% by wt
Ethylene glycol	0.4% by wt
Acetic acid	0.5% by wt
Succinic acid imide	4% by wt

The above substances are mixed together to make a basic fluid.

Using this basic mixture, various types of electroviscous fluids of the invention having the compositions given in Table 1 below were prepared: the ratios are by weight

Table 1

Example 1	Fluid : Antioxidant (A) = 99.7 : 0.3
Example 2	Fluid : Corrosion inhibitor (a) = 99.9 : 0.1
Example 3	Fluid : Antioxiant (A) : Corrosion inhibitor (a) = 99.6 : 0.3 : 0.1
Example 4	Fluid : Antioxidant (B) : Corrosion inhibitor (b) = 99.6 : 0.3 : 0.1
Example 5	Fluid : Antioxidant (A) : Corrosion inhibitor (a) = 97.9 : 2.0 : 0.1
Example 6	Fluid : Antioxidant (A) : Corrosion inhibitor (a) = 96.9 : 3.0 : 0.1
Example 7	Fluid : Antioxidant (A) : Corrosion inhibitor (a) = 98.5 : 0.5 : 1.0
Example 8	Fluid : Antioxidant (A) : Corrosion inhibitor (a) = 97.5 : 0.5 : 2.0
Comparative example	Fluid only

The viscosity of the mineral oil was adjusted in such manner that all of these samples have a viscosity of 80 cP at 40° C.

In the above table, 2,6-di-t-butylphenol was used as the antioxidant (A) and dioctyldiphenylamine was used as (B). A benzotriazole derivative was used as the corrosion inhibitor (a) and imidazole was used as corrosion inhibitor (b).

The properties of the samples of the fluid were tested as follows:

With the above electroviscous fluids at 40° C and 90° C, the following parameters were measured using a voltage-applicable rotation viscosimeter:

- Responsiveness:

Evaluated by the time (second) until viscosity is stabilized when AC electric field is changed from 0 to 2×10^6 (V/m).

- Reproducibility:

Evaluated by the ratio of viscosity change at the electric field of 2×10^6 (V/m) when AC electric field is repeatedly changed in a cycle of $1 - 2 \times 10^6$ (V/m) $\rightarrow$ 0.

-Durability:

Evaluated by the variation (%) of the viscosity over time when AC electric field is stabilized at 2 x 10^6 (V/m). (Measuring time: 5 hours)

-Electroviscous effect:

Evaluated by the ratio of the viscosity at a AC electric field of 2 x 10^6 (V/m) to the viscosity at an electric field of 0 (V/m).

The results of the evaluation are summarized in Table 2.

Table 2

		Responsiveness (sec.)	Reproducibility (%)	Durability (%)	Electroviscous effect (ratio)
Example 1	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	96	7
Example 2	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	95	7
Example 3	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	98	7
Example 4	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	97	7
Example 5	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	98	8
Example 6	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	94	7
Example 7	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	98	8
Example 8	40°C	1 or less	±2	100	4
	90°C	1 or less	±2	93	7
Comparative example	40°C	1 or less	±2	100	5
	90°C	1 or less	±2	90	7

As is evident from Table 2, when an antioxidant and/or corrosion inhibitor is added to the electroviscous fluid, excellent effects are obtained, such as responsiveness of viscosity change in wide temperature range up to high temperature, reproducibility, electroviscous effect and durability.

Claims

1. An electroviscous fluid comprising an electrically insulating fluid as the dispersant and (a) porous solid particles as the dispersed phase, (b) at least one substance selected from acids, salts and bases and (c) at least one substance selected from polyhydric alcohols and water, characterized in that it also contains (d) an antioxidant and/or corrosion inhibitor.

2. An electroviscous fluid as claimed in Claim 1, wherein the antioxidant is a phenol or amine.

3. An electroviscous fluid as claimed in Claim 2, wherein the antioxidant is 2,6-di-t-butyl-para-cresol or dioctyl diphenylamine.

4. An electroviscous fluid as claimed in Claim 2 or 3, wherein the antioxidant is present in an amount of 0.01 to 10 wt%.

5. An electroviscous fluid as claimed in Claim 1, wherein the corrosion inhibitor is a benzotriazole or

derivative thereof, imidazoline, pyrimidine derivative or compound containing sulfur and nitrogen.

6. An electroviscous fluid as claimed in Claim 5, wherein the corrosion inhibitor is present in an amount of 0.001 to 10 wt%.

7. An electroviscous fluid as claimed in any preceding claim, which also includes an agent which assist the dispersion of the solid particles.

8. An electroviscous fluid as claimed in Claim 7, wherein said agent is a sulphonate, phenate, phosphonate, succinic acid imide, amine or non-ionic dispersing agent.

9. An electroviscous fluid as claimed in any preceding claim, when used with an electric current passed therethrough, at a temperature of up to 100 °C.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 4402

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)
Y	US-A-3 047 507 (W.M. WINSLOW) * Claims 1-23; column 5, lines 16-45; column 7, line 3 - column 9, line 73 *	1-9	C 10 M 171/00
Y	US-A-3 367 872 (T.W. MARTINEK) * Claims 1-20; column 4, line 50 - column 5, line 63 *	1-9	
Y	US-A-2 751 352 (A.A. BONDI) * Claims 1-5; column 5, lines 19-26 *	1-9	
A	CHEMICAL ABSTRACTS, vol. 92, no. 2, 19th May 1980, page 127, abstract no. 166046u, Columbus, Ohio, US; S.D. LIKHTEROV et al.: "Electroviscous effect in oils containing additives", & KHIM. TEKHNOL. TOPL. MASEL 1980, (1), 43-5 * Abstract *	8	

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	15-06-1990	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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