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(54) **Electroviscous fluid.**

(57) The present invention relates to an electroviscous fluid which comprises a dispersion of 0.1 to 50 weight% of wet- method silica particles whose surface adsorbed water has been replaced by an organic compound having in its molecule at least one group selected from the group consisting of a nitrile group, hydroxyl group, and acid group, in an electrically insulating fluid. The wet-method silica particles have an average particle diameter of 10 to 500 micrometers and a pH that does not exceed 6.5. This electroviscous fluid provides a substantial increase in yield value at low voltages and an excellent shear stability.

The present invention relates to an electroviscous fluid which is a fluid whose viscosity can be changed by the impression or application of an external voltage.

Various types of these fluids have already been proposed, and they are typified by, for example, dispersions of porous inorganic particles (e. g., silica, alumina, talc) in an electrically insulating fluid. In each case, through the formation of an electrical double layer by means of water adsorbed on the particle surfaces, the particles become oriented in response to an external electric field and the viscosity increases (more specifically, the fluid is converted into a Bingham fluid, which exhibits a yield value). This effect is called the "Winslow effect". The following disadvantages have been associated with silica- based electroviscous fluids: they have limited application temperatures (approximately 10 ° C to 80 ° C), they abrade the surrounding machinery, and the particles sediment. Still, since silica is easily obtained on an industrial basis and is highly amenable to improvement and manipulation, it has been considered potentially useful for certain sectors of application, for example, machinery which would be used in the vicinity of room temperature and which would undergo little abrading motion. Silica-based electroviscous fluids are disclosed in United States Patent Number 3,047,507 and in Japanese Patent Application Laid Open [Kokai or Unexamined] Number 61-44998 [44,998/86], but in each case these exhibit an impractically weak Winslow effect. Also, Japanese Patent Application Laid Open Number 01-284595 [284,595/89] discloses an electroviscous fluid in the form of a dispersion in an electrically insulating fluid of wet-method silica whose surface adsorbed water has been replaced by polyvalent alcohol. Based on the formation of an electrical double layer by the polyvalent alcohol, this electroviscous fluid exhibits an electroviscous behavior more or less equal to that of the dispersion of the unmodified silica, but also retains its characteristics at higher temperatures (90 ° C). However, even in this case, the intensity of the Winslow effect is still merely more or less equal to that of the prior wet-method silica-based systems. Moreover, because the dielectric constant of the polyvalent alcohol declines with increasing temperature, the Winslow effect still declines at higher temperatures.

As a consequence, all of these heretofore proposed electroviscous fluids remain unsatisfactory from a practical standpoint.

The present invention introduces a silica dispersion- type electroviscous fluid which develops a Winslow effect sufficient to satisfy industrial applications. The present inventor carried out extensive investigations with a view to solving the aforementioned problems, and discovered as a result that the aforementioned problems are substantially reduced by the use as the disperse phase of silica prepared by replacing the water adsorbed on the surface of wet-method silica with a particular type of compound. The present invention was developed based on this discovery.

The object of the present invention is the introduction of an electroviscous fluid which develops an excellent Winslow effect. The object of the present invention is also to utilize a dispersion of 0.1 to 50 weight percent silica particles which comprise wet-method silica particles whose surface adsorbed water has been replaced by an organic compound which contains within its molecule at least one nitrile group, hydroxyl group, or acid group, and wherein the wet-method silica particles have an average particle diameter of 10 to 500 micrometers and have a pH that does not exceed 6.5, in an electrically insulating fluid. A further object of the present invention is to provide an electroviscous fluid which provides a substantial increase in yield value at low voltages and excellent shear stability.

The present invention relates to an electroviscous fluid comprising a dispersion of silica particles in an electrically insulating fluid, the improvement comprising using 0.1 to 50 weight% wet-method silica particles whose surface adsorbed water has been replaced by an organic compound having in its molecule at least one group selected from the group consisting of a nitrile group, hydroxyl group, or acid group, wherein the wet-method silica particles have an average particle size of 10 to 500 micrometers and a pH of not greater than 6.5. The pH (hydrogen ion concentration) of the wet-method silica particles are preferably measured in a 4 weight percent aqueous suspension, however the method of testing the particles for pH is not critical to the present invention.

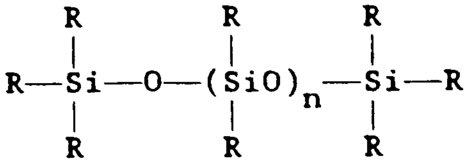
To explain the preceding in greater detail, the wet-method silica particles employed by the present invention are prepared by the production of silica by the addition of acid under wet conditions to water glass starting material. These wet-method silica particles are an ideal disperse phase for electroviscous fluids because their surfaces possess a layer of adsorbed water, which is ideal for the development of the Winslow effect, and because they have optimal particle sizes. Their average particle size should fall within the range of 10 to 500 micrometers and preferably falls within the range of 50 to 200 micrometers. When the particle size is less than 10 micrometers, the particles exhibit a large orientability, but the interparticle forces are small and a satisfactory viscosity will not be achieved. On the other hand, at particle sizes in excess of 500 micrometers, the orientability is diminished and the thickening effect is reduced. Moreover, at such dimensions, the particle size itself begins to pose significant problems. The particle shape should be as close to truly spherical as possible. When the particles substantially deviate from spherical, the effective interparticle contact area declines and the cohesive forces are then weak. With regard to the particle size distribution, the narrower the better. The particle orientability becomes increasingly uniform as the particle size distribution becomes narrower, which provides for a more efficient viscosity rise. Various methods can be devised for the production of silica particles which have a narrow particle size distribution and are as close to spherical as possible, but such particles are obtained mainly by devising a suitable drying process. For example, spray drying methods are ideal.

In addition to the properties discussed above, the quantity of ion in the silica is also a crucial factor in determining the targeted Winslow effect. While not limiting the present invention to any particular theory, it is believed that the principal ion present in the silica is the sodium ion, and this is mainly the excess from the sodium ion used in order to neutralize the solid acid present as an impurity in the water glass starting material. Accordingly, the fluidity of the silica is governed by the magnitude of this quantity of sodium ion. According to experiments by the inventor, the presence of free ion in the silica brings about a retardation in particle orientation. A clear example of this phenomenon is the instability in shear stress at a constant or variable shear rate that is observed when an electric field is applied to an electroviscous fluid prepared by the dispersion of free ion-containing wet-method silica. In the case of free ion-containing particles, this is thought to be due to an increase in the time required for orientation of the randomly distributed particles due to the relatively long time associated with ion movement. The result is the appearance of instability under dynamic conditions. It is for this reason that wet-method silica depleted of free ion (e. g., sodium ion, etc.) is optimal for the development of a useful Winslow effect. Pure wet-method silica generally exhibits fluidity in the acid region, therefore acidic silica is ideal. The fluidity index according to the present invention is defined as follows: the pH of a 4 wt% aqueous suspension of said silica must not exceed 6.5 and more preferably does not exceed 5.5. A useful Winslow effect does not appear at values in excess of 6.5. In order to obtain wet-method silica which has such a fluidity, the excess sodium ion must be removed to the maximum possible extent, or, alternatively, a pure water glass which contains only traces of solid acid must be employed as the starting material.

No specific restrictions are placed on the wet-method silica employed by the present invention as long as it satisfies the properties discussed above. It may be selected from among commercial wet-method silicas, for example, Nipsil A Q-S from Nippon Silica Kogyo Kabushiki Kaisha and its equivalents.

According to the present invention, the water adsorbed on the surface of this wet-method silica is then replaced by an organic compound which contains a nitrile group, hydroxyl group, or acid group. Thus, the surface of wet-method silica is normally covered with a layer of adsorbed water. While the particular weight proportion for this adsorbed water in the total silica weight will vary with the particular type of wet-method silica, in general it will fall within the range of 5% to 10%. Since this layer of adsorbed water is merely hydrogen bonded to a layer of structural water which resides immediately inward, it can be almost completely eliminated by heating to around 100 ° C. However, as discussed above, this adsorbed water layer plays a significant role in the development of the Winslow effect. The cause for this is believed to reside mainly in the high dielectric constant of the water (approximately 80 at room temperature). However, its ease of elimination by heating extinguishes the Winslow effect. In the present invention, this adsorbed water layer on the surface of wet-method silica is replaced with an organic compound which contains a nitrile group, hydroxyl group, or acid group. The nitrile group-containing organic compound as specified herein is exemplified by aliphatic nitriles such as acetonitrile, propionitrile, n-capronitrile, succinonitrile, etc., and by aromatic nitriles such as benzonitrile, alpha-tolunitrile, and so forth. The hydroxyl group-containing compound is exemplified by monovalent alcohols such as methanol and ethanol; by divalent alcohols such as ethylene glycol, 1,2-propanediol, and 1,4-butanediol; and by trivalent alcohols such as glycerol. The acid group- containing compound is exemplified by aliphatic acids such as acetic acid and propionic acid and by aromatic acids such as benzoic acid and phthalic acid. All of these are suitable and no particular restrictions apply to these compounds. Various methods can be devised for the replacement procedure, but the following method has proven to be simple and straightforward. First, the wet-method silica particles are placed under a nitrogen current at 150 ° C in order to remove the surface adsorbed water. After cooling to room temperature under the nitrogen current, the substituting compound is then added in a quantity corresponding to the weight loss due to the desorbed water with mixing to physical homogeneity in, for example, a mixer. After such a treatment, the surface of the wet-method silica particles will be covered by a layer of the substituting compound. Due to the high dielectric constant of same, a Winslow effect can be developed which is at least equivalent to that for the adsorbed water.

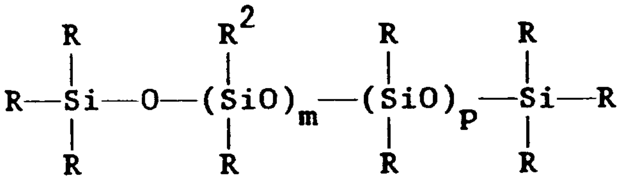
The electroviscous fluid according to the present invention comprises the dispersion of wet-method silica particles as specified hereinbefore in an electrically insulating fluid. However, the electrically insulating fluid itself is not particularly restricted as long as it is a liquid at room temperature and is electrically insulating. Such electrically insulating fluids are exemplified by mineral oils, dibutyl sebacate, chlorinated paraffins, fluorine oils, and silicone oils. Among the preceding, silicone oils are preferred for their strong electrical insulation, low temperature-dependent viscosity variation, and so forth. These silicone oils are exemplified by the fluid diorganopolysiloxanes with the following chemical structure:



$$\mathrm{R{-}\overset{R}{\underset{R}{Si}}{-}O{-}(\overset{R}{\underset{R}{Si}}O)_{n}{-}\overset{R}{\underset{R}{Si}}{-}R}$$

wherein R in the preceding formula comprises monovalent hydrocarbon groups as exemplified by alkyl groups such as methyl, ethyl, and propyl, and aryl groups such as phenyl and naphthyl. It is preferred within the present invention that methyl comprise at least 30% of the groups R. Moreover, while the degree of polymerization n is not particularly specified, it preferably does not exceed 1,000 in order to achieve a practical viscosity range. Values not exceeding 100 are even more preferred. Silicone oils with this structure are available in the form of a large number of commercial products, for example, SH200 from Toray Dow Corning Silicone Company, Limited.

Furthermore, among the silicone oils, fluoroalkyl-containing diorganopolysiloxanes are particularly preferred because they enhance the Winslow effect and inhibit the particle sedimentation caused by specific gravity differences. These are concretely expressed by the following structural formula:



$$\mathrm{R{-}\overset{R}{\underset{R}{Si}}{-}O{-}(\overset{R^{2}}{\underset{R}{Si}}O)_{m}{-}(\overset{R}{\underset{R}{Si}}O)_{p}{-}\overset{R}{\underset{R}{Si}}{-}R}$$

wherein R is defined as above, R2 is a fluoroalkyl group having 10 or fewer carbons, and m and p are integers with values not exceeding 1,000.

The structure of the aforementioned C<10 fluoroalkyl group is not particularly specified, but the 3,3,3-trifluoropropyl group is preferred from the standpoint of ease of synthesis. In order to obtain a substantial enhancement of the Winslow effect, it will be preferable for each molecule to contain at least 30 mole% fluoroalkyl group. Moreover, while the degree of polymerization m is again not particularly specified, it preferably does not exceed 1,000 in order to achieve a practical viscosity range. Values not exceeding 100 are even more preferred. The mechanism by which the fluoroalkyl group enhances the Winslow effect is not clear. It can be conjectured, however, that a strong intramolecular dipole is generated by the simultaneous presence in the molecule of the electronegative fluorine atom and electropositive silicon atom separated by a suitable distance. Polarization of the double layer is then promoted by contact between this dipole and the electrical double layer on the wet-method silica. Otherwise, fluorine- containing fluids tend to have larger specific gravities, which results in an accompanying inhibition of silica sedimentation.

These fluoroalkyl-containing diorganopolysiloxanes are commercially available, for example, as FS1265 from Toray Dow Corning Silicone Company, Limited.

The electroviscous fluid according to the present invention comprises the dispersion of wet-method silica particles as described hereinbefore in an electrically insulating fluid as described hereinbefore. The quantity dispersed should fall within the range of 0.1 to 50 wt% and preferably is in the range of 10 to 40 wt%. A satisfactory thickening effect is not obtained at less than 0.1 wt%. At values exceeding 50 wt%, the viscosity of the system is so substantially increased as to be impractical.

The electroviscous fluid according to the present invention as described above is useful as the working oil or functional oil in particular types of machinery, for example, machinery which will be employed in the vicinity of room temperature and where there will be little abrading motion.

The present invention will be explained in greater detail below through the use of illustrative and comparison examples. In the examples, cs = centistokes and the viscosity is the value at 25 ° C.

The electroviscous behavior was measured as follows. The test fluid was placed in an aluminum cup (interior diameter = 42 mm) into which an aluminum rotor (diameter = 40 mm, length = 60 mm) was subsequently inserted. The resulting cylindrical cell was set up vertically, and the cup was linearly accelerated from a shear rate (D) of zero to 330 s^{-1} over 40 seconds. During this period, the torque applied to the rotor was measured with a torque sensor, and this was converted into the shear stress (S) and the D-versus-S curve was drawn on an X-Y recorder. In addition, the rotor was electrically grounded and D-versus-S curves were also recorded while applying a direct-current voltage to the cup. The intersection of the extrapolation of the linear segment with the S-axis was designated as the yield value at the particular field strength. The thermal and shear stress stability and the sedimentability of the wet-method silica particles were also examined.

The electroviscosity test was also set up in such a manner that the cell temperature could be varied.

Example 1

Wet-method silica (Nipsil AQ-S from Nippon Silica Kogyo Kabushiki Kaisha) with an average particle size of 100 micrometers and pH = 5.5 to 6.5 (4 wt% aqueous suspension) was dried for 2 hours under a nitrogen current at 150 ° C. Drying caused this wet-method silica to suffer a weight loss of approximately 9 wt%. After the dried wet-method silica had been cooled to room temperature under a nitrogen current, acetonitrile was added in a quantity equal to the weight loss. Stirring in a mixer for about 1 hour afforded an acetonitrile-treated wet-method silica. 15 Weight parts of this acetonitrile-treated silica was suspended and dispersed into 85 weight parts trimethylsiloxy-terminated polydimethylsiloxane (viscosity = 100 cs). The electroviscous behavior of this suspension was then measured at a cell temperature of 25 ° C, and the measurement results are reported in Table 1 below.

Example 2

The electroviscous behavior of a suspension prepared as in Example 1 was measured at a cell temperature of 90 ° C, and these measurement results are reported in Table 1 below.

Example 3

Electroviscous fluid in the form of the suspension prepared in Example 1 was heated for 1 week at 90 ° C in an open system under air, then removed and cooled. After this heat treatment, the electroviscous behavior of the resulting suspension was measured, and these results are reported in Table 1.

Example 4

An electroviscous fluid in the form of a suspension was prepared as in Example 1, but in this case using 1,2- propanediol in place of the acetonitrile used in Example 1. The electroviscous behavior of this fluid was measured as in Example 1, and these results are reported in Table 1 below.

Example 5

An electroviscous fluid in the form of a suspension was prepared as in Example 1, but in this case using acetic acid in place of the acetonitrile used in Example 1. The electroviscous behavior of this fluid was measured as in Example 1, and these results are reported in Table 1 below.

Example 6

An electroviscous fluid was prepared as in Example 1, but in this case suspending and dispersing 15 wt% of the silica in a 3,3,3-trifluoropropylmethylpolysiloxane with a viscosity of 300 cs (FS1265-300CS from Toray Dow Corning Silicone Company, Limited) in place of the polydimethylsiloxane with viscosity = 100 cs used in Example 1. The electroviscous behavior of this suspension was measured at a cell temperature of 25 ° C, and these results are reported in Table 1 below.

Comparison Example 1

An electroviscous fluid in the form of a suspension was prepared as in Example 1, but in this case using the wet- method silica prior to its acetonitrile treatment in place of the acetonitrile-treated wet-method silica employed in Example 1. The electroviscous behavior of this fluid was measured as in Example 1, and these measurement results are reported in Table 1 below.

Comparison Example 2

The electroviscous behavior of the electroviscous fluid of Comparison Example 1 was measured at a cell temperature of 90 ° C, and these measurement results are reported in Table 1 below.

Comparison Example 3

Electroviscous fluid as prepared in Comparison Example 1 was heated for 1 week at 90 ° C in an open system under air, then removed and cooled. The electroviscous behavior of the electroviscous fluid obtained from this heat treatment was measured at a cell temperature of 25 ° C, and these results are reported in Table I.

Comparison Example 4

An electroviscous fluid in the form of a suspension was prepared as in Example 1, but in this case using wet-method silica particles with an average particle size of 4 micrometers and pH = 5.5 to 6.5 (4 wt% aqueous suspension) in place of the wet-method silica particles with an average particle size of 100 micrometers as used in Example 1. The electroviscous behavior of this fluid was measured as in Example 1, and these measurement results are reported in Table 1 below.

Comparison Example 5

An electroviscous fluid in the form of a suspension was prepared as in Example 1, but in this case using wet-method silica particles with an average particle size of 8.5 micrometers and pH = 10.0 to 11.0 (4 wt% aqueous suspension) in place of the wet-method silica particles with an average particle size of 100 micrometers as used in Example 1. The electroviscous behavior of this fluid was measured as in Example 1, and these measurement results are reported in Table 1 below.

Table I

EXAMPLE	THERMAL TREATMENT	YIELD VALUE		SHEAR STRESS STABILITY	PARTICLE SEDIMENT-ABILITY
		1 KV/mm	2KV/mm		
EX. 1	none	240	490	high	medium
EX. 2	none	205	460	high	medium
EX. 3	90°C/1 wk	75	160	high	medium
EX. 4	none	215	440	high	medium
EX. 5	none	200	390	medium	medium
EX. 6	none	315	660	high	low
COMPAR. EX. 1	none	220	460	high	medium
COMPAR. EX. 2	none	150	300	high	medium
COMPAR. EX. 3	90°C/1 wk	35	60	high	medium
COMPAR. EX. 4	none	135	290	high	medium
COMPAR. EX. 5	none	160	325	low	medium

Because the electroviscous fluid according to the present invention comprises a dispersion of 0.1 to 50 weight percent wet-method silica particles whose surface adsorbed water has been replaced by a particular type of organic compound in an electrically insulating fluid, this electroviscous fluid is characterized by a substantial increase in yield value at low voltages and an excellent shear stability.

Claims

1. In an electroviscous fluid comprising a dispersion of silica particles in an electrically insulating fluid, the improvement comprising using 0.1 to 50 weight% wet-method silica particles whose surface adsorbed water has been replaced by an organic compound having in its molecule at least one group selected from the group consisting of a nitrile group, hydroxyl group, and acid group, wherein the wet-method silica particles have an average particle size of 10 to 500 micrometers and a pH of not greater than 6.5.

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EUROPEAN SEARCH REPORT

Application Number

EP 91 11 8452

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	EP-A-0 342 041 (TOA NENRYO KOGYO K.K.) * page 3, line 53 - line 59; claims 1-6,10,13-16; examples 5-8 *	1	C10M171/00
Y	EP-A-0 311 984 (AMERICAN CYANAMID COMP.) * page 3, line 44 - line 52; claims 1-21 *	1	
A	EP-A-0 374 525 (BRIDGESTONE CORP.) * page 3, line 43 *	1	
A	FR-A-1 488 158 (TEXTRON ELECTRONICS) * the whole document *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 DECEMBER 1991	DE LA MORINERIE

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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