(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 516 394 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **92304793.0**

(51) Int. Cl.^{5} : **C10M 171/00**

(22) Date of filing : **27.05.92**

(30) Priority : **27.05.91 JP 151136/91**

(43) Date of publication of application :
02.12.92 Bulletin 92/49

(84) Designated Contracting States :
DE FR GB

(71) Applicant : **BRIDGESTONE CORPORATION**
10-1 Kyobashi 1-Chome, Chuo-Ku
Tokyo 104 (JP)

(72) Inventor : **Kurachi, Yasuo**
1-1-52-6 Kamiitabashi 3-chome
Itabashi-ku, Tokyo (JP)
Inventor : **Saito, Tasuku**
1265-2 Kamiarai, Tokorozawa-shi
Saitama-ken (JP)
Inventor : **Takagi, Koji**
3-6-305 Ogawahigashi-cho
Kodaira-shi, Tokyo (JP)
Inventor : **Kijima, Shigeru**
58-1-3-1 Higashitokorozawa 2-chome
Tokorozawa-shi, Saitama-ken (JP)

(74) Representative : **Stoner, Gerard Patrick et al**
Mewburn Ellis 2 Cursitor Street
London EC4A 1BQ (GB)

(54) Electrorheological fluid.

(57) A novel non-aqueous fluid possessing improved electrorheological effect is provided. Carbonaceous powder resulting from heat treatment of polyaniline powder is dispersed in an insulating oily medium to form an electrorheological fluid.

EP 0 516 394 A1

This invention relates to an electro rheological fluid.

Electrorheological fluid is a fluid whose viscoelasticity can be widely changed in a reversible manner by electrical control. Well known is the Winslow Effect that fluids having certain substances dispersed in oily media manifest an increase in apparent viscosity upon application of an electrical potential thereto. The old day electrorheological fluids which were typically composed of starch dispersed in mineral oil or lubricating oil were satisfactory for recognizing the significance of electrorheological effect, but lacked reproducibility so that their utility in industrial fields was impractical.

In order to provide fluids exhibiting improved electrorheological effect in a reproducible manner, a number of proposals were made with the main focus on powder as the dispersed phase. There are known a variety of powders, for example, a highly water-absorbing resin having an acid group such as polyacrylic acid (Japanese Patent Application Kokai = JP-A 93186/1978), an ion exchange resin (JP-A 31211/1985, and alumina silicate (JP-A 95397/1987). All these electrorheological fluids are composed of hydrophilic fine powder having water absorbed being dispersed in an insulating oily medium. With a high electrical potential externally applied to the fluid, the water helps the powder particles polarize so that bridging occurs between the particles in a potential direction, resulting in a viscosity increase. Prior research efforts had been made on these electrorheological fluids based on hydrous powder.

In order to overcome the drawbacks of the aqueous electrorheological fluids, it was recently proposed to use water-free particles to provide non-aqueous electrorheological fluids. There are known several non-aqueous electrorheological fluids using ferroelectric substances or semiconductor particles, for example, a fluid using organic semiconductor fine particles such as poly(acene-quinone) (JP-A 216202/1986 or GB 2 170 510 A published August 6, 1986), a fluid using dielectric fine particles obtained by coating organic solid particles on the surface with a conductive thin film and further coating with an electrically insulating thin film (JP-A 97694/1988), and a fluid using dielectric fine particles having a cavity (JP-A 172496/1989).

Research efforts are being made on these non-aqueous electrorheological fluids since they are expected of a possibility of eliminating the drawbacks of prior fluids due to the presence of water, for example, an increase of current flow during voltage application due to the presence of water ions and a marked current increase associated with a temperature rise. More particularly, on the assumption that the Winslow Effect is attributed to polarization at the surface of fine particles with external voltage applied thereto, many researches have been seeking for another approach for inducing polarization at the surface of fine particles, especially dielectric fine particles. Nevertheless, the non-aqueous electrorheological fluids, regardless of whether semiconductor particles of monophase compound or fine particles having an insulating layer formed on the surface thereof are used, have disadvantages including weak electrorheological effect as compared with the water-induced electrorheological effect, electrophoresis during DC conduction, and lack of stability.

Therefore, there is a need for development of a novel non-aqueous electrorheological fluid which can reduce these drawbacks.

Through investigations, the inventors reached the conclusion that the use of previously proposed dielectric substances and semiconductor particles has a limit in satisfying all the requirements including a further increase of electrorheological effect, prevention of electrophoresis upon DC conduction, stability and so forth. We continued further investigations in order to seek for particles susceptible to electrorheological effect other than the conventional known dielectric substances and semiconductor particles. As a result, we have found that carbonaceous particles resulting from heat treatment of polyaniline surprisingly exert effective electrorheological behavior even in the absence of water. By dispersing the carbonaceous particles in an oily medium, there is accomplished a novel electrorheological fluid.

Therefore, the present invention provides an electrorheological fluid comprising an oily medium having electrically insulating property and carbonaceous powder dispersed in the medium the carbonaceous powder having been produced by the heat treatment of polyaniline powder.

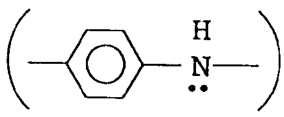
FIG. 1 is a diagram showing the particle size distribution of the carbonaceous powder used in Example 1.

FIG. 2 is a diagram showing the particle size distribution of the carbonaceous powder used in Example 2.

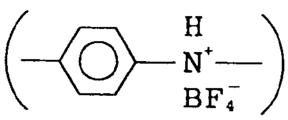
In accordance with the present invention, there is provided an electrorheological fluid in which carbonaceous powder resulting from heat treatment of polyaniline powder is dispersed in an insulating oily medium. This is a non-aqueous fluid which develops electrorheological effect without a need for water.

The polyaniline powder can be obtained by subjecting aniline to electrical or chemical oxidative polymerization. The particular polymerization procedure chosen is not critical. For example, in the case of electrical polymerization, it can apply a sufficient potential to cause aniline to polymerize. More particularly, polyaniline is prepared through electrical oxidative polymerization by immersing a pair of electrode plates, a working electrode and a counter electrode, in a solution of aniline monomer. A voltage higher than the oxidation potential of aniline is applied across the electrodes or a current flow is conducted under conditions to ensure a sufficient voltage to cause aniline to polymerize. Then polyaniline deposits on the working electrode. In the case of chemical oxidative polymerization, an oxidizing agent having an oxidation-reduction potential approximate to the polymerization potential of aniline is admitted into a solution of aniline monomer. Exemplary oxidizing agents are $(NH_4)_2S_2O_8$, MnO_2, PbO_2, and $FeCl_3$.

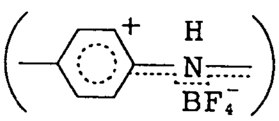
With regard to the preparation of polyaniline by electrical or chemical oxidative polymerization, it is known that the co-presence of an acid such as HBF_4, H_2SO_4, HCl and $HClO_4$, with aniline monomer in the polymerization system results in a highly conductive polyaniline because an acid anion is incorporated into the polyaniline being synthesized as a dopant. For example, oxidative polymerization of aniline monomer in the co-presence of HBF_4 generally yields a mixture of four species of polyaniline, that is, benzonoid-amine state (formula A), benzonoid-ammonium state (formula B), dope-semiquinone radical state (formula C), and quinoid-diimine state (formula D) polyanilines, formulae A to D being shown below. A polyaniline product containing a dope-semi-quinone radical state (formula C) is highly conductive. Since the mix ratio of these four species of polyaniline has eventually no influence on the electrorheological effect of the end product, any polyaniline product having a varying mix ratio may be used herein.



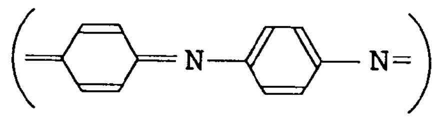
....(A)



....(B)

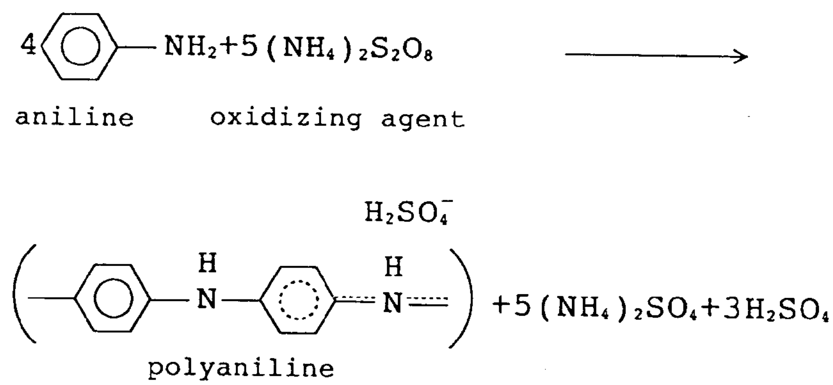


....(C)



....(D)

The synthesis of polyaniline is illustrated in more detail. When polyaniline is synthesized in accordance with electrical oxidative polymerization, plates or porous members of highly conductive material such as stainless steel, platinum and carbon are used as working and counter electrodes. The electrodes are immersed in an electrolytic solution containing aniline monomer and an acid such as H_2SO_4 and HBF_4. Electricity is conducted across the electrodes at a current density of about 0.1 to 100 mA/cm^2 whereupon aniline polymerizes and deposits on the working electrode. For the synthesis of polyaniline in accordance with chemical oxidative polymerization, 0.5 mol/liter of ammonium peroxodisulfate $(NH_4)_2S_2O_8$ as an oxidizing agent is admitted into an aqueous solution containing 1 mol/liter of H_2SO_4 and 0.4 mol/liter of aniline. The ammonium peroxodisulfate develops an oxidation-reduction potential of 2.0 V (vs. the normal electrode) that causes oxidative polymerization of aniline, whereby polyaniline precipitates. This reaction may be represented by the following scheme.



Where aniline is polymerized by the above-mentioned methods in the co-presence of acid, the structure of the resulting polyaniline largely varies with the type of acid used. For example, the polyaniline is fibril when HBF_4 is used and granular or sometimes powdery when H_2SO_4 is used. Various forms of polyaniline products may be used in the practice of the invention since they can be processed into an appropriate form by a powdering or granulating procedure. Preferably, polymerization is carried out under conditions such that the resulting polyaniline has an adequate particle size distribution. Although the particle size of polyaniline powder is not critical, a mean particle size of about 0.05 to about 200 μm, especially about 1 to about 100 μm is preferred.

Thereafter, the polyaniline is heat treated into a carbonaceous powder. The heat treating temperature is not particularly limited and may be properly selected in accordance with the requisite electrorheological effect and current value. Often, a temperature of about 250 to 800°C, especially about 450 to 600°C is selected. Heat treatment of polyaniline at temperatures below 250°C would fail to provide sufficient electrorheological effect depending on the polyaniline synthesis conditions. Temperatures above 800°C would yield a carbonaceous powder having too high conductivity and thus allowing excessive current flow. The remaining heat treating conditions including heating rate, treating time and treating atmosphere are not critical and may be determined without undue experimentation. For example, the treating atmosphere is preferably a non-oxidizing atmosphere, but an oxidizing atmosphere is acceptable at treating temperatures below 400°C.

A combination of oxidizing an non-oxidizing atmospheres is also acceptable. The carbonaceous powder resulting from heat treatment of polyaniline should preferably have a carbon retention of about 20 to 80%, especially about 25 to 70%.

The electrorheological fluid of the present invention is prepared by dispersing the thus obtained carbonaceous powder in an oily medium having electrically insulating property. The type of oily medium is not particularly limited. It may be selected from a variety of oily media having electrically insulating property including silicone oil, mineral oil, transformer oil, paraffin oil and halogenated aromatic oil.

The dispersing conditions are not particularly limited. Preferably, the carbon -aceous powder has an appropriate particle size distribution to disperse, for example, a mean particle size of about 0.05 to 200 μm, especially about 1 to 100 μm. As long as the polyaniline powder has a particle size within this preferred range, the heat treatment of the polyaniline generally yields a carbonaceous powder having a corresponding particle size within the preferred range. If the carbonaceous powder resulting from heat treatment had an extremely small or large mean particle size, the powder should be subsequently granulated or powdered by any appropriate means.

The amount of carbonaceous powder dispersed in oily medium may be properly determined in accordance with the intended use of electrorheological fluid and the like, more particularly a desired change of viscosity and other factors. The dispersion method is not particularly limited and any dispersion method capable of uniformly dispersing carbonaceous powder may be used.

The electrorheological fluid of the invention is advantageously utilized in the electric control of mechanical units such as engine mounts, shock absorbers, valves, actuators and clutches.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

Example 1

To 1 liter of an aqueous solution containing 0.4 mol/liter of aniline and 1.0 mol/liter of H_2SO_4 was added

0.5 mol of ammonium peroxodisulfate. With stirring the solution, polymerization was carried out for 5 hours. The resulting suspension was filtered and the solids were dried, obtaining 40 grams of polyaniline powder.

The polyaniline powder was heated up to 530°C at a rate of 3°C /min. in a nitrogen atmosphere and baked at the temperature for 1 hour, obtaining carbonaceous powder having a particle size distribution as shown in FIG. 1 and a carbon retention of 68%.

The carbonaceous powder, 50 grams, was dispersed in 150 grams of silicone oil (TSF 451-10 commercially available from Toshiba Silicone Co., Ltd.) to form an electrorheological fluid.

This electrorheological fluid was measured for electrorheological effect using a dual cylinder viscometer. The electrorheological effect was evaluated in terms of a viscosity at a shear rate of 366/sec. and a temperature of 25°C with a voltage of 0 to 2 kV applied between the-inner and outer cylinders. The results are shown in Table 1.

Example 2

Commercially available aniline black (Aniline Black No. 13 manufactured by Toyo Sikizai Industry Co., Ltd.) was heated up to 480°C at a rate of 3°C /min. in a nitrogen atmosphere and baked at the temperature for 1 hour, obtaining carbonaceous powder having a particle size distribution as shown in FIG. 2 and a carbon retention of 68%.

The carbonaceous powder, 50 grams, was dispersed in 150 grams of silicone oil (TSF 451-10) to form an electrorheological fluid. This fluid was measured for electrorheological effect as in Example 1. The results are also shown in Table 1.

Comparative Example 1

Without heat treatment, 50 grams of commercially available aniline black (Aniline Black No. 13) was dispersed in 150 grams of silicone oil (TSF 451-10) to form an electrorheological fluid. This fluid was measured for electrorheological effect as in Example 1. The results are also shown in Table 1.

Comparative Example 2

Without heat treatment, 50 grams of the polyaniline powder prepared in Example 1 was dispersed in 150 grams of silicone oil (TSF 451-10) to form an electrorheological fluid. This fluid was measured for electrorheological effect as in Example 1. The results are also shown in Table 1.

Table 1

	V=0 kV Viscosity (poise)	V=2 kV Viscosity (poise)	Viscosity change (poise)	V=2 kV Current Density (μ A/cm^2)
Example 1	5.54	17.54	12.09	14.98
Example 2	0.5	7.40	6.90	86.84
Comparative Example 1	0.6	1.50	0.9	Un-measur-able
Comparative Example 2	0.47	0.55*	0.03*	Un-measur-able

* measured at 800 V because unmeasurable above 800 V.

As seem from Table 1, the electrorheological fluids of the present invention exhibit satisfactory electrorheological effect.

There has been described an electrorheological fluid which is a novel non-aqueous fluid possessing improved electrorheological effect.

While the invention has been described in what is presently considered to be a preferred embodiment, other variations and modifications will become apparent to those skilled in the art. It is intended, therefore, that the invention not be limited to the illustrative embodiments.

Claims

1. An electrorheological fluid comprising carbonaceous powder dispersed in an oily medium having electrically insulating property, the carbonaceous powder resulting from heat treatment of polyaniline powder or polyaniline derivative powder.

2. The fluid of claim 1 wherein a mean particle size of polyaniline or its derivative is in a range of about 0.05 to about 200 μm.

3. The fluid of claim 2 wherein a mean particle size of polyaniline or its derivative is in a range of about 1 to about 100 μm.

4. The fluid of claim 1 wherein the heat treatment is at a temperature of about 250°C to about 800°C.

5. The fluid of claim 4 wherein the heat treatment is at a temperature of about 450°C to about 600°C.

6. The fluid of claim 1 wherein the carbonaceous powder resulting from heat treatment of polyaniline or its derivative has a carbon retention of about 20% to about 80%.

7. The fluid of claim 6 wherein the carbonaceous powder resulting from heat treatment of polyaniline or its derivative has a carbon retention of about 25% to about 70%.

8. The fluid of claim 1 wherein the carbonaceous powder has a mean particle size of about 0.05 to about

200 μm.

9. The fluid of claim 8 wherein the carbonaceous powder has a mean particle size of about 1 to about 100 μm.

10. A method of making an electrorheological fluid which comprises
obtaining polyaniline or a derivative thereof in a powder form;
heat treating the polyaniline or polyaniline derivative to form a carbonaceous powder;
dispersing the carbonaceous powder in an oily medium.

11. A method according to claim 10 wherein the polyaniline or polyaniline derivative is obtained from a polymerization treatment which is an electrical or chemical oxidative polymerization treatment,
and, optionally,
an acid selected from HBF_4, H_2SO_4, HCl and $HClO_4$ is included in the reaction medium during the polymerization step.

FIG.1

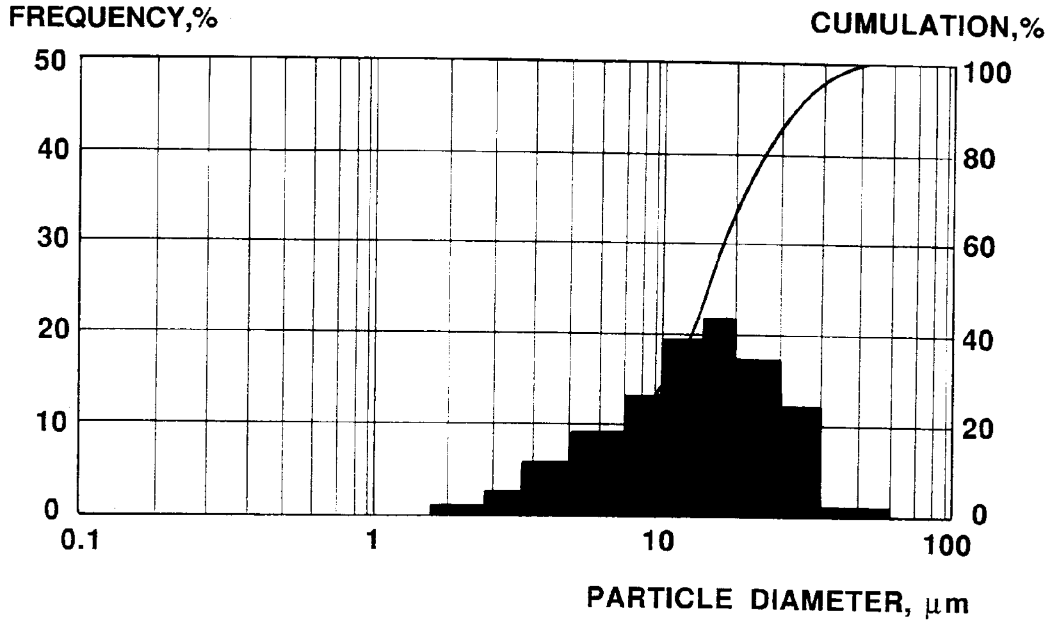
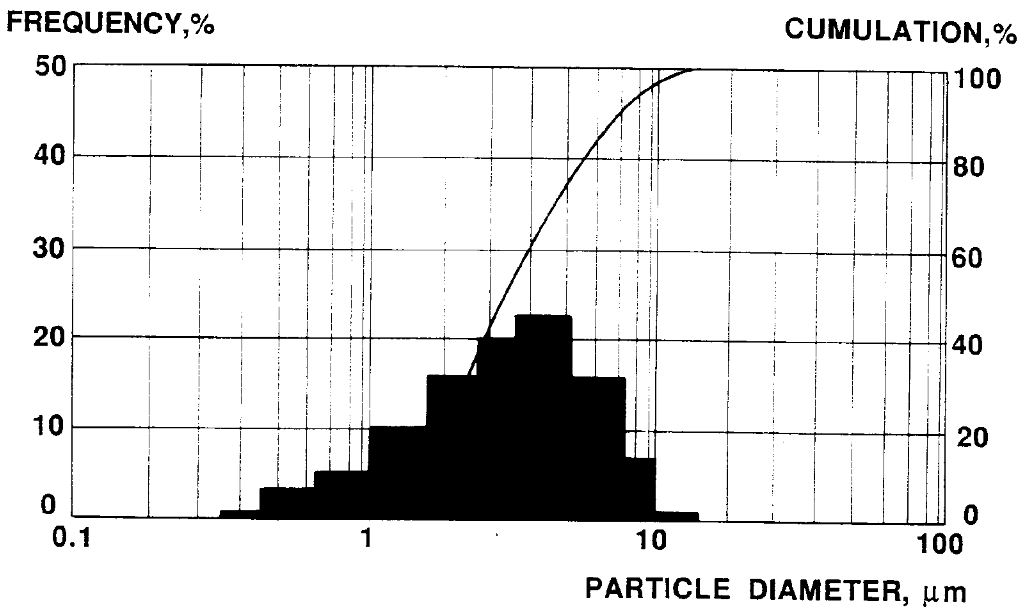

FREQUENCY,%
CUMULATION,%
50
40
30
20
10
0
100
80
60
40
20
0
0.1
1
10
100
PARTICLE DIAMETER, μm

FIG.2


FREQUENCY,%
CUMULATION,%
50
40
30
20
10
0
100
80
60
40
20
0
0.1
1
10
100
PARTICLE DIAMETER, μm

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4793

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)
A	EP-A-0 394 005 (NATIONAL RESEARCH DEVELOPMENT CORP.) * page 2, line 36 - line 43 * * page 3, line 3 - line 10; claim 1 * ---	1-3,10, 11	C10M171/00
A	EP-A-0 361 106 (BRIDGESTONE CORP.) * claim 1 * -----	1-9	
			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	01 JANUARY 1980	ROTSAERT 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