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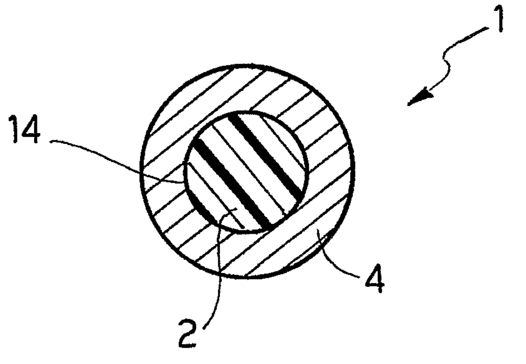
(54) **Title:** FLUID MAGNETO-RHEOLOGICAL COMPOSITION



(57) **Abstract:** The present invention relates to a fluid magneto-rheological composition containing ferromagnetic particles characterized by a low specific weight and a multilayer structure; in particular, the particles according to the present invention have a core made of a material with a low specific weight and a coating layer comprising a material with ferromagnetic properties.

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"FLUID MAGNETO-RHEOLOGICAL COMPOSITION"

The present invention relates to a fluid magneto-rheological composition. In particular, the present invention relates to a fluid magneto-rheological composition containing ferromagnetic particles characterized by a low specific weight.

The main property of fluid magneto-rheological or electro-rheological compositions is a variation of apparent viscosity when subject to a magnetic or electric field. Magneto-rheological fluids usually comprise ferromagnetic particles or typically with a diameter of about 1 μm, dispersed within a carrier fluid. In the presence of a magnetic field said particles get magnetized and orient the magnetic dipole parallel to the lines of force of the magnetic field, and arrange themselves as particle chains within the fluid. Particle chains operate so as to increase the apparent viscosity or global flow resistance of the fluid. If no magnetic field is present, the particles are again in an unorganized or free status and the apparent viscosity or discharge resistance of the material decreases accordingly. Magneto-rheological materials have a controllable behavior resembling the one of electro-rheological materials reacting to an electric field instead of a magnetic field.

Both electro-rheological and magneto-rheological materials are useful providers of variable damping forces within devices such as dampers, shock-absorbing devices and elastomeric supports.

Fluid magneto-rheological compositions as are known today, however, have a great disadvantage: the ferromagnetic or paramagnetic particles dispersed in the carrier fluid essentially consist of pure metals or alloys thereof, which have - as is known - molecular weights above the molecular weight of the carrier fluid and therefore strongly tend to sediment, thus jeopardizing the properties of behavior of the magneto-rheological fluid as a whole.

The problem of sedimentation can be overcome by mixing the fluid magneto-rheological composition: this operation, however, cannot be easily carried out if the composition has to be used for instance within a shock absorber.

The present problem has been dealt with in the past by modifying for instance the composition of the carrier fluid, i.e. by using a high density fluid - oil. Another known solution consists in adding to the carrier fluid a surfactant agent, which helps to keep the ferromagnetic particles in suspension through chemical interactions.

However, these solutions are unsatisfactory since - in the first case - there is not the necessary difference of viscosity between the active status - i.e. when the particles are in an organized status - and the passive status - i.e. when magnetization is not necessary and particles are in a disordered status - whereas in the second case chemical bonds are weak.

The present invention aims at overcoming the problem of sedimentation by providing a magneto-rheological fluid having the necessary difference of viscosity between active and passive status.

According to the invention said aim is achieved thanks to the solution specifically referred to in the appended claims.

In the embodiment now preferred, the invention relates to a magneto-rheological fluid containing ferromagnetic particles having a multilayer structure; in particular, the particles according to the present invention have a core made of a material with a low specific weight and a coating layer comprising a material with ferromagnetic properties. In a particular embodiment the ferromagnetic particles have a core with a central cavity.

Further characteristics and advantages of the fluid magneto-rheological composition according to the present invention will be evident from the following detailed description, given as a mere non-limiting example, with reference to the accompanying drawings, in which:

- Figure 1 is a sectioned view of a ferromagnetic particle according to the invention;

- Figure 2 is a sectioned view of a ferromagnetic particle with a hollow core.

With reference to Figure 1, number 1 refers to the particle as a whole. The particle 1 has a core 2 and a coating layer 4. On the interface between core and coating layer there is also a homogenous or inhomogeneous inter-phase 14 for the adhesion of the coating layer 4 onto the core 2.

Figure 2 shows a particle 1a having a core 8 with a central cavity 6 and a coating layer 10. Here again there is a homogenous or inhomogeneous inter-phase 16 for the adhesion of the coating layer 10 onto the core 8.

The material having a low specific weight constituting the core 2, 8 can be selected from the group comprising glass, aluminosilicates, microporous polymers or polymeric foams. The specific weight of the material constituting the core will be lower than the carrier fluid.

The size of the inner core 2, 8 will vary depending on the material, though always in the range from 5 to 300 microns. The size of the inner cavity 6, if present, can vary depending on the material of the core:

it should be greater the higher the specific weight of the material, so as to ensure that the particle as a whole has a lower specific weight than the carrier fluid.

The roughness of the surface of the inter-phase 14, 16 should be such as to ensure a good anchoring of the outer metal coating layer 4, 10.

The material constituting the coating layer 4, 10 can be selected from the group comprising iron (Fe), nickel (Ni), cobalt (Co) and alloys thereof Co-Ni, Fe-Ni, Fe-Co, Fe-Co-Ni.

The deposit thus obtained has no surface roughness and is very even and uniform, with a thickness of some microns to some dozens of microns.

Processes for depositing metals and/or metal alloys onto substrates made of glass, polycarbonate or microporous polymers are known at the state of the art.

The following describes as a mere non-limiting example two processes that can be used to obtain the coating layer - nickel in one case, cobalt in the other one - using a polymeric particle as substrate.

The production of ferromagnetic particles whose core is made of a polymeric material basically comprises the following steps:

- preparation of the surface of the polymeric particles,
- activation of the surface of the polymeric particles creating the inter-phase,
- deposit of the coating layer.

First of all, the polymeric particles undergo a preparatory step known as degreasing preconditioning step, consisting in suspending the particles under continuous stirring in a suitable solution containing basic salts such as carbonates or phosphates and, if necessary, surfactant agents, so as to clean their surfaces and simplify the following coating operations.

The activation step can be carried out with different methods, in particular carrying out sequentially the steps of pickling, neutralization, sensitization and activation with $PdCl_2$.

The so-called pickling step consists of a partial oxidation of the polymeric surface for a thickness of about 1 μm, which results in the formation on the surface of the polymeric particles of a network of submicroscopic pores enabling the subsequent anchoring of the stabilization element.

Then the oxidation products used in the pickling step are neutralized using solutions of neutralizing reducing agents.

The particles are then sensitized through a treatment with a solution of salts of Sn(II), thus obtaining the adsorption of Sn^{2+} cations.

The activation step, i.e. in which the inter-phase 14, 16 is created, consists in treating the polymeric particles having adsorbed on their surface the tin ions with a solution containing salts of Pd(II). Sn^{+2} ions are oxidized to Sn^{4+} ions, thus generating on the surface of the particles the inter-phase 14, 16, basically consisting of metal palladium microparticles, which act as nucleation centers for the growth of the ferromagnetic coating layer.

Alternatively, the preliminary pickling and neutralization treatments are followed by a treatment of sensitization and activation for each single stage (mixed process) by immersion in a bath containing salts of Sn(II) and Pd(II).

An electrolytic process leads to the deposition of the ferromagnetic material, nickel for instance, whose growth starts on the palladium nucleation centers, thus building island-like structures. The presence of a surfactant agent in the preconditioning bath increases uniformity in the distribution of the nucleation centers on the surface of the particles, which results in the uniformity of the coating layer.

The process by which the coating layer is obtained consists in depositing nickel by means of redox solutions containing salts of Ni^{2+} and hypophosphite ions ($H_2PO_2^-$). The process of chemical reduction of nickel salts is a self-catalytic process, in which metal reduction is caused by sodium hypophosphite ($NaH_2PO_2 \, H_2O$), the activated polymeric particles immersed in the bath acting as catalysts. Taking into consideration the main products reacting in the solution, the following reactions can be obtained:

$$(1)\quad H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H_2$$

$$(2)\quad Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+$$

i.e. hypophosphite ions in aqueous solution are catalytically oxidized to phosphite ions releasing gaseous hydrogen, whereas nickel cations are catalytically reduced to metal nickel by hypophosphite ions in the presence of water, while hypophosphite ions are oxidized to phosphite ions releasing at the same time hydrogen ions. Since nickel acts as a catalyst both for the first and for the second reaction, the process is "self-initializing". The result of the reaction is a coating layer made of a nickel-phosphor alloy in which the phosphor content depends on the concentration of phosphor in the solution and on its pH.

An alternative process for depositing the coating layer onto the polymeric material is the so-called polyol process.

Polyol process is known in the specific literature for the synthesis of monodispersed nano- and micrometric metal particles. In this process liquid polyol acts both as solvent for the metal precursor and as reducing agent; the metal precursor can be highly soluble in polyol (nitrate, chloride, acetate) or only slightly soluble (oxide, hydroxide). Metal atoms can be obtained by reduction of complexes of respective ions and then deposited onto the polymeric surface. This method is exploited above all for cobalt deposition.

In order to obtain a quantitative reduction of Co precursors so as to deposit the coating layer onto the polymeric particles, the reaction should be carried out in refluxing polyols. The steps constituting the polyol process basically comprise the dissolution of the metal precursor (cobalt hydroxide) in a mixture of polyol and polymeric microparticles: the suspension is stirred and heated to polyol boiling temperature. Then the dissolved species are reduced by means of the polyol: $Co^{2+} + 2e^{-} \rightarrow Co^{0}$, with subsequent nucleation and growth of metal particles $n\ Co^{0} \rightarrow Co_{n}$.

In order to prevent chemical-physical variations of the polymeric particles before metallization, said particles should be made of a polyol-inert material having degradation temperatures above polyol boiling temperature.

A suitable adjustment of test conditions (polyol reducing power, temperature, metal precursor concentration) enables to control precipitation kinetics by separating nucleation and growth of metal particles. In order to obtain a good metallization of polymeric particles it is extremely important to minimize the nucleation stage with respect to growth, thus polymeric particles will act as nucleation centers for cobalt atoms.

Polyol also acts as surfactant agent on polymeric particles coated with the cobalt coating layer, thus preventing aggregation between particles colliding because of Brownian movements. Polyol is adsorbed on the metal surface and protects the latter by means of short-ray effects of electronic and steric repulsion.

CLAIMS

1. Fluid magneto-rheological composition containing a carrier fluid and ferromagnetic particles, characterized in that said particles (1, 1a) have a specific weight that is slightly below, the same as or slightly above the specific weight of said carrier fluid.

2. Composition according to claim 1, characterized in that said particles (1, 1a) have a multilayer structure.

3. Composition according to claim 1 or 2, characterized in that said particles (1, 1a) have a core (2, 8) made of a material with a specific weight lower than the specific weight of said carrier fluid.

4. Composition according to any of the preceding claims, characterized in that said core (8) has a central cavity (6).

5. Composition according to any of the preceding claims, characterized in that said particles (1, 1a) have a coating layer (4, 10) outside said core (2, 8), made of a ferromagnetic material.

6. Composition according to any of the preceding claims, characterized in that said particles (1, 1a) have an inter-phase (14, 16) between said coating layer (4, 10) and said core (2, 8).

7. Composition according to any of the preceding claims, characterized in that said material having a low specific weight is selected from the group comprising glass, aluminosilicates, polymeric foams or microporous polymers.

8. Composition according to any of the preceding claims, characterized in that said ferromagnetic material is selected from the group comprising iron, nickel, cobalt and alloys thereof.

FIG. 1

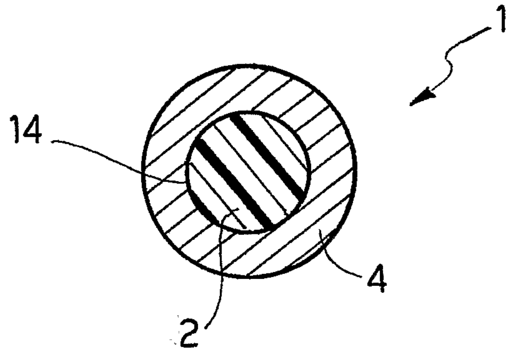
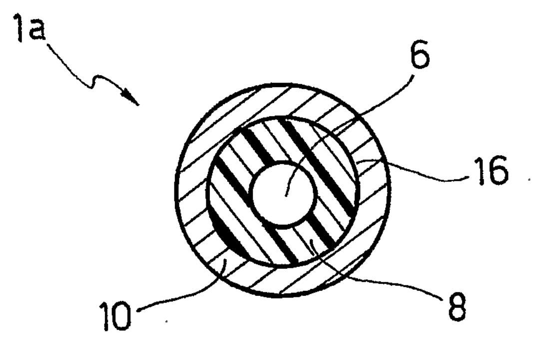


FIG. 2



INTERNATIONAL SEARCH REPORT

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IPC 7 H01F1/44 F16F9/53 F16J15/43 H01F1/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4 532 153 A (SOLC JITKA) 30 July 1985 (1985-07-30) the whole document	6,7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Gols, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

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