There is provided a process for the preparation of a suspension of magnetic particles in a polar carrier liquid. The process includes the step of coating the surface of the magnetic particles with an organic ligand having a hydrophilic chain prior to the suspension. For preparing a magnetically deformable mirror, the suspension of magnetic particles in a polar carrier liquid is coated with a reflective surface layer. A ferrofluid includes a suspension of magnetic particles coated with an organic ligand having a hydrophilic chain in a polar carrier liquid.
Declaration under Rule 4.17:
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(U))

Published:
— with international search report
CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35USC§119(e) of US provisional patent application 60/913,820 filed on April 25, 2007, the specification of which is hereby incorporated by reference.

TECHNICAL FIELD

[0002] The present invention relates to ferrofluids and, more particularly, to ferrofluids which are compatible with a reflective layer deposited on their surface to render them reflective. It also relates to magnetically deformable mirrors including a ferrofluid layer and a thin reflective surface film of reflective nanoparticles.

BACKGROUND OF THE INVENTION

[0003] Ferrofluids are colloidal dispersions (or suspensions) of magnetic nanoparticles in a liquid carrier that combine fluidic and magnetic properties to yield magnetically deformable liquids. Ferrofluids are well known and have many industrial applications including seals, coolants for loudspeakers and inks for printers. More recently, ferrofluids have been employed for the fabrication of a new kind of deformable liquid mirror (Brousseau, D.; Borra, E. F.; Jean-Ruel, H.; Parent, J.; Ritcey, A. Opt. Express 2006, 14, 11486, and Laird, P.; Borra, E. F.; Bergamesco, R.; Gingras, J.; Truong, L.; Ritcey, A. Proc. SPIE 2004, 5490, 1493). Application of a current through a conducting liquid generates magnetic fields so that the liquid can respond to the force resulting from an externally applied magnetic field. By using a magnetic field, it is possible to shape the surface of ferrofluids and thus of the resulting liquid mirrors.

[0004] Since ferrofluids are not highly reflective, this application requires that they be coated with a reflective layer for mirror applications. Surface films of silver nanoparticles for coating ferrofluids are typically based on reflective liquid-like films and denoted as MELLFs (for Metal Liquid-Like Films) (Yoge, D.; Efrima, S.; J. Phys. Chem, 1988, 92, 5754).

[0005] To achieve a stable suspension of magnetic particles in the liquid carrier,
stabilizing/dispersing agents are used to prevent particle aggregation and sedimentation. The choice of the stabilizing/dispersing agent depends on the nature of the liquid carrier in which the particles are dispersed. Ferrofluids composed of non-polar solvent, such as oils, usually include organic molecules containing relatively long alkyl chains, such as oleic acid, as the dispersing agent (E. Dubois, V. Cabuil, F. Boue and R. Perzynski, "Structural analogy between aqueous and oily magnetic fluids," J. Chem. Phys., Vol. 111, No. 15, (1999)). When anchored to the particle surface, the organic tails prevent the aggregation of the magnetic particles by introducing steric repulsion.

[0007] In known preparations in polar media, particle aggregation is prevented by electrostatic stabilization achieved through the introduction of surface charges with methods analogous to those developed for aqueous ferrofluids. Typical procedures employ the surface adsorption of citrate (Dubois, E.; Cabuil, V.; Boue F.; Perzynski, R. J. Chem. Phys. 1999, 111, 7147) or hydroxide (Tourinho, F. A.; Franck, R.; Massart, R. J. Mater. Sci. 1990, 25, 3249) ions to produce negatively charged particles. As described below, ethylene glycol based ferrofluids stabilized in this way are not compatible with the reflective surface films of silver nanoparticles. The reflective layer gradually cracks and flocculates to the bottom of the container when deposited on a ferrofluid containing citrate-coated nanoparticles.

[0008] A relatively large number of organic ligands, including, for example, fatty acids (Dubois, E.; Cabuil, V.; Boue, F.; Perzynski, R. J. Chem. Phys 1999, 111, 7147), ionic surfactants (Massart, R.; Neveu, S.; Cabuil-Marchal, V.; Brossel, R.; Fruchart, J.-M.; Bouchami, T.; Roger, J.; Bee-Debras, A.; Pons, J.-N.; Carpentier, M. Procede d'obtention de supports magnetiques finement divises par modification contrôlee de la surface de particules précurseurs magnetiques chargees et produits obtenus. French Patent 2,662,539, May 23, 1990) (Shafi, K.V.P.M.; Ulman, A.; Yan, X.; Yang N-L.; Estournes, C.; White, H.; Rafailovich, M. Langmuir 2001, 17, 5093), amines and alcohols (Boal, A.K.; Das, K.; Gray, M.; Rotello, V. Chem. Mater. 2002, 14, 2628) have been investigated as stabilizing agents for magnetic nanoparticles. In all cases, however, these ligands were employed to enable particle dispersion in organic media. Particle stabilization in polar carrier liquids, such as water or ethylene glycol, has been achieved rather through the introduction of surface charges. In known preparations, particle aggregation is prevented by electrostatic stabilization employing the surface adsorption of citrate (Dubois, E.; Cabuil, V.; Boue F.; Perzynski, R. J. Chem. Phys.
1999, 111, 7147) or hydroxide (Tourinho, F. A.; Franck, R.; Massart, R. J. Mater. Sci. 1990, 25, 3249). Ions to produce negatively charged particles. Bilayers of ionic surfactants have also been reported to provide electrostatic stabilization through the outer layer of charged head groups surrounding the particles (Maity, D.; Agrawal, D. C. J. Magn. Magn. Mater. 2007, 308, 46.)

SUMMARY OF THE INVENTION

[0009] It is therefore an aim of the present invention to address the above mentioned issues.

[0010] According to a general aspect, there is provided a process for the preparation of a suspension of magnetic particles in a polar carrier liquid. The process comprises the step of: coating the surface of the magnetic particles with an organic ligand having a hydrophilic chain prior to the suspension.

[0011] According to a general aspect, there is provided a process for the preparation of a magnetically deformable mirror. The process comprises the steps of: coating magnetic particles with an organic ligand having a hydrophilic chain; adding the ligand coated magnetic particles to a polar carrier liquid to create a ferrofluid including a suspension of the ligand coated magnetic particles in the polar carrier liquid; and coating the ferrofluid with a reflective surface layer.

[0012] According to a general aspect, there is provided a process for the preparation of a ferrofluid. The process comprises the steps: coating magnetic particles with an organic ligand including a hydrophilic chain; and introducing the ligand coated magnetic particles in a polar carrier liquid to create a suspension of the ligand coated magnetic particles in the polar carrier liquid.

[0013] According to another general aspect, there is provided a suspension of magnetic particles in a polar carrier liquid wherein the magnetic particles are coated with an organic ligand having a hydrophilic chain.

[0014] According to still another general aspect, there is provided a ferrofluid comprising a suspension of magnetic particles coated with an organic ligand having a hydrophilic chain in a polar carrier liquid.

[0015] According to a further general aspect, there is provided a magnetically
deformable mirror comprising a ferrofluid coated with a reflective surface layer wherein the ferrofluid comprises a suspension of magnetic particles in a polar carrier liquid wherein the particles are coated with an organic ligand having a hydrophilic chain.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Figure 1 shows a schematic representation of a synthetic route leading to $\gamma$-Fe$_2$O$_3$ nanoparticles coated with either (A) 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MOEEAA) or (B) citrate;

[0017] Figure 2 is a X-ray diffraction pattern of synthesized iron oxide nanoparticles compared to literature data of maghemite ($\gamma$-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$);

[0018] Figure 3 is a TEM micrograph of uncoated iron oxide nanoparticles dried from aqueous suspension on a Formvar coated nickel grid wherein the particle size distribution is shown in the inset;

[0019] Figure 4 shows a IR spectra of (a) dried iron oxide nanoparticles coated with MOEEAA and (b) pure MOEEAA;

[0020] Figure 5 shows a IR spectra of (a) dried iron oxide nanoparticles coated with trisodium citrate and (b) pure trisodium citrate;

[0021] Figure 6 is a graph showing thermograms of (a) dried uncoated iron oxide nanoparticles and (b) dried iron oxide nanoparticles coated with MOEEAA;

[0022] Figure 7 is a graph showing thermograms of (a) dried uncoated iron oxide nanoparticles and (b) dried iron oxide nanoparticles coated with trisodium citrate;

[0023] Figure 8 shows intensity weighted z-average particle size distributions obtained from dynamic light scattering measurements on ethylene glycol suspension of (a) uncoated iron oxide nanoparticles, (b) iron oxide nanoparticles coated with citrate, (c) iron oxide nanoparticles coated with MOEEAA and (d) iron oxide nanoparticles coated with MOEEAA and subsequently treated with sodium hydroxide;

[0024] Figure 9 includes Fig. 9a, 9b, and 9c and are photographs showing magnetically deformable liquid mirrors prepared from silver nanoparticles spread on the surface of ethylene glycol based ferrofluids containing respectively (a) iron oxide nanoparticles coated with citrate, after five to seven days, (b) iron oxide nanoparticles
coated with MOEEAA, and (c) the same liquid mirror as pictured in Fig. 9(b), after 70 days; and

[0025] Figure 10 is a graph showing peak-to-valley amplitude of deformation as a function of applied magnetic field for a liquid mirror prepared from an ethylene glycol based ferrofluid containing MOAAEE coated iron oxide nanoparticles and a thin film of silver nanoparticles deposited at the surface.

DETAILED DESCRIPTION OF EMBODIMENTS

[0026] In a process for the preparation of stable suspensions of magnetic particles in a polar carrier liquid, the surface of the magnetic particles is coated with an organic ligand having a hydrophilic chain prior to the suspension.

[0027] In a particular embodiment, there is provided a suspension of magnetic particles in a polar carrier liquid wherein the magnetic particles are coated with an organic ligand having a hydrophilic chain.

[0028] In another embodiment, there is provided a magnetically deformable mirror, which comprises a ferrofluid coated with a thin reflective layer, such as a reflective film of silver nanoparticles. The ferrofluid includes a suspension of magnetic particles in a polar carrier liquid wherein the magnetic particles are coated with an organic ligand having a hydrophilic chain.

Polar carrier liquid

[0029] Particularly, the polar carrier liquid is ethylene glycol, polyethylene glycol, glycerol, an ionic liquid or combinations thereof. In an embodiment, the polar carrier liquid has a relatively high surface tension (or polarity). More particularly, the polar carrier liquid is ethylene glycol, polyethylene glycol or glycerol. Most particularly, the polar carrier liquid is ethylene glycol.

Magnetic particles

[0030] In particular, the magnetic particles are nanoparticles. The nanoparticles have a diameter ranging between 2 and 14 nm. The nanoparticles can include iron oxides and, in a particular embodiment, they can include maghemite (γ-Fe₂O₃). It can also include magnetite (Fe₃O₄), other magnetic nanoparticles or a combination of various magnetic nanoparticles.
[0031] The concentration of magnetic nanoparticles in the polar carrier liquid ranges between 1 and 25 wt%. In an alternative embodiment, it ranges between 5 and 20 wt% and, in another alternative embodiment, it ranges between 10 and 20 wt%. Higher concentrations of magnetic nanoparticles in the polar carrier liquid maximizes deformation resulting from the magnetic field.

[0032] In alternative embodiments, the magnetic nanoparticles can include other non-iron oxide particles such as and without being limitative cobalt and nickel nanoparticles.

Organic ligand-coating

[0033] Particularly, the organic ligand has an hydrophilic chain and, more particularly, an oxyethylene chain. In an embodiment, the oxyethylene chain is selected from carboxylic acid-terminated organic molecules. More particularly, the organic molecule is a polar carbon chain, particularly a negatively charged terminated carbon chain such as negatively charged-terminated polyethylene glycol. Most particularly, the particles are coated with carboxylic acid-terminated polyethylene glycol of a structure as is shown below:

\[
\text{CH}_3\text{-O-}[\text{CH}_2\text{-CH}_2\text{-O}]_n\text{-CH}_2\text{-C}^{\text{O}}\text{-OH}
\]

wherein \(n\) is an integer ranging from 1 to 50. Particularly, the polymeric portion of the molecule can range from 1 to 30 repeating units (\(n\)), more particularly from 1 to 15, most particularly from 2 to 8, even most particularly \(n = 2\).

In alternative embodiments, it is appreciated that the organic ligand can include another oxyethylene chain and that the oxyethylene chain can include another attachment group which can be positive, negative or neutral.

In an embodiment, the concentration of organic ligand applied to the magnetic nanoparticles ranges between 1 and 15 wt% and, in an alternative embodiment, it ranges between 3 and 10 wt%.

Particular embodiment
In a particular embodiment, there is provided a stable suspension of magnetic nanoparticles in ethylene glycol where the magnetic particles are coated with 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MOEEAA; where n is 2). This organic molecule is highly soluble in polar liquids, i.e. the organic molecule has a relatively high chemical affinity for the polar liquid. This molecule is composed of a carboxylic acid group, which adsorbs to the particle surface, and a methoxy terminated chain of two ethoxy groups which ensures favourable interaction with the polar carrier liquid.

The improved polar ferrofluid reported herein shows excellent magnetic stability and does not precipitate.

These new MOEEAA-coated magnetic particles allow for the deposition of a reflective layer (MELLF) on the air-ferrofluid interface.

Reflective layer

The reflective layer can be made of colloidal particles, such as nanoparticles, which can be metallic or non-metallic. In an embodiment, the nanoparticles are silver particles, although any other suitable reflecting metallic particles from the periodic table can be used, such as gold, aluminum, or the like. Nanoparticles can be obtained by chemical means such as reduction, or non chemical means such as laser treatment or mechanical ablation from a solid. The reflecting particles can be coated with a surfactant, which are well-known to those skilled in the art, to stabilize the reflecting layer. Coated fluids usually result in high-reflectivity mirrors, especially when reflecting metallic nanoparticles are used.

In another embodiment, the ferrofluid can be covered with a flexible membrane that follows the deformation of the ferrofluid, and the latter may be made with numerous techniques. For example, the membrane may be made of Mylar™, Melinex™, polyimide, polyamide, gold coated nickel, silicon nitride or any coated or uncoated polymer film. If the membrane is uncoated, it forms the mirror surface. If the membrane is in direct contact with the ferrofluid, the coated or uncoated membrane forms the mirror surface and follows the deformation of the liquid substrate.

In another embodiment, the flexible membrane can be coated with a reflective layer using several techniques. For this coating purpose, one can use chemical deposition in aqueous or non-aqueous media, electrodeposition, vaporization, coating by sputtering from hot electrically heated elements, or any other method known
by one skilled in the art. In such a membrane arrangement, the ferrofluid supports the surface allowing a thinner membrane than is possible with mirrors employing membranes over an air gap. The ferrofluid provides a means to deform the membrane that is free of print through effects.

[0040] In another embodiment, a transparent rigid membrane can be disposed above and not directly in contact with the liquid reflective mirror. This transparent rigid membrane protects the optical surface from dust, evaporation or other contamination.

EXAMPLES

Example 1. Preparation of the magnetic particles

[0041] Particles were prepared by a precipitation technique and, more particularly, by coprecipitation involving the addition of an alkaline solution to an acidic aqueous mixture of ferrous and ferric salt. The procedure is similar, but not identical to, a previously reported method by Tourinho et al. (F. A. Tourinho, R. Franck, R. Massart, “Aqueous ferrofluids based on manganese and cobalt ferrites” J. Mater. Sci 25 (1990) 3249-3254).

[0042] Separate solutions of FeCl₃ and FeCl₂ were prepared in aqueous hydrochloric acid (0.09M). Concentrations were selected to maintain a molar ratio [Fe(II)/Fe(III)] = 0.5. The two solutions were heated to 70°C and combined for a total volume of 20OmL ([Fe]_°_t₈ = 0.15M), just prior to the next step.

[0043] 20 mL of a solution containing both NaOH (10M) and trisodium citrate dihydrate (0.085M) (6% molar ratio of [Fe]_°_t₈) was added quickly to the iron solution with both solutions being previously heated to 70°C. The resulting solution was maintained at 70°C and under vigorous stirring for 30 minutes. The resulting magnetite particles were collected with a strong magnetic field using a permanent magnet.

[0044] The Fe₂O₄ particles were washed three times by stirring the precipitate with 20OmL of nanopure water. Each nanopure water washing was followed by a washing with 20OmL of nitric acid (1M). The particles were decanted between each step with a strong magnetic field using a permanent magnet.

[0045] The particles were treated with nitric acid (2M) for 3 hours in order to introduce a positive charge on the surface.
The particles were collected with a magnet and re-dispersed in 100mL of water.

100mL of an aqueous iron(III) nitrate nonahydrate solution (0.5M) (or ferric nitrate) was added to the particle suspension and heated at 100°C under vigorous stirring. Stirring was continued for 30 minutes to oxidize at least a portion of magnetite ($\text{Fe}_3\text{O}_4$) to maghemite ($\gamma\text{-Fe}_2\text{O}_3$).

The particles were decanted with a strong magnetic field using a permanent magnet and washed twice with acetone (100mL) before being dispersed in 100mL of nanopure water.

Example 2. Addition of dispersing/stabilizing agents

Two different methods of stabilisation were employed.

2a. Stabilisation with MOEEAA:

The aqueous suspension of particles (prepared as described in example 1) was centrifuged at 3500 rpm to eliminate aggregates.

3.5 mL of 2-[2-(2-Methoxyethoxy)ethoxy]acetic acid (MOEEAA) was added to the particles dispersed in nanopure water previously heated at 90°C and the mixture was kept at this temperature and under vigorous stirring for 30 minutes. To isolate ligand-coated particles, an equivalent volume of acetone was added and particles were centrifuged at 15000 rpm for 90 minutes.


The aqueous suspension of particles (100mL) was heated to 90°C and 2 grams of sodium citrate were added under vigorous stirring. The particles were washed twice with acetone, being collected during decantation by a magnetic field.

The particles were re-dispersed in water and aggregates were eliminated by centrifugation at 2000 rotations/min for 15 minutes.

The various synthetic steps are summarized in Figure 1 for both MOEEAA and citrate coatings. Positively charged particles obtained after treatment with
Fe(NO\(_3\))\(_3\) without stabilizing coating, can be dispersed in ethylene glycol, but the suspension is not stable in the presence of a magnetic field. Both negatively charged citrate-coated particles (A) and positively charged particles functionalized with MOEEAA (B) form stable suspensions in ethylene glycol, but, as shown below, only the later are compatible with the MELLF. Positively charged particles functionalized with MOEEAA form stable suspensions also in glycerol.

Example 3. Preparation of the ferrofluid

[0055] The stabilized particles, obtained either through procedure 2a or procedure 2b were dispersed in ethylene glycol to obtain a weight percentage of particles of 19%.

Example 4. Preparation of the silver particles

[0056] The preparation of the silver particles was as described in United States Patent no. 6,951,398.

Example 5. Preparation of liquid mirrors

[0057] Magnetically deformable mirrors were prepared by coating the ferrofluid with a surface film of silver nanoparticles. Typical mirrors were prepared with 6 mL of ferrofluid, placed in an aluminum dish having a diameter of 7 cm. The metallic silver particles, prepared and concentrated as described (Gingras, J.; Dery, J. P.; Yockel-Lelievre, H.; Borra, E. F.; Ritcey, A. M. Colloids Surf., A 2006, 279, 79.) were sprayed onto the ferrofluid surface with a commercial paint spray gun connected to a nitrogen cylinder at a pressure of 275 kPa.

Example 6. Characterization of iron oxide nanoparticles particles

[0058] X-ray diffraction patterns of dry magnetic particles were obtained with a Siemens XRD system with Cu K radiation.

[0059] Figure 2 shows the x-ray diffraction pattern recorded for the iron oxide nanoparticles isolated before functionalization with MOEEAA or citrate. Although the co-precipitation method employed to prepare the particles has been previously reported to yield maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)). (Bee, A.; Massart, R.; Neveu, S. J. Magn. Magn. Mater. 1995, 149, 6) the possibility of obtaining mixtures containing residual magnetite (Fe\(_3\)O\(_4\)) has also been noted. (Maity, D.; Agrawal, D. C. J. Magn. Magn. Mater. 2007, 308, 46). Known x-ray diffraction patterns (Cornell, R. M.; Schertmann, U. The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses, VCH
Publishers, Weinheim, 2003) for $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ are thus also shown in Figure 2 for comparison. The position and relative intensities of the diffraction peaks reported in Table 1 indeed indicate that it is very difficult to distinguish between the two forms by this method. Given the oxidizing conditions used in particle preparation, it can be assumed that maghemite ($\gamma$-Fe$_2$O$_3$) is primarily obtained, but the possibility of residual magnetite remaining in the core of the particles cannot be excluded.

<table>
<thead>
<tr>
<th>Literature data</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Fe$_2$O$_3$ &amp; Fe$_3$O$_4$</td>
<td>26°</td>
</tr>
<tr>
<td>26°</td>
<td>1</td>
</tr>
<tr>
<td>23.86</td>
<td>12</td>
</tr>
<tr>
<td>26.21</td>
<td>14</td>
</tr>
<tr>
<td>30.29</td>
<td>30</td>
</tr>
<tr>
<td>35.72</td>
<td>100</td>
</tr>
<tr>
<td>43.38</td>
<td>15</td>
</tr>
<tr>
<td>53.90</td>
<td>9</td>
</tr>
<tr>
<td>57.45</td>
<td>20</td>
</tr>
<tr>
<td>63.07</td>
<td>40</td>
</tr>
<tr>
<td>74.61</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 1. X-ray diffraction data literature for maghemite ($\gamma$-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) compared to experimental data obtained from prepared iron oxide magnetic nanoparticles (for 2θ= 20° - 80°).

[0060] Transmission electron microscopy images of iron oxide nanoparticles were obtained with a JOEL JEM-1230 microscope operated at an acceleration voltage of 80 kV. Samples were prepared by evaporation of a drop of the particle suspension on a Formvar coated nickel grid.

[0061] A typical transmission electron micrograph of the iron oxide nanoparticles particles is shown in Figure 3. The particles were found to be roughly spherical with a mean diameter of about 6nm. The particle size distribution, as evaluated from manual measurements of about 1000 particles, is also shown in Figure 3 and agrees well with that typically obtained by the co-precipitation method of particle preparation (Tourinho, F. A.; Franck, R.; Massart, R. J. Mater. Sci. 1990, 25, 3249). Similar images were obtained for the particles functionalized with either citrate or MOEEAA.
Example 7. Characterization of surface functionalized particles

[0062] Particles functionalized with either MOEEAA or citrate were characterized by infrared spectroscopy and thermogravimetry. Infrared measurements provide information about the chemical nature of the coating layer, whereas thermogravimetry allows for the quantitative evaluation of the grafting density.

Infrared Spectroscopy

[0063] Infrared spectra of the dried particles were recorded using a Nicolet Magna IR 850 spectrometer equipped with a Golden Gate single reflection diamond ATR series MkII.

[0064] The infrared spectra of pure MOEEAA and of dried MOEEAA coated particles are shown in Figure 4. The absorption frequencies corresponding to the principal bands are reported in Table 2 along with peak assignments. In the case of pure MOEEAA, the most intense absorption bands are found at 1098 cm\(^{-1}\), 1740 cm\(^{-1}\) and 2881 cm\(^{-1}\), arising from vibrations characteristic of the constituent ether, carboxylic acid carbonyl and methylene groups, respectively. The spectrum of the coated particles exhibits bands corresponding to the ether and methylene stretching frequencies at 1093 cm\(^{-1}\) and 2866 cm\(^{-1}\), thus confirming the presence of MOEEAA. Bands arising from the carboxylate group are also evident, appearing at positions that differ significantly from that observed for the carbonyl of the free molecule. In fact, three relatively intense bands are observed at 1587 cm\(^{-1}\), 1404 cm\(^{-1}\) and 1316 cm\(^{-1}\). The strong band at 1587 cm\(^{-1}\) can be attributed to the carboxylate asymmetric stretch indicating that the free acid is deprotonated upon binding to the surface of the particle. The two bands at 1404 cm\(^{-1}\) and 1316 cm\(^{-1}\) can both be assigned to the symmetric stretching vibration of the carboxylate group, suggesting the presence of two different modes of surface coordination. In a detailed infrared study of the binding of a number of carboxylic acids to oxidized aluminium, Allara et al. (Allara, D. L.; Nuzzo, R. G. Langmuir 1985, 1, 52) also reported two distinct symmetric carboxylate stretching frequencies (1475 cm\(^{-1}\) and 1417 cm\(^{-1}\)). Although these authors attributed the observation of two bands to the presence of two types of adsorbate-substrate bonding, they were unable to provide specific structural assignments. Extensive studies of metal complexes of carboxylic acids indicate that the frequency difference between the asymmetric and symmetric stretching vibrations can be correlated with the bonding mode (Nakamoto, K. Infrared and Raman spectra of inorganic and coordination
compounds; John Wiley and Sons: New York, 1997). Bidentate complexes, in which both carboxylate oxygen atoms are bound to a single metal ion, exhibit frequency differences between the two vibrations of 40-70 cm\(^{-1}\). Bridging complexes in which the two oxygen atoms are bound to neighbouring metal ions show larger frequency differences, of the order of 140-170 cm\(^{-1}\). The largest frequency differences, in some cases exceeding 300 cm\(^{-1}\), are observed for unidentate complexes in which only one oxygen atom is bound to the metal. The IR spectrum of the MOEEAA functionalized magnetic particles exhibit two bands assigned to the symmetric carboxylate stretch, at frequencies corresponding to \([u_{\text{a}}(\text{COO}^-)-u_{\text{s}}(\text{COO}^-)]\) equal to 183 cm\(^{-1}\) and 271 cm\(^{-1}\), respectively. These frequency differences indicate that the ligand is bound to the surface both through bridging and unidentate structures.

<table>
<thead>
<tr>
<th>Band frequency / cm(^{-1})</th>
<th>MOEEAA coated (\gamma)-Fe(_2)O(_3) particles</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>2866</td>
<td>(u(\text{C-H})) for (-\text{CH}_2)</td>
</tr>
<tr>
<td>1740</td>
<td>-</td>
<td>(u(\text{C=O})) for free (-\text{COOH})</td>
</tr>
<tr>
<td>-</td>
<td>1587</td>
<td>(u(\text{COO}^-)) asym for adsorbed (\text{COO}^-)</td>
</tr>
<tr>
<td>-</td>
<td>1404</td>
<td>(u(\text{COO}^-)) sym (bridging coordination)</td>
</tr>
<tr>
<td>-</td>
<td>1316</td>
<td>(u(\text{COO}^-)) sym (unidentate coordination)</td>
</tr>
<tr>
<td>1200</td>
<td>1190</td>
<td>(u(\text{C-O-C})) asym</td>
</tr>
<tr>
<td>1098</td>
<td>1093</td>
<td>(u(\text{C-O-C})) sym</td>
</tr>
</tbody>
</table>

Table 2. Infrared band position and vibrational assignments for 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MOEEAA) and dried iron oxide nanoparticles coated with MOEEAA. ¹Nakamoto, K. *Infrared and Raman spectra of inorganic and coordination compounds;* John Wiley and Sons: New York, 1997.

[0065] Willis *et al.* (Willis, A. L.; Turro, N. J.; O'Brien, S. *Chem. Mater.* 2005, 17, 5970) recently reported that the infrared spectrum of oleic acid bound to \(\gamma\)-Fe\(_2\)O\(_3\), exhibits asymmetric and symmetric carboxylate stretching bands at 1527 cm\(^{-1}\) and 1430 cm\(^{-1}\), respectively. While the identification of a single symmetric stretching frequency implies a single bonding mode in this case, Willis *et al.* note that the bands are relatively large and attribute this to the presence of a mixture of compounds on the surface.
It is relevant to note that the symmetric carboxylate stretching frequencies observed for MOEEAA bound to iron oxide nanoparticles appear at significantly lower frequencies that those found for carboxylic acids on Al₂O₃ (Allara, D. L.; Nuzzo, R. G. Langmuir 1985, 1, 52). The stretching frequencies of coordinated carboxylates are known to vary significantly from one metal ion to another (Nakamoto, K.; McCarthy, P. J. Spectroscopy and Structure of Metal Chelate Compounds; John Wiley and Sons: New York, 1965). IR spectra of a series of n-alkanoic acids self-assembled on metal oxide surfaces indicate that both the carboxylate symmetric and asymmetric stretching frequencies shift to lower frequencies as stability of the ligand to surface bond increases. The relatively low frequencies observed for the MOEEAA functionalized particles thus imply relatively strong bonding.

Figure 5 shows the infrared spectrum of dried iron oxide nanoparticles coated with citrate. The spectrum of trisodium citrate is also shown for comparison. Both spectra exhibit bands characteristic of the asymmetric and symmetric stretching vibrations of the carboxylate moiety. In this case, the spectral changes that accompany surface bonding are less significant than those observed for MOEEAA coated particles. This is because the precursor ligand was introduced as a carboxylate salt rather than in the acid form. Furthermore, each ligand molecule contained three carboxylate groups and not all were involved in direct interactions with the surface. Nevertheless, small shifts to lower frequencies are observed for both asymmetric (1574 cm⁻¹ to 1565 cm⁻¹) and symmetric (1385 cm⁻¹ to 1380 cm⁻¹) stretching bands upon the adsorption of citrate to the particle surface.

Thermogravimetric analyses

Thermogravimetric analyses were performed with a Mettler Toledo instrument (model TGA/SDTA851©) using an aluminum oxide crucible. Samples were heated under a simultaneous flow of air and nitrogen at a rate of 50 mL/min for each gas. Samples were heated from 25°C to 900°C at the heating rate of 10°C/min.

The weight loss observed upon iron oxide nanoparticles coated with MOEEAA is plotted in Figure 6. The thermogram obtained for the uncoated particles is also provided for comparison. Upon heating between room temperature and 900°C, the uncoated particles show a weight loss of 9.4 % that can be attributed to water desorption from the surface. Over the same temperature range, the coated particles exhibit a greater weight loss due to the decomposition of the organic ligand. If it is
assumed that the coated and uncoated particles have the same water content, the weight percent of MOEEAA bound to the functionalized particles can be evaluated from the difference in weight loss between the two samples. In the present case, this difference is 5%. This result can be combined with the average particle size determined by TEM to estimate the grafting density of the MOEEAA chains on the particle surface as 1.2 molecule / nm². This relatively low grafting density provides a reasonable justification for the assumption that the water content of the particles is not significantly altered by the presence of the MOEEAA chains.

[0070] Figure 7 shows the thermograms obtained for the citrate coated particles. The functionalized particles exhibit a weight loss that exceeds that observed for the uncoated particles by 23%. If this difference is entirely attributed to the mass of citrate present, a grafting density of 6.4 molecules / nm² is obtained. It is, however, important to note that in the case of citrate adsorption, the assumption that the water content is unaltered by the presence of the ligand is probably not justified and the grafting density obtained in this way can only be considered as an estimate.

Example 8. Characterization of dispersed particles

[0071] Zeta potential and particle size were determined from dynamic light scattering measurements carried out with a Malvem Zetasizer nano series Nano-ZS. Particles were dispersed in ethylene glycol at a weight percentage of 0.6%. The viscosity of the pure solvent was employed in the particle size calculations.

[0072] Dynamic light scattering measurements were performed on ethylene glycol suspensions of uncoated iron oxide nanoparticles and of iron oxide nanoparticles coated with either citrate or MOEEAA. The resulting particle size distributions are plotted in Figure 8 (curves a, b and c). The three samples exhibit near identical particle size distributions centered near diameters of 100 nm. This average particle size is much greater than that evaluated from TEM images. Dynamic light scattering typically yields particle sizes that exceed those obtained by microscopy. This is in part because dynamic light scattering measures the hydrodynamic radius which is larger than the radius of a dry particle. In addition, the dynamic light scattering results are expressed as the intensity weighted z-average which is biased toward larger particles since the scattering intensity is proportional to the square of particle molecular weight. However, neither of these factors is sufficient to explain the large difference in particle size obtained here. Similar differences have been reported for maghemite particles.
dispersed in both water and dodecane and attributed to particle aggregation. The aggregation of magnetic particles in the absence of a magnetic field were theoretically investigated by the Monte Carlo technique. In the case of particles having a diameter of 10 nm, the attractive magnetostatic interaction energy between particles can be evaluated as being on the order of 10 kT. This attraction is sufficient to cause the formation of dynamic particle clusters containing on the order of 5-15 particles. The presence of such clusters in the particle suspensions would clearly explain why the hydrodynamic diameters obtained by dynamic light scattering are an order of magnitude larger than the diameters observed by TEM.

[0073] Dynamic light scattering was also employed to evaluate the zeta potential of the various particles. The results are summarized in Table 3. The uncoated particles were found to be positively charged, as expected from their prior treatment with nitric acid. The introduction of MOEEAA did not significantly alter the particle surface charge. This observation is consistent with the relatively low grafting density determined by thermogravimetry measurements.

<table>
<thead>
<tr>
<th>Nature of the particles</th>
<th>Zeta potential / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>+45</td>
</tr>
<tr>
<td>Coated with citrate</td>
<td>-50</td>
</tr>
<tr>
<td>Coated with MOEEAA</td>
<td>+44</td>
</tr>
<tr>
<td>Coated with MOEEAA - hydroxide treated</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3. Zeta potential of iron oxide nanoparticles with differing surface coatings, dispersed in ethylene glycol.

[0074] When dispersed in water, particles either coated with MOEEAA or not lead both to acidic ferrofluids at pH 4. The iron oxide nanoparticles coated with MOEEAA are unstable in aqueous solution between pH 5 to pH 10 as described in Hasmonay et al. (Hasmonay, E.; Bee, A.; Bacri, J.-C.; Perzynski, R. J. Phys. Chem. B 1999, 703, 6421) for similar iron oxide nanoparticles.

[0075] As discussed in further detail below, the presence of surface grafted MOEEAA has an important effect on the stability of the ferrofluid prepared in ethylene glycol. In order to determine whether the steric repulsion between particles generated by the MOEEAA chains is sufficient to prevent particle agglomeration, the positive particles were neutralized by the addition of sodium hydroxide ([NaOH] = 0.06 M). As
illustrated in Figure 8 (curve d), this treatment has an important effect on the particle size distribution, which is shifted to larger hydrodynamic diameters and significantly broadened, suggesting increased aggregation. This observation indicates that the particle suspension is primarily stabilized by electrostatic repulsions and the grafted MOEEAA chains alone do not provide sufficient steric stabilization.

Example 9. Characterization of ferrofluids and magnetically deformable mirrors

[0076] Ferrofluids were prepared by the dispersion of the various maghemite particles in ethylene glycol at a particle weight percent of 19%. The relative performance of the ferrofluids was evaluated from the amplitude of the surface deformation resulting from the application of a static magnetic field. For instance, the magnetic field can be created by means of permanent magnets, electromagnets, or a combination thereof. The deformation $h$ can be approximated as

$$h = \frac{\mu_0 (\mu_r - 1)}{2 \rho g} (\mu_r H_n^2 + H_t^2)$$

[0077] where $\rho$ is the density of the ferrofluid, $H_n$ and $H_t$ are the normal and tangential components of the magnetic field inside the ferrofluid, $\mu_r$ is the relative magnetic permeability and $\mu_0$ the permeability of free space. This equation indicates that for a fixed magnetic field strength, the observed deformation is a measure of $\mu_r$, which is, in turn, related to the magnetic susceptibility/ by

$$\mu_r = \chi + 1$$

[0078] Ferrofluids prepared from the uncoated particles showed unstable surface deformations when a magnetic field is applied. Ferrofluids prepared from particles coated with either MOEEAA or citrate, on the other hand, were stable and exhibited surface deformations that depend on the magnetic field strength.

[0079] Performance of the ferrofluid was evaluated by placing a sample on a single electromagnetic coil. Magnetic fields of the order of a few Gauss were generated by the application of a potential to the coil. As shown in Table 4, the MOEEAA-stabilized particles (A) demonstrated a similar performance - similar deformations at the same magnetic field as the citrate-stabilized particles (B).

[0080] For a given magnetic field strength, larger deformations were found for the
MOEEAA coated particles than for those stabilized with citrate. This may in part be a result of the lower grafting density of MOEEAA which results in a greater concentration of magnetic material in the ferrofluid suspension at a given weight fraction of particles.

<table>
<thead>
<tr>
<th>Actuator potential / V</th>
<th>Amplitude of deformation / µm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MOEEAA</td>
</tr>
<tr>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 4. Peak-to-valley amplitude of deformation as a function of applied voltage for ethylene glycol based ferrofluids prepared from iron oxide nanoparticles coated with either MOEEAA or citrate.

[0081] The clear advantage of the MOEEAA stabilized ferrofluid is demonstrated during coating with a thin reflective film of silver nanoparticles to fabricate magnetically deformable mirrors (Gingras, J.; Dery, J. P.; Yockell-Lelievre, H.; Borra, E. F.; Ritcey, A. M. Colloids Surf., A 2006, 279, 79). The photographs of mirrors prepared in this way are provided in Figure 9 for ferrofluids containing MOEEAA and citrate stabilized magnetic particles. The surface film of silver nanoparticles is clearly disrupted by the citrate stabilized suspension after five to seven days as shown in Figure 9a. More particularly, cracks having width of few millimetres appeared on the reflective surface about one week after deposition. Deposition of MELLF on a ferrofluid with citrate-stabilized particles showed instabilities.

[0082] Referring now to Figures 9b and 9c, there is shown that the liquid mirror spread on the MOEEAA stabilized ferrofluid, on the other hand, exhibits excellent reflectivity properties, comparable to those previously reported for silver nanoparticles spread on water and the MELLF optical quality remains stable for up to 70 days after the deposition (Gingras, J.; Dery, J. P.; Yockell-Lelievre, H.; Borra, E. F.; Ritcey, A. M. Colloids Surf., A 2006, 279, 79).

[0083] Thus, comparatively to citrate stabilized magnetic particles, the compatibility of MOEEAA-stabilized particles with the MELLF is higher.

[0084] The surface roughness of the silver coated ferrofluids was evaluated with a general purpose Zygo Mach-Zehnder interferometer. Magnetic deformations were
induced by placing an electromagnetic coil, capable of generating magnetic fields of the order of a few Gauss, directly below the mirrors as described in Massart, R. IEEE Trans. Magn. 1981, MAG-17, 1247. An Imagine Optics Shack-Hartmann wavefront analyser was employed to measure the resulting surface deformation.

[0085] Interferometry measurements indicate that the reflective film forms a smooth surface with a root mean square roughness (RMS) of approximately $\lambda / 20$ at 624 nm. Reflectivity of the film remained the same as reported for silver films spread on water. The reflectivity is typically around 60% in the visible and 80% in near infrared and beyond.

[0086] The stability of the liquid mirror was also investigated through repeated magnetic deformation over a period of three months. Figure 10 shows that the magnetic response remains constant over this time period, further illustrating the compatibility between the surface film of silver particles and the ferrofluid.

[0087] While it is clear that the MOEEAA coated particles allow for the preparation of a ferrofluid that is compatible with the reflective silver surface layer, the reason for this cannot be unambiguously identified. The MOEEAA (non-ionic) and citrate (ionic) stabilized particles differ not only in the chemical nature of the ligand, but also in the sign of the electrostatic charge. The MOEEAA coated particles are positive, whereas those stabilized with citrate are negatively charged. Unfortunately, it is difficult to evaluate the electrostatic charge of the silver nanoparticles. Although negatively charged when initially prepared in aqueous solution, the particles spontaneously flocculate to form a surface film upon coating with an organic ligand (Gingras, J.; Dery, J. P.; Yockell-Lelievre, H.; Borra, E. F.; Ritcey, A. M. Colloids Surf., A 2006, 279, 79). The expulsion of the particles from the aqueous phase during this step implies that their surface charge is significantly reduced. The sign of any residual charge, however, is unknown. If the silver particles carry a net positive charge, their compatibility with the MOEEAA stabilized ferrofluid could originate in electrostatic repulsions.

[0088] As noted above, the uncoated positively charged particles do not form a stable suspension in ethylene glycol. The presence of MOEEAA, even at a relatively low grafting density, allows for the preparation of a stable suspension. This ligand therefore clearly creates a repulsive barrier to particle aggregation and an increased affinity of the particles for the suspending medium. It is possible that the MOEEAA chains are also responsible for the screening of disruptive interactions between the
magnetic nanoparticles of the ferrofluid and the silver particles spread at its surface.

[0089] A novel polar liquid based ferrofluid and, in an embodiment, an ethylene glycol based ferrofluid was prepared and characterized. This ferrofluid is compatible with a surface MELLF and thus suitable for the fabrication of magnetically deformable liquid mirrors.

[0090] Ethylene glycol was identified as an appropriate carrier liquid for a ferrofluid and thus for magnetically deformable mirrors. The relatively high surface tension of this liquid allows for the deposition of a stable reflective film of silver nanoparticles. Furthermore, the relatively low vapor pressure of ethylene glycol slows evaporation.

[0091] The ferrofluid also includes positively charged iron oxide nanoparticles, such as maghemite nanoparticles, coated with an organic ligand having a hydrophilic chain, such as and without being limitative, MOEEAA. The ferrofluid exhibit a magnetic response that is equivalent, or perhaps even superior to that found for corresponding citrate stabilized particles.

[0092] Unlike the uncoated particles, maghemite nanoparticles coated with MOEEAA and dispersed in ethylene glycol remained stable in the presence of a magnetic field. MOEEAA should exhibit a strong affinity for the carrier liquid (ethylene glycol) due to the ethoxy group (-O-CH₂CH₂) within the chain.

[0093] Infrared spectra indicate that surface grafting occurs through the terminal carboxylate group which is bound to the γ-Fe₂O₃ particles both through bridging and unidentate structures. A surface grafting density of 1.2 molecules / nm² is determined from thermogravimetry measurements. Although MOEEAA functionalization increases the stability of maghemite nanoparticle suspensions in ethylene glycol, surface charge is also important for the prevention of particle agglomeration.

[0094] Furthermore, the presence of the terminal carboxylate group ensures stable grafting to the magnetic iron oxide nanoparticles.

[0095] Importantly, the MOEEAA based system is compatible with the deposition of surface films of silver nanoparticles, allowing the preparation of magnetically deformable liquid mirrors. Such mirrors exhibit optical quality surfaces and magnetic performance that remains stable over 70 days. Corresponding mirrors supporting by ferrofluids composed of citrate coated nanoparticles exhibit dull non-reflecting surfaces
with numerous cracks that appear shortly after the spreading of the reflective silver layer.

[0096] Optics and electronics are an enabling technologies. A large number of applications: telecommunications, projection systems, aspheric surfaces in optical systems (e.g. microscopes, telescopes, lithographic machines) can thus be foreseen for high-reflectivity mirrors. Moreover, the ferrofluid can be used as replacement for Micro Electro-Mechanical Systems (MEMS), which are used among others to redirect light in switches used in telecommunications.

[0097] Low-reflectivity optical elements, usually made of uncoated polished glass, are commonly used for optical-testing purposes. Magnetically shaped low-reflectivity liquids can be used for ophthalmologic applications. They can generate surfaces having complex shapes that are known and can be used to determine the shape of the lens of the human eye, the crystalline lens. This allows the measurement of high-order aberrations (optical defects) of the crystalline lens so that they can be corrected with the appropriate medical procedure, for example, surgery (e.g. with a laser beam) that reshapes the lens. The magnetically shaped reference surface can further be used to verify the correction made to the lens of the eye before, during or after the procedure. In current surgical procedures, one only removes the defocus aberration (correct the focal length). The advantage of measuring and removing high-order aberrations is that the vision of the patient can be further improved. One can thus envision removing Coma, Astigmatism and even even higher order aberrations.

[0098] The embodiments of the invention described above are intended to be exemplary only. The scope of the invention is therefore intended to be limited solely by the scope of the appended claims.
WHAT IS CLAIMED IS:

1. A process for the preparation of a suspension of magnetic particles in a polar carrier liquid, the process comprising the step of:

   coating the surface of the magnetic particles with an organic ligand having a hydrophilic chain prior to said suspension.

2. The process according to claim 1, wherein the hydrophilic chain of the organic ligand comprises an oxyethylene chain.

3. The process according to one of claims 1 and 2, wherein the organic ligand is a negatively-charged-terminated organic molecule.

4. The process according to claim 3, wherein the negatively-charged-terminated organic molecule is carboxylic acid-terminated polyethylene glycol.

5. The process according to claim 4, wherein the carboxylic acid-terminated polyethylene glycol is selected from the group consisting of:

   \[
   \text{CH}_3\text{-O-}(\text{CH}_2\text{-CH}_2\text{-O})_n\text{-CH}_2\text{-C}\text{\_OH}
   \]

   wherein \(n\) is an integer from 1 to 50.

6. The process according to claim 5, wherein the carboxylic acid-terminated polyethylene glycol is 2-[2-(2-methoxyethoxy)ethoxy]acetic acid.

7. The process according to anyone of claims 1 to 6, wherein the magnetic particles are nanoparticles comprising iron oxides.

8. The process according to claim 7, wherein the iron oxides comprise at least one of maghemite \(\text{CyFe}_2\text{O}_3\) and magnetite \(\text{Fe}_3\text{O}_4\).

9. The process according to anyone of claims 1 to 8, wherein the polar carrier liquid is a liquid selected from the group comprising ethylene glycol,
polyethylene glycol, glycerol, ionic liquids, and combinations thereof.

10. The process according to claim 9, wherein the polar carrier liquid comprises ethylene glycol.

11. The process according to anyone of claims 2 to 10, wherein the organic ligand is highly soluble in the polar carrier liquid.

12. A process for the preparation of a magnetically deformable mirror, the process comprising the steps of:
   - coating magnetic particles with an organic ligand having a hydrophilic chain;
   - adding the ligand coated magnetic particles to a polar carrier liquid to create a ferrofluid including a suspension of the ligand coated magnetic particles in the polar carrier liquid; and
   - coating the ferrofluid with a reflective surface layer.

13. The process according to claim 12, wherein the hydrophilic chain of the organic ligand comprises an oxyethylene chain.

14. The process according to one of claims 12 and 13, wherein the organic ligand is a negatively-charged-terminated organic molecule.

15. The process according to claim 14, wherein the negatively-charged-terminated organic molecule is carboxylic acid-terminated polyethylene glycol.

16. The process according to claim 15, wherein the carboxylic acid-terminated polyethylene glycol is selected from the group consisting of:

\[
\text{CH}_3\text{-O-}\text{(CH}_2\text{-CH}_2\text{-O)}_n\text{-CH}_2\text{-C}^\text{=O}\text{OH}
\]

wherein \(n\) is an integer from 1 to 50.

17. The process according to claim 16, wherein the carboxylic acid-terminated
polyethylene glycol is 2-[2-(2-methoxyethoxy)ethoxy]acetic acid.

18. The process according to anyone of claims 12 to 17, wherein the magnetic particles are nanoparticles comprising iron oxides.

19. The process according to claim 18, wherein the iron oxides comprise at least one of maghemite (\(\gamma-\text{Fe}_2\text{O}_3\)) and magnetite (\(\text{Fe}_3\text{O}_4\)).

20. The process according to anyone of claims 12 to 19, wherein the polar carrier liquid is a liquid selected from the group comprising ethylene glycol, ethylene glycol, polyethylene glycol, glycerol, ionic liquids, and combinations thereof.

21. The process according to claim 20, wherein the polar carrier liquid comprises ethylene glycol.

22. The process according to anyone of claims 12 to 21, wherein the organic ligand is highly soluble in the polar carrier liquid.

23. The process according to anyone of claims 12 to 22, wherein the reflective surface layer comprises a reflective film of reflective metallic particles.

24. The process according to claim 23, wherein the metallic particles comprises silver nanoparticles.

25. A process for the preparation of a ferrofluid, the process comprising the steps: coating magnetic particles with an organic ligand including a hydrophilic chain; and introducing the ligand coated magnetic particles in a polar carrier liquid to create a suspension of the ligand coated magnetic particles in the polar carrier liquid.

26. The process according to claim 25, wherein the hydrophilic chain of the organic ligand comprises an oxyethylene chain.

27. The process according to one of claims 25 and 26, wherein the organic ligand
is a negatively-charged-terminated organic molecule.

28. The process according to claim 27, wherein the negatively-charged-terminated organic molecule is carboxylic acid-terminated polyethylene glycol.

29. The process according to claim 28, wherein the carboxylic acid-terminated polyethylene glycol is selected from the group consisting of:

\[
\text{CH}_3\text{-O-}(\text{CH}_2\text{-CH}_2\text{-O})_n\text{-CH}_2\text{-C} - \text{OH}
\]

wherein \( n \) is an integer from 1 to 50.

30. The process according to claim 29, wherein the carboxylic acid-terminated polyethylene glycol is 2-[2-(2-methoxyethoxy)ethoxy]acetic acid.

31. The process according to anyone of claims 25 to 30 wherein the magnetic particles are nanoparticles comprising iron oxides.

32. The process according to claim 31, wherein iron oxides comprise at least one of maghemite (\( \gamma \text{-Fe}_2\text{O}_3 \)) and magnetite (\( \text{Fe}_3\text{O}_4 \)).

33. The process according to anyone of claims 25 to 32, wherein the polar carrier liquid is a liquid selected from the group comprising ethylene glycol, ethylene glycol, polyethylene glycol, glycerol, ionic liquids, and combinations thereof.

34. The process according to claim 33, wherein the polar carrier liquid comprises ethylene glycol.

35. The process according to anyone of claims 25 to 34, wherein the organic ligand is highly soluble in the polar carrier liquid.

36. A suspension of magnetic particles in a polar carrier liquid wherein the magnetic particles are coated with an organic ligand having a hydrophilic chain.
37. The suspension according to claim 36, wherein the hydrophilic chain of the organic ligand comprises an oxyethylene chain.

38. The suspension according to one of claims 36 and 37, wherein the organic ligand is a negatively-charged-terminated organic molecule.

39. The suspension according to claim 38, wherein the negatively-charged-terminated organic molecule is carboxylic acid-terminated polyethylene glycol.

40. The suspension according to claim 39, wherein the carboxylic acid-terminated polyethylene glycol is selected from the group consisting of:

\[
\text{CH}_3\text{-O-}\left(\text{CH}_3\text{-CH}_2\text{-O}\right)_{11}\text{-CH}_2\text{-C}^\text{\text{-OH}}
\]

wherein \(n\) is an integer from 1 to 50.

41. The suspension according to claim 40, wherein the carboxylic acid-terminated polyethylene glycol is 2-[2-(2-methoxyethoxy)ethoxy]acet ic acid.

42. The suspension according to anyone of claims 36 to 41, wherein the magnetic particles are nanoparticles comprising iron oxides.

43. The suspension according to claim 42, wherein the iron oxides comprise at least one of maghemite (\(\gamma\text{-Fe}_2\text{O}_3\)) and magnetite (\(\text{Fe}_3\text{O}_4\)).

44. The suspension according to anyone of claims 36 to 43, wherein the polar carrier liquid is a liquid selected from the group comprising ethylene glycol, glycerol, ethylene glycol, polyethylene glycol, ionic liquids, and combinations thereof.

45. The suspension according to claim 44, wherein the polar carrier liquid comprises ethylene glycol.

46. The suspension according to anyone of claims 36 to 45, wherein the organic
ligand is highly soluble in the polar carrier liquid.

47. A ferrofluid comprising a suspension of magnetic particles coated with an organic ligand having a hydrophilic chain in a polar carrier liquid.

48. The ferrofluid according to claim 47, wherein the hydrophilic chain of the organic ligand comprises an oxyethylene chain.

49. The ferrofluid according to one of claims 47 and 48, wherein the organic ligand is a negatively-charged-terminated organic molecule.

50. The ferrofluid according to claim 49, wherein the negatively-charged-terminated organic molecule is carboxylic acid-terminated polyethylene glycol.

51. The ferrofluid according to claim 50, wherein the carboxylic acid-terminated polyethylene glycol is selected from the group consisting of:

\[
\text{CH}_3\text{-O-(CH}_2\text{-CH}_2\text{-O)}_n\text{-CH}_2\text{-C-CH}_2\text{-OH}
\]

wherein \(n\) is an integer from 1 to 50.

52. The ferrofluid according to claim 51, wherein the carboxylic acid-terminated polyethylene glycol is 2-[2-(2-methoxyethoxy)ethoxy]acetic acid.

53. The ferrofluid according to anyone of claims 47 to 52, wherein the magnetic particles are nanoparticles comprising iron oxides.

54. The ferrofluid according to claim 53, wherein the iron oxides comprise at least one of maghemite \((\gamma\text{-Fe}_2\text{O}_3)\) and magnetite \((\text{Fe}_3\text{O}_4)\).

55. The ferrofluid according to anyone of claims 47 to 54, wherein the polar carrier liquid is a liquid selected from the group comprising ethylene glycol, ethylene glycol, polyethylene glycol, glycerol, ionic liquids, and combinations thereof.
56. The ferrofluid according to claim 55, wherein the polar carrier liquid comprises ethylene glycol.

57. The ferrofluid according to anyone of claims 47 to 56, wherein the organic ligand is highly soluble in the polar carrier liquid.

58. A magnetically deformable mirror comprising a ferrofluid coated with a reflective surface layer wherein the ferrofluid comprises a suspension of magnetic particles in a polar carrier liquid wherein the particles are coated with an organic ligand having a hydrophilic chain.

59. The magnetically deformable mirror according to claim 58, wherein the hydrophilic chain of the organic ligand comprises an oxyethylene chain.

60. The magnetically deformable mirror according to one of claims 58 and 59, wherein the organic ligand is a negatively-charged-terminated organic molecule.

61. The magnetically deformable mirror according to claim 60, wherein the negatively-charged-terminated organic molecule is carboxylic acid-terminated polyethylene glycol.

62. The magnetically deformable mirror according to claim 61, wherein the carboxylic acid-terminated polyethylene glycol is selected from the group consisting of:

\[
\text{CH}_3\text{-O-}(\text{CH}_2\text{-CH}_2\text{-O})_n\text{-CH}_2\text{-C}^\text{\textbullet}^\text{\textcircled{O}}\text{-OH}
\]

wherein \(n\) is an integer from 1 to 50.

63. The magnetically deformable mirror according to claim 62, wherein the carboxylic acid-terminated polyethylene glycol is 2-[2-(2-methoxyethoxy)ethoxy]acetic acid.
64. The magnetically deformable mirror according to anyone of claims 58 to 63, wherein the magnetic particles are nanoparticles comprising iron oxides.

65. The magnetically deformable mirror according to claim 64, wherein the iron oxides comprise at least one of maghemite ($\gamma$-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$).

66. The magnetically deformable mirror according to anyone of claims 58 to 65, wherein the polar carrier liquid is a liquid selected from the group comprising ethylene glycol, ethylene glycol, polyethylene glycol, glycerol, ionic liquids, and combinations thereof.

67. The magnetically deformable mirror according to claim 66, wherein the polar carrier liquid comprises ethylene glycol.

68. The magnetically deformable mirror according to anyone of claims 58 to 67, wherein the organic ligand is highly soluble in the polar carrier liquid.

69. The magnetically deformable mirror according to anyone of claims 58 to 68, wherein the reflective surface layer comprises a reflective film of reflective metallic particles.

70. The magnetically deformable mirror according to claim 69, wherein the metallic particles comprises silver nanoparticles.
Synthesised iron oxide

Maghemite

Magnetite

2θ (degrees)

FIG. 2
FIG. 3
**FIG. 4**

The diagram shows IR spectra with absorbance on the y-axis and wavenumber on the x-axis. Two curves labeled 'a' and 'b' are plotted. Key wavenumbers marked are 1587, 1404, and 1316 cm⁻¹. The spectrum at higher wavenumbers shows prominent peaks at 1740 cm⁻¹.
Figure 5
Figure 10: Amplitude of deformation vs. applied magnetic field.

- △ at deposition
- □ after 7 days
- ○ after 14 days
- ▼ after 35 days
- ○ after 56 days
- ◇ after 70 days

Y-axis: Amplitude of deformation / μm
X-axis: Applied magnetic field / Gauss
INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2008/000767

A. CLASSIFICATION OF SUBJECT MATTER
IPC: HOIF 1/44 (2006.01), BOIF 1/4744 (2006.01), BOIF 17/52 (2006.01), C09C 1/24 (2006.01), C09C 3/08 (2006.01), C09C 3/10 (2006.01) (more IPCs on the last page)
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)
IPC: HOIF 1/44 (2006.01), HOIF 1/42 (2006.01), G02B 5/08 (2006.01), G02B 1/06 (2006.01), G02B 1/10 (2006.01)
USPC: 977/383, 427/215, 427/217

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
CPD, WEST, Esp@cenet, CAPlus, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 2006/0286379 A1 (GAO) 21 December 2006 (21-12-2006) * paragraphs [0040], [0050], [0059], [0091], [0106], [0107], [0138], example 3 *</td>
<td>1-4, 7, 8, 11, 25-28, 31, 32, 35-39, 42, 43, 46-50, 53, 54, 57</td>
</tr>
</tbody>
</table>

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

A特 | Special categories of cited documents or referred to documents |
---|-------------------------------------------------------------|
“A” | document defining the general state of the art which is not considered to be of particular relevance |
“E” | earlier application or patent but published on or after the international filing date |
“L” | document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) |
“O” | document referring to anoral disclosure, use, exhibition or other means |
“P” | document published prior to the international filing date but later than the priority date claimed |
“T” | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
“X” | document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
“Y” | document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
“k” | document member of the same patent family |

Date of the actual completion of the international search
15 July 2008 (15-07-2008)

Date of mailing of the international search report
5 August 2008 (05-08-2008)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C1 14 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A OC0
Facsimile No.: 001-819-953-2476

Authorized officer
Jay Fothergill  819- 997-4842

Form PCT/ISA/210 (second sheet) (July 2008)
<table>
<thead>
<tr>
<th>Patent Document</th>
<th>Publication Date</th>
<th>Patent Family</th>
<th>Publication Date</th>
<th>Member(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DE 68905631 T2</td>
<td>15-07-1993</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0328497B1</td>
<td>31-03-1993</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 1243501A</td>
<td>28-09-1989</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 8800394A</td>
<td>09-08-1989</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 8800394D0</td>
<td>08-02-1988</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 8800394L</td>
<td>09-08-1989</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 4938686A</td>
<td>03-07-1990</td>
<td></td>
</tr>
<tr>
<td>WO 2006025627A1</td>
<td>09-03-2006</td>
<td>CA 2576975A1</td>
<td>09-03-2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 101014531A</td>
<td>08-08-2007</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 200851 1461T</td>
<td>17-04-2008</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 2006002 1536A</td>
<td>08-03-2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2008038361A1</td>
<td>14-02-2008</td>
<td></td>
</tr>
<tr>
<td>US 2006286379A1</td>
<td>21-12-2006</td>
<td>AU 2003262653A1</td>
<td>25-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 2003262653A8</td>
<td>25-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 2003262703A1</td>
<td>03-03-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2495244A1</td>
<td>26-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 1685076A</td>
<td>19-10-2005</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 10393052T5</td>
<td>01-09-2005</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 0503031 D0</td>
<td>23-03-2005</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 0523837D0</td>
<td>04-01-2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2407437A</td>
<td>27-04-2005</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2407437B</td>
<td>22-02-2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2422724A</td>
<td>02-08-2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2422724B</td>
<td>14-02-2007</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 7277296B2</td>
<td>02-10-2007</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 7327584B2</td>
<td>05-02-2008</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 7349226B2</td>
<td>25-03-2008</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2004031 1767A1</td>
<td>19-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 20040327 14A1</td>
<td>19-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 20040327 15A1</td>
<td>19-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2004037054A1</td>
<td>26-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 20042 12973A1</td>
<td>28-10-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 20051 35077A1</td>
<td>23-06-2005</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 20061 59860A1</td>
<td>20-07-2006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 20040 15548A2</td>
<td>19-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 20040 15548A3</td>
<td>06-05-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 200401 6417A2</td>
<td>26-02-2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 200401 6417A3</td>
<td>03-06-2004</td>
<td></td>
</tr>
<tr>
<td>JP 6061032A</td>
<td>04-03-1994</td>
<td>None</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Form PCT/ISA/210 (patent family annex) (July 2008)
<table>
<thead>
<tr>
<th>Classifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>G02B 7/70 (2006.01)</td>
</tr>
<tr>
<td>G02B 5/08 (2006.01)</td>
</tr>
<tr>
<td>HOIF 1/42 (2006.01)</td>
</tr>
</tbody>
</table>