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(54) **FERROFLUID SYSTEM CONTAINING GOLD PARTICLES**

(57) The invention relates to a ferrofluid system comprising:

- a first phase comprising magnetic particles dispersed in a first fluid F1,
 - a second phase comprising a second fluid F2,
 - an interface layer comprising gold particles,
- wherein the first fluid F1 and the second fluid F2 are not

miscible,

and wherein the gold particles are functionalized with a compound (SF1) soluble in the first fluid F1 and with a compound (SF2) soluble in the second fluid F2.

The invention also relates to using this ferrofluid system in the field of horology.

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Description

FIELD OF THE INVENTION

[0001] The invention relates to a ferrofluid system comprising a ferrofluid, gold particles and a second fluid. This composition may be used in the field of horology.

BACKGROUND OF THE INVENTION

[0002] Depending on the intended technological field, particles may require specific properties and therefore a specific assembly or specific formulation.

[0003] For instance, US 2016/0250612 discloses encapsulated particles having a core and a silica based and aluminum containing shell.

[0004] US 2013/0040292 teaches a nanoparticle biosensor having a magnetic core, a silica layer and an outer metal shell. The core material is made of cobalt ferrite. Peptide nucleic acid is immobilized onto the outer metal shell.

[0005] Some applications require that magnetic particles move, like a fluid, in the presence of a magnetic field. In that case, the magnetic particles are conditioned in a ferrofluid.

[0006] A ferrofluid may be used in a variety of different fields. For instance, US 2004/0195540 discloses ferrofluids and their use as liquids seals. These oil based ferrofluids have an improved stability over time due to the presence of an elemental modifier that prevents or delays the aging of the magnetic particles.

[0007] US 2018/0019049 teaches a deformable inductor having a liquid magnetic core within an elastomer body. The liquid magnetic core may be a ferrofluid made of a dispersion of magnetic particles in a viscous carrier liquid.

[0008] US 2010/0277820 discloses a ferrofluid comprising a suspension of magnetic iron particles in a polar carrier, for instance ethylene glycol. The magnetic iron particles are functionalized with ligands and coated with a reflective layer.

[0009] US 4,604,222 teaches a water free ferrofluid composed of magnetic particles, an organic liquid carrier, a dispersing agent and a cationic surfactant.

[0010] US 2015/0320889 teaches an oil in water emulsion comprising nanodroplets of an oil phase containing iron magnetic particles. Surfactants stabilize these nanodroplets in water.

[0011] WO 2017/103508 also teaches an oil in water emulsion having surfactants and oil droplets containing magnetic particles.

[0012] Typically, compositions comprising an oil phase and a water phase, such as the above oil in water emulsions, are stabilized by surfactants, which prevent the coalescence of the droplets containing the magnetic particles.

[0013] Although the above ferrofluids may exhibit satisfactory properties, they are not necessarily adapted for

a purpose that differs from their original technical field.

[0014] Indeed, adding pigments to ferrofluids generally afford unstable compositions. These compositions may also be subject to irreversible pigment leaching. Upon leaching, the pigments stick to the recipient containing the ferrofluid while the color of the ferrofluid turns to black i.e. the color of the magnetic particles.

[0015] Therefore, there is still a need for new ferrofluid compositions that are suitable for decorative applications. The Applicant has developed a stable ferrofluid composition that looks like a drop of liquid gold.

SUMMARY OF THE INVENTION

[0016] The invention relates to a ferrofluid system containing magnetic particles as well as gold particles and a second fluid. This ferrofluid system has a phase having the color of gold.

[0017] More specifically, the invention relates to a ferrofluid system comprising:

- a) a first phase comprising magnetic particles dispersed in a first fluid F1,
- b) a second phase comprising a second fluid F2,
- c) an interface layer comprising gold particles,

wherein the first fluid F1 and the second fluid F2 are not miscible,

and wherein the gold particles are functionalized with a compound (SF1) soluble in the first fluid F1 and with a compound (SF2) soluble in the second fluid F2.

[0018] This composition comprises two main phases having an interface corresponding to the intermediate layer of gold particles located between the first phase and the second phase.

[0019] The first phase is actually a ferrofluid since it comprises magnetic particles dispersed in a fluid.

[0020] The composition comprises two fluids that are not miscible. In general, one of the fluid is hydrophilic while the other fluid is hydrophobic. However, the ferrofluid of the composition is preferably either hydrophilic or hydrophobic fluid. The ferrofluid cannot be composed of hydrophilic and hydrophobic fluids. The ferrofluid system may relate to an emulsion when one of the phases is hydrophilic and the other one is hydrophobic.

[0021] A hydrophobic fluid is not miscible with hydrophilic fluid as they form two distinct phases when mixed together.

[0022] This ferrofluid system remains stable over time. The stability of the ferrofluid system relates to the absence of any color change and/or any gold particle migration outside of the interface layer. Typically, the composition according to the invention remains stable at 25 °C for over several months, even after being shaken regularly.

[0023] The first phase is a ferrofluid. It behaves like a liquid. It can be immobilized (held in space) in the presence of a magnetic field. It can also be displaced as it

follows the applied magnetic field.

[0024] The magnetic particles of the ferrofluid are ferromagnetic and/or ferrimagnetic particles, more preferably superparamagnetic particles. For instance, they may be particles containing elements such as iron, nickel or cobalt. They are preferably selected from the group consisting of iron oxide (for instance Fe_3O_4 or Fe_2O_3), cobalt iron oxide (for instance CoFe_2O_4), manganese iron oxide (for instance MnFe_2O_4), manganese zinc iron oxide (for instance $(\text{Mn,Zn})\text{Fe}_2\text{O}_4$), nickel iron oxide (for instance NiFe_2O_4), and mixtures thereof.

[0025] They are preferably iron oxide particles, more preferably $\gamma\text{-Fe}_2\text{O}_3$ particles.

[0026] They can have any shape. In particular, they can be spherical, spheroidal, ellipsoidal, cubic, parallel-epipedic or cylindrical (rod like).

[0027] The magnetic particles have a size preferably ranging from 2 nm to 5 μm , more preferably from 5 nm to 25 nm, for instance about 10 nm.

[0028] Typically, the size of an entity refers to the largest dimension of said entity, for instance the diameter of spherical particles or the length of parallelepipedic particles.

[0029] According to a particular embodiment, the magnetic particles represent from 0.1 to 80 wt% of the first phase, preferably from 2 to 15 wt%.

[0030] The magnetic particles may be functionalized with a stabilizing agent. This stabilizing agent is preferably selected from the group consisting of molecules containing one or more of the following: carboxyl-, catechol-, amino-, sulfur-, oxygen- and phosphorus-. For instance, it may be 2-hydroxypropane-1,2,3-tricarboxylic acid i.e. citric acid (CAS Number: 77-92-9).

[0031] It helps stabilizing the magnetic particles within the volume of the first phase. It enhances the stability of the suspension of magnetic particles in the first fluid F1. It is usually bound to the magnetic particles by any one of chemical bond, non-covalent interaction, for instance hydrogen bond and coordination bond, biophysical or physical interaction, for instance biotin-avidin or electrostatic interaction.

[0032] According to a particular embodiment, the stabilizing agent represents from 0.01 to 50 wt% of the first phase, preferably from 0.1 to 4.0 wt%, more preferably from 0.2 to 4.0 wt%.

[0033] The ferrofluid has a magnetic particles / stabilizing agent weight ratio that preferably ranges from 1 / 200 to 8000 / 1, more preferably from 100 / 1 to 4 / 1.

[0034] The first phase comprising the F1 fluid of the ferrofluid system is in contact with the second phase comprising the F2 fluid through the interface layer, which comprises gold particles. The gold particles are preferably plate-like particles and give a golden color to the first phase. They are made of gold having a purity that is preferably 14 carats or more. They may be made of 18 carat gold, 22 carat gold or even 24 carat gold. Preferably, gold is yellow gold, but white gold and red gold can also be considered.

[0035] Gold particles occupy preferably from 30 to 100 % of the area of the interface layer between the first phase and the second phase, more preferably from 95 to 100 %. Even though gold particles may overlap, the skilled person in the art will be able to adjust the quantity of gold particles depending on the volume of the first phase and/or the expected coverage.

[0036] The weight of the gold particles includes the functionalizing SF1 and SF2 molecules.

[0037] The gold particles are preferably anisotropic by shape.

[0038] These gold particles have preferably a plate-like shape, i.e., microplatelets or nanoplatelets. They may be a mix of particles having different shapes. For instance, they may be a mix of microplatelets and/or nanoplatelets including a minor amount of spherical gold particles, preferably of spherical particles having a sub-micron size.

[0039] Nevertheless, according to a particular embodiment, the gold particles are preferably free of spherical particles.

[0040] They have a size preferably ranging from 80 nm to 120 μm , more preferably from 0.5 μm to 80 μm , and even more preferably from 1 μm to 30 μm . As already mentioned, the size refers to the largest dimension of said particles e.g. the length, the diameter... depending on the shape of the particles.

[0041] They have a thickness that preferably ranges from 5 nm to 1 μm , more preferably from 10 nm to 500 nm, and even more preferably from 20 nm to 80 nm.

[0042] The size and the thickness of the gold microplatelets do not include the functionalizing SF1 and SF2 molecules. However, in general, the size and the thickness of the functionalized gold particles are within the ranges mentioned for the gold particles.

[0043] In general, the gold microplatelets are functionalized through chemical interactions. They preferably form non-covalent interactions with the molecules of SF1 and SF2 such as thiol-gold interaction and/or amine-gold interaction. Accordingly, both SF1 and SF2 compounds have preferably one or more -SH and/or -NH and/or -NH₂ functional groups. Thiol functional groups have usually a greater affinity to gold particles than amine functional groups.

[0044] One of the functionalizing compounds of the gold particles is preferably hydrophilic. It therefore affords oil in water surfactant properties to the gold particles. It preferably contains one or more OH groups and/or other polar moieties so as to improve its hydrophilic properties. It is preferably selected from the group consisting of one or more sulfur-, oxygen-, nitrogen- containing water soluble molecules. It is preferably thiocarbohydrate, for instance 2,3,4,5,6-pentahydroxy-N-(2-sulfanylethyl)hexanamide or other molecules such as compounds corresponding to any one of the following CAS numbers: 60-24-2; 1068-47-9, 19721-22-3; 59-52-9. This functionalizing compound is soluble in a hydrophilic fluid, preferably water. This compound may be the SF1 compound

when the F1 fluid is hydrophilic. It may be the SF2 compound when the F2 fluid is hydrophilic.

[0045] The other functionalizing compound of the gold particles is preferably hydrophobic. It therefore affords water in oil surfactant properties to the gold particles. It preferably contains one or more hydrocarbon chain, for instance $-(CH_2-CH_2)_n-$ with n ranging from 2 to 12 and/or cyclic compound part(s), so as to improve its hydrophobic properties. It is preferably selected from the group consisting of alkyl thiols and other hydrophobic thiol-containing molecules, for instance any one of $CH_3(CH_2)_nSH$ with n ranging from 5 to 17 (for instance 1-dodecanethiol (CAS 112-55-0)) and other molecules such as molecules having one of the following CAS numbers: 108-98-5; 1455-21-6; 2917-26-2; 626-04-0; 1569-69-3; 13333-97-6; 100-53-8; 771-62-0; 769-40-4; 1996-44-7; 371-42-6; 2885-00-9. This functionalizing compound is soluble in a hydrophobic fluid, preferably a mineral oil or a silicone oil. This compound may be the SF1 compound when the F1 fluid is hydrophobic. It may be the SF2 compound when the F2 fluid is hydrophobic.

[0046] The SF1 is soluble in the first fluid as 1 mass part of SF1 readily dissolves in 30 mass parts of first fluid, at 25 °C.

[0047] Since the gold particles are not soluble in the first fluid and in the second fluid, the SF1 and the SF2 compounds anchor gold particles on the interface between hydrophilic and hydrophobic fluid.

[0048] For instance, when the first fluid is a hydrophilic fluid and the second fluid is a hydrophobic fluid, the SF1 anchors the gold particles to the hydrophilic fluid while the SF2 anchors the gold particles to the hydrophobic fluid. When the first fluid is a hydrophobic fluid and the second fluid is a hydrophilic fluid, the SF1 anchors the gold particles to the hydrophobic fluid while the SF2 anchors the gold particles to the hydrophilic fluid.

[0049] Typically, the ferrofluid system contains a hydrophobic fluid and a hydrophilic fluid that are not miscible.

[0050] The hydrophobic fluid is preferably an oil, e.g. a mineral oil or a silicon oil. For instance, it may be selected from the group consisting of C_5 - C_{24} alkanes, C_5 - C_{24} cyclic hydrocarbon compounds, silicone oils, organohalides such as organochlorides and organofluorines. It is preferably selected from the group consisting of higher alkanes (C_{10} and above). Typically, oils comprise a mixture of compounds, for instance light oils may comprise a mixture of C_5 - C_9 alkanes.

[0051] The hydrophilic fluid is preferably selected from the group consisting of water; DMSO (dimethyl sulfoxide); DMF (dimethylformamide); glycols such as ethylene glycol; alcohols such as methanol, ethanol; and others. Most preferably, the hydrophilic fluid is water.

[0052] The SF2 is soluble in the second fluid as 1 mass part of SF2 readily dissolves in 30 mass parts of second fluid, at 25 °C. Nevertheless, the second fluid may also be air or another gas, for instance nitrogen or a noble gas, preferably argon or helium.

[0053] Due to the presence of both SF1 and SF2, the gold particles are at the interface between the first phase and the second phase.

[0054] The gold particles have a SF1 / SF2 weight ratio of preferably between 1/15 and 15/1, more preferably between 1/10 and 10 / 1, and even more preferably between 1 / 3 and 3/1.

[0055] Furthermore, according to a particular embodiment, the SF1 represent from 0.01 to 30 wt% by weight of the gold microplatelets, preferably 0.1 to 20 wt%, more preferably 2 to 10 wt%.

[0056] According to another particular embodiment, the SF2 represent from 0.01 to 30 wt% by weight of the gold microplatelets, preferably 0.1 to 20 wt%, more preferably 2 to 10 wt%.

[0057] In summary, the first phase comprises a suspension containing magnetic particles and, preferably, at least one stabilizing agent.

[0058] The ferrofluid system also comprises a second phase based on a second fluid F2 that is not miscible with the first fluid F1 .

[0059] The interface is comprised by SF1 and SF2 functionalized gold particles.

[0060] According to a particular embodiment, the ferrofluid system can have any first phase / second phase volume ratio between 1/3 and 1/20.

[0061] The first phase has a volume that preferably range from 50 μ L to 50 mL.

[0062] The first phase preferably defines a single volume that is located within the second phase. It is not an emulsion comprising a plurality of drops of a first phase dispersed in a second phase. Consequently, the ferrofluid system of the invention is preferably free of non-attached SF1 and/or SF2 stabilizing agents. The SF1 and SF2 molecules of the ferrofluid system are preferably all attached to the gold particles.

[0063] According to a particular embodiment, the ferrofluid system comprises:

- a) a first phase comprising magnetic particles dispersed in a first fluid F1, wherein F1 is a hydrophilic fluid, preferably water,
- b) a second phase comprising a second fluid F2, wherein F2 is a hydrophobic fluid preferably selected from the group consisting of alkanes, cyclic hydrocarbon compounds, silicone oils, mineral oils, and organohalides,
- c) an interface layer comprising SF1- and SF2-functionalized gold particles.

[0064] According to another particular embodiment, the ferrofluid system comprises:

- a) a first phase comprising magnetic particles dispersed in a first fluid F1, wherein F1 is a hydrophobic fluid preferably selected from the group consisting of alkanes, cyclic hydrocarbon compounds, silicone oils, mineral oils, and organohalides,

- b) a second phase comprising a second fluid F2, wherein F2 is a hydrophilic fluid, preferably water.
- c) an interface layer comprising SF1- and SF2-functionalized gold particles.

[0065] The invention also relates to the use of the ferrofluid system in the field of horology, for instance a time-piece comprising this ferrofluid system. For instance, it can afford aesthetic properties as it provides a visual display that behaves like a moving fluid in the presence of a magnetic field.

[0066] The invention also relates to a method for preparing the above described ferrofluid system according to the following steps:

- 1/ a suspension of magnetic particles is prepared as a first fluid F1,
- 2/ SF1 and SF2 functionalized gold particles are added to first fluid F1,
- 3/ the resulting composition is mixed with a second fluid F2.

[0067] As already mentioned, the magnetic particles may be functionalized with a stabilizing agent, for instance citric acid.

[0068] The gold particles may be prepared by reduction of auric salt, preferably HAuCl_4 . The reduction may preferably be carried out in the presence of compounds such as aniline and ethylene glycol.

[0069] The gold particles can be functionalized by the SF1 and the SF2 sequentially according to conventional reactions that are within the knowledge of the skilled person in the art. Indeed, the SF1 functionalization is preferably carried out in the F1 fluid or a solvent in which the SF1 compound is soluble while the SF2 functionalization is preferably first carried out in the F2 fluid or a solvent in which the SF2 compound is soluble. The order of functionalization (SF1 or SF2 at first) is not important. The SF1 and/or the SF2 functionalization(s) may also be carried out in the presence of the magnetic particles.

[0070] Steps 1/ through 3/ may be carried out at a temperature of between 0 °C and 90 °C, preferably above 15 °C.

[0071] The invention and its advantages will become more apparent to one skilled in the art from the following figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0072]

Figure 1 illustrates the first phase of the ferrofluid system according to the invention.

Figure 2 is a photography of the ferrofluid system according to the invention.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0073] The ferrofluid system has a first phase comprising magnetic particles and the second phase which is not miscible with the first one while an interface is occupied with gold particles. Figure 1 illustrate the first phase in which the magnetic particles (1) are dispersed in the fluid F1 (2).

[0074] The interface layer (3) comprises gold micro-platelets (4) that are functionalized with the SF1 and SF2 compounds.

[0075] Thanks to the SF1 and to the SF2, the gold particles (4) decorate an interface between the suspension of magnetic particles (1) and the second phase that comprises the second fluid in which the first fluid is not miscible.

[0076] However, the gold particles (4) do not act as a stabilizing agent since the gold particles do not prevent droplets of the first fluid F1 from collapsing together.

Claims

1. Ferrofluid system comprising:

- a) a first phase comprising magnetic particles dispersed in a first fluid F1,
- b) a second phase comprising a second fluid F2,
- c) an interface layer comprising gold particles,

wherein the first fluid F1 and the second fluid F2 are not miscible,
and wherein the gold particles are functionalized with a compound (SF1) soluble in the first fluid F1 and with a compound (SF2) soluble in the second fluid F2.

2. Ferrofluid system according to claim 1, **characterized in that** the magnetic particles are iron oxide particles, preferably $\gamma\text{-Fe}_2\text{O}_3$ particles.

3. Ferrofluid system according to any one of claims 1 to 2, **characterized in that** the magnetic particles have a size ranging from 2 nm to 5 μm , preferably from 5 nm to 25 nm.

4. Ferrofluid system according to any one of claims 1 to 3, **characterized in that** the magnetic particles are functionalized with a stabilizing agent that is selected from the group consisting molecules containing one or more of carboxyl-, catechol-, amino-, sulfur-, oxygen- and phosphorus-, preferably 2-hydroxypropane-1,2,3-tricarboxylic acid.

5. Ferrofluid system according to any one of claims 1 to 4, **characterized in that** the gold particles occupy from 30 % to 100 % of the area of interface layer

between the first phase and the second phase.

6. Ferrofluid system according to any one of claims 1 to 5, **characterized in that** the gold particles have a size ranging from 80 nm to 120 μm , preferably from 0.5 μm to 80 μm , more preferably from 1 μm to 30 μm . 5
7. Ferrofluid system according to any one of claims 1 to 6, **characterized in that** the gold particles have a thickness ranging from 5 nm to 1 μm , preferably from 10 nm to 500 nm, more preferably from 20 nm to 80 nm. 10
8. Ferrofluid system according to any one of claims 1 to 7, **characterized in that** the first fluid F1 is hydrophilic, preferably water, and **in that** the SF1 compound is selected from the group consisting of one or more sulfur-, oxygen-, nitrogen- containing water soluble molecules, preferably any one of 2,3,4,5,6-pentahydroxy-*N*-(2-sulfanylethyl)hexanamide and molecules having any one of the following CAS numbers 60-24-2, 1068-47-9, 19721-22-3 and 59-52-9. 15
9. Ferrofluid system according to any one of claims 1 to 8, **characterized in that** the second fluid F2 is hydrophobic and **in that** the SF2 compound is selected from the group of alkyl thiols and other hydrophobic thiol-containing molecules, preferably any one of 1-dodecanethiol and molecules having one of the following CAS numbers: 108-98-5; 1455-21-6; 2917-26-2; 626-04-0; 1569-69-3; 13333-97-6; 100-53-8; 771-62-0; 769-40-4; 1996-44-7; 371-42-6; and 2885-00-9. 20
10. Ferrofluid system according to any one of claims 1 to 9, **characterized in that** the gold particles have a SF1 / SF2 weight ratio of between 1/15 and 15/1, preferably between 1/10 and 10 / 1, and more preferably between 1/3 and 3 / 1. 25
11. Ferrofluid system according to any one of claims 1 to 10, **characterized in that** the ferrofluid system has any first phase / second phase volume ratio between 1/3 and 1/20. 30
12. Ferrofluid system according to any one of claims 1 to 11, **characterized in that** the first fluid F1 is a hydrophilic fluid, preferably water, and **in that** the second fluid F2 is a hydrophobic fluid, preferably selected from the group consisting of alkanes, cyclic hydrocarbon compounds, silicone oils, mineral oils, and organohalides. 35
13. Ferrofluid system according to any one of claims 1 to 7, **characterized in that** the first fluid F1 is hydrophobic, and the SF1 compound is selected from the group of alkyl thiols and other hydrophobic thiol-containing molecules, preferably any one of 1-dodecanethiol and molecules having one of the following CAS numbers: 108-98-5; 1455-21-6; 2917-26-2; 626-04-0; 1569-69-3; 13333-97-6; 100-53-8; 771-62-0; 769-40-4; 1996-44-7; 371-42-6; and 2885-00-9, and wherein the second fluid F2 is hydrophilic, preferably water, and the SF2 compound is selected from the group consisting of one or more sulfur-, oxygen-, nitrogen-containing water soluble molecules, preferably any one of 2,3,4,5,6-pentahydroxy-*N*-(2-sulfanylethyl)hexanamide and molecules having any one of the following CAS numbers 60-24-2, 1068-47-9, 19721-22-3 and 59-52-9. 40
14. Ferrofluid system according to any one of claims 1 to 13, **characterized in that** the first phase defines a single volume that is within the second phase. 45
15. Use of the ferrofluid system according to any one of claims 1 to 14, in the field of horology. 50
16. Ferrofluid system according to any one of claims 1 to 15, **characterized in that** the first phase defines a single volume that is within the second phase. 55

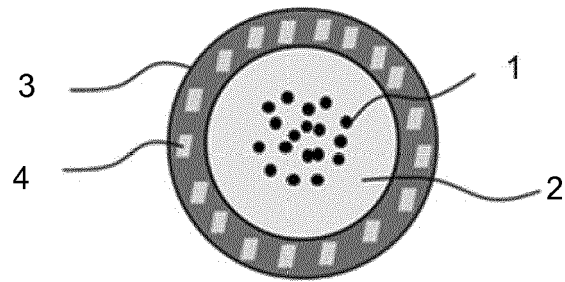


Fig.1

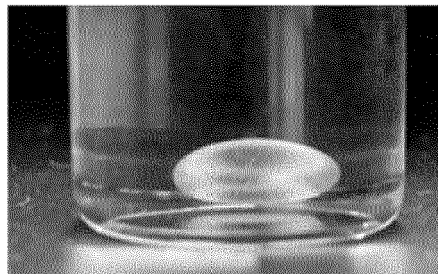


Fig.2



EUROPEAN SEARCH REPORT

 Application Number
 EP 19 18 7703

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Place of search		Date of completion of the search	Examiner
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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			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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