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(54) Title: MULTI-PHASE LIQUID COMPOSITION AND OPTICAL LENS DRIVEN BY ELECTROWETTING

(57) Abstract: The present invention relates to a multi-phase liquid composition comprising a conductive liquid and a non-conductive liquid, wherein a nanoparticle is dispersed in at least one of said liquids. The present invention also relates to an optical lens driven by electrowetting comprising such a multi-phase liquid composition, which optical lens is, or is included in, a variable focus liquid lens, an optical zoom, as well as to an apparatus comprising such an optical lens and a driver or electronic means for controlling said lens. The apparatus is a camera, a cell phone, an endoscope or a dental video.

Title: Multi-phase liquid composition and optical lens driven by electrowetting

The invention relates to a multi-phase liquid composition. The invention also relates to an optical lens driven by electrowetting containing a multi-phase liquid composition of the invention.

Optical lens driven by electrowetting and of variable focal length are described in European Patent EP-B1-1 166 157, the content of which is herein incorporated by reference. A cell is defined by two transparent non-conductive plates and side walls. The lower plate, which is non-planar, comprises a conical or cylindrical depression or recess, which contains a drop of a non-conductive or non-conductive liquid. The remainder of the cell is filled with an electrically conductive liquid, immiscible with the non-conductive liquid, having a different refractive index and substantially the same density. An annular electrode, which is open facing the recess, is positioned on the rear face of the lower plate. Another electrode is in contact with the conductive liquid. Through electrowetting phenomena it is possible to modify the curvature of the interface between the two liquids, according to the voltage V applied between the electrodes. For example, the curvature changes from the concave initial shape to the convex shape. Thus, a beam of light passing through the cell normal to the plates in the region of the drop will be focused to a greater or lesser extent according to the voltage applied. The conductive liquid may be an aqueous liquid containing salts or an organic liquid containing ionic compounds. The nonconductive liquid is typically an oil, an alkane or a mixture of alkanes, possibly halogenated.

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It has now been found that the conductive liquid and the non-conductive liquid must have some specific common properties in order to provide a very performing lens to be used as a variable focus liquid lens, an optical zoom and any other optical device using electrowetting in an inside or outside environment.

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In particular, it is an objective to provide a lens of strong optical power to have a difference of refractive index of the two liquids high enough, advantageously greater than or equal to about 0.2, preferably between about 0.2 and 0.4. Further, the non-conducting liquid and the conducting liquid need to have the same or a similar density.

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It is an object of the invention to provide multi-phase liquid compositions comprising a conductive liquid and a non-conductive liquid, the non-conductive liquid being immiscible

in the conductive liquid, these liquids having a high difference of refractive index, advantageously greater than or equal to about 0.2, preferably between about 0.2 and 0.4.

In one aspect, the invention relates to a multi-phase liquid composition comprising a conductive liquid and a non-conductive liquid, the non-conductive liquid being immiscible in the conductive liquid, the conductive liquid comprising nanoparticles.

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In another aspect, the invention relates to a multi-phase liquid composition comprising a conductive liquid and a non-conductive liquid, the non-conductive liquid being immiscible in the conductive liquid, the non-conductive liquid comprising nanoparticles.

In still another aspect, the invention relates to a multi-phase liquid composition comprising a conductive liquid and a non-conductive liquid, the non-conductive liquid being immiscible in the conductive liquid, the conductive liquid and the non-conductive liquid comprising nanoparticles.

Preferably, the difference of refractive index between both liquids is advantageously greater than or equal to about 0.2, preferably between about 0.2 and 0.4.

20 Preferably, the density of both liquids is the same or is similar. This means it is acceptable that the difference of densities may vary within a short range. Typically, it is preferred the difference of densities is not more than about 3.10⁻³ g/cm³ at 20°C.

Examples of possible solutions for improving Δn and density adjustment are summarized in the table below:

| | Low index conductive liquid | High index non-conductive liquid |
|---|---|--|
| 1 | Low index and high density nanoparticles, optionally surface functionalized to be dispersible in water. Mineral salt or organic salt or ionic liquid for conductivity | High index and low density nanoparticles, optionally surface functionalized to be dispersible in the non-conductive phase. Oil of high density |
| 2 | High density conductive liquid | High refractive index and high density nanoparticles, optionally surface functionalized to be dispersible in the non-conductive phase |
| 3 | Low index and high density nanoparticles, optionally surface functionalized to be dispersible in water. Mineral salt or organic salt or ionic liquid for conductivity | High refractive index organic compound |

Applicant has shown that the dispersion of nanoparticles in one or both liquid phases may have effective impact on density, refractive index and/or viscosity, as explained below. The person skilled in the art may select the nanoparticles (especially nature, size) and/or their amount that are useful to adjust the refractive index of one liquid phase and the difference of refractive index between both liquid phases. These particles may also be chosen to adjust other parameters, such as the density of the phase in order to adjust it as close as possible to that of the other phase.

In one embodiment, nanoparticles are used to increase the refractive index and the density of the non-conductive or the conductive liquid.

In another embodiment, nanoparticles are used to increase the refractive index of the non-conductive or the conductive liquid, without increasing or increasing too much the density. More specifically, nanoparticles are used to increase the difference between each refractive index of each liquid, without increasing or increasing too much the density.

In another embodiment, nanoparticles are used to increase the density of the non-conductive or the conductive liquid, without modifying or modifying too much the refractive index.

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Density is a function of volume fraction:

$$d^* = \phi d_P + (1 - \phi) d_L$$

with d* the composite liquid density, ϕ the volume fraction of particles and L and P refer to liquid and particles respectively.

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Viscosity can be obtained from the Chong's equation:

$$\eta = \eta_0 \left(1 + \frac{3}{4} \frac{\phi}{\phi_m - \phi} \right)^2$$

where η is the dynamic viscosity (in Pa.s), ϕ_m is the critical volume fraction and η_0 corresponds to the liquid viscosity. Kinematic viscosity ν is then related to dynamic

30 viscosity: $v = \frac{\eta}{\rho}$

Refractive index from the composite liquid is deduced from the Maxwell-Garnet equation (assuming a mean field approximation, valid for small volume fractions):

$$\varepsilon^* = \varepsilon_L \left(\frac{1 + 2\beta\phi}{1 - \beta\phi} \right) \text{ with } \beta = \frac{\varepsilon_P - \varepsilon_L}{\varepsilon_P + 2\varepsilon_L}$$

with ε the dielectric constant in the visible range.

Refractive index is then deduced from the dielectric constant using $n^* = \sqrt{\varepsilon^*}$

(In first approximation, a negligible imaginary dielectric constant is assumed, taking into account that particles and liquids are transparent in the visible range).

Measurements of dielectric constant have been performed using a silicone oil Dow Corning DC200 (2cS) and titanium oxide nanoparticles (having a 3/1 anatase to rutile phase ratio). Refractive indices have been calculated.

| -4 | _ |
|-----|----|
| - 1 | 1. |
| | |

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| | density | Viscosity (cS) | Refractive index | Dielectric constant |
|---------------|---------|----------------|--------------------|---------------------|
| Liquid | 0.872 | 2 | 1.389 | 1.929 |
| Composite 10% | 1.187 | 1.942 | 1.485 (Δn = 0.096) | 2.205 |
| Composite 20% | 1.498 | 2.187 | 1.584 (Δn = 0.195) | 2.508 |
| particles | 4 | ∞ | 2.60 | 6.76 |

Δn is the refractive index variation between the pure liquid and the liquid containing particles.

Have been represented the variations of density (Figure 1), viscosity (Figure 2), refractive index (Figure 3) as a function of particles volume fraction. Refractive index as a function of particles volume fraction is represented at Figure 4.

Increasing particles volume fraction has a larger impact on density than on viscosity and on refractive index. Hence, a reasonable volume fraction of about 10% should induce a refractive index variation $\Delta n = 0.1$ for a density variation $\Delta d = 0.315$.

Further increase of the refractive index may be obtained using particles and/or liquids or other components of higher refractive index.

A solution of silica nanoparticles in ethylene glycol has been used as a high density liquid, because this material has a relatively low refractive index. On the opposite, zirconia nanoparticles has been used in water and refractive index was increased by $\Delta n=0.05$ compared to pure water.

In the present invention, nanoparticles are nanometric solid materials, transparent in the visible range, small in size (the particles should not substantially or not at all diffuse light), for example particle size lower than about 50 nanometers, preferably lower than about 20

nanometers, more preferably lower than about 10 nanometers, and well dispersible in conductive and/or non conductive liquids.

Preferably the nanoparticles present a density of about 2 g/cm³ to about 20 g/cm³, preferably of about 4 g/cm³ to about 15 g/cm³.

The liquids containing the nanoparticles have good optical qualities; they are still transparent, present a low diffusion and high Abbe numbers (dispersive power).

The shape of the nanoparticles is preferably chosen to avoid light polarization and scattering. The particles are preferably spherical or close to a spherical shape.

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By extension, other materials could be used as nanoparticles to increase density and refractive index. Materials should be chosen depending on the optical requirements. As an example, titanium oxide could be used to screen UV light.

Nanoparticles can also be used to make conductive a liquid which is non conductive *per se*, in other words nanoparticles are useful to confer conductivity to a non conductive liquid, such as for example a non conductive liquid which is non miscible with another non conductive liquid.

In another embodiment, nanoparticles are made of but are not limited to silver, platinum or carbon and dispersed in a poorly conducting liquid to increase the conductivity.

According to another feature, nanoparticles dispersed in one or both liquids are made of one or more materials having a strong absorption in the UV light wavelength range, typically at wavelength below about 360 nm, but a very low absorption in the visible light wavelength range. These materials are made of titanium oxide or cerium oxide for example. Such particles are deemed to absorb the UV light coming through the electrowetting device and thus protect some liquids and/or insulating layer and/or hydrophobic coatings comprised in the electrowetting device from UV degradation.

According to another feature, nanoparticles dispersed in one or both liquids are made of one or more materials having a strong absorption in the IR wave lengths, particularly in the Near-IR, preventing from implementing an IR filter on the lens. Such a filter is necessary when the electrowetting device is an optical device comprising a numerical imaging sensor, usually sensitive to IR wave lengths, particularly in the Near-IR wave lengths.

According to another embodiment, nanoparticles comprise at least one visible light transparent material, such as silica, and containing IR absorbing molecules embedded in the materials. These molecules are preferentially absorbing infrared and transparent to visible light.

- According to a preferred embodiment, the IR absorbing molecules embedded in the particles are organic metal complex infrared absorbing dyes.

 In another preferred embodiment, the organic metal complex is of the aminothiophenolate type, as described in US patent application 2002/0125464 A1.
- According to another feature, the multiphase composition is made of two non miscible liquids and only one of them comprises nanoparticles being conductive. In this specific feature, the dispersing medium is thus more conducting than the other liquid, allowing electrowetting phenomenon to occur with liquids that are not necessarily conductive in the beginning. This feature allows the use of a much broader range of liquids, including liquids being much more chemically stable.

This is particularly relevant when using liquid not containing water, an example of such liquid being a high refractive index liquid made of oily molecules on the one side, and a low refractive index liquid like fluorinated solvent on the other side, particles being dispersed either in the high or low refractive index liquid.

It should also be understood that mixtures of two or more different materials can be used as nanoparticles to be dispersed in one or both of the liquids.

As stated above, various materials could be used as nanoparticles to modify the liquid properties, fluorides and/or oxides inorganic compounds being preferred, and among them the following are more preferred:

| | n (500 nm) | density (g/cm³) |
|------------------|-------------|-----------------|
| ZrO_2 | 2 | 5.56 |
| Y_2O_3 | 1.75 | 4.84 |
| TiO ₂ | 2.49-2.9 | 4.23 |
| ZnO | 2.008-2.029 | 5.7 |
| Gd_2O_3 | 1.8 | 7.4 |
| HfO ₂ | 2 | 9.7 |
| SiO ₂ | 1.45-1.5 | 2.2 |

| | n (500 nm) | density (g/cm³) |
|------------------|------------|-----------------|
| AI_2O_3 | 1.63 | 4.97 |
| CeO ₂ | 2.05-2.2 | 7.1 |
| YbF_3 | 1.56 | 8.2 |
| CaF ₂ | 1.23-1.42 | 3.18 |
| YF_3 | 1.52 | 5.07 |
| GdF_3 | 1.57 | 7.05 |

Other oxides and/or fluorides may be used, and for example those chosen from among indium fluoride (InF₃), indium oxide (In₂O₃), tin fluorides (SnF₂ or SnF₄), tin oxide (SnO₂), barium fluoride (BaF₂), barium oxide (BaO), bismuth fluoride (BiF₃) and bismuth oxide (Bi₂O₃).

Particles can be coated by organic ligands in order to increase the colloidal stability, especially in organic solvent or media.

Ligands are usually molecules similar to the dispersing media and chemically functionalized to bind the surface of the inorganic particles. Functionalizing groups are chosen to have a strong affinity to the chemical nature of the inorganic particle. They can be silane derivatives, such as those of formula R-Si-OH, carboxylic group(s)-containing compounds, such as R-COOH, for example citric acid, phosphine oxides, such as those of general formula R₃-P=O, phosphines, such as those of formula R₃-P, polymer materials, such as for example poly (ethylene oxides), or any chelating molecule that would bind to the inorganic core.

EXAMPLES

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1. Use of nanoparticles in the non-conductive liquid to increase the refractive index.

In order to increase the refractive index of the non-conductive liquid without increasing too much the density, nanoparticles based on silica, titanium or aluminum oxide can be dispersed in an non-conductive oil. PDMS (polydimethylsiloxane) may be used to functionalize silica to facilitate the dispersion.

Shape of the nanoparticles is spherical to avoid light polarization and scattering.

Experiments have been performed with titanium oxide particles, mean 2.5 nm in diameter, made and dispersed by nano-H Company in a silicon oil SIP6827 (phenyltrimethoxysilane, company ABCR). Liquids have been characterized with and without particles:

| | Without particles | With TiO ₂ | Variation | Theory |
|---------------------------|-------------------|-----------------------|-----------|--------|
| Density at 20°C (g/cm³) | 0.924 | 0.9489 | 2.69% | 4.22% |
| Refractive index at 20°C | 1.43779 | 1.45128 | 0.94% | 0.64% |
| Viscosity at 20°C (mm²/s) | 4 | 5.21 | 30.25% | -1.25% |
| ABBE number | 40.97 | 35.93 | -12.30% | - |

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| Initial aspect | yellow |
|--------------------|-----------|
| State at -40°C | liquid |
| After 12h at -40°C | unchanged |

Oil containing the nanoparticles is light yellow, and doesn't freeze at -40°C. Density variations are slightly below theoretical calculations. This can be explained by the fact that we didn't take into account the nanoparticles coating having a lower density. A better agreement is found assuming that particles have a density of 3 instead of 4.23 (bulk value). This corresponds to a realistic coating shell, e = 2Å in thickness and having a density of d = 1.

Viscosity is also higher than expected, presumably because the model only considers the nanoparticles as hard spheres whereas it is coated by molecules having an intrinsic viscosity.

Similarly, yttria particles (Y_2O_3) have been dispersed in the same oil SIP6827 (ABCR) at 50 g/L and characterized:

| η (mm²/s) | 560 |
|-------------|---------|
| ρ (g/cm3) | 0.9517 |
| n (489 nm) | 1.45131 |
| Abbe number | 42.89 |

| λ (nm) | n |
|--------|---------|
| 400 | 1.46325 |
| 448 | 1.45579 |

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| λ (nm) | n |
|--------|---------|
| 489 | 1.45131 |
| 541 | 1.44709 |
| 589.3 | 1.44421 |
| 654.6 | 1.44129 |
| 703 | 1.43958 |

Addition of nanoparticles has thus modified the oil properties:

| Δn (589.3 nm) | 0.00642 |
|---------------|---------|
| Δρ (g/cm³) | 0.0377 |
| Δη (mm²/s) | 556 |

2. Use of nanoparticles in the non-conductive liquid to increase the density and the refractive index.

In the case where the conductive phase has a high density, typically higher than 1.2, nanoparticles can be dispersed in the non-conductive phase in order to increase the density as well as the refractive index. Nanoparticles based on ytterbium, gadolinium, titanium, indium, tin, bismuth, zirconium, barium have a density high enough in order to increase the density of the non-conductive phase already at low concentration of nanoparticles.

Dispersion of the nanoparticles can be done in the oil by the mean of an organic surface around the metal oxide or fluoride.

The size of the nanoparticles may be around 5 nm in order to avoid the diffraction and the diffusion of the light. By this way, the suspension stays clear and transparent.

3. Use of nanoparticles in the conductive phase to increase the density.

Nanoparticles can be dispersed in the conductive phase, either in water or in ethylene glycol which are already components of the conductive phase. In this case, the density can be adjusted to be equilibrated with the oil.

Examples of nanoparticles are depicted in the following table.

 SiO_2 was purchased from Nyacol nanotechnogies (reference product DP 5820, 30% in ethylene glycol). ZrO_2 was purchased from Nyacol nanotechnologies (product stabilized 20% in acetic acid).

| λ(nm) / n | ZrO ₂ (in a diluted acetic acid solution) | SiO₂ in ethylene glycol |
|----------------|--|----------------------------|
| 401.5 | 1.39929 | 1.44813 |
| 435.8 | 1.39571 | 1.44458 |
| 486.1 | 1.39182 | 1.44076 |
| 546.1 | 1.38848 | 1.43756 |
| 589.3 | 1.38659 | 1.43575 |
| 656.3 | 1.38426 | 1.43353 |
| 703 | 1.38305 | 1.43238 |
| Abbe number | 51.13 | 60.27 |
| density | 1.2542 | 1.2996 |
| viscosity (cS) | 4 | 58.86 |

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In the concentrations indicated above, the viscosity is rather low and the density has been significantly increased. The refractive index stays reasonably low. The liquid is reasonably dispersive since the Abbe number is higher than 50.

Under thermal conditions, the parameters of the suspensions of nanoparticles ZrO₂ and SiO₂ evolves as described in Figures 5-6. The variation of the densities in temperature is rather similar with both nanoparticles (Figure 5). Figure 6 shows refractive index as a function of temperature, and variation is also very similar.

Some formulations having high refractive index difference have been done for the zoom application. As an example, the following liquids containing ZrO₂ dispersed in the acetic acid allows a difference of refractive index of 0.299 and a density of 1.19.

| Liquids | Quantity | Compound | n | ABBE | d |
|----------|----------|---|----------------------|-------|----------------------|
| Liquid 1 | 100% | Santolight [™] LS5267 [‡] | 1.67365 | * | 1.1980 |
| | | | $\Delta n = 0.29905$ | | $\Delta d = -0.0012$ |
| Liquid 2 | 2% | LiBr (10%) | 1.3746 | 52.36 | 1.1992 |
| | 18% | water | | | |
| | 80% | ZrO ₂ (20%) in acetic acid (15%) and water (65%) | | | |

^{‡:} SantolightTM SL-5267 is a polyphenyl ether high refractive index compound provided by NUSIL Silicone technology.

Electrowetting experiments have been done on these liquids. The hydrophobic substrate was Parylene C on stainless steal. The applied voltage increased from 0 to 120 V. Under these conditions, the contact angle of the oil in the conductive phase increased from 45 to 105 without saturation phenomena. (See Figure 7). Hysteresis stays rather low. The interfacial tension was 30.82 mN/m

Several compositions have been made where the proportion of nanoparticles can vary (SiO_2 : about 20 nm; ZrO_2 : about 5 to about 10 nm):

compounds

| | 0.20% | Na ₂ SO ₄ |
|----|-----------|---------------------------------|
| | 41.80% | water |
| | 14.0% | glycerol |
| | 37.0% | trifluoroethanol |
| | 7.0% | SiO ₂ |
| 10 | | |
| | ratio (%) | compounds |
| | 0.20% | Na ₂ SO ₄ |
| | 33.80% | water |
| | 10.0% | MPG |
| | 8.0% | SiO ₂ |
| | 40.0% | trifluoroethanol |
| | 8.0% | ZrO ₂ (AC) |
| | ratio (%) | compounds |
| | 65.0% | LiBr 10% |
| | 25.0% | trifluoroethanol |
| | 10.0% | ZrO ₂ (AC) |
| | ratio (%) | compounds |
| | 0.20% | Na ₂ SO ₄ |
| | 30.80% | water |
| | 15.0% | MPG |
| | | |

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Ratio (%)

45.0%

9.0%

trifluoroethanol

ZrO2 (AC)

| ratio (%) | compounds |
|-----------|-----------------------|
| 2.00% | LiBr 10% |
| 26.00% | water |
| 72.00% | ZrO ₂ (AC) |
| 72.0070 | 2.02 (1.0) |
| ratio (%) | compounds |
| 2.00% | LiBr 10% |
| 17.30% | water |
| 80.70% | ZrO ₂ (AC) |
| ratio (%) | compounds |
| 2.00% | LiBr 10% |
| 19.80% | water |
| 78.20% | ZrO ₂ (AC) |
| ratio (%) | compounds |
| 2.00% | LiBr 10% |
| 16.00% | water |
| 82.00% | ZrO₂ (AC) |
| ratio (%) | compounds |
| 2.00% | LiBr 10% |
| 20.50% | water |
| 77.40% | ZrO ₂ (AC) |
| 0.10% | BenzAl-Chloride |
| ratio (%) | compounds |
| 2.00% | LiBr 10% |
| 20.55% | water |
| 77.40% | ZrO_2 (AC) |
| 0.01% | BenzAl-Chloride |
| ratio (%) | compounds |
| 2.00% | LiBr 10% |
| 22.00% | water |
| 76.00% | ZrO ₂ (AC) |
| | |

Fluorinated material like ytterbium fluoride (YbF₃) (density = 8.17 g cm⁻³, n = 1.56) and gadolinium fluoride (GdF₃) can also be used. Fluorinated metals are the most dense and exhibit usually low refractive index.

Experiments were conducted with citric acid/GdF₃ nanoparticles in water. The synthesis of GdF₃ was realized following published procedures (F. Evanics; P. R. Diamente; F. C. J. M van Veggel; G. J. Stanisz; R. S. Prosser: *Chem. Mat.*, *18*(10), (2006), 2499-2505), starting with Gd(NO₃)₃ and NaF in the presence of citric acid. The refractive indices and the densities have been measured with the various concentrations of 1 g/ml to 0.0 6g/ml, as shown on Figure 8.

Very high concentrations of nanoparticles in water have been obtained, until 1 kg/L. Such a concentrated solution exhibit a refractive index of 1.328 and a density of 1.3 (Commercial zirconia gave d = 1.1992, n = 1.3746). These results clearly shows that fluorinated nanoparticles where efficient to increase the density without too much increasing the refractive index. Such solutions are compatible with antifreezing agents like ethylene glycol. Nevertheless, such highly concentrated aqueous solutions can induce some light diffusion. The density can be increased using fluorinated organic shell for instance.

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The result of these different uses of nanoparticles follows a same purpose: increasing the Δn between a pair of immiscible and isodensity conductive and insulating (non-conducting) liquids.

According to another feature, the electrical conductive liquid comprises at least one conventional freezing-point lowering agent. As freezing-point lowering agent, mention may be made of alcohol, glycol, glycol ether, polyol, polyetherpolyol and the like, or mixtures thereof. Examples thereof include the following agents: ethanol, ethylene glycol (EG), monopropylene glycol (MPG), 1,2-propane diol, 1,2,3-propane triol (glycerol), and the like, and mixtures thereof.

Still according to another feature, the multi-phase liquid composition comprises a non-conductive liquid that is immiscible in the conductive liquid. This said non-conductive liquid comprising an organic or an inorganic (mineral) compound or mixture thereof. Examples of such organic or inorganic compounds include a Si-based monomer or oligomer, a Ge-based monomer or oligomer, a Si-Ge-based monomer or oligomer, a hydrocarbon, or a mixture thereof.

The hydrocarbon may be linear or branched and may contain one or more saturated, unsaturated or partially unsaturated cyclic moiety(ies). The hydrocarbon has advantageously from 10 to 35 carbon atoms, preferably from 15 to 35 carbon atoms. Hydrocarbons having less than 10 carbon atoms are less preferred since miscibility into the conductive liquid may occur.

The hydrocarbon may comprise one or more insaturation(s) in the form of double and/or triple bond(s). More than 2 or 3 double or triple bonds are not preferred considering the risk of decomposition with UV radiations. Preferably the hydrocarbon does not contain any double or triple bonds, in which case the hydrocarbons are referred to as alkanes in the present specification.

The hydrocarbon may further comprise one or more heteroatoms, as substituants and/or as atoms or group of atoms interrupting the hydrocarbon chain and/or ring. Such heteroatoms include, but are not limited to, oxygen, sulfur, nitrogen, phosphor, halogens (mainly as fluorine, chlorine, bromine and/or iodide). Care should be taken that the presence of one or more heteroatom(s) does not impact the immiscibility of the two liquids.

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May be used mixtures containing more than 99.8 % of alkanes. These mixtures may contain little amount of aromatic groups and/or unsaturated moieties in a ratio lower than 1 weight % (preferentially lower than 0.5%). Chlorine may also be present in said alkane, in a ratio lower than 10 weight %, preferentially lower than 7%. Such impurities may be present as sub-product resulting from the preparation of the alkanes, e.g. when they are obtained by distillation process.

According to various features of the present invention, the hydrocarbon is or comprises:

- a linear or branched alkane, such as decane ($C_{10}H_{22}$), dodecane ($C_{12}H_{24}$), squalane ($C_{30}H_{62}$), and the like;
- an alkane comprising one or more rings, such as tert-butylcyclohexane (C₁₀H₂₀), and the like:
- a fused ring system, such as α -chloronaphthalene, α -bromonaphthalene, cis, trans-decahydronaphthalene ($C_{10}H_{18}$), and the like;
- a mixture of hydrocarbons, such as those available as Isopar[®] V, Isopar[®] P (from ExxonMobil); and the like,

and mixtures thereof.

The nanoparticles can be dispersed in one or several of the following silicon-based compound:

- a siloxane of the formula 1a, 1b or 1c:

wherein each of R1, R2 and R' independently represents alkyl, (hetero)aryl, (hetero)arylalkyl, (hetero)arylalkenyl or (hetero)arylalkynyl and n is comprised between 1 and 20, preferably between 1 and 10, more preferably n is 1, 2, 3, 4 or 5 and with the precision that n is greater than 2 in formula 1c;

- a silane of formula 2:

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$$(R')_{3}Si = \begin{cases} R1 \\ Si = \frac{1}{m}Si(R')_{3} \end{cases}$$

wherein R1, R2 and R' are as defined above and m is comprised between 1 and 20, preferably between 1 and 10, more preferably m is 1, 2 or 3;

- a monosilane of formula 3:

wherein R1 and R2 are as defined above, and each of R3 and R4 independently represents alkyl, (hetero)aryl, (hetero)arylalkyl, (hetero)arylalkynyl.

In the above formulae:

- alkyl means a straight or branched alkyl radical having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms; preferred alkyl includes methyl, ethyl, n-propyl, iso-propyl; alkyl radical may be halogenated, for instance may comprise a 1,1,1-trifluopropyl group;
- (hetero)aryl means an aromatic or heteroaromatic radical containing from 5 to 12 atoms, forming at least one, preferably one, aromatic and/or heteroaromatic ring, said ring(s) being optionally substituted by one or more halogens, preferably 1, 2 or 3 halogen atoms (mainly fluorine, chlorine and/or bromine), and being optionally

fused with one or more saturated, partially saturated or unsaturated ring system; preferred (hetero)aryl is phenyl or naphthyl, optionally substituted with 1, 2 or 3 halogen atoms;

- (hetero)arylalkyl is as defined above for each of the alkyl and (hetero)aryl radical; preferred (hetero)arylalkyls include benzyl, phenethyl, optionally substituted with 1, 2 or 3 halogen atoms;
- (hetero)arylalkenyl and (hetero)arylalkynyl correspond to radicals wherein the (hetero)aryl moiety is as defined above, and alkenyl and alkynyl represent a straight or branched alkyl radical, as defined above, further comprising one or more, preferably one, double bond or one or more, preferably one, triple bond, respectively.

The nanoparticles can be dispersed in one or several of the following specific siliconbased species:

- hexamethyldisilane, diphenyldimethylsilane, chlorophenyltrimethylsilane, phenyltrimethylsilane, methylsilane,
 - phenethyltris(trimethylsiloxy)silane, phenyltris(trimethylsiloxy)silane, polydimethylsiloxane, poly(3,3,3-trifluoropropylmethylsiloxane), 3,5,7-triphenylnonamethylpentasiloxane, 3,5-diphenyloctamethyltetrasiloxane,
 - 1,1,5,5-tetraphenyl-1,3,3,5-tetramethyltrisiloxane, and hexamethylcyclotrisiloxane.

The nanoparticles can be dispersed in one or several of the following germane based species:

- germanoxane of formula 4
- 25 germane of formula 5

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- germane of formula 6

wherein R', R1, R2, R3, R4 and n are as defined above.

The non-conductive liquid may contain one or several of the following specific germane based species: hexamethyldigermane, diphenyldimethylgermane, phenyltrimethylgermane.

According to another feature, the non-conductive liquid comprises at least one Si- and/or Ge-based compound substituted by one or more phenyl groups and/or other groups like fluorinated or non fluorinated alkyl (ethyl, *n*-propyl, *n*-butyl), linear or branched alkyls, chlorinated or brominated phenyl groups, benzyl groups, halogenated benzyl groups; or a mixture of Si- and/or Ge-based compounds wherein at least one compound is substituted by one or more phenyl groups and/or other groups like fluorinated or non fluorinated alkyl (ethyl, *n*-propyl, *n*-butyl), linear or branched alkyls, chlorinated or brominated phenyl groups, benzyl groups, halogenated benzyl groups.

The nanoparticles can be dispersed in the non-conducting liquid in the presence of wetting agents.

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Examples of organic or inorganic (mineral) compounds - and/or of wetting agents, specifically on Parylene or Cyclotene, or other non-conductive (isolating) layer or coating having a high surface energy (> 30 mN/m) - are presented in Tables 1, 2 and 3 below:

-- Table 1 --

| Compound | Density at 20°C (g/cm3) | Refractive index at 589.3nm at 20°C | viscosity at 20°C (cSt) | Surface tension at 20°C |
|---------------------------------------|-------------------------------|---|----------------------------|-------------------------------|
| 1-Bromononane | 1.0895 | 1.4545 | 1.93 | 28.69 |
| 1,2-Dibromohexane | 1.5812 | 1.50258 | 1.6843 | 30.52 |
| Bromocyclohexane | 1.3347 | 1.49541 | 1.79 | 31.57 |
| 1-Chloro-2-methyl-2- phenylpropane | 1.0423 | 1.52444 | 3.2455 | 34.36 |
| 1,9-Dichlorononane | 1.0102 | 1.4599 | 3.93 | 34.49 |
| 1,8-Dichlorooctane | 1.0261 | 1.45921 | 3.21 | 34.52 |
| 1,10-Dichlorodecane | 0.9966 | 1.46085 | 4.76 | 34.54 |
| Cycloheptylbromide | 1.3085 | 1.50451 | 2.4078 | 35.05 |
| 1-Chloro-3-phenylpropane | 1.0478 | 1.52223 | 2.3959 | 35.94 |
| 2-phenylethylbromid | 1.37 | 1.55729 | 2.3115 | 37.69 |
| 1,8-Dibromooctane | 1.4657 | 1.49927 | 4.08 | 37.73 |
| 1-Bromo-3-phenylpropane | 1.3127 | 1.545 | 2.7 | 37.92 |
| 1,6-Dibromohexane | 1.608 | 1.5073 | 2.7 | 38.39 |
| 1,9-Dibromononane | 1.4115 | 1.49639 | 4.85 | 39 |
| 1,1,2-Tribromoethane | 2.61 | 1.593 | 300 | 43.16 |

-- <u>Table 2</u> --

| Compound | density at 20°C (g/cm3) | refractive index at 589.3nm at 20°C | viscosity at 20°C (cSt) | Surface tension at 20°C |
|----------------------------------|-------------------------------|---|----------------------------|-------------------------------|
| Cyclohexylbenzene | 0.9424 | 1.52576 | 2.98 | 30.62 |
| 1,2-Dichlorobenzene | 1.3061 | 1.55136 | 1.13 | 31.56 |
| 1-Chloro-2-fluorobenzene | 1.2405 | 1.50104 | 0.78303 | 31.82 |
| 2-Chloro-1,4- dimethylbenzene | 1.056 | 1.52347 | 1.04 | 31.9 |
| Chlorobenzene | 1.1066 | 1.52479 | 0.74284 | 32.63 |
| 1-Bromo-4-propylbenzène | 1.286 | 1.5363 | 1.55 | 33.15 |
| 1-Bromo-4-ethylbenzène | 1.3395 | 1.54455 | 1.08 | 33.65 |
| Bromobenzene | 1.4964 | 1.55972 | 0.81 | 33.99 |
| 1-Phenyl-1-cyclohexene | 0.99 | 1.56842 | | 37.25 |
| Cyclopropyl phenyl sulfide | 1.0619 | 1.58233 | 2.7 | 38.43 |
| 4-Chlorodiphenyl ether | 1.1916 | 1.58854 | 4.69 | 39.13 |
| Thioanisole | 1.0584 | 1.58703 | 1.5401 | 39.23 |
| Phenyl sulfide | 1.1123 | 1.6328 | 4.26 | 41.36 |
| 4-Bromodiphenyl ether | 1.4213 | 1.60819 | 5.8813 | 42.12 |
| 2-Fluorobenzophenone | 1.1853 | 1.58562 | 17.831 | 42.44 |
| 1-Bromonaphtalene | 1.4889 | 1.65815 | 3.68 | 43.57 |
| 2-Bromothioanisole | 1.542 | 1.63377 | 3.3203 | 44.58 |

-- <u>Table 3</u> --

| Compound | density at 20°C (g/cm3) | refractive index at 589.3nm at 20°C | |
|---------------------------|-------------------------|-------------------------------------|--|
| Diphenyldimethylgermanium | 1.18 | 1.573 | |

CLAIMS

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1. Use of nanoparticles in an optical electrowetting device comprising a first and a second liquids, said liquids being non miscible, said nanoparticles being dispersed in at least one of the liquids.

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- Use of claim 1, wherein the diameter of said nanoparticles is lower than 50 nanometers, preferentially lower than 20 nanometers, preferably lower than 10 nanometers.
- 3. Use of claim 1, wherein said nanoparticles are made of silica (SiO₂), titanium oxide 15 (TiO₂), aluminum oxide (Al₂O₃), zirconium oxide (ZrO₂), ytterbium fluoride (YbF₃), gadolinium fluoride (GdF₃), yttrium oxide (Y₂O₃), zinc oxide (ZnO), hafnium oxide (HfO₂), cerium oxide (CeO₂), calcium fluoride (CaF₂), yttrium fluoride (YF₃), indium . fluoride (InF₃), indium oxide (In₂O₃), tin fluorides (SnF₂ or SnF₄), tin oxide (SnO₂), barium fluoride (BaF2), barium oxide (BaO), bismuth fluoride (BiF3) or bismuth oxide (Bi₂O₃).

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4. Use of claim 1, wherein one of the liquid is a non conductive liquid and the other liquid is a conductive liquid, the nanoparticles being dispersed in the non-conductive liquid.

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5. Use of claim 4, wherein said nanoparticles are made of silica (SiO₂), titanium oxide (TiO₂), aluminum oxide (Al₂O₃).

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6. Use of claim 1, wherein one of the liquid is a non conductive liquid and the other liquid is a conductive liquid, the nanoparticles being dispersed in the conductive liquid.

7. Use of claim 6, wherein said nanoparticles are made of silica (SiO₂), zirconium oxide (ZrO₂), ytterbium fluoride (YbF₃), gadolinium fluoride (GdF₃).

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Use of claim 1 in a variable focus liquid lens driven by electrowetting.

9. A multi-phase liquid composition comprising two non miscible liquids, wherein nanoparticles are dispersed in at least one of the liquids.

10. The multi-phase liquid composition of claim 9, wherein the diameter of said nanoparticles is lower than 50 nanometers, preferentially lower than 20 nanometers, preferentially lower than 10 nanometers.

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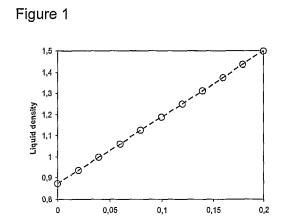
- 11. The multi-phase liquid composition of claim 9, wherein said nanometric solid material is made of silica (SiO₂), titanium oxide (TiO₂), aluminum oxide (Al₂O₃), zirconium oxide (ZrO₂), ytterbium fluoride (YbF₃), gadolinium fluoride (GdF₃), yttrium oxide (Y₂O₃), zinc oxide (ZnO), hafnium oxide (HfO₂), cerium oxide (CeO₂), calcium fluoride (CaF₂), yttrium fluoride (YF₃), indium fluoride (InF₃), indium oxide (In₂O₃), tin fluorides (SnF₂ or SnF₄), tin oxide (SnO₂), barium fluoride (BaF₂), barium oxide (BaO), bismuth fluoride (BiF₃) or bismuth oxide (Bi₂O₃).
- **12.** The multi-phase liquid composition of claim 9, wherein said nanoparticles are dispersed in one of the liquids to increase its conductivity.
- 13. The multi-phase liquid composition of claim 9, wherein one of the liquid is a non conductive liquid and the other liquid is a conductive liquid, the nanoparticles being dispersed in the non-conductive liquid.
 - **14.** The multi-phase liquid composition of claim 13, wherein said nanoparticles are made of silica (SiO₂), titanium oxide (TiO₂), aluminum oxide (Al₂O₃).
 - **15.** The multi-phase liquid composition of claim 9, wherein one of the liquid is a non conductive liquid and the other liquid is a conductive liquid, the nanoparticles being dispersed in the conductive liquid.
- 30 16. The multi-phase liquid composition of claim 15, wherein said nanoparticles are made of silica (SiO₂), zirconium oxide (ZrO₂), ytterbium fluoride (YbF₃), gadolinium fluoride (GdF₃).
- **17.** An optical electrowetting device comprising a multi-phase liquid composition of claim 9.

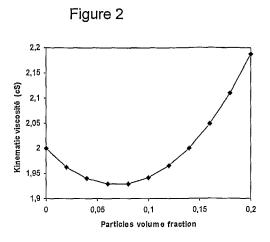
18. The optical electrowetting device of claim 17 which is a variable focus liquid lens, an optical zoom, an optical aperture.

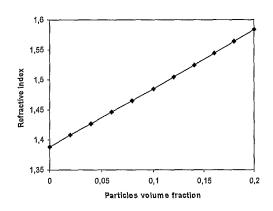
- 19. An apparatus comprising an optical device of claim 17.
- 20. An apparatus of claim 19, which is a camera, an endoscope, a cell phone, a dental

video camera.

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Particles volume fraction

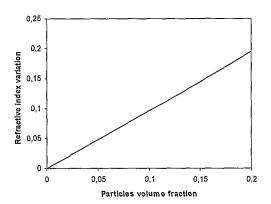


Figure 3

Figure 4

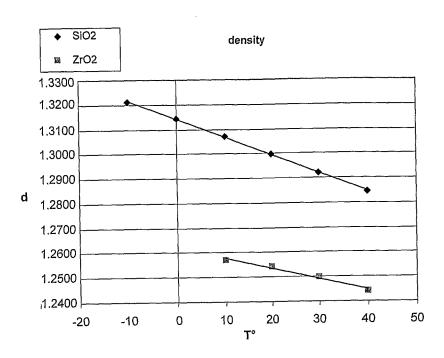


Figure 5

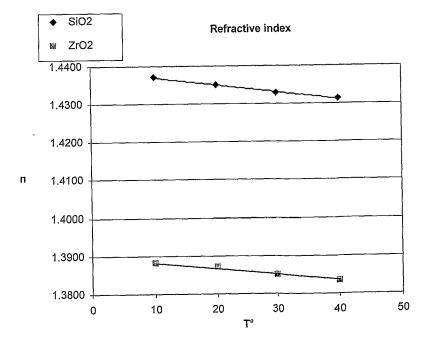


Figure 6

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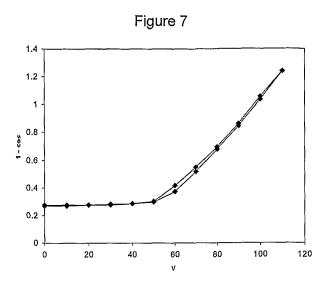
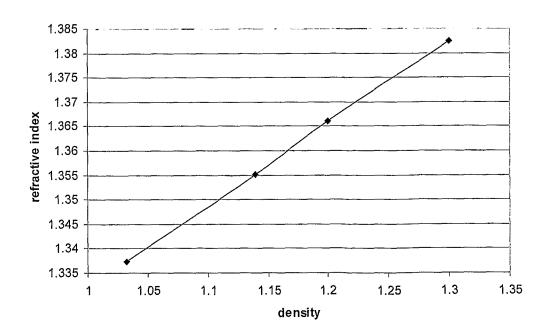


Figure 8

Refractive index and density of GdF₃/citric acid



INTERNATIONAL SEARCH REPORT

International application No PCT/IB2007/000839

A. CLASSIFICATION OF SUBJECT MATTER INV. G02B3/14 G02B26/02

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

B. FIELDS SEARCHED

 $\begin{tabular}{ll} \textbf{Minimum documentation searched (classification system followed by classification symbols)} \\ \textbf{G02B} \end{tabular}$

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

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

EPO-Internal, WPI Data

| C. DOCUM | ENTS CONSIDERED TO BE RELEVANT | |
|-----------|--|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| | | |

| Further documents are listed in the continuation of Box C. | X See patent family annex. |
|--|--|
| pecial categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document but published on or after the international filing date 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) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention cannot be considered novel or cannot be considered novel or cannot be considered novel or cannot be considered to involve an inventive step when the 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. *** document member of the same patent family | |
| Date of the actual completion of the international search | Date of mailing of the international search report |
| 17 August 2007 | 24/08/2007 |
| Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 | Authorized officer |
| NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | THEOPISTOU, P |

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/000839

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