



- (51) International Patent Classification:
G02F 1/167 (2006.01)
- (21) International Application Number:
PCT/US2014/047627
- (22) International Filing Date:
22 July 2014 (22.07.2014)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
13/952,136 26 July 2013 (26.07.2013) US
- (71) Applicant: **E INK CALIFORNIA, LLC** [US/US]; 47485 Seabridge Drive, Fremont, California 94538 (US).
- (72) Inventors: **DU, Hui**; 47485 Seabridge Drive, Fremont, California 94538 (US). **LIN, Craig**; 47485 Seabridge Drive, Fremont, California 94538 (US). **WANG, Ming**; 47485 Seabridge Drive, Fremont, California 94538 (US). **ZANG, HongMei**; 47485 Seabridge Drive, Fremont, California 94538 (US).
- (74) Agents: **KUNG, Viola T.** et al.; Perkins Coie LLP - PAO, P. O. Box 1208, Seattle, Washington 98111-1208 (US).
- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: ELECTROPHORETIC FLUID

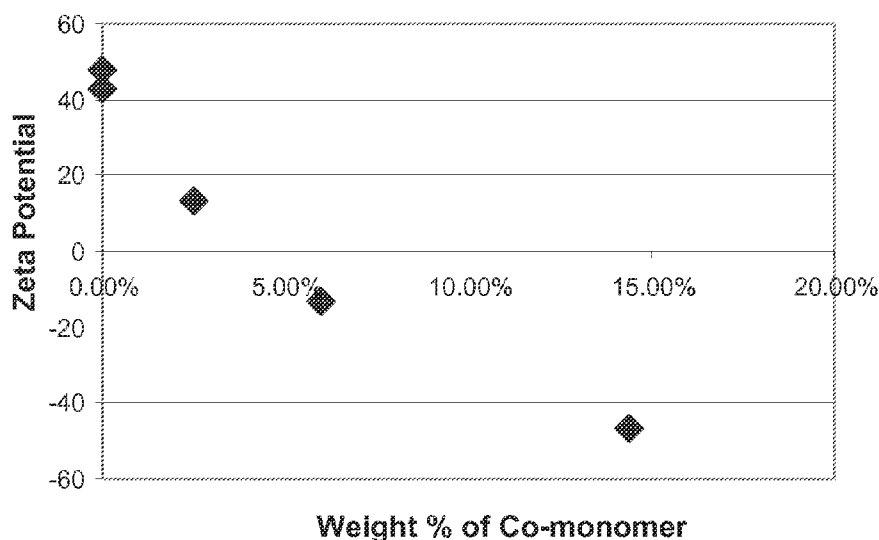


Figure 3

(57) Abstract: The present invention is directed to a display fluid comprising charged composite pigment particles dispersed in a solvent. The composite pigment particle comprises at least a core pigment particle, a shell coated over the core pigment particle and steric stabilizer molecules on the surface of the composite pigment particle, wherein the shell is formed from a monomer and a co-monomer. A display fluid comprising the composite pigment particles provides improved display performance.



Declarations under Rule 4.17:

Published:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))* — *with international search report (Art. 21(3))*

ELECTROPHORETIC FLUID

FIELD OF THE INVENTION

5 The present invention is directed to the preparation of composite pigment particles that can be used to form an electrophoretic fluid, and the resulting display fluid.

BACKGROUND OF THE INVENTION

10 An electrophoretic display (EPD) is a non-emissive device based on the electrophoresis phenomenon influencing charged pigment particles dispersed in a dielectric solvent. An EPD typically comprises a pair of spaced-apart plate-like electrodes. At least one of the electrode plates, typically on the viewing side, is transparent. An electrophoretic fluid composed of a dielectric solvent with charged pigment particles dispersed therein is enclosed between the two electrode plates.

15 An electrophoretic fluid may have one type of charged pigment particles dispersed in a solvent or solvent mixture of a contrasting color. In this case, when a voltage difference is imposed between the two electrode plates, the pigment particles migrate by attraction to the plate of polarity opposite that of the pigment particles. Thus, the color showing at the transparent plate may be either the color of the solvent or the color of the pigment particles. Reversal of plate polarity will cause the particles to migrate back to the opposite plate, thereby reversing the color.

25 Alternatively, an electrophoretic fluid may have two types of pigment particles of contrasting colors and carrying opposite charges, and the two types of pigment particles are dispersed in a clear solvent or solvent mixture. In this case, when a voltage difference is imposed between the two electrode plates, the two types of pigment particles would move to the opposite ends (top or bottom) in a display cell. Thus one of the colors of the two types of the pigment particles would be seen at the viewing side of the display cell.

30 In another alternative, pigment particles of additional colors are added to an electrophoretic fluid for forming a highlight or multicolor display device.

For all types of the electrophoretic displays, the fluid contained within the individual display cells of the display is undoubtedly one of the most crucial parts of the device. The composition of the fluid determines, to a large extent, the lifetime, contrast ratio, switching rate and bistability of the device.

5

In an ideal fluid, the charged pigment particles remain separate and do not agglomerate or stick to each other or to the electrodes, under all operating conditions. In addition, all components in the fluid must be chemically stable and compatible with the other materials present in an electrophoretic display.

10

Currently, the pigment particles in an electrophoretic fluid often have a density which is much higher than that of the solvent in which the particles are dispersed, thus causing performance issues, such as poor grey level bistability and vertical settling problems.

15

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1a and 1b show the composite pigment particles of the present invention.

Figure 2 shows reaction steps of a process suitable for the preparation of the composite pigment particles of the present invention.

Figures 3 and 4 demonstrate the possibility of tuning the charge polarity and charge level with a co-monomer in the method of synthesis of the composite pigment particles.

20

SUMMARY OF THE INVENTION

The present invention is directed to a display fluid comprising charged composite pigment particles dispersed in a solvent, wherein each of said composite pigment particles comprises at least a core pigment particle, a shell coated over the core pigment particle and steric stabilizer molecules on the surface of the composite pigment particles.

25

In one embodiment, the density of the composite pigment particles substantially matches to that of the solvent.

30

In one embodiment, the difference between the density of the composite pigment particles and the density of the solvent is less than 2 g/cm³.

In one embodiment, the core pigment particle is an inorganic pigment particle and the core pigment particles may be surface treated or surface untreated. The shell may also be formed from an organic material, and in that case, the organic content of the composite pigment particles may be at least 20% by weight, preferably 20% to 70% by weight and more preferably 20% to 40% or 30% to 50%, by weight.

In one embodiment, the core pigment particle may be an organic pigment particle. In this embodiment, the core pigment particle may also be surface treated or surface untreated. The polymer content of the composite pigment particles with an organic core particle may be at least 20%, preferably 30% to 70% by weight and more preferably 40% to 60% or 30% to 50% by weight.

In one embodiment, the shell may be completely incompatible or relatively incompatible with the solvent.

In one embodiment, the surface of the shell may comprise functional groups to enable charge generation or interaction with a charge control agent.

In one embodiment, the steric stabilizer molecules may be formed from polyacrylate, polyethylene, polypropylene, polyester, polysiloxane or a mixture thereof.

In one embodiment, the fluid may further comprise a second type of charged pigment particles. In one embodiment, the second type of charged pigment particles is composite pigment particles comprising at least a core pigment particle, a shell coated over the core pigment particle and steric stabilizer molecules on the surface of the composite pigment particles. The two types of composite pigment particles in the fluid are of contrasting colors. In one embodiment, the fluid may comprise more than two types of pigment particles and each type has a color different from the colors of other types.

In one embodiment, the solvent in which the composite pigment particles are dispersed may be a hydrocarbon solvent or a mixture of a hydrocarbon solvent and another solvent, such as a halogenated solvent or a silicone oil type solvent.

In one embodiment, the composite pigment particles may be prepared by dispersion polymerization or living radical polymerization.

Another aspect of the invention is directed to a composite pigment particle for an electrophoretic display comprises at least a core pigment particle, a shell coated over the core pigment particle and steric stabilizer molecules on the surface of the composite pigment particle, wherein the shell is formed from a monomer and a co-monomer.

A further aspect of the invention is directed to a method for tuning the charge level of a composite pigment particle, which method comprises adding a co-monomer to a composition comprising a monomer for forming a shell of the composite pigment particle.

DETAILED DESCRIPTION OF THE INVENTION

The first aspect of the present invention is directed to the composite pigment particles, as shown in Figures 1a and 1b. The composite pigment particles (10) may have one or more core pigment particles (11). The core particle(s) (11) is/are coated with a shell (12). There are steric stabilizer molecules (13) on the surface of the composite pigment particles.

The core pigment particles may be of any colors (e.g., black, white, red, green, blue, cyan, magenta, yellow or the like).

The composite pigment particles may be closely density matched to a solvent in which they are dispersed, especially in a hydrocarbon solvent.

In one embodiment, the core particles may be formed from an inorganic material, such as TiO_2 , BaSO_4 , ZnO , metal oxides, manganese ferrite black spinel, copper chromite black spinel, carbon black or zinc sulfide pigment particles.

The inorganic core particles may be optionally surface treated. The surface treatment would improve compatibility of the core pigment particles to the monomer in a reaction medium or chemical bonding with the monomer, in forming the shell of the composite pigment particles. As an example, the surface treatment may be carried out with an organic silane

having functional groups, such as acrylate, vinyl, $-\text{NH}_2$, $-\text{NCO}$, $-\text{OH}$ or the like. These functional groups may undergo chemical reaction with the monomers.

The core particles can also be surface treated with an inorganic material, such as silica, aluminum oxide, zinc oxide or the like or a combination thereof. Sodium silicate or tetraethoxysilane may be used as a common precursor for silica coating.

In case of an inorganic treatment, the structure of the coating may be porous to reduce density.

An organic shell may be formed from an organic polymer, such as polyacrylate, polyurethane, polyurea, polyethylene, polyester, polysiloxane or the like. For example, a polyacrylate shell may be formed from monomer, such as styrene, methyl acrylate, methyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, vinyl pyridine, n-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate or the like. A polyurethane shell may be formed from monomer or oligomer, such as multifunctional isocyanate or thioisocyanate, primary alcohol or the like. A polyurea shell may be formed from monomer containing reactive groups, such as amine/isocyanate, amine/thioisocyanate or the like. A person skilled in the art would be able to select proper monomer or oligomer and its variations, based on the concept of the present invention.

In case of an organic shell, the "organic content" of the resulting composite pigment particles from inorganic core particles would be at least 20% by weight, preferably 20% to 70% by weight and more preferably 20% to 40% by weight. In this embodiment, the term "organic content" is determined by the total weight of the shell (12) and the steric stabilizers (13) divided by the total weight of the core pigment particles (11), the shell (12) and the steric stabilizers (13).

The density of the shell is preferably low, lower than 2g/cm^3 and more preferably 1g/cm^3 . The shell thickness may be controlled, based on the density of the shell material and the desired final particle density.

The shell material is either completely incompatible or relatively incompatible with the display fluid in which the composite pigment particles are dispersed. Relatively "incompatible" as used herein, means that no more than 5%, preferably no more than 1%, of the shell material is miscible with the display fluid.

5

In order to achieve this complete or relative incompatibility, a polymeric shell material may have polar functionality on its main chain or a side chain. Examples of such polar functionality may include $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{O-R}$, $-\text{NH-R}$ and the like (wherein R is an alkyl or aryl group). Each of the side chains, in this case, preferably has less than 6 carbon atoms. In one embodiment, the main chain or the side chain may contain an aromatic moiety.

In addition, the core pigment particle(s) and the shell should behave as one single unit. This may be achieved by cross-linking or an encapsulation technique, as described below.

15

The steric stabilizer (13) in Figure 1 is usually formed of high molecular weight polymers, such as polyethylene, polypropylene, polyester, polysiloxane or a mixture thereof. The steric stabilizers should be compatible with the solvent in which the composite pigment particles are dispersed to facilitate dispersion of the composite pigment particles in the solvent.

20

In addition to the steric stabilizer, the surface of the shell may optionally have functional groups that would enable charge generation or interaction with a charge control agent.

25

In another embodiment of the present invention, the core particles may be formed from an organic material, such as CI pigment PR 254, PR122, PR149, PG36, PG58, PG7, PY138, PY150, PY20, PY83, PB15 or the like, which are commonly used organic pigment materials described in the color index handbook "New Pigment Application Technology" (CMC Publishing Co, Ltd, 1986) and "Printing Ink Technology" (CMC Publishing Co, Ltd, 1984). Specific examples may include Clariant Hostaperm Red D3G 70-EDS, Hostaperm Pink E-EDS, PV fast red D3G, Hostaperm red D3G 70, BASF Irgazine red L 3630, Cinquasia Red L 4100 HD, Irgazin Red L 3660 HD, Clariant Novoperm yellow HR-70-EDS, Blue B2G, Green GNX and the like. The composite pigment particles formed from the organic core particles are usually colored, such as red, green, blue, cyan, magenta, yellow or the like.

30

The surface of the organic core particles may be treated or untreated. The surface treatment would improve compatibility of the core pigment particles to the monomer in a reaction medium or chemical bonding with the monomer, in forming the shell of the composite color particles. The pre-treated functional molecules can be either chemically bonded or
5 physically absorbed onto the pigment particle surface. The functional molecules may be a dispersant, surfactant or the like.

The shell for organic core particles is usually formed from an organic shell material, as described above.

10 The stabilizers for the composite pigment particles prepared from organic core particles may also be prepared as described below.

The “polymer content” of the composite pigment particles prepared from organic core
15 particles may be at least 20% by weight, preferably 30% to 70% by weight and more preferably 40% to 60% or 30% to 50%, by weight. The term “polymer content” is determined by the total weight of the shell (12) and the steric stabilizers (13) divided by the total weight of the core pigment particles (11), the shell (12) and the steric stabilizers (13).

20 The second aspect of the present invention is directed to the preparation of the composite pigment particles of the present invention, which may involve a variety of techniques.

1. Dispersion Polymerization

25 For example, they may be formed by dispersion polymerization. During dispersion polymerization, monomer is polymerized around core pigment particles in the presence of a steric stabilizer polymer soluble in the reaction medium. The solvent selected as the reaction medium must be a good solvent for both the monomer and the steric stabilizer polymer, but a non-solvent for the polymer shell being formed. For example, in an aliphatic hydrocarbon
30 solvent of Isopar G®, monomer methylmethacrylate is soluble; but after polymerization, the resulting polymethylmethacrylate is not soluble.

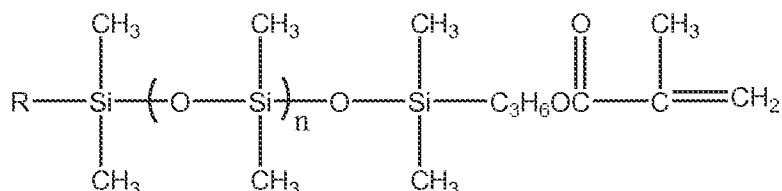
The polymer shell formed from the monomer must be completely incompatible or relatively incompatible with the solvent in which the composite pigment particles are dispersed. Monomers suitable for forming the shell may be those described above, such as styrene, methyl acrylate, methyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, vinyl pyridine, n-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate or the like.

The steric stabilizer polymer may be a reactive and polymerizable macromonomer which adsorbs, becomes incorporated or is chemically bonded, onto the surface of the polymer shell being formed. The macromonomer as a steric stabilizer, determines the particle size and colloidal stability of the system.

The macromonomer may be an acrylate-terminated or vinyl-terminated macromolecule, which are suitable because the acrylate or vinyl group can co-polymerize with the monomer in the reaction medium.

The macromonomer preferably has a long tail, R, which may stabilize the composite pigment particles in a hydrocarbon solvent.

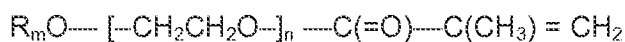
One type of macromonomers is acrylate terminated polysiloxane (Gelest, MCR-M11, MCR-M17, MCR-M22), as shown below:



Another type of macromonomers which is suitable for the process is PE-PEO macromonomers, as shown below:

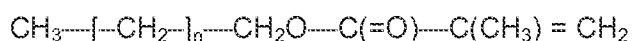


or



The substituent R may be a polyethylene chain, n is 1-60 and m is 1-500. The synthesis of these compounds may be found in Dongri Chao et al., Polymer Journal, Vol. 23, no.9, 1045 (1991) and Koichi Ito et al, Macromolecules, 1991, 24, 2348.

A further type of suitable macromonomers is PE macromonomers, as shown below:



The n, in this case, is 30-100. The synthesis of this type of macromonomers may be found in Seigou Kawaguchi et al, Designed Monomers and Polymers, 2000, 3, 263.

2. Living Radical Dispersion Polymerization

Alternatively, the composite pigment particles may be prepared by living radical dispersion polymerization, as shown in Figure 2.

The living radical dispersion polymerization technique is similar to the dispersion polymerization described above by starting the process with pigment particles (21) and monomer dispersed in a reaction medium.

The monomers used in the process to form the shell (22) may include styrene, methyl acrylate, methyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, vinyl pyridine, n-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate and the like.

However in this alternative process, multiple living ends (24) are formed on the surface of the shell (22). The living ends may be created by adding an agent such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), a RAFT (reversible addition-fragmentation chain transfer) reagent or the like, in the reaction medium.

In a further step, a second monomer is added to the reaction medium to cause the living ends (24) to react with the second monomer to form the steric stabilizers (23). The second monomer may be lauryl acrylate, lauryl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, hexyl acrylate, hexyl methacrylate, n-octyl acrylate, n-octyl methacrylate, n-octadecyl acrylate, n-octadecyl methacrylate or the like.

3. Non-aqueous Emulsion Poly-condensation

Further alternatively, the composite pigment particles may be formed by coating core pigment particles by non-aqueous emulsion poly-condensation.

In this alternative process, the shell of the composite pigment particles may be a polyurethane or polyurea material. The steric stabilizers may be non-polar long chain hydrocarbon molecules. Polyurethane and polyurea usually are not compatible to a non-polar hydrocarbon solvent and their hardness and elastic property can be tuned through the monomer composition.

This synthesis method is similar to emulsion or dispersion polymerization, except that polycondensation occurs, inside micelles, with polyurethane monomer and the inorganic core pigment particles.

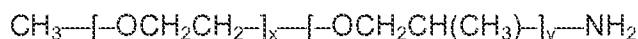
The polyurethane or polyurea coating system may be considered as an oil-in-oil emulsion, which contains two incompatible solvents, one of which is a non-polar organic solvent and the other is a polar organic solvent. The system may also be referred to as non-aqueous emulsion polycondensation, in which the non-polar solvent is the continuous phase and the polar solvent is the non-continuous phase. The monomer and the inorganic pigment particles are in the non-continuous phase. Suitable non-polar solvents may include the solvents in the Isopar® series, cyclohexane, tetradecane, hexane or the like. The polar solvents may include acetonitrile, DMF and the like.

An emulsifier or dispersant is critical for this biphasic organic system. The molecular structure of the emulsifier or dispersant may contain one part soluble in the non-polar solvent, and another part anchoring to the polar phase. This will stabilize the micelles/droplets

containing the monomer and the inorganic pigment particles and serving as a micro-reactor for particle formation through polycondensation.

Suitable emulsifiers or dispersants may include di-block co-polymers, such as poly (isoprene)-b-poly(methyl methacrylate), polystyrene-b-poly(ethene-alt-propene) (Kraton) or the like.

Also, a co-emulsifier may be added to form chemical bonding with the particles. For example, amine terminated hydrocarbon molecules can react with the particles during polycondensation and bond to surface as robust steric stabilizers. Suitable co-emulsifiers may include surfonamine (B-60, B-100 or B-200) as shown below:



wherein x is 5-40 and y is 1-40.

In one approach, the process may continue growing polyacrylate steric stabilizers after the polycondensation reaction in the microreactor is completed. In this case, the shell is formed from polyurethane while the steric stabilizers may be polyacrylate chains. After the emulsifier or dispersant used in the process is washed away from the particle surface, the composite pigment particles are stable in the non-polar solvent (i.e., display fluid) with the polyacrylate stabilizers. Some materials that can initiate acrylate polymerization include isocyanatoethyl acrylate, isocyanatostyrene or the like.

Monomers for the steric stabilizer may be a mixture of hydroxyethyl methacrylate and other acrylate that are compatible to the non-polar solvent, such as lauryl acrylate, lauryl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, hexyl acrylate, hexyl methacrylate, n-octyl acrylate, n-octyl methacrylate, n-octadecyl acrylate, n-octadecyl methacrylate or the like.

In any of the processes described above, to incorporate functional groups for charge generation, a co-monomer may be added in the reaction medium. The co-monomer may either directly charge the composite pigment particles or have interaction with a charge control agent

in the display fluid to bring a desired charge polarity and charge density to the composite pigment particles. Suitable co-monomers may include vinylbenzyl-aminoethylamino-propyl-trimethoxysilane, methacryloxypropyltrimethoxysilane, acrylic acid, methacrylic acid, vinyl phosphoric acid, 2-acrylamino-2-methylpropane sulfonic acid, 2-(dimethylamino)ethyl methacrylate, N-[3-(dimethylamino)propyl]methacrylamide and the like.

A co-monomer, in the context of the present invention, is a monomer different from a monomer already in a composition for forming the shell of composite pigment particles. When both a monomer and a co-monomer are present in a reaction medium for forming the shell, the charge polarity or intensity of the composite pigment particles may be tuned to a desired level.

For example, a yellow pigment (Clariant Hostaperm H4G-EDS) prepared from a standard synthesis method (methyl methacrylate used as the monomer for forming the shell and PDMS (polydimethylsiloxane) acrylate used as the stabilizer polymer) shows a positive zeta potential. However, if a fluorinated co-monomer, e.g., 2-perfluorobutylethyl acrylate, is added in the reaction medium for forming the shell, the zeta potential of the yellow pigment may be brought to be in the negative range (see Figure 3).

In a further example, a blue pigment (Clariant Hostaperm B2G-EDS) produced from a standard synthesis method (methyl methacrylate used as the monomer for forming the shell and PDMS (polydimethylsiloxane) acrylate used as stabilizer polymer) shows a very low positive charge level. But when a co-monomer, 2-(dimethylamino)ethyl methacrylate, is added in the synthesis of the shell, the charge level of the blue pigment increases as the amount of the co-monomer added increases (see Figure 4).

As shown, the charge polarity of a pigment material may be changed from negative to positive or vice versa by the addition of a co-monomer in the reaction medium for forming the shell. The charge level of a pigment material may also be tuned by this method.

The co-monomers that can introduce a negative charge may include, but are not limited to, fluorinated acrylate or fluorinated methacrylate. Specific examples include 2-perfluorobutylethyl acrylate, 2,2,2 trifluoroethyl methacrylate, 2,2,3,3 tetrafluoropropyl methacrylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate, 1,1,1,3,3,3-hexafluoroisopropyl

methacrylate, 2,2,3,3,3-pentafluoropropyl acrylate, 2,2,3,3-tetrafluoropropyl acrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate, 2,2,3,3,4,4,4-heptafluorobutyl methacrylate or the like.

5 The co-monomers that can introduce a positive charge may include, but are not limited to, 2-(dimethylamino)ethyl methacrylate, N-[3-(dimethylamino)propyl]-methacrylamide. The functional groups on these positive charge generating co-monomers include, but are not limited to, -NHR, -NR₂, -NH-, -NH₂ or the like (wherein R is up to 4 carbon atoms).

10 The main monomers for forming the shell are listed above in this application. For example, they may be styrene, methyl acrylate, methyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, vinyl pyridine, n-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate or the like. In some cases, the main monomer may be acrylate, methacrylate or styrene with hydrocarbon side chains.

15 Some examples of suitable monomer-comonomer pair are methylmethacrylate and 2-(dimethylamino)ethyl methacrylate, methylmethacrylate and 2-perfluorobutylethyl acrylate, 20 methylmethacrylate and 2,2,2 trifluoroethyl methacrylate, and the like.

25 The molar ratio of charge tuning co-monomer to the total monomers (main monomer plus co-monomer) can be in between 0.1% to 50% based on desired charge intensity of particles, preferably in between 1% to 10%.

30 The quantities of the reagents used (e.g., the inorganic core pigment particles, the shell materials and the material for forming the steric stabilizers) in any of the processes described above may be adjusted and controlled to achieve the desired organic content in the resulting composite pigment particles.

 The third aspect of the present invention is directed to a display fluid comprising the composite pigment particles of the present invention, which composite pigment particles are dispersed in a solvent. A preferred solvent has a low dielectric constant (preferably about 2 to

3), a high volume resistivity (preferably about 10^{15} ohm-cm or higher) and a low water solubility (preferably less than 10 parts per million). Suitable hydrocarbon solvents may include, but are not limited to, dodecane, tetradecane, the aliphatic hydrocarbons in the Isopar® series (Exxon, Houston, Tex) and the like. The solvent can also be a mixture of a hydrocarbon and a halogenated carbon or silicone oil base material.

The present invention is applicable to a one-particle, two-particle or multiple particle electrophoretic display fluid system. In a multiple particle system, there may be more than two types of pigment particles and each type has a color which is different from the colors of other types.

In other words, the present invention may be directed to a display fluid comprising only the composite pigment particles prepared according to the present invention which are dispersed in a hydrocarbon solvent. The composite pigment particles and the solvent have contrasting colors.

Alternatively, the present invention may be directed to a display fluid comprising two types of pigment particles dispersed in an organic solvent and at least one of the two types of the pigment particles is prepared according to the present invention. The two types of pigment particles carry opposite charge polarities and have contrasting colors. For example, the two types of pigment particles may be black and white respectively. In this case, the black particles may be prepared according to the present invention, or the white particles may be prepared according to the present invention, or both black and white particles may be prepared according to the present invention.

The composite pigment particles prepared according to the present invention, when dispersed in an organic solvent, have many advantages. For example, the density of the composite pigment particles may be substantially matched to the organic solvent, thus improving performance of the display device. In other words, the difference between the density of the composite pigment particles and the density of the solvent is less than 2 g/cm^3 , more preferably less than 1.5 g/cm^3 and most preferably less than 1 g/cm^3 .

In the two particle system, if only one type of the pigment particles is prepared according to the present invention, the other type of pigment particles may be prepared by any other methods. For example, the particles may be polymer encapsulated pigment particles. Microencapsulation of the pigment particles may be accomplished chemically or
5 physically. Typical microencapsulation processes include interfacial polymerization/crosslinking, *in-situ* polymerization/crosslinking, phase separation, simple or complex coacervation, electrostatic coating, spray drying, fluidized bed coating and solvent evaporation, etc.

10 The composite pigment particles prepared by the previously known techniques may also exhibit a natural charge, or may be charged explicitly using a charge control agent, or may acquire a charge when suspended in the organic solvent. Suitable charge control agents are well known in the art; they may be polymeric or non-polymeric in nature, and may also be ionic or non-ionic, including ionic surfactants such as sodium dodecylbenzenesulfonate,
15 metal soap, polybutene succinimide, maleic anhydride copolymers, vinylpyridine copolymers, vinylpyrrolidone copolymer, (meth)acrylic acid copolymers or N,N-dimethylaminoethyl (meth)acrylate copolymers), Alcolec LV30 (soy lecithin), Petrostep B100 (petroleum sulfonate) or B70 (barium sulfonate), Solsperse 17000 (active polymeric dispersant), Solsperse 9000 (active polymeric dispersant), OLOA 11000 (succinimide ashless dispersant),
20 OLOA 1200 (polyisobutylene succinimides), Unithox 750 (ethoxylates), Petronate L (sodium sulfonate), Disper BYK 101, 2095, 185, 116, 9077 & 220 and ANTI-TERRA series.

EXAMPLES

Example 1

25 **Step A: Deposition of Vinylbenzylaminoethylaminopropyl-trimethoxysilane on Black Pigment Particles**

To a 1 L reactor, Black 444 (Shepherd, 40 g), isopropanol (320 g), DI water (12 g), ammonium hydroxide (28%, 0.4 g) and Z-6032 (Dow Corning, 16 g, 40% in methanol) were added. The reactor was heated to 65°C with mechanical stirring in a sonication bath. After 5
30 hours, the mixture was centrifuged at 6000 rpm for 10 minutes. The solids were redispersed in isopropanol (300 g), centrifuged and dried at 50°C under vacuum overnight to produce 38 g of desired pigment particles.

Step B: Preparation of Polymer Coating on Pigment Particles through Dispersion Polymerization

Two (2) g of polyvinylpyrrolidone (PVP K30) was dissolved in a mixture of 94.5g water and 5.5g ethanol. The solution was purged with nitrogen for 20 minutes and heated to 65°C. The pigment particles (4 g) prepared from Step A was dispersed in a mixture of 3.0g lauryl acrylate, 0.2g divinylbenzene and 0.03g AIBN (azobisisobutyronitrile) to form a uniform suspension. This suspension was added into the PVP solution at 65°C. With stirring, the polymerization reaction lasted about 12 hours.

Then a mixture of 3.0g octadecyl acrylate and 0.03g AIBN was added into the above reaction flask and the reaction was continued for 12 hours.

The solids produced were separated from the liquid through centrifugation and then washed with isopropanol and methylethylketone to remove PVP K30 and other chemicals that were not bonded on the pigment particles. The solids were dried at 50°C under vacuum to produce final composite black particles. The organic content of the particles produced was about 34% by weight, tested through TGA (thermal gravimetric analysis).

Example 2

Synthesis of Colored Composite Pigment Particles

Hostaperm Red D3G 70-EDS (Clariant, 2.5g), methyl methacrylate (8g) and toluene (2g) were added into a 20 ml vial and sonicated for 2 hours. To a 250 mL reactor, the above mixture, MCR-M22 (Gelest, 5.7g) and DMS-T01 (Gelest, 30g) were added. The reactor was heated to 70°C with magnetic stirring and purged with nitrogen for 20 minutes, followed by the addition of lauroyl peroxide (0.07 g). After 19 hours, the mixture was centrifuged at 5000 rpm for 15 minutes. The solids produced were redispersed in hexane and centrifuged. This cycle was repeated twice and the solids were dried at room temperature under vacuum to produce the final particles. The polymer content of the particles produced was about 49 % by weight, tested through TGA (thermal gravimetric analysis).

While the present invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes

may be made and equivalents may be substituted without departing from the scope of the invention.

WHAT IS CLAIMED IS:

1. A method for tuning the charge level of a composite pigment particle, comprising

5 (i) providing a composition comprising a monomer,

(ii) selecting a co-monomer to be added to the composition wherein the co-monomer is capable of introducing a positive charge or a negative charge to the composite pigment particle or altering the charge level of the composite pigment particle, and

(iii) forming a shell of the composite pigment particle using the composition.

10 2. The method of claim 1, wherein the monomer is styrene, methyl acrylate, methyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, vinyl pyridine, n-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate or dimethylaminoethyl methacrylate.

15 3. The method of claim 1, wherein the monomer is acrylate, methacrylate, or styrene with a hydrocarbon side chain.

20 4. The method of claim 1, wherein the co-monomer is selected from the group consisting of vinylbenzyl-aminoethylamino-propyl-trimethoxysilane, methacryloxypropyltrimethoxysilane, acrylic acid, methacrylic acid, vinyl phosphoric acid, 2-acrylamino-2-methylpropane sulfonic acid, 2-(dimethylamino)ethyl methacrylate, and N-[3-(dimethylamino)propyl]methacrylamide.

25 5. The method of claim 1, wherein the co-monomer is a fluorinated acrylate, or fluorinated methacrylate, to introduce a negative charge.

30 6. The method of claim 1, wherein the co-monomer is 2-perfluorobutylethyl acrylate, 2,2,2 trifluoroethyl methacrylate, 2,2,3,3 tetrafluoropropyl methacrylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate, 1,1,1,3,3,3-hexafluoroisopropyl methacrylate, 2,2,3,3,3-pentafluoropropyl acrylate, 2,2,3,3-tetrafluoropropyl acrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate, or 2,2,3,3,4,4,4-heptafluorobutyl methacrylate, to introduce a negative charge.

7. The method of claim 1, wherein the co-monomer is 2-(dimethylamino)ethyl methacrylate or N-[3-(dimethylamino)propyl]-methacrylamide, to introduce a positive charge.

8. The method of claim 1, wherein the co-monomer comprises a functional group selected from the group consisting of -NHR, -NR₂, -NH- and -NH₂, wherein R is an alkyl of up to 4 carbon atoms, to introduce a positive charge.

9. The method of claim 1, wherein pair of the monomer and the co-monomer is methylmethacrylate and 2-(dimethylamino)ethyl methacrylate, methylmethacrylate and 2-perfluorobutylethyl acrylate, or methylmethacrylate and 2,2,2 trifluoroethyl methacrylate.

10. The method of claim 1, wherein the molar ratio of the co-monomer to the total of the monomer and the co-monomer is between 0.1 to 50%.

11. The method of claim 10, wherein the molar ratio of the co-monomer to the total of the monomer and the co-monomer is between 1 to 10%.

12. A composite pigment particle for an electrophoretic display comprises at least a core pigment particle, a shell coated over the core pigment particle, and steric stabilizer molecules on the surface of the composite pigment particle, wherein the shell is formed from a monomer and a co-monomer, wherein the monomer is styrene, methyl acrylate, methyl methacrylate, n-butyl acrylate, n-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, vinyl pyridine, n-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate.

13. The particle of claim 12, wherein the co-monomer is 2-perfluorobutylethyl acrylate, 2,2,2 trifluoroethyl methacrylate, 2,2,3,3 tetrafluoropropyl methacrylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate, 1,1,1,3,3,3-hexafluoroisopropyl methacrylate, 2,2,3,3,3-pentafluoropropyl acrylate, 2,2,3,3-tetrafluoropropyl acrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate, or 2,2,3,3,4,4,4-heptafluorobutyl methacrylate.

14. The particle of claim 12, wherein the co-monomer is 2-(dimethylamino)ethyl methacrylate or N-[3-(dimethylamino)propyl]-methacrylamide.

15. The particle of claim 12, wherein the molar ratio of the co-monomer to the
5 total of the monomer and the co-monomer is between 0.1 to 50%.

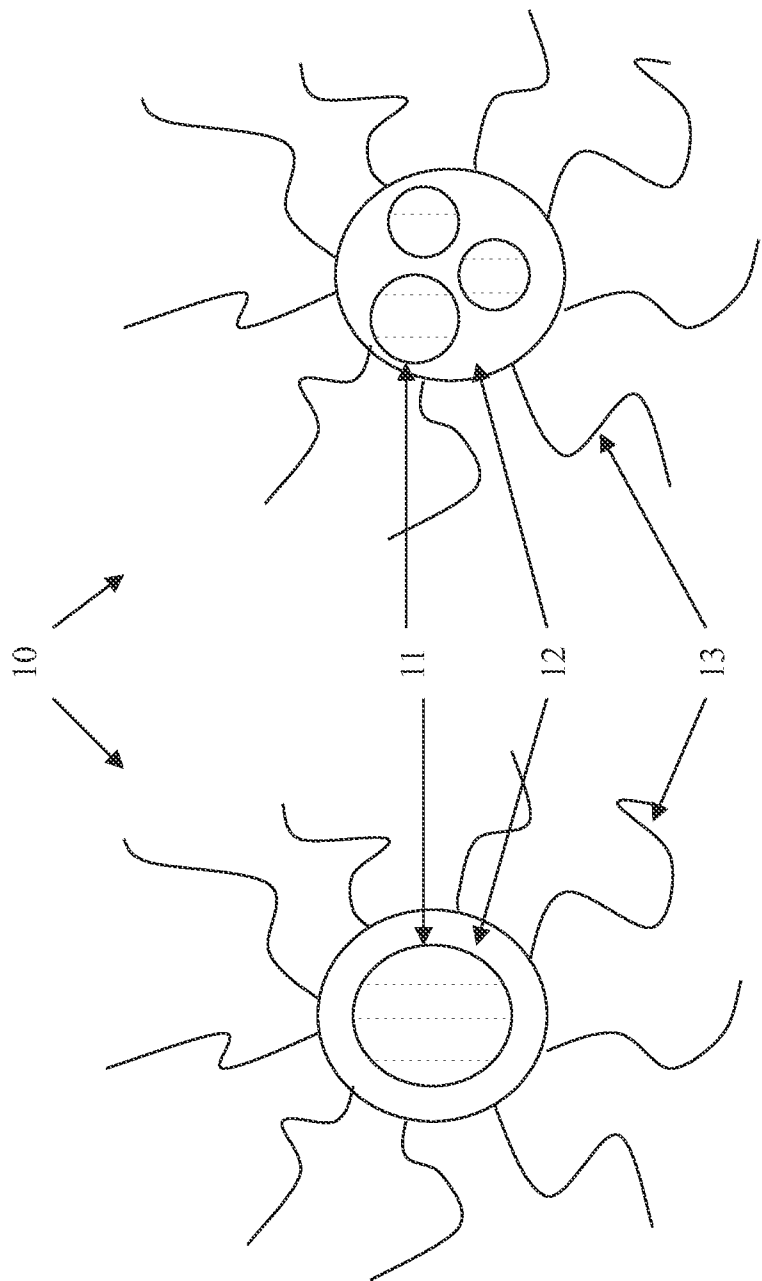


Figure 1b

Figure 1a

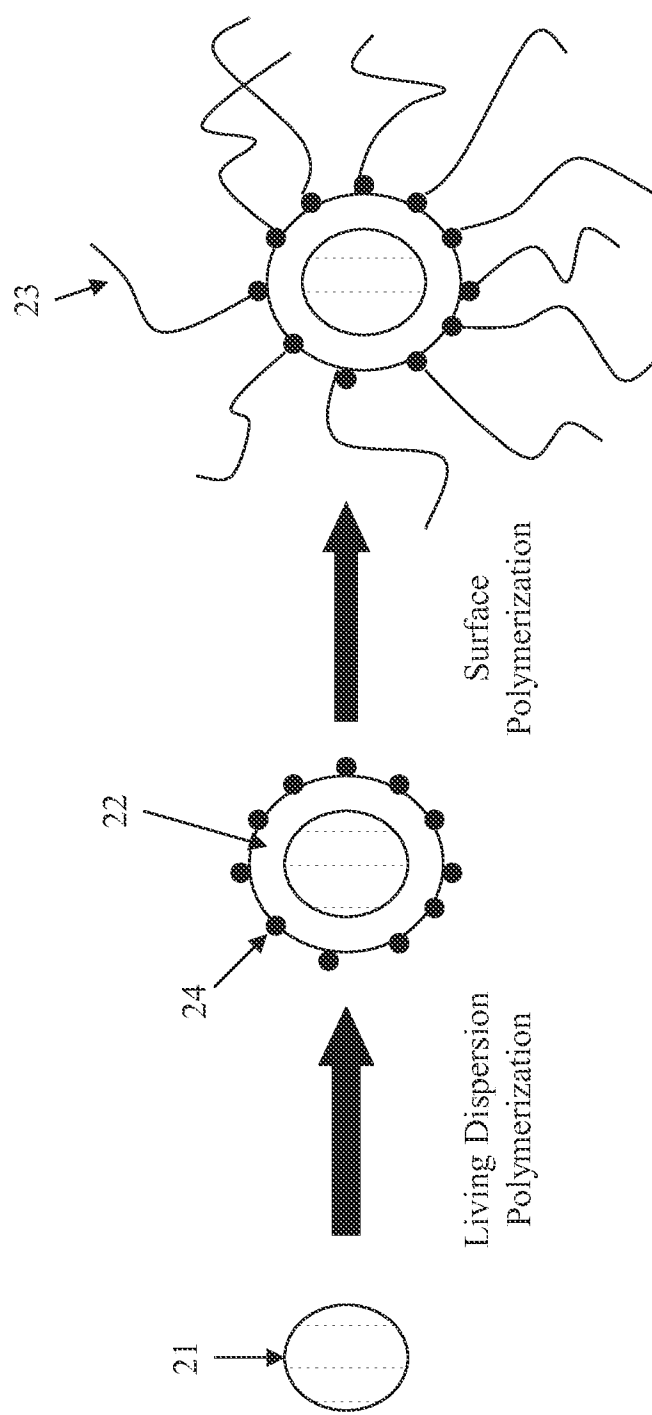


Figure 2

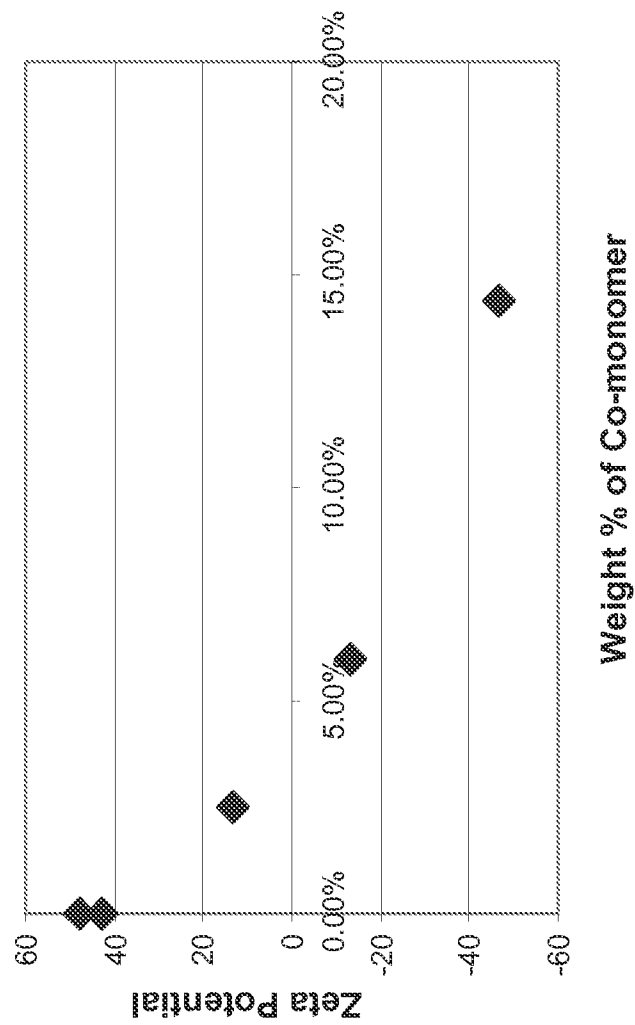


Figure 3

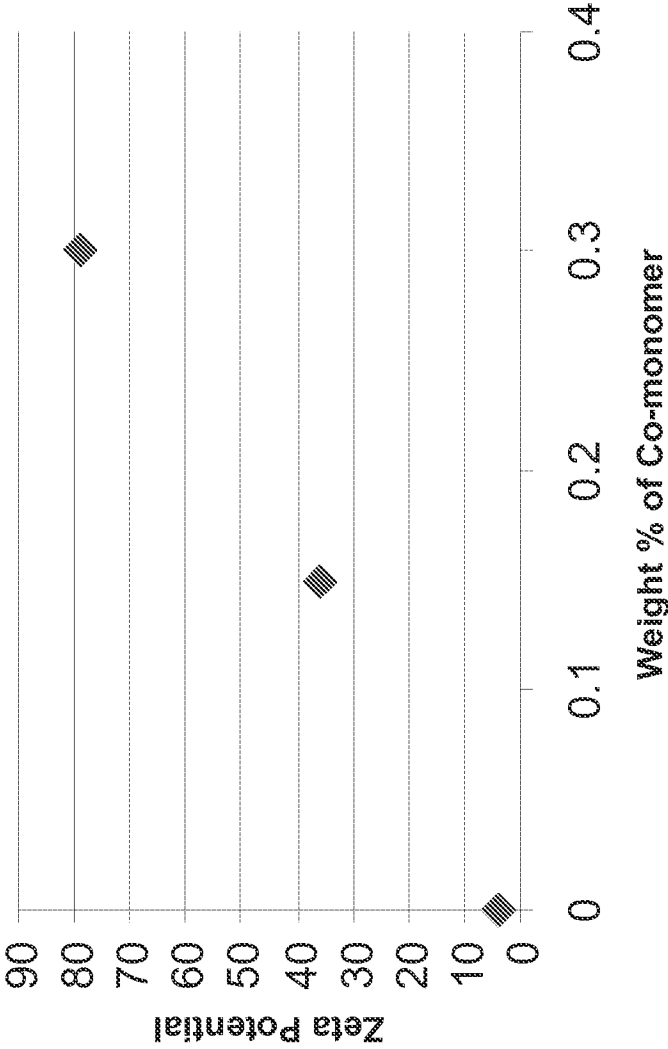


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/047627**A. CLASSIFICATION OF SUBJECT MATTER****G02F 1/167(2006.01)i**

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)

G02F 1/167; H01B 1/12; A61K 8/73; G02B 26/00; C08F 8/00; A61K 31/795; H01B 1/00; B32B 27/02; C08L 33/12; A61K 8/81

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: monomer, co-monomer, charge, shell, pigment particle

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0199798 A1 (HUI DU et al.) 09 August 2012 See paragraphs [0011], [0029], [0042]-[0061]; and figure 2.	1-4
Y		12
A		5-11, 13-15
Y	US 4387138 A (WARREN H. GIFT) 07 June 1983 See column 4, lines 32-36; and figure 1.	12
A	US 2011-0256085 A1 (RUELA TALINGTING PABALAN et al.) 20 October 2011 See paragraphs [0036], [0203], [0272]; and figure 3.	1-15
A	US 2011-0286957 A1 (MARY G. PRIEVE et al.) 24 November 2011 See paragraphs [0314], [0337], [0440]-[0443]; and figure 4 .	1-15
A	US 2008-0100906 A1 (GABRIEL IFTIME et al.) 01 May 2008 See paragraphs [0033], [0060], [0122]; and figure 1.	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited 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 an oral 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

"&" document member of the same patent family

Date of the actual completion of the international search

06 November 2014 (06.11.2014)

Date of mailing of the international search report

06 November 2014 (06.11.2014)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

LEE, Dong Yun

Telephone No. +82-42-481-8734



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/047627

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012-0199798 A1	09/08/2012	CN 102645813 A TW 201235760 A	22/08/2012 01/09/2012
US 04387138 A	07/06/1983	US 4341883 A	27/07/1982
US 2011-0256085 A1	20/10/2011	CA 2791853 A1 CN 102858883 A EP 2534205 A2 RU 2012138119 A WO 2011-100665 A2 WO 2011-100665 A3	18/08/2011 02/01/2013 19/12/2012 20/03/2014 18/08/2011 15/12/2011
US 2011-0286957 A1	24/11/2011	AU 2009-246321 A1 AU 2009-246327 A1 AU 2009-246329 A1 AU 2009-246332 A1 AU 2009-313358 A1 CA 2724014 A1 CA 2724105 A1 CA 2724455 A1 CA 2724472 A1 CA 2734917 A1 CA 2742880 A1 CA 2742955 A1 CN 102065902 A CN 102066444 A CN 102076328 A CN 102083878 A CN 102083878 B CN 102272179 A CN 102272179 B CN 103342789 A EP 2281011 A2 EP 2281011 B1 EP 2285853 A2 EP 2285853 B1 EP 2296627 A2 EP 2296708 A2 EP 2331069 A1 EP 2352522 A1 EP 2364330 A2 EP 2620161 A1 JP 2011-520901 A JP 2011-521054 A JP 2011-522070 A JP 2011-523641 A JP 2012-500793 A JP 2012-507581 A JP 2012-508284 A	19/11/2009 19/11/2009 19/11/2009 19/11/2009 14/05/2010 19/11/2009 19/11/2009 19/11/2009 19/11/2009 25/02/2010 14/05/2010 14/05/2010 18/05/2011 18/05/2011 25/05/2011 01/06/2011 10/07/2013 07/12/2011 12/03/2014 09/10/2013 09/02/2011 27/02/2013 23/02/2011 27/02/2013 23/03/2011 23/03/2011 15/06/2011 10/08/2011 14/09/2011 31/07/2013 21/07/2011 21/07/2011 28/07/2011 18/08/2011 12/01/2012 29/03/2012 05/04/2012

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/047627

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008-0100906 A1	01/05/2008	KR 10-2011-0020803 A	03/03/2011
		KR 10-2011-0020804 A	03/03/2011
		KR 10-2011-0026424 A	15/03/2011
		KR 10-2011-0033124 A	30/03/2011
		KR 10-2011-0095292 A	24/08/2011
		MX 2011004242 A	20/07/2011
		US 2011-0123636 A1	26/05/2011
		US 2011-0129921 A1	02/06/2011
		US 2011-0142951 A1	16/06/2011
		US 2011-0143434 A1	16/06/2011
		US 2011-0143435 A1	16/06/2011
		US 2011-0281354 A1	17/11/2011
		US 2011-0281934 A1	17/11/2011
		US 2012-0021514 A1	26/01/2012
		US 8822213 B2	02/09/2014
		WO 2009-140421 A2	19/11/2009
		WO 2009-140421 A3	25/02/2010
		WO 2009-140423 A2	19/11/2009
		WO 2009-140423 A3	25/02/2010
		WO 2009-140427 A2	19/11/2009
		WO 2009-140427 A3	04/03/2010
		WO 2009-140429 A2	19/11/2009
		WO 2009-140429 A3	25/02/2010
		WO 2009-140432 A2	19/11/2009
		WO 2009-140432 A3	04/03/2010
		WO 2010-021770 A1	25/02/2010
		WO 2010-053596 A1	14/05/2010
		WO 2010-053597 A2	14/05/2010
		WO 2010-053597 A3	03/02/2011
		WO 2010-054266 A2	14/05/2010
		WO 2010-054266 A3	29/07/2010
		CA 2607508 A1	30/04/2008
		JP 2008-112166 A	15/05/2008
		US 7545557 B2	09/06/2009