



- (51) **International Patent Classification:**
G02B 5/02 (2006.01) *B01J 13/02* (2006.01)
- (21) **International Application Number:**
PCT/EP2013/069163
- (22) **International Filing Date:**
16 September 2013 (16.09.2013)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (71) **Applicants:** **LIGHT IN LIGHT S.R.L.** [IT/IT]; Via G. Ferrari, 14, I-22100 Como (IT). **UNIVERSITA' DEGLI STUDI DELL'INSUBRIA** [IT/IT]; Via Ravasi, 2, I-21100 Varese (IT).
- (72) **Inventors:** **MENG, Xia**; Greifenseestrasse, 38, CH-8050 Zurich (CH). **XIE, Delong**; c/o Hua WU, Alpenstrasse, 5, CH-8600 Dübendorf (CH). **JIN, Lu**; c/o Hua WU, Alpenstrasse, 5, CH-8600 Dübendorf (CH). **DI TRAPANI, Paolo**; Via Sarfatti, 2, I-22020 Cavallasca (CO) (IT). **WU, Hua**; Alpenstrasse, 5, CH-8600 Dübendorf (CH). **MORBIDELLI, Massimo**; Wehntalerstrasse, 291, CH-8046 Zurich (CH).
- (74) **Agent:** **GISLON, Gabriele**; MARIETTI, GISLON e TRUPIANO S.r.l., Via Larga, 16, I-20122 Milan (IT).
- (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, 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).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

(54) **Title:** COMPOSITE SYSTEM COMPRISING A POLYMER MATRIX AND CORE-SHELL NANOPARTICLES, PROCESS FOR PREPARING IT AND USE THEREOF

(57) **Abstract:** A polymer matrix/nanoparticle composite (PMNC) comprises core-shell nanoparticles, where the core is made of a material that is different from the polymer matrix and at least part of the shell is made of the same monomer or polymer that is used for said polymer matrix, or is made of a monomer or polymer compatible with said matrix. The core of the nanoparticles has a refractive index that is different from the refractive index of the polymer used for the matrix, at least the matrix is made of transparent materials that do not absorb light.



COMPOSITE SYSTEM COMPRISING A POLYMER MATRIX AND CORE-SHELL NANOPARTICLES, PROCESS FOR PREPARING IT AND USE THEREOF

Background of the invention

5 The present invention relates to a composite system comprising a polymer matrix and nanoparticles, to a process for preparing said system and to uses of said system. In particular, the composite system of the present invention comprises a polymer matrix that includes a uniform and random dispersion of polymer or/and inorganic nanoparticles, the nanoparticles are of the core-shell type and have a polymer or/and inorganic core and at least one shell that preferably is a polymer.

Description of the prior art

Nanoparticles or colloidal particles (for simplicity, all of them are referred to here as nanoparticles) can be used as fillers, generally functional fillers, in polymer matrices to produce polymer matrix/nanoparticle composites (PMNCs) with particular properties.

Examples of application of PMNCs are e.g.:

- WO 2009/156348 and WO 2009/156347 that disclose a light diffuser obtained from a transparent polymer matrix that includes a dispersion of inorganic nanoparticles; very stringent requirements for the polymer matrix and the dispersed nanoparticles are set.

- US 7,033,524, that relates to composites obtained from annealed core-shell nanoparticles that optionally are void to incorporate further materials; in particular polypyrrole particles are provided with a shell and annealed to provide a conductive film.

The PMNCs have potential applications in various fields such as in optics, optoelectronics, magneto-optics, mechanical enhancement, etc. For most of these applications, the major and critical requirement is that the nanoparticles have to be uniformly and randomly distributed within the polymer matrix. This has been shown in literature to be extremely difficult to perform, not only in large commercial scale productions but also in lab-scale experiments,

because nanoparticles always tend to aggregate during their integration into polymer matrices.

Summary of the invention

It is an aim of the present invention to solve the above problems and to
5 provide a method for preparing a nanocomposite system in which a polymer matrix has a uniform distribution of nanoparticles.

With the wording "*uniform distribution*" it is meant that nanoparticles are homogeneously distributed within a polymer matrix, i.e. with an average density which is virtually constant across the system, wherein said average
10 density is measured over volumes larger than 0.1 mm^3 , namely over volumes of 1 mm^3 .

It is a further aim of the invention to have a random distribution of the nanoparticles; with the wording "*random distribution*" it is meant that there is no aggregation of nanoparticles, or minimal aggregation of nanoparticles,
15 wherein by aggregation it is meant the formation of clusters of packed nanoparticles which can be much smaller than the 0.1 mm^3 of above, as for example the case of clusters of hundreds, or tens, or even few nanoparticles only.

Aggregation is an important problem, in particular in optical applications of
20 nanoparticles in PMNCs. In fact, independently from the capability of the observer of visually resolving the size of the cluster, the optical interference effect arising due to the contact of several nanoparticles dramatically modifies the scattering properties of the final composite material, the cluster behaving as a new particle whose size is substantially larger than the primary
25 nanoparticle size. Notably said modifications might be relevant even in the presence of very few clusters since the efficacy of the scattering increases dramatically with the increase of the said cluster size (for example it increases with the 6th power of the size in the Rayleigh regime).

As a consequence one of the aims of the present invention is to avoid the
30 formation of clusters wherein several nanoparticles are in contact one another. More precisely the scope is to guarantee the existence of a

minimum distance between the surfaces of any two neighbouring nanoparticles, this distance being at least 0.2, preferably 0.5, most preferably 0.7 times the nanoparticle size. In the case of nanoparticles having core and shell structure, the size of the nanoparticle is measured as the size, i.e. the dimension, of the core. According to the present invention, in the claimed system the nanoparticles are spaced by a distance that is at least 10 nm, preferably 30nm, more preferably 50nm: this result could not be achieved by means of the prior art methods and systems.

A further aim of the invention is also to guarantee that, in the event of the formation of a region in the composite system wherein the nanoparticles are positioned as close as possible one another, the distance between neighbouring nanoparticles is not only larger than a minimum value, preferably the cited 10 nm, but varies randomly within a distribution above said minimum, for example between 0.2 and 0.7 times the nanoparticle size. In fact said randomness in the nanoparticle distance might quench the coherence among scattering contributions from different nanoparticles and thus further contribute in hindering the appearance of optical interference effects. In other terms, one of the aims of the invention is to guarantee both a minimum distance between the nanoparticles surface and, the fact that in the presence of a cluster the actual distance between neighbouring nanoparticles follows a random distribution above said minimum value.

With the wording "*uniform and random distribution*" it is meant a combination of the above definitions, whereby nanoparticles are distributed within a polymer matrix in a statistically disordered manner, without agglomeration among them and without any correlation in their respective position.

It is a further aim of the invention to provide a polymer matrix/nanoparticle composite material that is suitable to be used for the production of a light diffuser that can chromatically separate white visible light into at least two chromatic components: one in which the blue component is dominant and one in which the blue component is low. The diffuser of the present invention should be able to perform the same function of the diffuser disclosed in the

above mentioned application WO 2009/156348.

Description of preferred exemplary embodiments

These aims are reached by the present invention, that provides a composite system according to claim 1.

5 The system comprises a polymer matrix that includes nanoparticles; the polymer material used for preparing the matrix is a material that *per se* is transparent and does not absorb light, i.e. the polymer matrix without nanoparticles is transparent and does not absorb light. The nanoparticles are core-shell nanoparticles, the core of the nanoparticles is made of a material
10 that is different from the polymer matrix and has a refractive index that is different from the refractive index of the matrix to provide a scattering of at least a portion of the light transmitted through said system or a product containing said system. Preferably, the core is made of one or more materials that do not absorb light. However, in certain embodiments the
15 possibility of using cores made of materials which absorb light is admitted. In a preferred embodiment, the core material is selected from a polymer, optionally cross-linked, an inorganic material, preferably metal oxides such as TiO₂, SiO₂, ZnO, ZrO₂, Fe₂O₃, Al₂O₃, Sb₂SnO₅, Bi₂O₃, CeO₂, or a combination of thereof.

20 At least part of the shell of the nanoparticles is obtained from the same material, e.g. a monomer or a polymer, as that used for preparing said polymer matrix or obtained from a monomer or polymer compatible with said matrix. The polymer of the shell might be cross linked.

The polymer matrix/nanoparticle composite system above disclosed
25 preferably provides a Rayleigh scattering or a Rayleigh-like scattering of at least a portion of the transmitted light.

In the present application a “*composite system*” is used to define (and protect) both the final PMNC product and the separate starting materials, the polymer for the matrix and the nanoparticles to be dispersed therein.

30 With the wording “*compatible*” it is meant a monomer or a polymer that is completely dispersible or soluble in the matrix before the matrix is

polymerized. Preferably, the shell or at least part of it, is made of a polymer of the same type of the matrix, e.g. PMMA (poly-methylmethacrylate) for both the shell and the matrix; this will enable an excellent dissolution of the shell and dispersion of the nanoparticles in the matrix before polymerizing and optionally cross-linking the matrix.

5 The polymer material used for preparing the matrix is not absorbing and transparent, i.e. the final matrix, without nanoparticles, is made of a material in which the transmission of light is essentially regular and which has a high transmittance in the visible region of the spectrum. The same preferably
10 applies to the material used for the shell, too.

The matrix can have any shape and can be made of any material that can be used for the purpose and that has the above mentioned properties of being transparent and not light absorbing. Exemplary embodiments of a matrix are a panel, e.g. in PMMA or other polymer, a film and a paint, namely the layer
15 that remains on the substrate after the paint has been applied and the solvent has evaporated.

The dimensions of the nanoparticles are small enough to provide a Rayleigh scattering of the type discussed and disclosed e.g. in WO 2009/156348; exemplary average dimensions of the core of the nanoparticles are in the
20 range of 10 to 240 nanometers.

The composite system is said to be a Rayleigh-like diffuser if said system or at least a portion of it produces a haze, as defined in the ASTM Designation E284-09a, which is at least 1.5 times larger, preferentially 2 times, more preferentially 3 times, for an impinging light in the spectral interval 400-450
25 nm than in the interval 600-650 nm, said property being verified for at least one direction of the impinging light beam with respect to the composite system, and wherein by a portion of composite system it is meant, for example, a thin slice if the system is shaped as a bulk solid material or a thin layer if the system is for example a liquid coating or paint.

30 In fact in the case of thick samples, for example a large tin of paint, multiple scattering can hinder the property of preferentially scattering the short

wavelength component of the impinging light with respect to the longer one. Notably the Rayleigh like scattering property appears when a sufficiently thin layer of material is used, where multiple scattering does not occur.

In the present description, unless differently and specifically defined, the
5 meaning of terms and words is to be referred to ASTM E284 – 09a and to the following standards (as long as they are not in contrast with ASTM E2884-09a): ASTM D1746 – 09; ASTM D 1003 – 07; ISO 13468-2:1999(E);

The core of the nanoparticle can be a linear polymer, or a cross-linked polymer or an inorganic material. In an exemplary embodiment the core is
10 made of a cross-linked polymer; in any case, as mentioned, the core material has a refractive index that is different from the refractive index of the polymer of the matrix, said matrix being made of transparent materials that do not absorb light

The nanoparticle of the invention preferably has at least one shell
15 substantially surrounding the core and made of a material (usually a polymer) that is suitable to act as a "sacrificial shell" and to provide a dispersion of the nanoparticle in the material of the matrix. To this purpose, the shell might be a linear (i.e. not cross-linked) polymer.

In a preferred embodiment, the nanoparticle has a first shell that is cross-
20 linked and at least a second shell, externally to the first shell, that is not cross-linked. The second shell is usually obtained in a second step of production of the nanoparticle. At least said second shell is obtained from the same monomer or polymer that is used for preparing said polymer matrix, or from a monomer or polymer compatible with polymer that is used for
25 preparing the polymer matrix , so as to enhance random and uniform dispersion of the nanoparticles in the the matrix before matrix polymerization and/or crosslinking.

In an exemplary embodiment of the polymer matrix/nanoparticle composite (PMNC) according to the present invention, the core is made of cross-linked
30 polystyrene, the first, cross-linked, shell is made of polymethyl methacrylate (PMMA) and the second shell, as well as the matrix, are made of polymethyl

methacrylate (PMMA).

The dimensions of the shell, either with a single or multiple layers, are dependent on the minimum distance required between the external surfaces of two adjacent cores in the final composite material. For example, if the
5 required minimum surface-to-surface distance for the core is l , the first shell thickness is $l/2$. As a matter of fact, embodiments are possible where the shell is thinner than what required by the minimum distance between nanoparticles. But nevertheless said shell works to statistically keep nanoparticles apart and prevent aggregation, e.g. for the case of fairly dilute
10 PMNCs.

Suitable materials for the core nanoparticles are polycarbonate, polyester resins, polystyrene, poly(styrene-acrylonitrile), polytetrafluoroethylene, modified polytetrafluoroethylene resins, polyvinylchloride, polyvinylidene fluoride and inorganic materials. Preferred inorganic materials
15 are selected from metal oxides such as TiO_2 , SiO_2 , ZnO , ZrO_2 , Fe_2O_3 , Al_2O_3 , Sb_2SnO_5 , Bi_2O_3 , CeO_2 , or a combination of thereof. A preferred metal oxide is TiO_2 .

Suitable materials for the shell and matrix are resins having excellent optical transparency selected from thermoplastic, thermosetting and photocurable
20 resins. Suitable resins are in particular acrylic resins (e.g. PMMA), epoxy resins, polyester resins such as polyethylene or polybutylene terephthalates and polycaprolactone; polystyrene resins (e.g. Polystyrene); PTFE and similar fluorinated resins and fluorene resins; polyamide resins (e.g. nylon); polyimide resin; polycarbonate; polysulfone; polyphenylene ethers;
25 polyvinylalcohol resins; vinyl acetate resins; polyether sulfone; amorphous polyolefins; polyarilate; liquid crystal polymers.

In a certain embodiment, the composite system is made as a rigid and self-sustaining panel, *i.e.* a panel which substantially does not bend when suspended horizontally from any two sides. For example, a said composite
30 system might be shaped as a parallelepiped featuring a thickness in the range 0.5 - 5% of its length, wherein thickness and length are here defined as the

smallest and largest side of the panel, respectively. A typical length of said rigid panel is in the range 0.5 - 3 m. A preferred molecular weight for the linear polymer of the matrix is in the range of 450.000 to 2.000.000 g/mol.

In a further embodiment, the composite system is made as a foil, here
5 defined as a rigid but not self-sustaining panel, *i.e.*, a panel which, in analogy with the rigid panel, is not flexible (*i.e.* it breaks when it is bended along short-curvature angles, *e.g.* when it is bended by 180°) but which does not keep its shape when suspended horizontally. For examples, foil composite systems might have thickness smaller than 0.005 times the length. In
10 analogy with the rigid panel case, foils might feature a matrix made of a polymer of high molecular weight.

According to still another embodiment of the invention, the composite system is made as flexible film, here defined as non-rigid sheet, *i.e.* a sheet which does not break when it is bended along short-curvature angles, *e.g.* when it
15 is bended by 180°. For example, a flexible-film composite-system might have thickness in the range from 10 micron to 1mm, preferentially from 50 micron to 0.5 mm. In addition, it might comprise a plastifier and/or a polymeric shock absorber and/or a co-polymer made from a plurality of different monomers tailored in order to achieve the desired flexibility.

20 In a preferred embodiment, the composite system is configured as a sky-sun diffuser *i.e.* a diffuser capable of separating an impinging white light into a bluish diffused and a yellowish transmitted component, as the sky does with the white impinging sunlight. More generally, said composite system might contain a number of nanoparticles per unit area which suffices to guarantee
25 that at least a few % (*e.g.* 5%) of an impinging white light is scattered by the system in Rayleigh-like regime. For example, the composite system might be shaped as a rigid panel, or a foil or a flexible film and, independently from the thickness, it might feature a nanoparticle areal density, namely the number N of nanoparticles per square meter, *i.e.* the number of nanoparticles within a
30 volume element delimited by a portion of the panel, foil or film surface having an area of 1 m², wherein N satisfies the condition $N \geq N_{min}$, *e.g.*

$2N_{min} \leq N \leq 13N_{min}$, preferably N is in the range $3N_{min}$ to $10N_{min}$, most preferably $N \approx 6N_{min}$ and wherein:

$$N_{min} = \nu \frac{10^{-29}}{D^6} \cdot \left| \frac{m^2 + 2}{m^2 - 1} \right|^2$$

wherein ν is a dimensional constant equal to 1 meter⁶, N_{min} is expressed as a number/meter², the effective diameter D , which is given by the nanoparticle diameter times the matrix refractive index, is expressed in meters and wherein m is equal to the ratio of the refractive index of the nanoparticle core to the refractive index of the matrix material.

In another, different, embodiment, the composite system is made as a paint, i.e. as a dispersion of resins and additives in a solvent, e.g. in an organic or aqueous solvent. In the typical case, the paint composite system features a nanoparticle concentration (i.e. a number of nanoparticles per unit volume) such to guarantee that the condition $N \geq N_{min}$, e.g. $2N_{min} \leq N \leq 13N_{min}$, preferably $3N_{min} \leq N \leq 10N_{min}$, most preferentially $N \approx 6N_{min}$, is fulfilled for a paint layer that after drying has a thickness in the range 1 - 50 microns. Typical embedding matrix for said systems are polymers such as PET, PVC, EVA and similar, for the case of films, and polymers such as acrylics, vinylics, polyurethane and similar for the case of paints.

In some embodiments, and particularly when the system is shaped as a panel, a foil or a film, showing a surface of size much larger than the system thickness, the request for the system of exhibiting a visually uniform Rayleigh like scattering across the surface translates in having an average areal density N , measured over areas larger than of 0.25 mm², which is substantially constant across the surface. Notably this feature does not necessarily require the nanoparticles volume density to be constant across the sample since any fluctuation or variation of the nanoparticles volume density in the direction perpendicular to the surface is not perceived, since the observer only perceives the integrated effect.

In a further embodiment, the composite system is made as a complex-shape

elongated object, *i.e.* an object whose shape differs from the parallelepiped and is such that the smallest circumscribed ellipsoid has a flattening $f > 0.5$, where $f = (a-b)/a$, wherein a is the semi-major axis and b is the semi-minor axis; said elongation is suitable in order to allow different portions of the same object to scatter light with different colours, as the sky does during sunset or sunrise, etc.

In a different embodiment the sandwiched sky-sun diffuser might comprise two glass external layers and an central layer shaped as a film comprising a dispersion of nanoparticles in an polymer matrix in order to obtain a new glass panel or window which behaves both as a safety glass for what concerns the mechanical properties and as a Rayleigh like diffuser for what concerns the optical properties. In addition, said sandwiched sky-sun diffuser might also comprise two layers of adhesive materials which might optically and/or mechanically match the composite system internal layer with the external layers, *i.e.* prevent multiple reflections and provide the elasticity required to compensate for different thermal expansion of internal and external layers. Suitable adhesive materials are EVA (ethylene vinyl acetate) and PVB (Polyvinyl butyral).

A different object of the present invention is a painted sky-sun diffuser, *i.e.* a structure comprising a transparent panel, *e.g.* glass, polycarbonate, or similar material, coated by the composite-system paint as above discussed.

Both the sandwiched and the painted sky-sun diffuser provide an important advantage with respect, *e.g.*, to the bare composite-system panel or foil, given by the superior fire retardant properties, which are substantially defined by the characteristics of the external substrate instead of the composite system itself.

A still further object of the invention is a process for preparing polymer matrix/nanoparticle composite (PMNC), according to claim 11.

Preferably the core of the nanoparticles is made of a polymer (*e.g.* polymer B) that can also be cross-linked; a preferred preparation process for the core nanoparticle is through emulsion polymerization in an aqueous solvent.

In general, initially the type of nanoparticles and the type of polymer matrix are selected; then the first step in the process is to prepare the core-shell nanoparticles, where the core and shell are the chosen nanoparticle and polymer matrix, respectively. Each core-shell nanoparticle contains only one
5 core, and the thickness of the shell depends on the minimum requirement of the interparticle distance in the PMNC. As mentioned for example, if the required minimum surface-to-surface distance for the core is l , the shell thickness is $l/2$ (i.e. $0.5 l$).

Any of the known different techniques to make the shell for the core
10 nanoparticle, such as physical coating or adsorption can be used. A preferred preparation process for the core nanoparticle is through emulsion polymerization in an aqueous solvent. Emulsion polymerization is preferred also because it is possible to use the same reactor first to prepare the core nanoparticles and then to provide them with a shell (in one or two layers).

15 In general, the starting nanoparticles could be a cross linked polymer, e.g. polystyrene or other polymers, previously obtained in a known way by emulsion polymerization with the required dimensions.

To prepare a shell with two layers, the feeding time for the first shell layer is in general from 2 to 10 hours; the amount of cross linker for the first shell is
20 1% to 10% by weight (w/w). The feeding time for the second shell is from 2 to 10 hours, the second shell preferably being without cross linker to dissolve in the matrix material, monomer and/or polymer.

Any conventional initiators for free-radical emulsion polymerization can be applied here. The amount of the initiator for the first shell is 0.1% to 0.5% of
25 the total monomer, and part of the initiator is injected at the beginning and the remaining part is fed continuously together with the monomer. The amount of the initiator for the second shell is 0.1% to 0.5% of the total monomer, and part of the initiator is injected at the beginning and the remaining part is fed continuously together with the monomer.

30 The core-shell nanoparticles thus obtained are separated from the aqueous medium in which they have been prepared, e.g. by drying.

Any suitable process for treatment of the nanoparticles obtained after the emulsion is finished and the core-shell nanoparticles are ready may be used to prepare the polymer matrix/nanoparticles system. If a film is required, direct drying and melting is used, otherwise the nanoparticles are coagulated and dried. The dry nanoparticles can be dispersed in the material e.g. a monomer and/or a polymer, that will form the bulk of the final matrix, and subsequently polymerized in a known way. Alternatively, the obtained nanoparticles can be dispersed in a matrix containing polymers, an example of this embodiment of the invention is a paint or an ink that comprises a plurality of nanoparticles. In a composite system that is represented by a paint or ink comprising the invention nanoparticles, the matrix is formed by the resins, additives and solvents normally present in such products, to which the invention nanoparticles have been added. The resulting product is a "preliminary system", i.e. the paint or ink usually does not provide the required scattering when it is in a tin or similar container, but the scattering effect will be provided as soon as a layer of paint or ink has been applied to a transparent substrate.

In general the concentration of nanoparticles in the final product is in the range of 0.001% to 20% by weight, according to the requirement of the final composite product and according to the nature of the nanoparticles; in general, the required amount of nanoparticles having a core at least in part inorganic is much less than the amount required for polymer-core nanoparticles.

In a preferred embodiment, the core of the invention's core-shell nanoparticle comprises either a single inorganic nanoparticle or a cluster of inorganic nanoparticles or a cluster of inorganic nanoparticles and a polymer, depending on the size of said inorganic nanoparticles. In the case of the core composed of a cluster of inorganic nanoparticles and a polymer, preferably, the polymer is cross-linked to form an "integral" core together with the inorganic nanoparticles, and the overall dimensions of the core are within the above mentioned ones.

In a preferred embodiment the inorganic nanoparticles are metal oxides as above mentioned, e.g. and preferably TiO_2 . The TiO_2 component, which has a high refractive index, contributes for efficient light scattering, the polymer portion of the core coats the inorganic particles and provides a first shell of cross-linked polymer around the TiO_2 particles. In this embodiment, the polymer used for the core extends outside the core to provide a first shell that is cross-linked.

Preferably, an outer shell of a linear polymer helps to increase the compatibility and re-dispersibility of the composites with an organic solvent.

Core-shell nanoparticles as above discussed with reference to the process and to the PMNC system, are therefore an object of the present invention; in particular core-shell nanoparticles having a cross-linked core, a first, internal, shell that is cross-linked and a second external shell that is a linear polymer, i.e. a not cross linked polymer, external to the cross-linked shell layer.

A preferred embodiment of the invention is the polymer matrix/nanoparticle composite (PMNC) system in which the material of the core of the nanoparticles has a refractive index that is different from the refractive index of the material of the matrix and wherein the dimensions of the core of the nanoparticles are small enough to provide a Rayleigh like scattering e.g. a scattering like the one described in patent application WO 2009/156348 i.e. a scattering process which preferentially diffuses the short-wavelength component of the impinging light with respect to the long one. Exemplary average dimensions of the core of the nanoparticles are in the range of 10 to 240 nanometers, preferentially 30 to 150 nanometers, more preferentially 50 to 100 nanometers.

These PMNCs were surprisingly found to provide excellent light diffusers, capable of chromatic separation as per above mentioned applications.

The present invention provides several advantages over the prior art.

By providing a shell of the selected polymer it is possible to greatly facilitate the uniform and random dispersion of the core nanoparticles in the matrix.

By providing a compatible cross linked shell it is possible to maintain the

cores separated by the correct distance also in the final matrix; this is ensured especially by having a first layer of cross-linked polymer with the required thickness, e.g. $l/2$ if the final distance between two adjacent cores must be l . The additional second layer of non cross-linked polymer, identical
5 to the polymer used for the matrix, will act as a carrier for the core and cross-linked first shell; in a case where the matrix is initially liquid, the “sacrificial shell” dissolves in the monomer of the matrix to thus “transport” the nanoparticles into it and ensure an excellent distribution of the nanoparticles in the final PMNC product.

- 10 The invention will now be further disclosed with reference to the following examples and explanations.

Example 1 – Preparation of PTFE-core nanoparticles.

- Polymerization was carried out in a glass reactor equipped with a reflux condenser, magnetic stirrer (200-300 rpm), nitrogen inlet, and a water jacket
15 for temperature control. The formulation is given in Table 1. In particular, the initial reactor charge was purged with nitrogen to remove dissolved oxygen while heated, followed by addition of a part of the initiator solution. The monomer mixture and the remaining initiator solution were then fed to the reactor over a prescribed period of time (e.g., 3.5 hours) by a pump,
20 respectively.

- The reactor temperature was kept at 80 ± 2 °C during the polymerization. At the end of the monomer feeding, the reaction system was maintained at 85 °C for 1 hour to complete the monomer conversion. Then, the system was cooled down to 40 °C, and its pH was adjusted to 7. The final latex was
25 filtered with a filter of 25 micron openings to remove any possible coagulum formed during the polymerization.

Table 1 Typical recipe for emulsion polymerization of PTFE-MMA/BA particles for sky-sun diffusers.

	Chemicals	Weight (g)	Note
Monomer feed	MMA	50-100	The MMA/BA ratio depends on Tg
	BA	0-50	
Initial reactor charge	H ₂ O	125	
	NaHCO ₃	0.3	
	Surfactant (K30)	0.5	
	PTFE latex	30 ($\phi_{wt}=33\%$)	
Initiator solution	KPS	0.35	
	H ₂ O	24	
Total		275 ($\phi_{wt}=40\%$)	

Example 2 – Preparation of polystyrene-core nanoparticles.

Cross linked polystyrene latex with nanoparticle size of 65 nm (diameter measured by dynamic light scattering) was used for seeded emulsion polymerization.

1650 g polystyrene latex, 800 g water, 6 g SDS (surfactant, sodium dodecyl sulfate) and 1.6 g KPS, (potassium persulfate, initiator) were charged in the reactor under mechanical stirring. Then 285 g of MMA mixed with 15 g of cross linker (5% w/w of cross linker DTTA, di-trimethylolpropane-tetraacrylate) was slowly added to the reactor within 3 hours at 80°C. The system was kept at 80°C for another 2.5 hours to finish the first shell.

Then, 300 g MMA and 1.4 g KPS were added and fed at 80°C during two hours; the mixture was heated for another 1 hour to finish the reaction and was then cooled to room temperature. The average size of the nanoparticles was found to be 90 nm, with narrow distribution, and the solid content was about 28% by weight. After polymerization, the latex was mixed with an ion exchange resin and stirred for 2 hours to remove the surfactant.

Example 3 – Preparation of inorganic cores for core-shell nanoparticles.

The following steps were carried out.

1. Synthesizing TiO₂ particles in organic solvent under relatively low temperature.

In a typical process, precursor TiCl₄ is dropwise added into ethanol. After the heat production is released completely, the mixture is poured into pre-heated benzyl alcohol. The system is maintained by stirring and heating for more

than 8.5 hours. When the hydrolysis process finishes, TiO_2 nanocrystallized particles are thoroughly precipitated by adding ether, followed by centrifugation and re-dispersion in ethanol.

2. Hydrophobic modification of TiO_2 .

- 5 TiO_2 primary particles form nanoclusters in ethanol. To make them compatible with organic solvents, silane coupling agent is added and chemically attaches to the surface of the clusters. Excess silane is removed by centrifuging. The treated nanoclusters are then used to prepare core-shell nanoparticles.

10 3. Preparation of core-double-shell structure

The modified TiO_2 nanoclusters are well dispersed in a mixture of monomer (e.g., methyl methacrylate or styrene) and cross linker (e.g., di-trimethylolpropane tetraacrylate or divinylbenzene). The dispersion is dropwise added, under stirring and N_2 , to an aqueous solution of the steric
15 surfactant, forming a homogeneous mixture with the assistance of sonication or mechanical separation. After nitrogen purging and mechanical stirring, an aqueous solution of the initiator (potassium persulfate) is introduced into the system and the first emulsion polymerization is carried out, while the N_2 bubbling and stirring are still maintained.

- 20 After the first layer has been polymerized and cross-linked, the second linear shell is provided on the external surface of the nanoparticles. For this second linear shell, a monomer is fed continuously at a low feeding rate, and corresponding amount of initiator is added, without using a cross-linking agent. After the second polymerization process is completed core-shell
25 nanoparticles of the invention are obtained from aqueous phase by freezing.

There are two main processes for post-treating the nanoparticles obtained according to the invention: direct drying and melting for preparing a film, and coagulation and drying for preparing a PMNC system by redispersion in a monomer.

30 **Technique A: Direct drying and melting**

If the PMNCs are required in the form of films, the typical techniques for

making films from polymer latexes can be used. In particular, the obtained core-shell nanoparticles latex can be dried directly to eliminate water, and then the temperature is increased to above the T_g (glass transition temperature) of the polymer constituting the shell, leading to the formation of the PMNCs in the form of films.

Technique B: Powder moulding

This technique includes two steps:

Step 1: Coagulation of the core-shell particles

Coagulation or aggregation methods are used to separate the core-shell nanoparticles from the disperse medium. A coagulation process leads the core-shell nanoparticles to form clusters or aggregates with sizes from at least a few tens of microns to hundreds of microns or even to millimetres, thus easy to be separated from the disperse medium by any standard techniques such as filtration, floatation, sedimentation, centrifugation, etc.

Due to the advantage of the core-shell structure, within the dried clusters or aggregates or powders, the minimum distance among the nanoparticles is maintained by the designed thickness of the shell. To ensure the uniform and random distribution of the nanoparticles within the clusters, coagulation under shear is preferred, since it forms compact clusters with randomly distributed particles. In particular, three types of coagulation are preferred:

a) Coagulation of latexes in mechanically stirred tanks with addition of a proper amount of electrolytes. The electrolytes can be chosen amongst any salts or base or acid. The use of the electrolytes is required to partially or completely eliminate the electrostatic repulsive interactions among the particles so as to ease the coagulation.

b) Coagulation of latexes in intense shear flow without making use of electrolytes. In this case, the energy generated by the intense shear flow should be high enough, capable of forcing the particles to overcome the interaction barrier, leading to aggregation. Typical processes that are able to generate so high energies are, for example, forcing the latexes to pass through a microchannel, as described in the open literature (Wu H, Zaccone

A, Tsoutsoura A, Lattuada M, Morbidelli M. High shear-induced gelation of charge-stabilized colloids in a microchannel without adding electrolytes. Langmuir. 2009; 25:4715-23).

Further, if there are specific requirements for the nanoparticle concentrations within the PMNCs, which cannot be satisfied only by the produced thickness of the shell, then, particles of the same materials as the shell (i.e., the same as the polymer matrix), but without the nanoparticle core, are produced using the same emulsion polymerization technique. The obtained latex where the particles do not contain the nanoparticle core will be mixed with the latex where the particles contain the nanoparticle core, in proper ratios based on the requirements in the nanoparticle concentration. The obtained latex mixtures are then coagulated using the techniques described above, so as to produce the dried powders.

c) Coagulation by freezing.

The latex of example 2 was stored in a freezer at -18°C. After defreezing the latex, the mixture was centrifuged. The solid wet powder was recovered and dried.

Step 2: Preparation of the composite.

The nanoparticle powder thus obtained is then used for preparing the required matrix composite. After having obtained the dried powders where the nanoparticles are distributed, with the required minimum distance among the nanoparticles core being ensured by the presence of the shell, various standard techniques can be used to easily produce the desired, different forms of the PMNCs.

A preferred technique is bulk polymerization, in which the nanoparticles powder is weighed and dissolved in the monomer of the matrix, before crosslinking it. Re-dispersion is carried out so as to obtain a uniform dispersion of the nanoparticles, that is ensured thanks to the presence of one or, preferably, two layers of the shell; proper agitation and/or use of ultrasonic energy may be advantageous.

For example, the powder obtained after freezing and drying the nanoparticles

of example 2 was weighed and dissolved in MMA. The transparent dispersion was sonicated for 2 hours to get the nanoparticles well dispersed in MMA. A standard bulk polymerization technique was used to convert the monomers into the polymer matrix, in which the nanoparticles are
5 homogeneously distributed, leading to the required PMNCs.

Other techniques may be used, such as injection moulding, reaction injection moulding, compression moulding, transfer moulding, extrusion moulding, rotomoulding, blow moulding, calendering, knife coating, etc. This possibility
10 of having a starting material that can undergo many different treatments is one of the key advantages of the present invention.

In another embodiment, nanoparticles having a core with the required refractive index, with or without a polymer, and a non cross-linked shell, are dispersed in a matrix and sonicated until they reach the required uniform dispersion. The matrix is then polymerized and optionally cross-linked.

CLAIMS

1. A composite system (PMNC), comprising a polymer matrix that contains a plurality of nanoparticles, wherein said polymer material used for preparing a matrix is a material that *per se* is transparent and does not
5 absorb light, characterized in that said nanoparticles are core-shell nanoparticles, wherein said core of the nanoparticles is made of a material that is different from the polymer matrix and has a refractive index that is different from the refractive index of the polymer of the matrix to provide a scattering of at least a portion of the light transmitted through
10 said system or a product containing said system, and in that at least part of the shell of the said nanoparticles is obtained from the same monomer or polymer that is used for said polymer matrix, or is obtained from a monomer or polymer compatible with said matrix.
2. A polymer matrix/nanoparticle composite system according to claim 1,
15 wherein said scattering of at least a portion of the transmitted light is a Rayleigh and/or a Rayleigh-like scattering.
3. A polymer matrix/nanoparticle composite system according to claim 1 or 2, wherein the material of said core is selected from polymers and inorganic compounds.
- 20 4. A polymer matrix/nanoparticle composite system according to any claim 1 to 3, wherein said core is made of one or more materials that do not absorb light.
5. A polymer matrix/nanoparticle composite system according to any previous claim, wherein said core and/or said shell and/or said matrix is
25 cross-linked.
6. A polymer matrix/nanoparticle composite system according to claim 5, comprising a first shell that is a cross-linked shell and at least a second shell layer, externally to said first shell, at least said second shell being obtained from the same monomer or polymer from which said polymer
30 matrix is obtained, or from a monomer or polymer compatible with it, wherein said second shell is not cross-linked.

7. A polymer matrix/nanoparticle composite system according to any previous claim, wherein said core is made of cross-linked polystyrene, said matrix and said shell layers are made of polymethylmethacrylate (PMMA).
- 5 8. A polymer matrix/nanoparticle composite system according to any claim 1 to 6, wherein said core is made of an inorganic material, preferably selected from metal oxides, most preferably from TiO_2 , SiO_2 , ZnO , ZrO_2 , Fe_2O_3 , Al_2O_3 , Sb_2SnO_5 , Bi_2O_3 , CeO_2 .
9. A polymer matrix/nanoparticle composite system according to any claim 10 to 8, wherein the minimum distance between the cores of two nanoparticles is at least 10 nm.
10. A polymer matrix/nanoparticle composite system according to any claim 1 to 9, wherein the number of nanoparticles within a volume element delimited by a portion of the panel, foil or film surface having an area of 1 m^2 , is N , wherein $N \geq N_{\min}$, preferably $2N_{\min} \leq N \leq 13N_{\min}$, more preferably N is in the range $3N_{\min}$ to $10N_{\min}$, most preferably $N \approx 6N_{\min}$ and wherein:

$$N_{\min} = \nu \frac{10^{-29}}{D^6} \cdot \left| \frac{m^2 + 2}{m^2 - 1} \right|^2$$

where ν is a dimensional constant equal to 1 meter⁶, N_{\min} is expressed as a number/meter², the effective diameter D , which is given by the nanoparticle diameter times the matrix refractive index, is expressed in meters and wherein m is equal to the ratio of the refractive index of the nanoparticle core to the refractive index of the matrix material.

11. A process for preparing a composite system that is a polymer matrix/nanoparticle composite (PMNC) system, wherein a plurality of nanoparticles is dispersed in a polymer matrix, wherein the polymer material used for preparing a matrix is a material that *per se* is transparent and does not absorb light, characterized in comprising the following steps:
- a) preparing a plurality of nanoparticles of a material (B);

5 b) providing said nanoparticles with at least one shell obtained from a monomer or polymer (A) to give a core-shell nanoparticle wherein the material (B) of the core of the nanoparticle is different from the monomer or polymer to be used for the matrix and has a refractive index that is different from the refractive index of the polymer of the matrix;

10 c) dispersing said core-shell nanoparticles into the monomer or polymer from which said matrix will be obtained, said monomer or polymer of the matrix being the same as or being compatible with said monomer or polymer (A) of the shell, so as to obtain a dispersion of the nanoparticles in the matrix before polymerization;

d) polymerizing the matrix, and

e) optionally cross-linking the matrix

15 whereby said polymer matrix/nanoparticle composite system provides a scattering of at least a portion of the light transmitted through said PMNC system or through a product containing said system.

20 12.A process according to claim 11, wherein said polymer matrix/nanoparticle composite system provides a Rayleigh or a Rayleigh-type scattering of at least a portion of the light transmitted through said system or through a product containing said system.

13.A process according to claim 11 or 12, wherein said matrix is a paint comprising polymer resins and at least a solvent, and wherein said scattering is provided by said polymer matrix/nanoparticle composite system after said solvent has evaporated from a layer of paint.

25 14.A process according to any claim 11 to 13, comprising the step of cross-linking said core and/or said shell of the nanoparticles.

30 15.A process according to claim 14, comprising the steps of preparing a nanoparticle having a core comprising a polymer, optionally cross-linking said polymer in said core, preparing a first shell comprising a polymer and cross-linking said polymer of the first shell, providing said core-shell

nanoparticle with an additional shell, said additional shell comprising a polymer that is not cross-linked.

16. A process according to any claim 11 to 15 characterized in comprising the steps of preparing a core of inorganic nanoparticles or a cluster of inorganic nanoparticles.
17. A process according to any claim 11 to 16, comprising the steps of preparing a core of a cluster of inorganic nanoparticles and a monomer, polymerizing said monomer and preferably cross-linking it, to provide a core comprising inorganic nanoparticles and a polymer, preferably a cross-linked polymer.
18. A process according to any claim 11 to 17, wherein said core of the nanoparticles is prepared by emulsion polymerization.
19. A process according to any claim 11 to 18, further comprising the steps of preparing nanoparticles from the monomer or polymer that is used to prepare said shell (A), wherein said nanoparticles do not comprise said core material (B), and mixing said core-free nanoparticles with an amount of nanoparticles having a core, whereby said core-free nanoparticles provide a starting material for said matrix.
20. A process according to any previous claim, comprising the step of sonicating or shearing a dispersion of nanoparticles in a matrix material.
21. Core-shell nanoparticles as obtainable from a process according to any claim 11 to 20.
22. Core-shell nanoparticles as disclosed in any claim 1 to 10.
23. Core-shell nanoparticles according to claim 21 or 22, having a core, a cross linked shell layer and a second shell layer, not cross linked, external to the said cross-linked shell.
24. Core-shell nanoparticles according to any claim 21 to 23, wherein said core consists of at least one inorganic nanoparticle.
25. Core-shell nanoparticles according to any claim 21 to 23, wherein said core comprises inorganic nanoparticles and a polymer, preferably a cross-linked polymer.

26. Core-shell nanoparticles according to any claim 21 to 25, that are dry.
27. A light diffuser comprising a polymer matrix/nanoparticle composite system according to any claim 1 to 10.
28. The use of core-shell nanoparticles for the production of PMNC systems,
5 wherein said nanoparticles have a core, a first shell layer that is a cross-linked polymer, and at least a second shell layer, located externally to said first layer, at least said second shell being made of the same polymer that is used for said polymer matrix, or of a polymer compatible with it, the polymer of said second layer being not cross linked.
- 10 29. The use according to claim 28, wherein the PMNC system is part of a light diffuser.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/069163

A. CLASSIFICATION OF SUBJECT MATTER
INV. G02B5/02 B01J13/02
ADD.

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)
G02B B82Y B01J

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 345 701 A2 (PPG IND OHIO INC [US]) 20 July 2011 (2011-07-20)	1-5,7,9, 11-15, 17,18, 20-22, 25-29
Y	page 8, paragraph 47 - paragraph 50 -----	10,19
X	EP 2 020 428 A1 (BOREALIS TECH OY [FI]) 4 February 2009 (2009-02-04) page 8, paragraph 42 - paragraph 43 page 7, paragraph 39 - paragraph 40 -----	1-4,7-9, 20-22, 24,26,27
X	EP 0 745 622 A1 (ICI PLC [GB]) 4 December 1996 (1996-12-04) page 6, line 5 - line 8 page 5, line 20 - line 50 ----- -/-	1-7,9, 20-23, 26-29



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

20 May 2014

Date of mailing of the international search report

27/05/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Le Masson, Nicolas

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/069163

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/142808 A1 (IZU NORIYA [JP] ET AL) 7 June 2012 (2012-06-07) page 6, paragraph 86 - paragraph 91 -----	1-5, 7-12,16, 20-22, 24,26,27
X	WO 2009/156347 A1 (LIGHT IN LIGHT S R L [IT]; DI TRAPANI PAOLO [IT]; PIGAZZINI MARTA CECI) 30 December 2009 (2009-12-30) cited in the application	1-29
Y	claims 2-5 -----	10
Y	US 2003/136946 A1 (KUMACHEVA EUGENIA [CA]) 24 July 2003 (2003-07-24) cited in the application claim 1 -----	19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/069163

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2345701	A2	20-07-2011	AR 058819 A1 27-02-2008
			AT 553134 T 15-04-2012
			AU 2006309059 A1 10-05-2007
			BR PI0619715 A2 11-10-2011
			CA 2627735 A1 10-05-2007
			CN 101300314 A 05-11-2008
			DK 1951825 T3 23-07-2012
			DK 2345701 T3 18-03-2013
			EP 1951825 A2 06-08-2008
			EP 2345701 A2 20-07-2011
			ES 2383201 T3 19-06-2012
			ES 2399858 T3 03-04-2013
			HK 1123063 A1 08-03-2013
			JP 4759619 B2 31-08-2011
			JP 2009514027 A 02-04-2009
			JP 2011138173 A 14-07-2011
			KR 20080065000 A 10-07-2008
			NZ 567355 A 25-05-2012
			NZ 592648 A 28-09-2012
			PT 1951825 E 30-05-2012
			PT 2345701 E 26-02-2013
			UA 90558 C2 11-05-2010
			US 2007100026 A1 03-05-2007
			US 2010328764 A1 30-12-2010
			US 2012100375 A1 26-04-2012
			WO 2007053409 A2 10-05-2007
EP 2020428	A1	04-02-2009	EP 2020428 A1 04-02-2009
			EP 2176337 A2 21-04-2010
			WO 2009016188 A2 05-02-2009
EP 0745622	A1	04-12-1996	AT 191491 T 15-04-2000
			CA 2220411 A1 28-11-1996
			CN 1185165 A 17-06-1998
			DE 69607613 D1 11-05-2000
			DE 69607613 T2 17-08-2000
			DK 0828772 T3 14-08-2000
			EP 0745622 A1 04-12-1996
			EP 0828772 A1 18-03-1998
			ES 2145453 T3 01-07-2000
			JP 5410868 B2 05-02-2014
			JP H11505871 A 25-05-1999
			JP 2007321158 A 13-12-2007
			JP 2009270115 A 19-11-2009
			MY 134601 A 31-12-2007
			PT 828772 E 31-07-2000
			TW 442502 B 23-06-2001
			US 6172135 B1 09-01-2001
			WO 9637531 A1 28-11-1996
US 2012142808	A1	07-06-2012	CN 102625817 A 01-08-2012
			JP 4682368 B2 11-05-2011
			JP 2011057960 A 24-03-2011
			KR 20120064666 A 19-06-2012
			TW 201107239 A 01-03-2011
			US 2012142808 A1 07-06-2012
			WO 2011018939 A1 17-02-2011

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/069163

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009156347	A1	30-12-2009	EP 2304478 A1 06-04-2011
			EP 2304480 A1 06-04-2011
			US 2011194270 A1 11-08-2011
			US 2011216542 A1 08-09-2011
			WO 2009156347 A1 30-12-2009
			WO 2009156348 A1 30-12-2009

US 2003136946	A1	24-07-2003	NONE
