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(54) **Title**: A COMPOSITION INCLUDING A LUMINESCENT COMPOUND

(57) **Abstract**: The present invention provides a composition comprising a semi-crystalline polymer and a luminescent compound, and a solar concentrator including a collector that comprises such composition.

Description

A composition including a luminescent compound

Cross-reference to related applications

[0001] This application claims priority from European application No. 15171214.8, filed on 9th June 2015, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention pertains to a composition comprising a semi-crystalline polymer and a luminescent compound, and to a solar concentrator including a collector that comprises such composition.

Background Art

[0003] Luminescent solar concentrators operate on the principle of collecting radiation over a large area, converting it by luminescence (commonly using a fluorescent compound) and directing the generated radiation into a smaller area output target.

A luminescent solar concentrator (LSC) typically comprises a luminescent material coupled to or embedded with a material acting as a waveguide to form a radiation collector and at least one photovoltaic cell coupled to said collector.

The collector is typically an optically transparent sheet made of a composition comprising a polymer and a luminescent compound.

A substantial fraction of incident solar radiation is absorbed by the luminescent compound trapped in the collector and directed via internal reflection to at least one output surface of said collector. The luminescent compound is responsible for conversion of at least a part of the incident solar light into a radiation with a longer wavelength which is advantageous for the silicon cell, which has maximum external quantum efficiency around 1100 nm. The photovoltaic cells coupled to the output surfaces of the collector then convert the emitted electromagnetic radiation into electric current.

In the older and more widespread design, LSCs comprise parallel thin, flat layers of alternating luminescent and transparent materials, placed to gather incoming radiation on their (broader) faces and emit concentrated

radiation around their (narrower) edges.

More recently, other configurations were made available, such as doped or coated optical fibers, or contoured stacks of alternating layers.

[0004] Sheets or layers made from polymers such as polycarbonate and poly(methyl methacrylate) are typically used as waveguides, because of their high optical transparency and high refractive index.

[0005] For example, **US 2009/0126778** (SABIC INNOVATIVE PLASTICS IP B.V.) 5/21/2009 discloses a LSC comprising a primary waveguide and a photovoltaic cell, wherein the primary waveguide is made from a composition comprising a polymer, typically a polycarbonate or an acrylic ester polymer such as poly(methylmethacrylate), and a fluorescent colorant selected from the group consisting of a dye, a pigment and a quantum dot.

[0006] However, the need is still unmet for a luminescent solar concentrator advantageously exhibiting enhanced durability and weatherability properties in the long term over conventional luminescent solar concentrators, together with outstanding mechanical and optical properties.

Summary of invention

[0007] The present invention achieves these objectives by providing a composition (C) comprising:

- at least one semi-crystalline polymer (P) having a heat of fusion of at most 35 J/g and comprising recurring units derived from ethylene and at least one of chlorotrifluoroethylene (CTFE), and tetrafluoroethylene (TFE);
- at least one luminescent compound (L),

wherein the composition comprises at most 0.5% in weight, with respect to the total weight of the composition, of a polymer formed of recurring units deriving from acrylate monomers (polyacrylate A).

[0008] These objectives are also met by the present invention via the provision of a collector for a luminescent solar concentrator comprising at least one portion exposed to radiations (portion (F)) comprising the composition (C) as defined above, and of a luminescent solar concentrator comprising said collector.

[0009] The present invention achieves these objectives by providing a process for the manufacture of a collector for a luminescent solar concentrator, said process comprising:

(i) providing the composition (C) as defined above and

(ii) processing into a layer the composition (C) provided in step (i).

Brief description of drawings

[0010] Figure 1: optical efficiency vs concentration of luminescent compound (L) in the composition of the invention

[0011] Figure 2: optical efficiency vs distance from the cell (triangles = comparison composition, squares = composition of the invention)

[0012] Figure 3: degradation of dye upon weatherability tests (measurements at wavelength = 570 nm, circles = comparison composition, squares = composition of the invention)

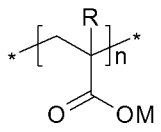
Description of embodiments

[0013] Unless otherwise specified, in the context of the present invention all percentages of a component of a mixture are referred to the weight, or number of moles, of the component with respect to the total weight, or total number of moles, of the mixture.

[0014] Unless otherwise specified, in the context of the present invention the indication that a composition “comprises” one or more component(s) includes the compositions that consist up to 100% of such component(s).

[0015] Unless otherwise specified, in the context of the present invention the indication that a polymer “consists essentially of” one or more recurring unit(s) means that they form at least 95% of the total of the recurring units.

[0016] In the context of the present invention, the term "polyacrylate" indicates a polymer comprising substantially, or consisting of, recurring units derived at least one monomer (H) comprising at least one carboxylic acid ester group of formula -COOM, wherein M is a C_1-C_5 alkyl group. Generally, the polyacrylate (A) is of formula (A-1):



(A-1)

wherein M is a C_1-C_5 alkyl group, R is H or -CH_3 and n is an integer such

that the number average molecular weight of the polyacrylate (A) is of from 1000 to 1000000, typically of from 2000 to 100000, more typically of from 3000 to 60000. A typical example of such polyacrylate (A) is polymethylmethacrylate (PMMA).

[0017] The amount of polyacrylate can be determined via any of the methods known to the person skilled in the art, such as by MALDI MS/MS techniques (e.g. those reported in G. Montaudo et al. *Prog. Polym. Sci.* **2006**, *31*, 277–357, and references cited therein).

[0018] For the purpose of the present invention, the term "luminescent compound [compound (L)]" is intended to denote either a fluorescent compound [compound (L-F)] or a phosphorescent compound [compound (L-P)].

[0019] The terms "luminescent", "fluorescent" and "phosphorescent" are used in the present invention according to their usual meanings. Specifically, the term "luminescent" indicates a compound capable of spontaneous emission of radiation when electronically or vibrationally excited and not in thermal equilibrium with its environment.

The compound (L) is able to re-emit an absorbed electromagnetic radiation when passing from an excited state to a ground state. The wavelength of the re-emitted radiation is usually longer that the wavelength of the absorbed radiation. Preferably, compound (L) is a fluorescent compound, that is a compound that re-emits the radiation essentially only during the irradiation of a substance by an electromagnetic radiation.

[0020] The choice of the compound (L) is not particularly limited.

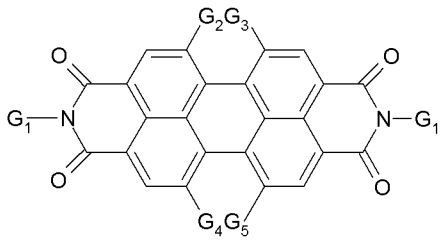
The compound (L) is typically selected from the group consisting of luminescent organic or inorganic compounds. Mixtures of one or more organic compounds (L) and one or more inorganic compounds may be used in the composition (C) of the invention. In alternative, an luminescent organic compound alone or mixtures of luminescent organic compounds may be separately used. Preferably, the composition of the invention comprises at least one luminescent compound (L) that is a fluorescent compound.

Non-limiting examples of inorganic luminescent compounds (L) include

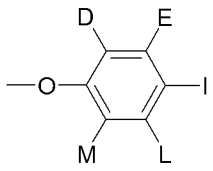
quantum dots or nanoparticles, e.g. CIS ($CuInS_2$), CdSe/CdS or PbSe/PbS quantum dots, BAM (barium magnesium aluminate doped with Europium or other elements), phosphors such as BAM:Ce^{2+}; YAG:Ce^{3+}; $(Sr,Ba)SiO_4:Eu^{2+}$; LuAG:Ce^{3+}.

[0021] Non-limiting examples of organic compounds (L) typically include polycyclic aromatic compounds, preferably those comprising a perylene dimiide core (also indicated as bis-diimide of peri-dinaphthalene, perilene or dibenz[*de,kl*]anthracene), linear conjugate systems such as polyparaphenylene/arylene, planar benzofused systems such as rubrene, coumarin dyes and metallorganic compounds containing Ir, B, Al or Pt (for example BODIPY, i.e. boron-dipyrromethene, Alq3, i.e. tris(8-hydroxyquinolinato)aluminium).

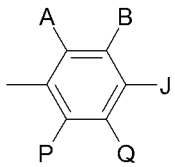
[0022] The organic compound (L) is preferably of formula (L-1):



(L-1)



(X)



(Y)

wherein:

- G_1 is a linear or branched alkyl group or oxygen-containing alkyl group of formula $C_nH_{2n+1}O_m$, wherein n is an integer of from 1 to 44 and m is lower than n/2, or a group (Y) as depicted above, wherein each of A, B, P, J and Q is independently a hydrogen atom, a fluorine atom, a methoxy group or a C_nH_{2n+1} alkyl group, wherein n is an integer from 1 to 16,
- each of G_2, G_3, G_4 and G_5 is independently a hydrogen atom, a fluorine atom, a methoxy group, a C_nH_{2n+1} alkyl group, wherein n is an integer from 1 to 16, or a group (X) as depicted above, wherein each of D, E, I, L and M is independently a hydrogen atom, a fluorine atom, a methoxy group or a C_nH_{2n+1} alkyl group, wherein n is an integer from 1 to 16.

Preferably, in the formula (L-1) G_1 is a group (Y) as described above.

[0023] As non-limiting example, organic compounds (L) of formula (L-1) suitable for use in the composition (C) of the invention are those having the following CAS numbers: 112100-07-9 (1, 6, 7, 12-tetraphenoxyperylene-N, N'-Bis-(2, 6-diisopropylphenyl)-3, 4:9, 10-tetracarboxdiimide, Lumogen F Red® by BASF); 848841-82-7 (Lumogen Violet 570® by BASF),

[0024] 82953-57-9 (N,N'-Bis(2,6-diisopropylphenyl)-3,4,9,10- perylene tetracarboxylic Diimide, perlyene orange, Lumogen F Orange 240 ® by BASF), 848841-83-8 (Lumogen F Blue 650 ® by BASF), 147-14-8 8 (Lumogen F Green 850 ® by BASF), Lumogen Yellow 083 ® by BASF, Lumogen Yellow 170® by BASF and Lumogen Pink 240® by BASF.

[0025] In a preferred embodiment, the luminescent compound (L) in composition (C) of the invention comprises, or consists of, 1, 6, 7, 12-tetraphenoxy perylene-N, N'-Bis-(2, 6-diisopropylphenyl)-3, 4:9, 10-tetracarboxdiimide (CAS number: 112100-07-9), corresponding to the structure wherein in formula (L-1) G_1 is a group (Y), each of G_2, G_3, G_4 and G_5 is a group (X), each of A and P is a isopropyl group and each of B, J, D, E, I, L and M is a hydrogen atom.

[0026] In a preferred embodiment of the invention, the amount of the at least one luminescent compound (L) in composition (C) is from 0.00005 to 5%, preferably 0.005 to 4%, more preferably from 0.025 to 3% or from 0.05 to 2% or from 0.1 to 1% in weight with respect to the total weight of the composition.

[0027] In a more preferred embodiment, luminescent compound (L) in composition (C) is 1, 6, 7, 12-tetraphenoxyperylene-N, N'-Bis-(2, 6-diisopropylphenyl)-3, 4:9, 10-tetracarboxdiimide (CAS number 112100-07-9) in amount from 0.0005 to 3%, preferably 0.005 to 1%, more preferably from 0.025 to 0.75% or from 0.05 to 0.5% in weight with respect to the total weight of the composition.

[0028] In a more preferred embodiment, luminescent compound (L) in composition (C) is the perylene compound having CAS number 848841-82-7 (Lumogen Violet 570®) in amount from 0.0005 to 3%, preferably 0.001 to 1%, more preferably from 0.025 to 0.75% or from 0.05

to 0.5% in weight with respect to the total weight of the composition.

[0029] The composition (C) may further comprise one or more additives selected from the group consisting of UV blockers, fillers, lubricating agents, heat stabilizers, anti-static agents, acid scavengers, flame-retardants, smoke-suppressing agents, IR-reflectors, thermal conductive fillers and the like.

[0030] The composition (C) may preferably further comprise at least one metal or semi-metal compound in the form of nanoparticles.

[0031] The selection of the UV blockers is not particularly limited; both organic and inorganic compounds may be used. Preferred UV blockers are notably based on CeO_2, ZnO and/or TiO_2. Nanoparticles of ZnO and/or TiO_2, optionally coated with coupling agents such as silane coupling agents, may also be used.

[0032] The composition (C) typically comprises:

- from 90% to 99.99% by weight over the total weight of (C) of at least one thermoplastic polymer (P),
- from 0.01% to 10% by weight over the total weight of (C) of at least one compound (L).

[0033] The composition (C) preferably comprises:

- from 95% to 99.975% by weight, over the total weight of (C), at least one thermoplastic polymer (P),
- from 0.025% to 5% by weight, over the total weight of (C), of at least one compound (L), more preferably from 97 to 99.95 of (P) and 3 to 0.05 of (L) in weight over the total weight of (C).

[0034] Preferably, in the composition (C) of the invention the polymer (P) comprises:

(a) from 30 to 48%, preferably from 35 to 45 % by moles of recurring units derived from ethylene (E);

(b) from 52 to 70%, preferably from 55 to 65%, by moles of recurring units derived from chlorotrifluoroethylene (CTFE) or tetrafluoroethylene (TFE) or mixture thereof; and

(c) from 0 to 5%, preferably from 0.5 to 2.5 % by moles of recurring units derived from one or more fluorinated and/or hydrogenated comonomer(s),

different from E, CTFE and TFE,

wherein all the percentages are with respect to the total number of moles of recurring units in (P).

[0035] Preferably, in the composition (C) of the invention the polymer (P) is an ECTFE copolymer, said ECTFE copolymer being copolymer of ethylene and CTFE and optionally said third monomer.

[0036] The polymer (P) may further comprise from 0.1% to 5% by moles, based on the total amount of monomers (a') and (b'), of recurring units deriving from at least one other monomer selected from the group consisting of fluorinated monomers (F) and hydrogenated monomers (H).

[0037] Non-limiting examples of monomers (F) suitable for polymers (P) include, notably, monomers (F) selected from the group consisting of perfluoroalkylvinylethers, perfluoroalkylethylenes such as perfluorobutylethylene, perfluorodioxoles and vinylidene fluoride. Among them, the preferred monomer (F) is perfluoropropylvinylether of formula CF_2=CFO-C_3F_7.

[0038] Non-limiting examples of monomers (H) suitable for polymers (P) include, notably, monomers (H) of formula (H-1):

CH_2=CH-$(CH_2)_nR_1$ (H-1)

wherein:

- R_1 is a -OR_2 or a -$(O)_tCO(O)_pR_2$ group, wherein t and p are integers equal to 0 or 1,

- R_2 is a hydrogen atom or a hydrogenated linear or branched alkyl or cycloalkyl group having from 1 to 20 carbon atoms, optionally containing heteroatoms and/or chlorine atoms, the heteroatoms preferably being O or N, and - n is an integer in the range of from 0 to 10.

[0039] In formula (H-1), R_2 optionally contains one or more functional groups, preferably selected from the group consisting of OH, COOH, epoxide, ester and ether groups. R_2 may optionally contain double bonds. In formula (H-1), R_2 is preferably an alkyl group having from 1 to 10 carbon atoms containing hydroxyl functional groups and n is an integer in the range of from 0 to 5. Preferred monomers (H) suitable for polymers (P) are selected from the group consisting of monomers (H) of any of formulas

(H-2) to (H-5):

- acrylic monomers of formula (H-2):

CH_2=CH-CO-O-R_2 (H-2)

such as ethyl acrylate, n-butyl acrylate, acrylic acid and hydroxyalkyl acrylates such as hydroxyethyl acrylate, hydroxypropyl acrylate and (hydroxy)ethylhexyl acrylate, provided that such monomers do not form a polyacrylate structure by homopolymerization,

- vinylether monomers of formula (H-3):

CH_2=CH-O-R_2 (H-3)

such as propylvinylether, cyclohexylvinylether and 4-hydroxybutylvinylether,

- vinyl monomers of the carboxylic acid of formula (H-4):

CH_2=CH-O-CO-R_2 (H-4)

such as vinyl acetate, vinyl propionate and vinyl-2-ethylhexanoate, and

- unsaturated carboxylic acid monomers of formula (H-5): CH_2=CH-(CH_2)$_n$-COOH (H-5)

wherein n has the above mentioned meaning such as vinylacetic acid.

[0040] Most preferred monomers (H) suitable for polymers (F-2) are selected from the group consisting of the acrylic monomers of formula (H-2) as defined above.

[0041] Nevertheless, ECTFE polymers free from other monomers are most preferred.

[0042] Preferably, in the composition (C) of the invention the polymer (P) is an ECTFE copolymer and has a melting temperature not exceeding 210°C, preferably not exceeding 200°C, more preferably not exceeding 198°C, more preferably not exceeding 195°C, more preferably not exceeding 193°C, even more preferably not exceeding 190°C, even more preferably not exceeding 180°C. Preferably, in the composition (C) of the invention the polymer (P) is an ECTFE copolymer and possesses a melting temperature of advantageously at least 120°C, preferably of at least 130°C, still preferably of at least 140°C, more preferably of at least 145°C, even more preferably of at least 150°C. In the context of the present invention, the melting temperature can be determined, for example, by

Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/min, according to ASTM D 3418.

[0043] The heat of fusion of polymer (P) can be determined by Differential Scanning Calorimetry (DSC) using a method known to the person skilled in the art, e.g. at a heating rate of 10°C/min according to ASTM D 3418.

[0044] Polymer (P) possesses a heat of fusion of at most 35 J/g, preferably of at most 30 J/g, more preferably of at most 25 J/g, even more preferably below 20 J/g.

[0045] Nevertheless, it is essential for polymer (P) of being a semi-crystalline polymer, i.e. a polymer having a detectable melting point when determined according to ASTM D 3418. Without lower limit for heat of fusion being critical, it is nevertheless understood that polymer (P) will generally possess a heat of fusion of at least 1 J/g, preferably of at least 2 J/g, more preferably of at least 5 J/g, determined according To the aforementioned method.

[0046] In a preferred embodiment, the heat of fusion of polymer (P) in the composition according to the invention is from 30 to 1 J/g, more preferably from 2 to 25 J/g, even more preferably from 5 J/g to 20 J/g (e.g. determined according to ASTM D3418 at a heating rate of 10°C/min).

[0047] Preferably, in the composition (C) of the invention the polymer (P) is an ECTFE copolymer and consists essentially (i.e. by more than 99.9 mole % with respect to the total number of moles of recurring units) of:

(a) from 30 to 48%, more preferably 35 to 47%, even more preferably from 38 to 41% by moles, with respect to the total number of moles of recurring units, of recurring units derived from ethylene (E);

(b) from 70 to 52%, more preferably 53 to 65%, even more preferably from 62 to 59 by moles, with respect to the total number of moles of recurring units, of recurring units derived from chlorotrifluoroethylene (CTFE).

[0048] The melt flow rate of the ECTFE polymer (P), for example measured following the procedure of ASTM 3275-81 at 230°C and 2.16 Kg, ranges generally from 0.01 to 75 g/10 min, preferably from 0.1 to 50 g/10 min, more preferably from 0.5 to 30 g/10 min.

[0049] In a preferred embodiment, the amount of polyacrylate polymers in the

composition (C) according to the invention is lower than 0.05%, preferably lower than 0.01%, even more preferably lower that 0.001% in weight with respect to the total weight of the composition, i.e. no polyacrylate polymer is detectable in composition (C) . Such amount can be determined by any suitable analytical method known to the person skilled in the art. The substantial absence of polyacrylate in the composition according to the present invention is advantageous, as polyacrylates are subject to radical degradation, particularly upon exposure to solar light and electromagnetic radiations in general, which results in shorter service life of the articles comprising polyacrylates. In addition, in weathering tests it was found that acrylates cause a relevant degree of degradation of luminescent dyes, such as perylene-based dyes. In a preferred embodiment of the invention, the amount of semi-crystalline polymer (P) in the composition (C) is at least 95%, preferably 97.5%, more preferably at least 99% in weight with respect to the total weight of the composition.

[0050] In addition to its use in luminescent solar collectors, the composition according to the present invention is particularly suitable for manufacturing protective films, including films for protecting photovoltaic (PV) modules, in particular for front-sheets or back-sheets of PV cells, but also architectural membranes and films for agricultural purposes.

[0051] Another aspect of the present invention concerns a process for manufacturing the thermoplastic fluoropolymer composition (C) as above described, said process comprising mixing :

- the polymer (P), as above detailed; and
- the luminescent compound (L).

[0052] According to a preferred variant of the invention, said process comprises advantageously mixing by dry blending and/or melt compounding the polymer (P) and the compound (L), as above detailed.

[0053] Generally, the process comprises a first step wherein the polymer (P) is provided under the form of powder and is dry-blended with said compound (L) in the form of particles, optionally under the form of a dispersion of particles in a liquid medium so as to obtain a powder/paste mixture and a second step wherein said powder/paste mixture is melt compounded.

[0054] As an alternative, polymer (A) and the luminescent compound particles (L) can be directly mixed by melt compounding.

[0055] Advantageously, the polymer (A) and the luminescent compound (L) particles are melt-compounded in continuous or batch devices. Such devices are well-known to those skilled in the art.

[0056] Examples of suitable continuous devices to melt-compound the thermoplastic fluoropolymer composition of the invention are notably screw extruders. Thus, polymer (A) and the luminescent compound (L) particles, and optionally other ingredients, are advantageously fed in an extruder and the thermoplastic fluoropolymer composition of the invention is extruded. This operating method can be applied either with a view to manufacturing finished product such as, for instance, hollow bodies, pipes, laminates, calendared articles, or with a view to having available granules containing the desired composition, optionally additives and fillers, in suitable proportions in the form of pellets, which facilitates a subsequent conversion into finished articles. With this latter aim, the thermoplastic fluoropolymer composition of the invention is advantageously extruded into strands and the strands are chopped into pellets.

[0057] Preferably, the polymer (A) and the luminescent compound particles are melt compounded in single-screw or twin-screw extruder. Examples of suitable extruders well-adapted to the process of the invention are those available from Leistritz, Maris America Corp., Werner and Pfleiderer and from Farrel.

[0058] Still another object of the invention is the use of the thermoplastic fluoropolymer composition as defined above for the manufacturing of films.

[0059] Techniques for manufacturing films are well known in the art. The composition of the invention will be preferably processed under the form of a film by cast extrusion or hot blown extrusion techniques, optionally with mono- or bi-axial orientation.

[0060] A technique particularly suitable for the manufacture of films of the composition of the invention involves extruding the molten composition through a die having elongated shape so as to obtain an extruded tape and casting/calendering said extruded tape so as to obtain a film.

[0061] Tape can be calendered into a film by passing through appropriate rolls, which can be maintained at appropriate temperatures, and whose speed can be adjusted so as to achieve the required thickness.

[0062] Films and layers obtained from the composition of the invention are preferably transparent films and layers, i.e. films and layers having a total transmittance (and/or haze) of more than 80%, preferably more than 85%, even more preferably more than 92 % when determined on films having a thickness of about 50 μm, when measured according to ASTM D 1003 standard in air.

[0063] Total transmittance and haze can also be determined according to ASTM D1003 standard in water, e.g. by placing the film in a quartz cuvette filled with deionized water.

[0064] When measured in water, as above detailed, total transmittance of films and layers obtained from the inventive composition is generally of more than 85%, more preferably of more than 90%, even more preferably of more than 94%.

[0065] Further, in addition, films and layers obtained from the composition of the invention are preferably such that in transmission, the scattering of light, responsible for the reduction of contrast of images viewed through it, is limited. In other words, films and layers obtained from the composition of the invention have values of haze of less than 15%, preferably of less than 10%, even more preferably of less than 7%, when determined on films and layers having a thickness of about 50 μm, when measured according to ASTM D 1003 standard in air.

[0066] Similarly, when haze is measured in water, as above detailed for total transmittance, it is generally preferred for the films and layers obtained from the inventive compositions to possess a haze of less than 12%, more preferably of less than 8%, even more preferably of less than 5%.

[0067] Films and layers so obtained and comprising the composition (C) as defined above are another object of the present invention.

[0068] The film of the invention can be advantageously assembled in a multilayer structure. Multilayer structures comprising the film of the invention are also objects of the present invention.

[0069] Assemblies which have been found particularly useful to the purposes of the invention are those wherein the film of the invention is assembled with a film made from a composition comprising at least one semi-crystalline polymer comprising recurring units derived from ethylene and at least one of chlorotrifluoroethylene (CTFE) and tetrafluoroethylene (TFE). The selection of this latter polymer is not particularly restricted; it may be notably selected among polymers having a heat of fusion below or beyond 35 J/g. It is nevertheless understood that, for the aim of increasing mechanical properties and of ensuring outstanding water vapour barrier properties, in preferred assemblies the film as above detailed is assembled with at least one layer made from a composition comprising at least one semi-crystalline polymer comprising recurring units derived from ethylene and at least one of chlorotrifluoroethylene (CTFE) and tetrafluoroethylene (TFE), said polymer having a heat of fusion of more than 35 J/g [polymer (B)].

[0070] In an embodiment, the present invention provides a sheet or layer comprising composition (C) as described above, that is suitable to be used as a collector in a luminescent solar concentrator.

[0071] In an embodiment, the present invention provides a luminescent solar concentrator comprising at least one collector comprising composition (C) as described above and at least one photovoltaic cell.

[0072] It was surprisingly found that the composition (C) significantly contributes to increasing the optical efficiency of the luminescent solar concentrator of the invention with respect to an analogue composition comprising a semi-crystalline polymer having a heat of fusion higher than 35 J/g for high geometric gains (A collector / A photovoltaic cell).

[0073] It has been also surprisingly found that the composition (C) significantly contributes to improving durability and weatherability properties of the collector in the luminescent solar concentrator of the invention with respect to the previously available collectors.

[0074] The collector of the present invention advantageously shows outstanding optical transparency and haze properties, while successfully exhibiting reduced waveguide losses and thus enhanced optical efficiency for high

geometric gains. Also, the collector of the present invention advantageously shows excellent interlayer adhesion properties and mechanical properties and can be suitably used in a luminescent solar concentrator. The composition (C) is typically comprised in the outer layer of the collector that is directly exposed to the incident electromagnetic radiation.

[0075] The collector may further comprise at least one back layer (layer (B)). For the purpose of the present invention, the term “back layer (layer (B))” is intended to denote the inner layer of the collector, which is not directly exposed to the incident radiation.

[0076] In the configurations where the collector comprises at least one layer (B), said at least one layer (B) is typically adhered to at least one layer (F) that comprises or consists of composition (C) according to the present invention. The layer (B) is preferably made of either glass or of a composition comprising at least one thermoplastic polymer. The thermoplastic polymer may be the thermoplastic polymer (P) or a different polymer with suitable characteristics.

[0077] In the configurations where the collector further comprises at least one layer (B), it may also further comprise at least one adhesive layer [layer (Ad1)] between at least one layer (F) and at least one layer (B).

[0078] The nature of the material constituting the layer (Ad1) is not particularly limited, provided that said layer (Ad1) ensures suitable adhesion between the layer (F) and the layer (B) of the collector.

[0079] The layer (Ad1) is typically made of at least one polymer such as a thermoplastic polymer.

[0080] The collector preferably consists of:

- at least one layer (F),
- optionally, at least one layer (B), and
- optionally, between said at least one layer (F) and said at least one layer (B), at least one layer (Ad1).

[0081] In the configurations where the collector further comprise at least one layer (B), the layer (F) of the collector of the invention typically has a thickness of from 0.01 mm to 1 mm, preferably of from 0.01 mm to 0.5 mm.

[0082] In the configurations where the collector does not comprise at least one layer (B), the layer (F) of the collector of the invention typically has a thickness of from 0.01 mm to 100 mm, preferably of from 0.01 mm to 10 mm.

[0083] The collector of the invention is typically optically transparent.

[0084] For the purpose of the present invention, the term “optically transparent” indicates that the incident electromagnetic radiation is allowed to pass through a material without being scattered or absorbed. The collector of the invention is advantageously optically transparent to incident electromagnetic radiation having a wavelength of from about 250 nm to about 2500 nm, preferably of from about 400 nm to about 800 nm.

[0085] The collector of the invention preferably has a total transmittance of more than 80%, preferably of more than 85%, more preferably of more than 90%, as measured on a collector having a thickness of about 50 μm according to ASTM D1003 in air.

[0086] Further, the collector of the invention preferably has values of Haze of less than 15%, preferably of less than 10%, more preferably of less than 7%, as measured on a collector having a thickness of about 50 μm according to ASTM D1003 in air.

[0087] The layer (F) typically has a refractive index n_1 comprised between 1 and 2.

[0088] The layer (B), when present, typically has a refractive index n_2 comprised between 1 and 2, and preferably has a refractive index n_2 higher than the refractive index n_1 of the layer (F).

[0089] The layer (Ad1), when present, typically has a refractive index n_3 comprised between 1 and 2.

[0090] The collector according to the present invention typically has a refractive index n_4 comprised between 1 and 2.

[0091] The refractive index can be measured according to any suitable method.

[0092] The present invention pertains to a luminescent solar concentrator comprising at least one collector including composition (C) as defined above and at least one photovoltaic cell.

[0093] At least one photovoltaic cell of the luminescent solar concentrator of the

invention is typically adhered to at least a portion of the collector.

The photovoltaic cell is preferably adhered to at least a portion of the collector by means of at least one adhesive layer [layer (Ad2)].

The layer (Ad2) typically has a refractive index n_5 comprised between 1 and 2 and has a refractive index n_5 substantially equal to the refractive index n_4 of the collector.

[0094] The layer (Ad2), equal to or different from the layer (Ad1), is typically made of at least one polymer such as a thermoplastic polymer.

The layer (Ad2) is usually made of a polyurethane polymer (particularly for devices wherein the photovoltaic cells are on the edges of the LSC) or of a EVA (ethyl vinyl acetate) polymer.

[0095] The photovoltaic cell typically has an absorption surface receiving electromagnetic radiation emitted by the collector.

[0096] According to a first embodiment of the invention, the plane of the absorption surface of at least one photovoltaic cell of the luminescent solar concentrator is substantially parallel to the plane of the layer (F) of at least one collector.

[0097] The collector of this first embodiment of the invention typically has a thickness of from 0.01 mm to 1 mm, preferably of from 0.05 mm to 0.5 mm.

[0098] According to a second embodiment of the invention, the plane of the absorption surface of at least one photovoltaic cell of the luminescent solar concentrator is substantially perpendicular to the plane of the layer (F) of at least one collector. Typically, in this embodiment the photovoltaic cell is placed on the edge of the collector surface. The collector of this second embodiment of the invention typically has a thickness of from 0.01 mm to 100 mm, preferably of from 0.05 mm to 10 mm.

[0099] The person skilled in the art is able to select the proper thickness of the collector having regard to the configuration of the luminescent solar concentrator according to either the first or the second embodiment of the invention.

[0100] The photovoltaic cell of the invention typically comprises at least one semiconductor photoactive layer. For the purpose of the present invention,

the term “semiconductor photoactive layer” is intended to indicate a layer endowed with photoelectric conversion property and able to perform photovoltaic conversion. The specific materials used for forming such semiconductor photoactive layer include single crystal silicon semiconductor, non-single crystal silicon semiconductor (e.g. an amorphous silicon (a-Si) semiconductor or a polycrystalline silicon semiconductor), compound semiconductors and junctions such as $CuInSe_2$, $CuInS_2$, GaAs, CdS/Cu_2S, CdS/CdTe, CdS/InP, and $CdTe/Cu_2Te$, and organic semiconductors such as polymers and small-molecule compounds like polyphenylene vinylene, copper phthalocyanine (a blue or green organic pigment) and carbon fullerenes. The semiconductor photoactive layer formed of either of the above semiconductor is typically either a “pn junction” or a “pin junction” or a Schottky junction.

[0101] The photovoltaic cell may further comprise at least one optically transparent electroconductive layer.

For the purpose of the present invention, the term “electroconductive layer” is intended to denote an upper-side electrode (i.e. an electrode having a light receiving surface). Specific examples of materials suitable for use in the optically transparent electroconductive layer include In_2O_3, SnO_2, In_2O_3-SnO_2 (ITO), ZnO, TiO_2, Cd_2SnO_4, crystalline semiconductor layers doped with a high concentration of an impurity, like notably fluorine-doped tin oxide (SnO_2:F, or “FTO”), doped zinc oxide (e.g. : ZnO:Al) and flexible organic conductors, like, e.g. carbon nanotube networks embedded in a transparent polymer matrix.

[0102] The layer may be formed by resistance-heating vapor deposition, sputtering, spraying, chemical vapour deposition (CVD), impurity diffusion, and like methods. In case of flexible organic conductors, typical polymer processing technologies are also available, including laminating, casting, extrusion and the like.

[0103] A grid-type collecting electrode may be provided on the optically transparent electroconductive layer in order to efficiently collect the generated current. Specific examples of materials suitable for use in the collecting electrode include Ti, Cr, Mo, W, Al, Ag, Ni, Cu, Sn, and alloys

thereof, and an electroconductive paste such as a silver paste. The collecting electrode may be formed by sputtering, resistance heating, and CVD employing a mask pattern; metal film deposition and subsequent etching for patterning; direct grid electrode pattern formation by photo-assisted CVD; formation of a negative pattern mask of the grid electrode and subsequent metal plating; printing with electroconductive paste, bonding of metal wires, and like methods. The electroconductive paste generally includes a dispersion of powder of silver, gold, copper, nickel, carbon or the like in a polymeric binder. The polymeric binder includes polyester resins, epoxy resins, acrylic resins, alkyd resins, polyvinyl acetate resins, rubbers, urethane resins, and phenol resins. Otherwise, a wire made of a metal such as Cu may be provided on the transparent conductive layer.

[0104] The photovoltaic cell may also further comprise at least one electroconductive substrate.

[0105] For the purpose of the present invention, the term “electroconductive substrate” is intended to denote a base member for the photovoltaic cell as well as a lower-side electrode. Examples of materials thereof include silicon, tantalum, molybdenum, tungsten, stainless steel, aluminium, copper, titanium, carbon sheet, lead-plated steel, and resin films, and ceramics and glass having an electroconductive layer formed thereon. On the above electroconductive substrate, a backside reflection layer may be formed from a metal layer, a metal oxide layer, or a lamination thereof. The metal layer can be formed from Ti, Cr, Mo, W, Al, Ag, Ni, Cu, and the like. The metal oxide layer can be formed from ZnO, TiO_2, SnO_2, In_2O_3 -SnO_2 (ITO), and the like. The metal layer and the metal oxide layer may be formed by resistance heating vapor deposition, electron beam vapor deposition, sputtering, or a similar method.

[0106] The luminescent solar concentrator is generally equipped with output terminals for extracting photovoltaic current. The output terminals are typically in electric connection with the electroconductive substrate and the collecting electrode, respectively. A metal piece such as a copper tab can be used as output terminal at the electroconductive substrate side,

connected to the electroconductive substrate by spot welding or soldering. On the other hand, a metal may be electrically connected to the collecting electrode by means of conductive paste or solder.

[0107] In an embodiment, the present invention provides a process for the manufacture of a collector for a luminescent solar concentrator, said process comprising:

(i) providing the composition (C) as described above and

(ii) processing into a layer the composition (C) provided in step (i).

[0108] Preferably, in the process of the invention the composition (C) provided in step (i) further comprises at least one organic solvent.

[0109] Preferably, in the process of the invention the composition (C) is processed into a layer in liquid phase, preferably wherein the composition (C) provided in step (i) is free from organic solvents.

[0110] Preferably, in the process of the invention wherein under step (ii) the composition (C) is processed into a layer in molten phase.

[0111] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0112] The following examples are provided to illustrate typical embodiments of the invention and do not have the purpose to limit its scope.

[0113] Experimental part

[0114] **Raw materials**

[0115] ECTFE-c (comparative polymer) is a commercially available ethylene/chlorotrifluoroethylene (E/CTFE, molar ratio 1:1) copolymer having a melting point (T_{m2}) of 242°C and a heat of fusion (ΔH_{2f}) of 42 J/g and a MFI of 18 g/10min (275°C/2.16 kg).

ECTFE 1 (polymer (P) according to the present invention): is a 41/59 mole% E/CTFE copolymer having a melting point (T_{m2}) of 180°C, a heat of fusion (ΔH_{2f}) of about 18 J/g and a MFI of 1.4 g/10min (230°C/2.16 kg).

[0116] Luminescent compound (L) is Lumogen F 305 Red® by BASF.

[0117] **General manufacturing procedure of the compositions of the invention**

The polymer, under the form of powder, and the organic luminescent

particles were pre-mixed in a rapid mixer equipped with a three-stage paddles mixer so as to obtain a homogeneous powder mixture having required weight ratio between mentioned ingredients.

Powder mixture was then processed by extrusion in a double screw conical extruder (Brabender), equipped with 4 temperature zones and a 3 mm^2 holes die. Processing set points were set as follows, for ECTFE-c (Table 1) and ECTFE-1 (Table 2), respectively:

[0118] **Table 1 - ECTFE-c processing conditions**

Table 0001

T1 (head)	T2	T3	T4
230	240	260	270

Screws speed was set at 20 rpm, with a torque of 15%, so as to yield a throughput rate of about 4.6 kg/h, and a melt extrudate temperature of 274°C.

[0119] **Table 2 - ECTFE-1 processing conditions**

Table 0002

T1(head)	T2	T3	T4
210	220	230	240

Screws speed was set at 20 rpm, with a torque of 40%, so as to yield a throughput rate of about 4.7 kg/h, and a melt extrudate temperature of 244°C.

Extruded strands were cooled in a water bath, dried, calibrated and cut in a pelletizer.

General procedure for the manufacture of films

For manufacturing thin films, pellets were processed in a 19 mm single screw extruder equipped with conventional three zones screw (L/D= 25) without mixing elements. The die used was a flat-die 100 mm wide having a die gap of 500 μm. Upon exit from the die, molten tape was casted on a three subsequent chill rolls, whose speed was adapted so as to obtain a film thickness of about 50 μm. Conditions are

summarized in Table 3.

[0120]

Table 3

Condition	Unit	ECTFE-1	ECTFE-c
T1	°C	200	235
T2	°C	210	250
T3	°C	220	260
T4 (head)	°C	230	270
T MELT (@ clamp)	°C	235	276
Head pressure	bar	150	31
Screw speed	rpm	15	15

[0121] Device fabrication

[0122] All LSC devices have been fabricated using bulk plates, made with a (fluoro)polymer, as waveguide. Waveguides were prepared from slabs of (fluoro)polymers, prepared by molding from pellets. Pellets were prepared by extrusion, starting from a powder obtained by mixing the polymer and the luminescent dye. The luminescent dye was used in different concentrations (0.0005 – 0.5 wt. %).

[0123] The standard dimensions of the plate used for the waveguide were 25x25 mm^2, 2 mm thick.

[0124] Each plate was then coupled to one or more mc-Si PV cells so that one or more edges of the waveguide were connected to the photoactive area of one or more PV cells. Bonding was performed by means of a hotmelt thermosoftening polyurethane adhesive (but also other index-matching optically clear bonding media can be used) that was placed on the active face of the PV cell after positioning the PV cell face-up on a 140°C hot-plate. Once softening of the polyurethane film was achieved (approximately 2 min at 140°C), each edge of the LSC glass substrate was pressed onto the adhesive film for about 30 s to ensure a good optical contact with the PV cell. The LSC system was then allowed to cool down to room temperature so that hardening of the polyurethane could be achieved.

[0125] Measurement protocol

[0126] For the PV characterization of the illuminated LSC devices, current-voltage (I-V) curves have been collected by means of a source-measure unit under AM 1.5G solar illumination at 100 mW cm^{-2} (1 sun), calibrated with a NREL certified reference cell. I-V testing has been carried out in air by performing scans between - 0.2 V and 0.6 V with 10 mV step intervals on the illuminated LSC device and by recording the current response. The solar simulator power output was monitored by means of a power-meter with thermopile sensor.

[0127] Performance evaluation

[0128] The PV response of the LSC devices has been evaluated considering the following figures of merit:

[0129] 1. The power conversion efficiency of the LSC device η_{LSC} defined as:

[0130] $\eta_{LSC} = (FF \bullet (I_{SC}/A_{LSC}) \bullet V_{OC})/P_{IN}$

[0131] where FF (-) is the fill factor, I_{SC} (mA) is the short circuit current and V_{OC} (V) is the open circuit voltage extracted from the PV cells attached to the LSC waveguide, A_{LSC} (cm^2) is the area of the LSC top surface, and P_{IN} (mW cm^{-2}) is the incident solar power density.

[0132] 2. The optical efficiency of the LSC device is defined as Jsc LSC/ Jsc PV, wherein Jsc LSC = Isc LSC/Area LSC and Jsc PV = IscPV/Area PV.

[0133] Weathering tests

[0134] LSC devices have been subjected to weathering tests with a QUVB apparatus according to the international standard ISO 4892-3 (Light source: type 2 (UVB-313); exposure cycle: Method C (8 h dry, 0.48 W/nm*m^2 at 310 nm, 70°C, 4 h condensation, light off, 50°C))

[0135] Light irradiation is tested every 500 h with a calibrated photodiode

[0136] LSC devices were periodically taken out of the weather-o-meter chamber for PV characterization, as described in the next section.

[0137] Haze/TT measurements of a slab comprising ECTFE–c or ECFTE-1 as is, or containing 0.025% wt of Lumogen F Red® (L).

[0138]

Table 4

Material	Haze %	Haze variation	Film Thickness

ECTFE-c	1.81 ± 0.06	-	40.78 ± 2.39
ECTFE-c + 0.025 (L)	53.43 ± 1.53	29.5 times	37.44 ± 2.00
ECTFE-1	0.63 ± 0.26	-	50.11 ± 2.26
ECTFE-1 + 0.025 (L)	1.80 ± 0.12	2.85 times	46.44± 5.05

[0139] These result indicate that the use of the copolymer P(E-CTFE) with a different ratio between Ethylene and CTFE imparts a higher transparency to the slab used for the waveguide.

[0140] Haze values were measured on films of comparable thickness. Thickness values were averaged on 9 different points while Haze values were averaged on three points on the same film. The addition of Lumogen Red to a ECTFE-c film leads to a significant increase (29 x) in haze while only a slight increase (2.85) was measured on ECTFE-1 according to the invention. Since Haze is the property that should be most affected by a bad dispersion of Lumogen, it can be inferred that a suitable dispersion of Lumogen Red is obtained in ECTFE-1 and not in ECTFE-c, having a heat of fusion above 35 J/g. Notably, the suitable dispersion is obtained in the substantial absence of PMMA.

[0141] A better dispersion of Lumogen in ECTFE-1 leads to a higher optical efficiency in LSCs. The higher performance of ECTFE-1 becomes more evident increasing the captation area of LSCs (references: J.Roncali and F.Garnier “Photon transport properties of LSC: analysis and optimization” *Applied Optics* **1984** pag 2809 and J.M.Drake “Organic dyes in PMMA in a planar luminescent solar collector: a performance evaluation” *Applied Optics***1982** pag 294.

[0142] Weatherability tests: the data shown in Figure 2 demonstrate that a slower degradation of the dye is observed for the compositions of the invention, comprising ECTFE -1, with respect to the comparative composition (ECTFE-c).

[0143] Average optical efficiency vs distance from cell (Figure 3). The optical efficiency was measured at increasing distance from the cell, i.e. from the photovoltaic cell (PC). As known to the person skilled in the art, apparently small variations in the optical efficiency (e.g. 0.5 % or higher) in this type of measurements actually result in significantly higher overall performance of

the luminescent solar concentrator. The optical efficiency of the composition according to the invention (comprising ECTFE-1) at a distance between 3 and 6 cm from the PC is higher than that of the comparative composition (comprising ECTFE-c), which indicates that superior performances in terms of electric current are obtainable using a luminescent solar concentrator according to the invention.

Claims

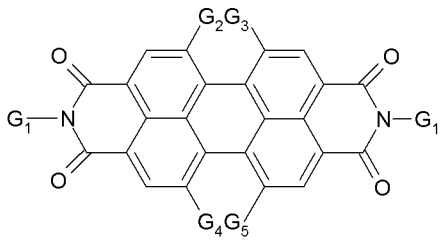
1. A composition (C) comprising:

   - at least one semi-crystalline polymer (P) having a heat of fusion of at most 35 J/g and comprising recurring units derived from ethylene and at least one of chlorotrifluoroethylene (CTFE), and tetrafluoroethylene (TFE);

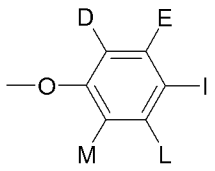
   - at least one luminescent compound (L),

   wherein the composition comprises at most 0.5% in weight, with respect to the total weight of the composition, of a polymer formed of recurring units deriving from acrylate monomers (polyacrylate A).

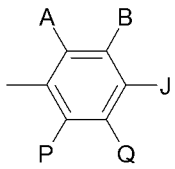
2. The composition (C) according to claim 1, wherein the luminescent compound is at least one compound of formula (L-1):



(L-1)



(X)



(Y)

wherein:

- G_1 is a linear or branched alkyl group or oxygen-containing alkyl group of formula $C_nH_{2n+1}O_m$, wherein n is an integer of from 1 to 44 and m is lower than n/2, or a group (Y) as depicted above, wherein each of A, B, P, J and Q is independently a hydrogen atom, a fluorine atom, a methoxy group or a C_nH_{2n+1} alkyl group, wherein n is an integer from 1 to 16,

- each of G_2, G_3, G_4 and G_5 is independently a hydrogen atom, a fluorine atom, a methoxy group, a C_nH_{2n+1} alkyl group, wherein n is an integer from 1 to 16, or a group (X) as depicted above, wherein each of D, E, I, L and M is

independently a hydrogen atom, a fluorine atom, a methoxy group or a C_nH_{2n+1} alkyl group, wherein n is an integer from 1 to 16, preferably wherein each of G_2, G_3, G_4 and G_5 is (X), each of D, E, I, M, L is H, each of G_1 is (Y), J, P and Q are H and A and P are isopropyl.

3. The composition (C) according to any of the preceding claims, wherein the polymer (P) comprises:

   (a) from 30 to 48%, preferably from 35 to 45 % by moles of recurring units derived from ethylene (E);

   (b) from 52 to 70%, preferably from 55 to 65% by moles of recurring units derived from chlorotrifluoroethylene (CTFE) or tetrafluoroethylene (TFE) or mixture thereof; and

   (c) from 0 to 5%, preferably from 0.5 to 2.5 % by moles of recurring units derived from one or more fluorinated and/or hydrogenated comonomer(s), different from E, CTFE and TFE,

   wherein all the percentages are with respect to the total number of moles of recurring units in (P).

4. The composition (C) according to claim 3, wherein the polymer (P) is selected from the group consisting of ECTFE copolymers, said ECTFE copolymers being copolymers of ethylene and CTFE and optionally said third monomer.

5. The composition (C) according to claim 4, wherein the ECTFE copolymer has a melting temperature not exceeding 210°C, preferably not exceeding 200°C, more preferably not exceeding 198°C, preferably not exceeding 195°C, more preferably not exceeding 193°C, even more preferably not exceeding 190°C, and has a melting temperature of advantageously at least 120°C, preferably of at least 130°C, still preferably of at least 140°C, more preferably of at least 145°C, even more preferably of at least 150°C, wherein the melting temperature is determined by Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/min, according to ASTM D 3418.

6. The composition (C) of claim 4 or 5, wherein at least 95% of the recurring units of the ECTFE copolymer consist of:

   (a) from 35 to 47% by moles, with respect to the total number of moles of recurring units, of recurring units derived from ethylene (E);

   (b) from 53 to 65% by moles, with respect to the total number of moles of

recurring units, of recurring units derived from chlorotrifluoroethylene (CTFE).

7. The composition (C) according to any of the preceding claims, wherein the amount of polyacrylate (A) is lower than 0.05%, preferably lower than 0.01% in weight with respect to the total weight of the composition.
8. The composition (C) according to any of the preceding claims, wherein the amount of the at least one luminescent compound (L) is from 0.00005 to 5%, preferably 0.005 to 4%, more preferably from 0.025 to 3% or from 0.05 to 2% or from 0.1 to 1% in weight with respect to the total weight of the composition and wherein the amount of semi-crystalline polymer (P) is at least 95%, preferably 97.5%, more preferably at least 99% in weight with respect to the total weight of the composition.
9. A collector for a luminescent solar concentrator which comprises at least one layer exposed to radiations (layer (F)) comprising the composition (C) according to any of the preceding claims.
10. A process for the manufacture of a collector for a luminescent solar concentrator, said process comprising:
    (i) providing the composition (C) according to any of the claims 1-8 and
    (ii) processing into a layer the composition (C) provided in step (i).
11. The process according to claim 10, wherein the composition (C) provided in step (i) further comprises at least one organic solvent.
12. The process according to claim 10, wherein under step (ii) the composition (C) is processed into a layer in liquid phase, preferably wherein the composition (C) provided in step (i) is free from organic solvents.
13. The process according to claim 12, wherein under step (ii) the composition (C) is processed into a layer in molten phase.
14. A luminescent solar concentrator comprising at least one collector according to claim 9 and at least one photovoltaic cell.
15. The luminescent solar concentrator according to claim 14, wherein at least one photovoltaic cell is adhered to at least a portion of at least one collector.

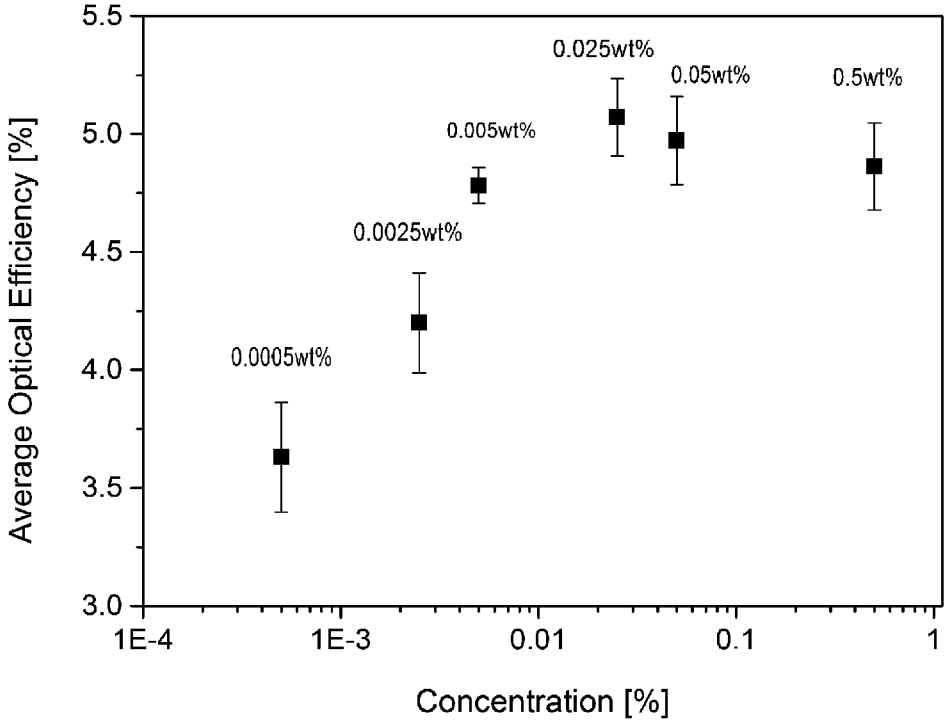

Average Optical Efficiency [%]
5.5
5.0
4.5
4.0
3.5
3.0
1E-4
1E-3
0.01
0.1
1
Concentration [%]
0.0005wt%
0.0025wt%
0.005wt%
0.025wt%
0.05wt%
0.5wt%

Fig. 1

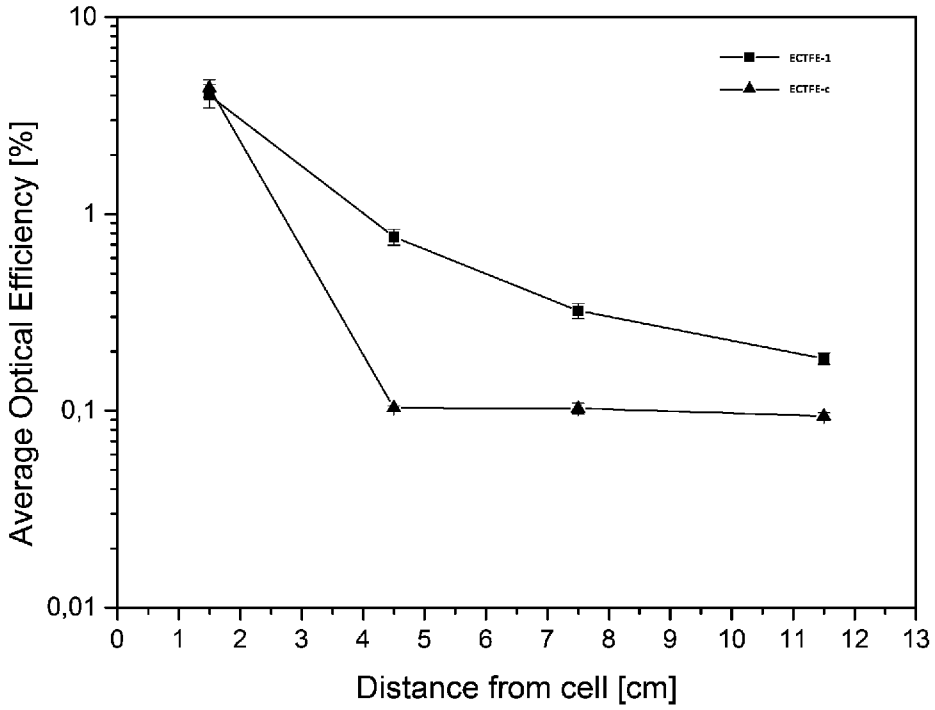

Average Optical Efficiency [%]
10
1
0,1
0,01
0
1
2
3
4
5
6
7
8
9
10
11
12
13
Distance from cell [cm]
ECTFE-1
ECTFE-c

Fig. 2

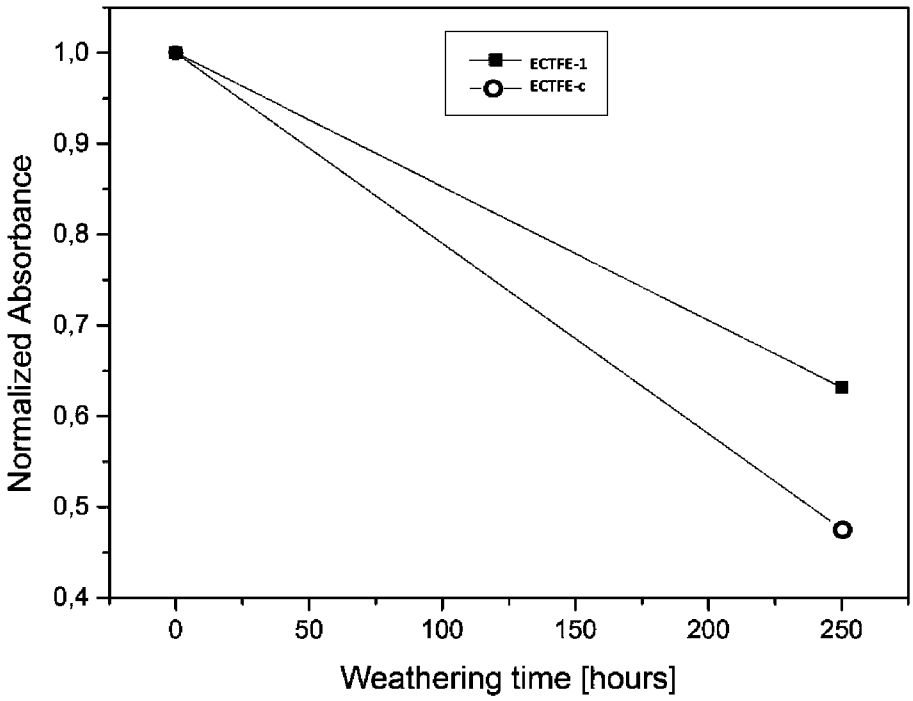

ECTFE-1
ECTFE-c
Normalized Absorbance
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0
50
100
150
200
250
Weathering time [hours]

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/063103

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/06 H01L31/055 C07D471/06 C09B5/62 C08L27/18
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)
C09K H01L C07D C09B C08L

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, INSPEC, 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	CN 104 022 175 A (ZHONGTIAN PHOTOVOLTAIC MATERIALS CO LTD) 3 September 2014 (2014-09-03)	1,3,7,8
A	paragraphs [0001], [0014]	2,4-6, 9-15
A	WO 2012/049242 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]; CARELLA SERELLA [IT]; BASSI MATTIA) 19 April 2012 (2012-04-19) paragraphs [0002], [0014], [0015], [0020], [0022] - [0025], [0041]	1-15
A	EP 0 939 088 A1 (DU PONT [US]) 1 September 1999 (1999-09-01) paragraphs [0002], [0012] - [0017], [0039]; tables 1,3	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 August 2016	02/09/2016

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/063103

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 2015/023574 A1 (NITTO DENKO CORP [JP]; LIN WEIPING [US]; ZHANG HONGXI [US]; RACHWAL MI) 19 February 2015 (2015-02-19) claim 1	1-15
A	WO 2015/073586 A1 (SIMAVORYAN SERGEY [US]; WANG PENG [US]; LIN WEIPING [US]; ZHANG HONGXI) 21 May 2015 (2015-05-21) paragraphs [0001], [0069]	1-15
A	EP 2 578 075 A1 (ASAHI GLASS CO LTD [JP]) 10 April 2013 (2013-04-10) paragraphs [0019], [0082]	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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