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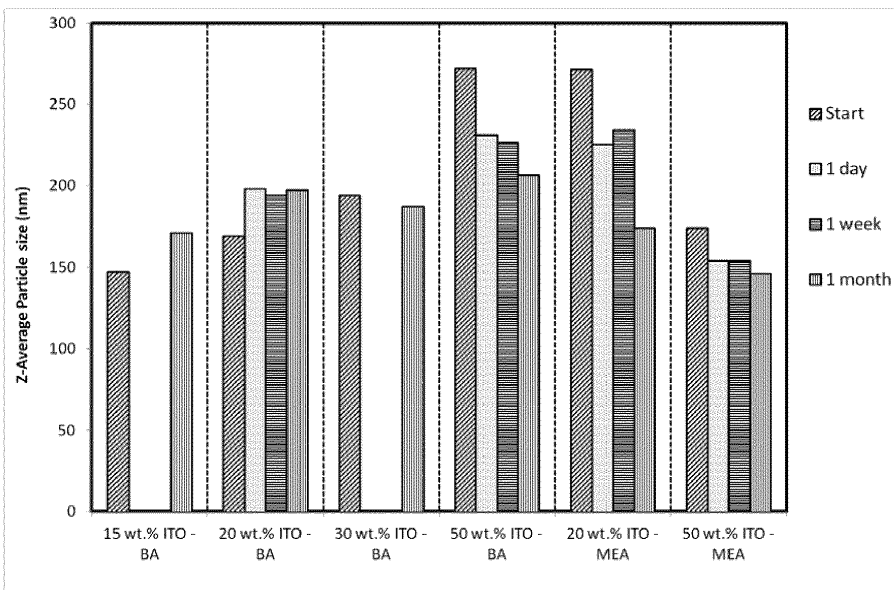
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(54) **DISPERSIONS OF METALS AND/OR METAL COMPOUNDS**

(57) Dispersion comprising
a) solid particles comprising at least one metal element in elemental form and/or at least one metal compound of at least one metal element, wherein the metal element is selected from (i) elements of group IA except hydrogen, (ii) elements of group IIA, (iii) elements of group IIIA, (iv) elements of group IVA except carbon, (v) arsenic, anti-

mony, bismuth, tellurium, polonium and astatine, (vi) elements of groups IB, IIB, IIIB, IVB, VB, VIB, VIIB, VIIIB and VIIIIB, (vii) lanthanides, (viii) actinides and (ix) mixtures thereof,
b) at least one surfactant comprising a β -keto carboxylic acid group, and
c) a fluid dispersing medium.

Figure 1



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Description**TECHNICAL FIELD**

5 [0001] The present invention relates to dispersions of solid particles made of a metal and/or a derivative thereof in a fluid dispersing medium with the help of a surfactant.

BACKGROUND

10 [0002] Dispersions of solid particles made of metals and dispersions of solid particles made of metal compounds (such as borides, carbides, nitrides, oxides and sulfides) have found increasing interest in the recent years for a multitude of different applications. For example, metal dispersions and metal oxide dispersions have been widely used for the manufacture of conductive or semiconductive films through facile deposition processes on substrates.

15 [0003] Especially in cases where transparency is needed, nanoparticulate dispersions of metals or of metal compounds are commonly used and it is important to avoid agglomeration of the nanoparticles. As long as the nanoparticles are not agglomerated, no or only little light diffusion occurs due to the small size of the particles which is beneficial for the transparency and for lower haze.

20 [0004] Furthermore, especially in cases where electrical or ionic conductivity is needed (where nanoparticulate dispersions of metals and nanoparticulate dispersions of various metal compounds are commonly used), it is important to avoid agglomeration of the nanoparticles. As long as the nanoparticles are not agglomerated, the packing density of the particles can be higher and hence conductivity can be higher.

[0005] A further requirement is the stability of the dispersion. If the metal or the metal compound settles down too rapidly, no homogenous films can be obtained. Therefore, it is common to add a surfactant to the dispersion to stabilize same. However, addition of a surfactant leads to a number of issues.

25 [0006] It has been found that the surfactant should be removed as completely as possible after deposition on the substrate as remaining surfactant is usually detrimental to the final film's properties. This is particularly the case when electrical, ionic and thermal conductivities are concerned. Remaining organics can also be detrimental to the thermal stability and stability over time of the films.

30 [0007] In addition to conductive films, dispersions based on metals and/or on metal compounds have found significant interest as fillers in organic matrices where they are used to add a specific functionality to the organic material. As an example, metal oxides can be used as anti-UV agents in polymers to decrease yellowing of the polymer on the mid-term caused by UV degradation. Metal oxides (e.g. alumina) and various metal compounds, including carbides (e.g. silicon carbide, boron carbide and tungsten carbide) and nitrides (e.g. boron nitride), can also be used as mechanical reinforcer in polymer matrices. In that context, stable dispersions of metal-based nanoparticles are required when solvent

35 blending with polymer solutions is the selected incorporation approach. However, remaining surfactants can decompose during processing the metal or metal compound - polymer composite, leading to inuniformities inside the polymer sample (eg. bubbles) or can even trigger the polymer decomposition during processing or storage.

[0008] In fuel cells and other energy storage devices, bipolar metal plates (e.g. aluminum plates) are advantageously surface-treated with a metal, a metal nitride or a metal carbide (e.g. Ti, Au, Nb, TiN, TiC, TiCN, CrN) to form collectors. The so-treated bipolar plates have good strength, elasticity, dimensional stability, heat resistance, corrosion resistance, structural integrity, and core properties. Metal nitrides and metal carbides provide superior corrosion resistance and wear resistance. Again, remain surfactants can affect the properties of the plate, in particular its heat resistance and its corrosion resistance.

40 [0009] Metal oxides, metal sulfides and other metal chalcogenides are commonly used as inorganic luminescent materials or pigments that can be deposited as thin films. Presence of residual organics severely impairs the color brightness of devices based on such films.

45 [0010] Numbers of metal, metal oxides and other metal compounds are used for their catalytic properties and can be used in heterogeneous catalysis in the gas and liquid phases. These catalysts are usually deposited on a substrate in order to increase the surface area, to avoid leaching and, in some cases, to take advantage of the synergy of the two components (catalyst and substrate) for the catalytic reaction. Residual surfactants at the surface of the catalyst would obviously severely impair its catalytic performances by reducing the available surface for the catalytic reaction and by inducing secondary reactions. An energy and economically disadvantageous heat treatment is therefore required to remove the remaining surfactant. In addition, the heat treatment can be responsible for reagglomeration of the metal-based particles reducing the surface area available for the reaction. If the dispersions are deposited on flexible substrates

50 which are often based on polymers, the removability of the surfactant should be given at temperatures below the temperature of deformation of the substrate, and/or below the glass transition temperature thereof.

55 [0011] Alike, if composites made of polymer and of metal-based particles are concerned, removal of the surfactant should be preferably performed at temperatures below the glass transition of the polymer itself and, in any cases, below

the processing temperature.

[0012] EP-A 524 630 discloses compositions for use in a transparent and electrically conductive film. The compositions comprise a composite compound based on an inorganic indium salt, an organic tin salt and an organic compound capable of coordinating with indium and tin. The organic compound may be based on α or β -keto acid group containing compounds. The dispersions are coated on substrates with high temperature resistance and a firing step at a temperature of 500 °C is necessary to obtain the desired oxide compounds from the salts. The compositions of this reference are thus not suitable for substrates with deformation temperatures below 500°C.

[0013] WO 2005/105963 relates to the use of compounds having a hydrophobic moiety attached to a hydrophilic moiety, wherein the hydrophilic moiety comprises a β -keto carboxylic acid group, as a surfactant. Dispersions comprising solid particles and the said surfactant are also claimed. No dispersions comprising metals or metal compounds are disclosed or suggested.

[0014] WO 2010/071641 describes, inter alia, a process for the manufacture of cerium oxide nanoparticles. It is said that a stabilizer is normally needed during the manufacture of the nanoparticles to prevent undesirable agglomeration and a number of stabilizers are mentioned, including carboxylic acids, α -hydroxycarboxylic acids and α -ketocarboxylic acids or mixtures thereof.

[0015] There exists an ongoing need for dispersions of metals and/or metal compounds which may be used for the applications described hereinabove and still other applications, and in which a surfactant is used which is not detrimental to the desired properties of the final product and which may be removed under moderate conditions.

[0016] There also exists an increasing need for conductive films or semiconductive films based on metals and/or metal compounds on substrates having low deformation temperatures as same are useful in (organic) electronic devices which have been the subject of intense research in the recent years.

[0017] It was thus an object of the present invention to provide dispersions comprising metals and/or metal compounds on one hand and surfactants on the other hand from which the surfactants may be removed under mild conditions without detrimental effect.

SUMMARY OF THE INVENTION

[0018] This object has been achieved with the dispersion in accordance with claim 1.

[0019] The following is an itemized listing of various facets and embodiments of the invention, and combinations thereof :

- item 1 : dispersion comprising
 - a) solid particles comprising at least one metal element in elemental form and/or at least one metal compound of at least one metal element, wherein the metal element is selected from (i) elements of group IA except hydrogen, (ii) elements of group IIA, (iii) elements of group IIIA, (iv) elements of group IVA except carbon, (v) arsenic, antimony, bismuth, tellurium, polonium and astatine, (vi) elements of groups IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIIIB, (vii) lanthanides, (viii) actinides and (ix) mixtures thereof,
 - b) at least one surfactant comprising a β -keto carboxylic acid group, and
 - c) a fluid dispersing medium ;
- item 2 : dispersion as described in item 1, wherein the surfactant comprises a hydrophobic moiety attached to the β -keto carboxylic acid group via a bond from a carbon or an oxygen atom of the hydrophobic moiety to a carbon atom of the β -keto carboxylic acid group ;
- item 3 : dispersion as described in item 2, wherein the hydrophobic moiety is attached through a carbon atom of the hydrophobic group to the β -carbon atom of the β -keto carboxylic acid group ;
- item 4 : dispersion as described in item 2 or 3, wherein the hydrophobic group is selected from a straight-chain, branched-chain or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic group; an unsubstituted or substituted aromatic group; an unsubstituted or substituted hydrophobic polyoxyalkylene group; an unsubstituted or substituted perfluoroalkyl group; an unsubstituted or substituted polysiloxane group; a lignin or rosin derivative; and any combination thereof;
- item 5 : dispersion as described in item 1, wherein the surfactant is benzoyl acetic acid;
- item 6 : dispersion as described in any one of the preceding items, wherein the weight of the surfactant, based on the weight of the fluid dispersing medium, is of at least 2 wt. % ;
- item 7 : dispersion as described in item 6, wherein the weight of the surfactant, based on the weight of the fluid dispersing medium, is of at least 5 wt. %, possibly at least 10 wt. % or at least 15 wt. % ;
- item 8 : dispersion as described in any one of the preceding items, wherein the weight of the surfactant, based on the weight of the fluid dispersing medium, is of at most 50 wt. % ;

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- item 9 : dispersion as described in item 8, wherein the weight of the surfactant, based on the weight of the fluid dispersing medium, is of at most 35 wt. %, possibly at most 30 wt. % or at most 15 wt. % ;
- item 10 : dispersion as described in any one of the preceding items, wherein the solid particles comprise at least one metal element in elemental form ;
- 5 - item 11 : dispersion as described in item 10, wherein the solid particles comprise one and only one metal element in elemental form ;
- item 12 : dispersion as described in item 10, wherein the solid particles comprise a metal alloy comprising at least two metal elements in elemental form ;
- 10 - item 13 : dispersion as described in any one of the preceding items, wherein the solid particles comprise at least one metal compound ;
- item 14 : dispersion as described in item 13, wherein the metal compound belongs to at least one class of compounds chosen from the class of metal hydride compounds, the class of metal beryllide compounds, the class of metal boride compounds, the class of metal aluminide compounds, the class of metal carbide compounds, the class of metal silicide compounds, the class of metal germanide compounds, the class of metal stannide compounds, the class of metal pnictide compounds, the class of metal oxide compounds, the class of metal chalcogenide compounds, the class of metal halide compounds and the class of intermetallic compounds ;
- 15 - item 15 : dispersion as described in item 14, wherein the metal compound belongs to at least one class of compounds chosen from the class of metal boride compounds, the class of metal carbide compounds, the class of metal pnictide compounds, the class of metal oxide compounds and the class of metal chalcogenide compounds ;
- 20 - item 16 : dispersion as described in item 15, wherein the metal compound is a metal oxide compound ;
- item 17 : dispersion as described in item 16, wherein the metal oxide compound is selected from oxides, oxychalcogenides, oxyhalides and mixtures thereof;
- item 18 : dispersion as described in item 17, wherein the metal oxide compound is a mixed oxide of indium and tin ;
- 25 - item 19 : dispersion as described in any one of the preceding items, wherein either
 - the solid particles comprise at least one metal element in elemental form and are free of any metal compound, wherein the weight of the metal element in elemental form, based on the weight of the solid particles, is above 50 wt. %, preferably of at least 90 wt.% and more preferably of at least 99 wt. %
 - or
 - 30 • the solid particles comprise at least one metal compound and are free of any metal element in elemental form, wherein the weight of the metal compound, based on the weight of the solid particles, is above 50 wt. %, preferably of at least 90 wt.% and more preferably of at least 99 wt. %
 - or
 - 35 • the solid particles comprise at least one metal element in elemental form and at least one metal compound, wherein the combined weight of the metal element in elemental form and of the metal compound, based on the weight of the solid particles, is of above 50 wt. %, preferably of at least 90 wt.% and more preferably of at least 99 wt. % ;
- 40 - item 20 : dispersion as described in item 19, wherein either
 - the solid particles consist essentially of or consist of at least one metal element in elemental form
 - or
 - the solid particles consist essentially of or consist of at least one metal compound
 - or
 - 45 • the solid particles consist essentially of or consist of at least one metal element in elemental form and at least one metal compound ;
- item 21 : dispersion as described in any one of the preceding items, wherein the weight of the solid particles, based on the weight of the dispersion, ranges from 0.5 to 75 wt. % ;
- 50 - item 22 : dispersion as described in item 21, wherein the weight of the solid particles, based on the weight of the dispersion, is of at least 1 wt. % ;
- item 23 : dispersion as described in item 22, wherein the weight of the solid particles, based on the weight of the dispersion, is of at least 5 wt. %, possibly at least 10 wt. %, at least 20 wt. % or even at least 35 wt. % ;
- item 24 : dispersion as described in item 21, 22 or 23, wherein the weight of the solid particles, based on the weight of the dispersion, is of at most 65 wt. %, possibly at most 55 wt. % or at most 45 wt. % ;
- 55 - item 25 : dispersion as described in any one of the preceding items, wherein the solid particles have an average particle diameter (D_{50} median diameter computed on the basis of the intensity weighed particle size distribution) of less than or equal to 300 nm, preferably of less than or equal to 200 nm, more preferably of less than or equal to

- 150 nm ;
- item 26 : dispersion as described in item 25, wherein the average particle diameter is less than 100 nm, possibly less than 50 nm ;
 - item 27 : dispersion as described in item 25 or 26, wherein the average particle diameter is of at least 1 nm, possibly of at least 3 nm ;
 - item 28 : dispersion as described in any one of the preceding items, wherein the fluid dispersing medium is a liquid dispersing medium ;
 - item 29 : dispersion as described in item 28, wherein the liquid dispersing medium comprises one or more than one organic liquid(s) ;
 - item 30 : dispersion as described in item 29, wherein the organic liquid is chosen from methyl ethyl ketone, 1-methyl-2-pyrrolidone isopropanol, 2-isopropoxy ethanol, tetrahydrofuran and mixtures thereof ;
 - item 31 : dispersion as described in any one of the preceding items, wherein the combined weight of the solid particles, of the surfactant and of the fluid dispersing medium, based on the weight of the dispersion, is of at least 90 wt. %, preferably at least 95 wt. % and more preferably at least 99 wt. % ;
 - item 32 : dispersion as described in item 31, wherein the dispersion consists essentially of or consists of the solid particles, the surfactant and the fluid dispersing medium ;
 - item 33 : dispersion in accordance as described in any one of the preceding items except item 32, further comprising liquid droplets and/or gas bubbles which is (are) dispersed in the fluid dispersing medium ;
 - item 34 : use of the dispersion as described in any one of the preceding items for depositing a functional film on a solid substrate or in a bulk form ;
 - item 35 : use as described in item 34 for depositing a functional film on a solid substrate ;
 - item 36 : use as described in item 35, wherein the solid substrate has a temperature of deformation of 400 °C or less ;
 - item 37 : use as described in item 35 or 36, wherein the solid substrate is a polymer, metal, glass, ceramic or paper, or has a hybrid nature ;
 - item 38 : process for the manufacture of a conductive film on a substrate having a temperature of deformation of less than 400 °C comprising
 - a) providing the substrate,
 - b) depositing the dispersion as described in any one of items 1 to 33 on the substrate, and
 - c) removing the surfactant by thermodecomposition at a temperature below the deformation temperature of the substrate ;
 - item 39 : functional film obtained by using the dispersion as described in any one of items 1 to 33 or by the process as described in item 38.;
 - item 40 : functional film obtainable by using the dispersion as described in any one of items 1 to 33 or by the process as described in item 38.

DETAILED DESCRIPTION OF THE INVENTION

- [0020] Usually, the invented dispersion comprises solid particles dispersed, as an internal phase, in a fluid (preferably, in a liquid), as an external phase, by means of a surfactant, as a dispersing agent.
- [0021] The dispersion in accordance with the present invention comprises at least metal and/or at least one metal compound. In accordance with the present invention, the metal is selected from (i) elements of group IA except hydrogen, (ii) elements of group IIA, (iii) elements of group IIIA, (iv) elements of group IVA except carbon, (v) arsenic, antimony, bismuth, tellurium, polonium and astatine, (vi) elements of groups IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIIIB, (vii) lanthanides, (viii) actinides and (ix) mixtures thereof.
- [0022] For the avoidance of doubt, the different groups of elements are herein numbered in accordance with the CAS system.
- [0023] Generally, metals are the elements in the periodic system which are located left to the diagonal extending from boron (atomic number 5) to astatine (atomic number 85)).
- [0024] Metals of group IA (Li, Na, K, Rb, Cs, Fr) are also known as alkali metals and metals of group IIA (Be, Mg, Ca, Sr, Ba and Ra) are generally referred to as alkaline earth metals.
- [0025] The metals of group IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIIIB are often referred to as transition metals. This group comprises the elements with atomic number 21 to 30 (Sc to Zn), 39 to 48 (Y to Cd), 72 to 80 (Hf to Hg) and 104 to 112 (Hf to Cn).
- [0026] The lanthanides encompass the metals with atomic number 57 to 71 and the actinides the metals with the atomic number 89 to 103.
- [0027] Some of the elements encompassed by the description above and understood to be metals for the purpose of

the present invention, are sometimes also referred to as metalloids. The term metalloid is generally designating an element which has properties between those of metals and non-metals. Typically, metalloids have a metallic appearance but are relatively brittle and have a moderate electrical conductivity. The six commonly recognized metalloids are boron, silicon, germanium, arsenic, antimony, and tellurium. Other elements also recognized as metalloids include aluminum, polonium, and astatine. On a standard periodic table all of these elements may be found in a diagonal region of the p-block, extending from boron at one end, to astatine at the other (as indicated above).

[0028] In the invented dispersion, all the solid particles comprising at least one metal element in elemental form and/or at least one metal compound of at least one metal element can be of the same chemical nature; for example, all the solid particles can consist of the same metal in elemental form, of the same metal alloy, of the same metal compound or of the same mixture of metal compounds (for example, core-shell particles wherein the shell is made of a first metal oxide and the core is made of another metal oxide). Alternatively, the solid particles element can be of different chemical nature; for example, some solid particles can consist of a certain metal oxide while other particles consist of another metal oxide.

METALS IN ELEMENTAL FORM AND METAL ALLOYS

Metals in elemental form

[0029] According to a first facet A of the present invention, the solid particles comprise at least one metal element in elemental form.

[0030] The metal in elemental form can be :

- a metal of group IA, such as Li, Na, K or Rb
- a metal of group IIA, such as Be, Mg, Ca, Sr or Ba
- a metal of group IIIA, such as B, Al, Ga, In or Tl
- a metal of group IVA, such as Si, Ge, Sn or Pb
- As, Sb, Bi, Te, Po or At
- a transition metal
- a metal of group IIIB, such as Sc or Y
- a metal of group IVB, such as Ti, Zr or Hf
- a metal of group VB, such as V, Nb or Ta
- a metal of group VIB, such as Cr, Mo or W
- a metal of group VIIB, such as Mn
- a metal of group VIIIB, such as Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn or Cd
- a lanthanide, such as La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu
- an actinide, such as Ac, Th, Pa or U.

[0031] In first embodiment of facet A, the solid particles comprise one and only one metal element in elemental form.

[0032] In another embodiment of facet A, the solid particles comprise a metal alloy comprising at least two metal elements in elemental form.

Metal alloys

[0033] A metal alloy can be viewed as a solid metal-solid metal mixture wherein a primary metal acts as solvent while other metal(s) act(s) as solute; in a metal alloy and wherein the concentration of the metal solute does not exceed the limit of solubility of the metal solvent.

[0034] The metal alloy may be notably selected from the group consisting of Au-Pt, Pt-Pd, Sn-Ni, Pt-Bi and Pt-Fe alloys. Metal alloy particles wherein the alloy is selected from this group may for example be used in catalyst and electrochemical storage applications.

METAL COMPOUNDS

[0035] According to a second facet B of the present invention, the solid particles comprise at least one metal compound.

[0036] The chemical nature of the metal compound is not particularly limited.

[0037] In general, the metal compound belongs to at least one class of compounds chosen from the class of metal hydride compounds, the class of metal beryllide compounds, the class of metal boride compounds, the class of metal aluminide compounds, the class of metal carbide compounds, the class of metal silicide compounds, the class of metal germanide compounds, the class of metal stannide compounds, the class of metal pnictide compounds, the class of

metal oxide compounds, the class of metal chalcogenide compounds, the class of metal halide compounds and the class of intermetallic compounds. It often belongs to at least one class of compounds chosen from the class of metal boride compounds, the class of metal carbide compounds, the class of metal pnictide compounds, the class of metal oxide compounds and the class of metal chalcogenide compounds.

5 **[0038]** Some metal compounds useful for the invented dispersion can belong to several classes of compounds. For example, oxychalcogenides belong the class of metal oxide compounds and to the class of metal chalcogenide compounds, oxyhalides belong the class of metal oxide compounds and to the class of metal halide compounds, and oxynitrides belong the class of metal oxide compounds and to the class of metal nitride compounds.

10 **Metal hydride compounds**

[0039] In accordance with a first embodiment of facet B, the metal compound is a metal hydride compound.

[0040] Metal hydride compounds comprise typically at least one metal atom (wherein the metal is as above defined) which is chemically bound to at least one hydrogen atom, wherein the electronegativity of the hydrogen atom is higher than the electronegativity of the metal atom.

15 **[0041]** Binary metal hydride compounds consist of at least one metal atom and at least one hydrogen.

[0042] An example thereof is beryllium hydride.

20 **Metal beryllide compounds**

[0043] In accordance with a second embodiment of facet B, the metal compound is a metal beryllide compound.

[0044] Metal beryllide compounds comprise typically at least one beryllium atom and at least one other metal atom which is chemically bound to the beryllium atom, wherein the electronegativity of the beryllium atom is higher than the electronegativity of the other metal atom.

25 **[0045]** The (or at least one) other metal atom comprised in the metal beryllide compound can be notably :

- a metal of group IA, as in LiBe, LiBe₂, Li₂Be, LiBe₃, Li₃Be, Li₂Be₃, Li₃Be₂, LiBe₄ Li₄Be and Na₂Be
- a metal of group IIA, as in CaBe₁₃
- a metal of group IVB, as in ZrBe₁₃ and TiBe₁₂
- 30 - a metal of group VB, as in VBe₁₃, Nb₂Be₁₇ and Ta₂Be₁₇
- a metal of group VIB, as in CrBe₂, or
- a lanthanide as in LaBe₁₃.

35 **Metal icosagenide compounds**

[0046] Certain metal compounds useful for facet B of the present invention are metal icosagenide compounds. Metal icosagenide compounds include metal boride compounds, metal aluminide compounds and metal gallide compounds such as vanadium gallide (V₃Ga, which is an intermetallic compound).

40 **Metal boride compounds**

[0047] In accordance with a third embodiment of facet B, the metal compound is a metal boride compound.

[0048] Metal boride compounds comprise typically at least one boron atom and at least one other metal atom which is chemically bound to the boron atom, wherein the electronegativity of the boron atom is higher than the electronegativity of the other metal atom.

45 **[0049]** The (or at least one) other metal atom comprised in the metal boride compound can be notably :

- a metal of group IIA, as in MgB₂ (superconductor), MgAlB₁₄ and BeB₂
- a metal of group IIIA, as in AlC₄B₂₄ and AlB₂
- 50 - a metal of group IIIB, as in YB₂₅ and YB₅₀
- a metal of group IVB, as in TiB₂, ZrB₂ and HfB₂
- a metal of group VB, as in VB, VB₂, NbB, NbB₂, TaB and TaB₂
- a metal of group VIB, as in Cr₂B, Cr₅B₃, CrB, Mo₂B₅ and W₂B₅
- a metal of group VIIIB, as in FeB, Fe₂B, CoB, Co₂B, NiB and Ni₂B, or
- 55 - a lanthanide as in LaB₆ and LnAlB₁₄ wherein Ln denotes a lanthanide atom.

Metal aluminide compounds

[0050] In accordance with a fourth embodiment of facet B, the metal compound is a metal aluminide compound.

[0051] Metal aluminide compounds comprise typically at least one aluminum atom and at least one other metal atom which is chemically bound to the aluminum atom, wherein the electronegativity of the aluminum atom is higher than or equal to the electronegativity of the other metal atom.

[0052] The (or at least one) other metal atom comprised in the metal aluminide compound can be notably :

- a metal of group IIA, as in MgAl
- a metal of group IVB, as in TiAl, or
- a metal of group VIII B, as in Ni₃Al.

Metal crystallogenide compounds

[0053] Certain metal compounds useful for facet B of the present invention are metal crystallogenide compounds. Metal crystallogenide compounds include metal carbide compounds, metal silicide compounds, metal germanide compounds and metal stannide compounds.

Metal carbide compounds

[0054] In accordance with a fifth embodiment of facet B, the metal compound is a metal carbide compound.

[0055] Metal carbide compounds comprise typically at least one carbon atom and at least one metal atom which is chemically bound to the carbon atom; the electronegativity of the carbon atom is obviously higher than the electronegativity of the metal atom.

[0056] The (or at least one) metal atom comprised in the metal carbide compound can be notably:

- a metal of group IA, as in Na₂C₂ (sodium percarbide) and Li₄C₃ (lithium sequecarbide)
- a metal of group IIA, as in Be₂C, CaC₂ (calcium percarbide) and Mg₂C₃ (magnesium sesquicarbide)
- a metal of group IIIA, as in B₄C which is an example of a covalent carbide
- a metal of group IVA, as in SiC which is another example of a covalent carbide
- bismuth, as in BiC
- a metal of group IVB, as in TiC and HfC
- a metal of group VB, as in TaC and VC
- a metal of group VIB, as in Cr₃C₂, Mo₂C₅ and WC
- a metal of group VIIIB, as in Fe₃C, or
- a lanthanide, as in LaC₂ (lanthanum percarbide) and Ln₂C₃ (sesquicarbide, wherein Ln denotes a lanthanide).

Metal silicide compounds

[0057] In accordance with a sixth embodiment of facet B, the metal compound is a metal silicide compound.

[0058] Metal silicide compounds comprise typically at least one silicon atom and at least one other metal atom which is chemically bound to the silicon atom, wherein the electronegativity of the silicon atom is higher than or equal to the electronegativity of the other metal atom.

[0059] The (or at least one) other metal atom comprised in the metal silicide compound can be notably :

- a metal of group IVB, as in TiSi₂, Ti₅Si₃, Ti₅Si₅ and TiSi
- a metal of group VIB, as in MoSi₂ and WSi₂,
- a metal of group VB, as in TaSi₂, or
- a metal of group VIIIB, as in CoSi₂ and NiSi.

Metal germanide compounds

[0060] In accordance with a seventh embodiment of facet B, the metal compound is a metal germanide compound.

[0061] Metal germanide compounds comprise typically at least one germanium atom and at least one other metal atom which is chemically bound to the germanium atom, wherein the electronegativity of the germanium atom is higher than or equal to the electronegativity of the other metal atom.

[0062] Examples of metal germanide compounds are molybdenum germanide (MoGe₂) and the mixed germanides of manganese and of another metal of group IVB, such as ZrMnGe and TiMnGe.

Metal stannide compounds

[0063] In accordance with a eighth embodiment of facet B, the metal compound is a metal stannide compound.

[0064] Metal stannide compounds comprise typically at least one tin atom and at least one other metal atom which is chemically bound to the tin atom, wherein the electronegativity of the tin atom is higher than or equal to the electronegativity of the other metal atom.

[0065] Examples of metal stannides compounds are :

- alkali metal stannides, such as K_4Sn_9 and KSn
- molybdenum stannide $MoSn_2$
- transition metal stannides, such as Os_4Sn_{17} , $RhSn_3$, $RhSn_4$ and $IrSn_4$.

Metal pnictide compounds

[0066] In accordance with a ninth embodiment of facet B, the metal compound is a metal pnictide compound, in particular a metal nitride compound or a metal phosphide compound.

[0067] Metal pnictide compounds comprise typically at least two different atoms, namely at least one first atom which is a pnictogen atom (which itself is or is not a metal atom) and at least one other atom which is a metal atom (which itself is or is not a pnictogen atom), wherein the electronegativity of the first atom is higher than or equal to the electronegativity of the other atom.

[0068] The first atom can be notably a nitrogen atom (the case being, the pnictide is a nitride), a phosphorus atom (the case being, the pnictide is a phosphide), an arsenic atom (the case being, the pnictide is an arsenide), an antimony atom (the case being, the pnictide is an antimonide) or a bismuth atom (the case being, the pnictide is an bismuthide).

Metal nitride compounds

[0069] Metal nitride compounds comprise typically at least one nitrogen atom and at least one metal atom which is chemically bound to the nitrogen atom; the electronegativity of the nitrogen atom is obviously higher than the electronegativity of the metal atom.

[0070] The (or at least one) metal atom comprised in the metal nitride compound can be notably:

- a metal of group IA, as in Li_3N , or in $LiMoN_2$ and Li_7MnN_4 lithium transition metal nitrides
- a metal of group IIA, as in $CaTaO_2N$, $SrTaO_2N$, $BaTaO_2N$ or $BaNbO_2N$
- a metal of group IIIA, as in AlN , InN or GaN
- a metal of group IVA, as in Si_3N_4 or Si_2N_2O
- a metal of group IIIB, as in ScN or YN
- a metal of group IVB, as in TiN , ZrN or HfN
- a metal of group VB, as in $TaON$
- a metal of group VIB, as in CrN , Cr_2N , MoN , Mo_2N , WN , W_2N
- a metal of group VIIB, as in Li_7MnN_4 , TcN
- a metal of group VIIIB, as in CoN , FeN , Co_3N , Ni_3N_2 , or
- a lanthanide , as in LaN or $LaTaON_2$.

[0071] Early transition metal nitrides, such as TiN , VN , NbN , Mo_2N , W_2N and CrN , exhibit high chemical stability and functional physical properties such as hardness, high wear resistance, electrical conductivity, or even superconductivity.

[0072] In some embodiments, the metal nitride is an oxynitride (i.e. a compound that qualifies as metal nitride compound and as metal oxide compound).

[0073] Examples thereof are :

- tantalum oxynitride ($TaON$)
- perovskite oxynitrides, such as $CaTaO_2N$, $SrTaO_2N$, $BaTaO_2N$, $LaTaON_2$ and $BaNbO_2N$, and
- silicon oxynitride (Si_2N_2O).

Metal phosphide compounds

[0074] Metal phosphide compounds comprise typically at least one phosphorus atom and at least one metal atom which is chemically bound to the phosphorus atom, wherein the electronegativity of the phosphorus atom is higher than the electronegativity of the metal atom.

[0075] Examples of metal phosphides compounds are :

- transition metal phosphides (known as hydrodesulphurisation & hydrodenitrogenation catalysts), including :
 - monometallic phosphides such as molybdenum phosphide (MoP) or tungsten phosphide (WP)
 - bimetallic phosphides such as nickel molybdenum phosphide NiMoP
 - "metal rich phosphides" (phosphides of a metal of group VIII B) such as Ni₂P, Fe₂P or Co₂P
- metal oxyphosphides such as cobalt oxyphosphide Co₄P₂O₉, which is an oxygen reduction electrocatalyst in proton exchange membrane fuel cell.

Metal arsenide compounds

[0076] Metal arsenide compounds comprise typically at least one arsenic atom and at least one other metal atom which is chemically bound to the arsenic atom, wherein the electronegativity of the arsenic atom is higher than the electronegativity of the metal atom.

[0077] Examples of metal arsenide compounds are :

- ZrCuSiAs (which is a superconductor)
- mixed arsenides of a lanthanide (especially, europium) and of a metal of group VIII B, such as EuMe₂As₂ wherein Me is Fe, Co or Ni and LnFeAs wherein Ln is a lanthanide (especially, Ce, Pr or Nd)
- arsenide oxides such Sm₂CuAs₃O.

Metal oxide compounds

[0078] In accordance with a tenth embodiment of facet B to which the highest preference is herein given notably because of its especially high practical importance from an industrial standpoint, the metal compound is a metal oxide.

[0079] Metal oxide compounds comprise typically at least one oxygen atom and at least one metal atom which is chemically bound to the oxygen atom; the electronegativity of the oxygen atom is obviously higher than the electronegativity of the metal atom.

[0080] Certain metal oxides are solid ionic compounds. In certain other metal oxides, the metal atom and the oxygen atom are covalently bonded.

[0081] The metal oxide compound itself is preferably selected from oxides, oxychalcogenides and oxohalides. As above explained, oxychalcogenides and oxohalides comprise respectively, in addition to the at least one oxygen atom in their chemical formula, at least one chalcogenide atom or at least one halide atom. Wherever used in the present specification, the term "chalcogenide" denotes an element of group VIA of the periodic system other than oxygen.

[0082] The metal oxide compound in the dispersions of the present invention may be a single oxide or a mixed oxide.

Single metal oxides

[0083] A single metal oxide is typically composed of one or more metal atom(s) of a same, unique metal element and one or more oxygen atom(s).

[0084] The metal atom comprised in the single metal oxide can be notably :

- a metal of group IA, as in Li₂O, Na₂O, K₂O, Rb₂O and Cs₂O
- a metal of group IIA, as in BeO, MgO, CaO, SrO and BaO
- a metal of group IIIA, as in B₂O₃, Al₂O₃, Ga₂O₃, In₂O₃ and Tl₂O₃
- a metal of group IVA, as in SiO₂, GeO₂, SnO₂, Sn₂O₃, Sn₃O₄ and PbO₂
- arsenic as in As₂O₃, antimony as in Sb₂O₃, bismuth as in Bi₂O₃, tellurium as in TeO₂, or polonium as in PoO₂
- a metal of group IB, as in CuO, Cu₂O, AgO, Ag₂O₂, Ag₂O₃ and Ag₃O₄
- a metal of group IIB, as in ZnO, CdO and HgO
- a metal of group IIIB, as in Sc₂O₃ and Y₂O₃
- a metal of group IVB, as in TiO₂ and ZrO₂
- a metal of group VB, as in VO₂, V₂O₅, Nb₂O₅, Ta₂O₅
- a metal of group VIB, as in Cr₂O₃, MoO₃, MoO₂ and WO₃
- a metal of group VIIB, as in MnO, Mn₂O₃, Mn₃O₄ and Mn₂O₇
- a metal of group VIIIB, as in FeO, Fe₂O₃, Fe₃O₄, CoO, Co₃O₄, NiO and RuO₂ a lanthanide Ln, as in CeO₂ and in Ln₂O₃, or

- an actinide, as in ThO₂.

Mixed metal oxides

5 **[0085]** A mixed metal oxide is typically composed of one or more metal atom(s) of different metal elements and one or more oxygen atom(s). Many metals can form mixed oxides with one or more other metals. Mixed oxide minerals appear in a great variety in nature and synthetic mixed oxides find use as components of different materials used in advanced technological applications.

10 **[0086]** Only by way of example a number of mixed oxides are described below:

- transparent conducting doped zinc oxides, such as ZnO:Al, ZnO:Cu, ZnO:Ag, ZnO:Ga, ZnO:Mg, ZnO:Cd, ZnO:In, ZnO:Sn, ZnO:Sc, ZnO:Y, ZnO:Co, ZnO:Mn, ZnO:Cr and ZnO:B
- cuprates superconductors, such as YBa₂Cu₃O_{7-x}, Bi₂Sr₂CuO₆, Bi₂Sr₂CaCu₂O₈, Bi₂Sr₂Ca₂Cu₃O₆, Tl₂Ba₂CuO₆, Tl₂Ba₂CaCu₂O₈, Tl₂Ba₂Ca₂Cu₃O₁₀, TlBa₂Ca₃Cu₄O₁₁, HgBa₂CuO₄, HgBa₂CaCu₂O₆ and HgBa₂Ca₂Cu₃O₈,
- 15 - ACrO₄ with A = Zn, Cd, Cu, Ca, Pb, Ba or Sr
- AWO₄ and AMoO₄ where A = Ni, Mg, Mn, Fe, Co, Zn, Cu, Ca, Sr, Ba or Pb
- ATaO₄ and ANbO₄ where A = Cr, Fe, Rh or V
- ASbO₄ where A = Al, Cr, Fe, Rh or Ga
- AVO₄ where A = Cr, Fe, Al, In, Bi, Fe or Al
- 20 - Y_{1-x-y}Gd_xLn_yBO₃ where Ln represents a lanthanide metal, 0 < x < 1 and 0 < y < 1
- A₃NbO₇ where A = Bi, Y or a lanthanide metal
- perovskites, such as LaGaO₃, Na_{1-x}Bi_xTiO₃ with 0 < x < 1,
- perovskite oxides, such as La_{1-x}Sr_xMeO_{3-δ} (Me = Co or Cu) with 0 < x < 1,
- ion conductors, such as Bi₂V_{1.9}Cu_{0.1}O_{5.35}, Ge_{0.9}Gd_{0.1}O_{1.95} or La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}·(ZrO₂)_{0.9}(Y₂O₃)_{0.1}
- 25 - CuZnFe₂O₄, CoMn₂O₄, PbCrO₄
- Zr_{1-x}Ti_xO₂, Ba₆Ti₁₇O₄₀, BaZrO₃, PbTiO₃, SrTiO₃, Ba_{1-x}Sr_xTiO₃, PbZrO₃, PbTi_{1-x}Zr_xO₃ where 0 < x < 1
- doped yttrium oxides and lanthanide oxides, namely Y₂O₃:Ln and Ln₂O₃:Ln wherein Ln is a lanthanide atom,
- titanium-tin mixed oxide Sn_{1-x}Ti_xO₂ with 0 < x < 1,
- yttrium, rhodium or lanthanide niobates, tantalates and vanadates A_{1-x}X_xMeO₄ where A = Y, Rh or Ln, X = Bi or Ln provided A and X are different from each other, Ln represents a lanthanide atom, Me = Nb, Ta or V and 1 ≥ x > 0
- 30 - indium-gallium-zinc oxide (IGZO) of formula InGaZn₂O₅
- transparent conducting Delafossite CuFeO₂ and other related ternary compounds of Delafossite structure of general chemical formula A_xX_yO_z where A is Ag, Pd or Pt and X is Co, Cr, Sr, Ba, Al, Ga, In, Sc, Y, La, Pr, Nd, Sm or Eu, and wherein x, y and z values are depending on the oxidation states of A and X
- 35 - transparent conducting Delafossite-type quaternary compounds: CuA_{2/3}Sb_{1/3}O₂ where A = Mn, Ca, Al, AgA_{2/3}Sb_{1/3}O₂ (A = Ni, Zn), and
- mixed oxides of indium and tin, commonly referred to as ITO, which denotes a solid solution of indium(III) oxide (In₂O₃) and tin(IV) oxide (SnO₂), consisting essentially of or consisting of from 80 wt. % up to 95 wt. % of In₂O₃ and from 5 wt. % to 20 wt. % of SnO₂, in some cases about 90 wt. % In₂O₃ and about 10 wt. % SnO₂; in particular for organic electronic device applications, ITO has been profitably used in the recent past.
- 40

Oxychalcogenides

45 **[0087]** Representative examples of oxychalcogenides are the following:

- rare earth oxysulphides A_{2-x}X_xO_yS_z where A = Y or a lanthanide metal, X = Gd or a lanthanide metal, 0 < x < 1, y > 0, z > 0, y + z = 3 e.g. Y_{1.8}Gd_{0.2}O₂S
- BiCu₁₋₂O_aS_bSe_cTe_d, where 0 ≤ z ≤ 0.2; 0 < a < 2, 0 ≤ b < 2, 0 ≤ c < 2, 0 ≤ d < 2 and a + b + c + d = 2 with a = 1 or 2, e.g. BiCuOS
- 50 - Bi_{1-x}Me_xCu_{1-y-ε}Me'_yOS where Me is an element or a combination of elements chosen from the group (g1), namely Pb, Sn, Hg, Ca, Sr, Ba, Sb, In, Tl, Mg and rare earth metals, and wherein Me' is an element or a combination of elements chosen from the group (g2) : Ag, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, Mg, Al and Cd, wherein x and y are numbers below 1 with at least one of the numbers x and y being different from 0 and 0 ≤ ε < 0.2, and
- Bi_{1-x}M_xAg_{1-y-ε}M'_yOS wherein M is an element or a combination of elements from the group (A) : Pb, Sn, Hg, Ca, Sr, Ba, Sb, In, Tl, Mg, rare earth metals and M' is an element or a combination of elements from the group (B) : par Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Al, Cd, Pt, Pd, x and y are numbers below 1 and 0 ≤ ε < 0.2.
- 55

Oxohalides

[0088] Representative examples of oxohalides of transition metals are shown below, sorted by the oxidation state of the metal:

- 5
- oxohalides wherein the transition metal has 3 as oxidation state, such as VOCl, VOBr and FeOCl
 - oxohalides wherein the transition metal has 4 as oxidation state, such as $[\text{TiOCl}_4]^{2-}$, $\text{Cl}_3\text{TiOTiCl}_3$, VOCl_2 , $[\text{VOCl}_4]^{2-}$
 - oxohalides wherein the transition metal has 5 as oxidation state, such as VOX_3 , VO_2X , $[\text{CrOF}_4]$, $[\text{CrOF}_5]^{2-}$, MnOCl_3 , TcOCl_3 , VOF_3 , VOCl_3 and NbOCl_3
 - 10 - oxohalides wherein the transition metal has 6 as oxidation state, such as MnO_2Cl_2 , CrO_2X_2 , $[\text{CrO}_3\text{Cl}]^-$, ReOX_4 , ReO_2F_2 , OsOF_4 , CrO_2F_2 , CrO_2Cl_2 , WO_2Cl_2 and WOCl_4
 - oxohalides wherein the transition metal has 7 as oxidation state, such as MnO_3Cl , ReOF_5 , ReO_2F_3 , ReO_3Cl , OsOF_5
 - oxohalides wherein the transition metal has 8 as oxidation state, such as OsO_2F_4 , OsO_3F_2 .

15 **Metal chalcogenide compounds**

[0089] In accordance with an eleventh embodiment of facet B, the metal compound is a metal chalcogenide. "Chalcogenide" is the designation for the elements of group VIA of the periodic system except oxygen.

20 [0090] Metal chalcogenide compounds comprise typically at least two different atoms, namely at least one first atom which is a chalcogen atom (which itself is or is not a metal atom) and at least one other atom which is a metal atom (which itself is or is not a chalcogen atom), wherein the electronegativity of the first atom is higher than or equal to the electronegativity of the other atom.

25 [0091] The first atom can be notably a sulphur atom (the case being, the chalcogen is a sulphide), a selenium atom (the case being, the chalcogen is a selenide), a tellurium atom (the case being, the chalcogen is a telluride) or a polonium atom (the case being, the chalcogen is a polonide).

Metal sulphide compounds

30 [0092] Then, metal sulphide compounds comprise typically at least one sulphur atom and at least one metal atom which is chemically bound to the sulphur atom; the electronegativity of the sulphur atom is obviously higher than the electronegativity of the metal atom.

[0093] The (or at least one) metal atom comprised in the metal sulphide compound can be notably :

- a metal of group IA, as in Li_2S , $\text{Li}_2\text{CdSnS}_4$
- 35 - a metal of group IIA, as in $\text{BaGa}_2\text{GeS}_6$
- a metal of group IIIA, as in CuInS_2 or $\text{Cu}_2\text{ZnSnS}_4$ (CZTS)
- a metal of group IVA, as in PbS or Pb_2S_3
- antimony as in Sb_2S_3 , or bismuth as in Bi_2S_3
- a metal of group IB as in CuS , Cu_2S or Ag_2S
- 40 - a metal of group IIB as in ZnS , CdS or PbHgS
- a metal of group IVB, as in TiS_2
- a metal of group VB, as in NbS_2
- a metal of group VIB, as in MoS_2
- a metal of group VIIB, as in FeS_2 or Co_9S_8
- 45 - a metal of group VIIIB, as in CoN , FeN , Co_3N or Ni_3N_2 , or
- a lanthanide, as in LaN or LaTaON_2 .

[0094] Thin chalcogenide films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors and sensors. Metal sulphide compounds of choice for this application include Bi_2S_3 , PbS , As_2S_3 , Sb_2S_3 , Ag_2S , CdZnS , CuInS_2 , PbHgS and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS).

Metal selenide compounds

55 [0095] Metal selenide compounds comprise typically at least one selenium atom and at least one metal atom which is chemically bound to the selenium atom, wherein the electronegativity of the selenide atom is higher than the electronegativity of the metal atom.

[0096] The (or at least one) metal atom comprised in the metal selenide compound can be notably:

- a metal of group IA, as in $KPSe_6$, $NaAsSe_2$, $Na_2Ge_2Se_5$ or Li_2Se
- a metal of group IIA, as in $BaGa_2GeSe_6$
- a metal of group IIIA, as in $CuIn_xGa_{1-x}Se_2$ (CIGS) with $0 < x < 1$
- a metal of group IVA, as in $PbSe$ or Pb_2Se_3
- 5 - a metal of group IB as in above cited CIGS (which is useful for solar cell applications)
- a metal of group IIB as in $CdSe$, $CdPbSe$ or $ZnSe$
- a metal of group IVB, as in $TiSe_2$
- a metal of group VB, as in $NbSe_2$, or
- a metal of group VIB, as in WSe_2 (which is a semiconductor).

Metal telluride compounds

[0097] Metal telluride compounds comprise typically at least one tellurium atom and at least one other metal atom which is chemically bound to the tellurium atom, wherein the electronegativity of the selenide atom is higher than or equal to the electronegativity of the metal atom.

[0098] Non limitative examples of metal telluride compounds are Pb_2Te_3 , $CdTe$, $SbTe_3$ and Bi_2Te_3 .

Metal halide compounds

[0099] In accordance with a twelfth embodiment of facet B, the metal compound is a metal halide.

[0100] Metal halide compounds comprise typically at least one halogen atom other than astatine and at least one metal atom which is chemically bound to the halogen atom; the electronegativity of the halogen atom other than the astatine atom is obviously higher than the electronegativity of the metal atom.

[0101] The halogen atom can be a fluorine atom (the case being, the halide is a fluoride), a chlorine atom (the case being, the halide is a chloride), a bromine atom (the case being, the halide is a bromide) or an iodine atom (the case being, the halide is an iodide).

[0102] The (or at least one) metal atom comprised in the metal halide compound can be notably:

- a metal of group IIIA, as in $AlCl_3$
- a metal of group IVA, as in $SiCl_4$
- a metal of group IB, as in $AgBr$
- a metal of group IVB, as in $TiCl_3$
- a metal of group VIB, as in $MoCl_3$, or
- a metal of group VIIIB, as in $FeCl_3$.

Intermetallic compounds

[0103] In accordance with a last embodiment of facet B, the metal compound is an intermetallic compound.

[0104] The terms "intermetallic compound" are commonly used to denote a compound having at least one first metal atom as defined above which is at least partially chemically bound to at least one other metal atom. The chemical bonding may be covalent and/or ionic, and is often at least partly ionic. Likewise a metal alloy, an intermetallic compound can be viewed as a solid metal-solid metal mixture wherein a primary metal acts as solvent while other metal(s) act(s) as solute; however, in an intermetallic compound and in contrast with what happens in an alloy, the concentration of the metal solute usually exceeds the limit of solubility of the metal solvent, causing a particular metal-metal arrangement.

[0105] The intermetallic compound can be a metal compound consisting of at least one first metal atom chosen from beryllium atom, aluminum atom and gallium atom on one hand and at least one second metal atom other than the first metal. In particular, the intermetallic compound can be a metal compound consisting of at least one first metal atom chosen from beryllium atom, aluminum atom and gallium atom on one hand and at least one second metal atom chosen from transition metal atoms and lanthanide atoms on the other hand.

[0106] Examples of intermetallic compounds include $LaBe_{13}$, $ZrBe_{13}$, VBe_{13} , $CrBe_2$, $MgAl$, $TiAl$, Ni_3Al , V_3Ga and europium gallides such as $EuGa_4$, $EuGa_2$, Eu_3Ga_5 , Eu_5Ga_9 , $EuGa$, Eu_8Ga_7 , Eu_3Ga_2 and $Eu_{28}Ga_{11}$.

[0107] The solid particles comprised in the dispersion in accordance with the present invention are preferably nanoparticles.

[0108] The term nanoparticles, as used herein, denotes particles having an average particle diameter of less than than or equal to 300 nm, preferably of less than or equal to 200 nm and more preferably of less than or equal to 150 nm. In certain cases, it has proven advantageous that the average particle diameter be less than 100 nm, particularly preferred less than 50 nm. Normally, the average particle diameter is of at least 1 nm, or in some cases of at least 3 nm.

[0109] The term average particle diameter when used herein refers to the D_{50} median diameter computed on the basis

of the intensity weighed particle size distribution as obtained by the so called Contin data inversion algorithm. Generally said, the D_{50} divides the intensity weighed size distribution into two equal parts, one with sizes (diameters) smaller than D_{50} and one with sizes (diameters) larger than D_{50} .

[0110] In general, the average particle diameter as defined above is determined according to the following procedure.

First, if needed, the particles are isolated from a medium in which they may be contained (as there are various processes for the manufacture of such particles, the products may be available in different forms, e.g. as neat dry particles or as a suspension in a suitable dispersion medium. The neat particles are then used for the determination of the particle size distribution preferably by the method of dynamic light scattering. In this regard the method as described in ISO Norm Particles size analysis - Dynamic Light Scattering (DLS), ISO 22412:2008(E) is recommended to be followed. This norm provides notably for instructions relating to instrument location (section 8.1.), system qualification (section 10), sample requirements (section 8.2.), measurement procedure (section 9 points 1 to 5 and 7) and repeatability (section 11). Measurement temperature is usually at 25 °C and the refractive indices and the viscosity coefficient of the respective dispersion medium used should be known with an accuracy of at least 0.1 %. After appropriate temperature equilibration the cell position should be adjusted for optimal scattered light signal according to the system software. Before starting the collection of the time autocorrelation function the time averaged intensity scattered by the sample is recorded 5 times. In order to eliminate possible signals of dust particles moving fortuitously through the measuring volume an intensity threshold of 1.10 times the average of the five measurements of the average scattered intensity may be set. The primary laser source attenuator is normally adjusted by the system software and preferably adjusted in the range of about 10,000 cps. Subsequent measurements of the time autocorrelation functions during which the average intensity threshold set as above is exceeded should be disregarded.

[0111] Usually a measurement consists of a suitable number of collections of the autocorrelation function (e.g. a set of 200 collections) of a typical duration of a few seconds each and accepted by the system in accordance with the threshold criterion explained above. Data analysis is then carried out on the whole set of recordings of the time autocorrelation function by use of the Contin algorithm available as a software package, which is normally included in the equipment manufacturer's software package.

[0112] The particles, in particular the nanoparticles, may have any shape, i.e. they may e.g. be particulate or fibrous, depending on the chemical composition of the oxide compounds. The term "particulate" in this respect is to be understood as referring to particles having a more or less isometric structure like spherical, substantially spherical, ovoidal or substantially ovoidal particles. Such particulate particles usually differ from acicular particles, platy particles as well as fibrous particles in the aspect ratio.

[0113] Platy particles are well known by the persons skilled in the art. Typically, platy particles consist essentially of, or even consist of, particles having the shape of, or resembling to a plate, i.e. the particles are flat or substantially flat and their thickness is small in comparison with the other two dimensions.

[0114] Acicular particles are also well known by the skilled in the art. Typically, acicular particles have the shape of, or resembling a needle.

[0115] The metal oxide compound may also be present in the form of fibrous particles, i.e. particles which are slender and greatly elongated, and their length is very high in comparison with the other two dimensions.

[0116] Wherever used hereinafter, the terms "metal-based material" denote a set of composed of at least one metal element in elemental form and/or at least one metal compound of at least one metal element.

[0117] In the invented dispersion, the weight of the metal-based material, based on the weight of the solid particles, is advantageously above 50 wt. %, preferably of at least 90 wt.% and more preferably of at least 99 wt. %; still more preferably, the solid particles consist essentially of or consist of the metal-based material. It results therefrom that:

- when the solid particles comprise at least one metal element in elemental form and are free of any metal compound, the weight of the metal element in elemental form, based on the weight of the solid particles, is advantageously above 50 wt. %, preferably of at least 90 wt.% and more preferably of at least 99 wt. %; still more preferably, the solid particles consist essentially of or consist of at least one metal element in elemental form;
- when the solid particles comprise at least one metal compound and are free of any metal element in elemental form, the weight of the metal compound, based on the weight of the solid particles, is advantageously above 50 wt. %, preferably of at least 90 wt.% and more preferably of at least 99 wt. %; still more preferably, the solid particles consist essentially of or consist of at least one metal compound;
and
- when the solid particles comprise at least one metal element in elemental form and at least one metal compound, the combined weight of the metal element in elemental form and of the metal compound, based on the weight of the solid particles, is of advantageously above 50 wt. %, preferably of at least 90 wt.% and more preferably of at least 99 wt. %; still more preferably, the solid particles consist essentially of or consist of at least one metal element

in elemental form and at least one metal compound.

[0118] In the invented dispersion, the weight of the solid particles, based on the weight of the dispersion, ranges advantageously from 0.5 to 75 wt. %. The weight of the solid particles, based on the weight of the dispersion, is preferably of at least 1 wt. %, more preferably of at least 5 wt. % and is possibly of at least 10 wt. %, at least 20 wt. % or even at least 35 wt. %. Besides, the weight of the solid particles, based on the weight of the dispersion, is preferably of at most 65 wt. %, possibly at most 55 wt. %.

[0119] The dispersion in accordance with the present invention comprises, as component b) at least one surfactant comprising a β -keto carboxylic acid group.

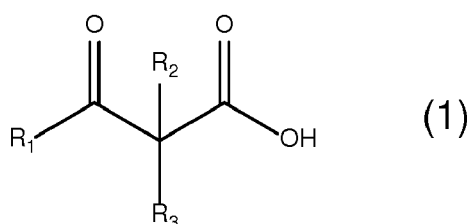
[0120] The term "surfactant" generally denotes a compound which lowers the surface tension between a liquid and a solid in a dispersion, thereby stabilizing the dispersion.

[0121] Preferred surfactants for use in the dispersions in accordance with the present invention are compounds having a hydrophobic moiety attached to a hydrophilic moiety, wherein the hydrophilic moiety comprises a β -keto acid group and the hydrophobic moiety is attached via a bond from a carbon or an oxygen of the hydrophobic moiety to a carbon of the β -keto acid group.

[0122] The term hydrophobicity is used herein to describe a property of a molecule which is seemingly repelled from a mass of water. The hydrophobic interaction is mostly an entropic effect originating from the disruption of hydrogen bonds between liquid molecules of water by the non-polar hydrophobic solute. According to IUPAC hydrophobicity is the association of non-polar groups or molecules in an aqueous environment which arises from the tendency of water to exclude non-polar molecules.

[0123] In accordance with another preferred embodiment, the β -carbon of the β -keto acid group does not form part of a carboxyl or ester group, or a salt thereof.

[0124] Preferred surfactants for use in the dispersion in accordance with the present invention are represented by general formula (1)



or a salt of such compounds.

[0125] Surfactants of this type are generally susceptible to temperature controlled decomposition, depending on pH, into volatile reaction products and an oil-like (if liquid), hydrophobic residue.

[0126] The temperature at which decomposition occurs is in most cases below 200 °C, preferably below 150 °C and even more preferably not significantly exceeding 100°C. The decomposition products are volatile compounds which can be easily removed from the final products obtained from the dispersion.

[0127] Most preferred are surfactants which decompose to volatile products to at least 90 % in ten minutes at a temperature of not more than 150°C.

[0128] For the purpose of this invention, the term decomposition temperature is the temperature at which, in the thermal gravimetric analysis, a weight loss of 60% or more is observed when using a temperature gradient program starting at 25°C and an increase rate of 5°C/min.

[0129] The rate of decomposition of surfactants of this type can be effectively controlled by temperature. The rate of decomposition generally increases with increasing temperature. Furthermore, the decomposition rate of the surfactant may be accelerated by catalysts, such as decarboxylases, or simple amino acids, like glycine. Neither the attachment of the hydrophobic moiety to the hydrophilic moiety via a bond from a carbon of the hydrophobic moiety, nor from an oxygen of the hydrophobic moiety, are susceptible to premature degradation and/or thermally uncontrolled degradation under the above-presented conditions.

[0130] In many common situations, e.g. for many commonly used hydrophobic moieties, the hydrophobic moiety is preferably attached via a bond from a carbon of the hydrophobic moiety. With reference to formula I, this is the equivalent of the hydrophobic moiety being $-\text{C}-\text{R}^4$, wherein R^4 is a hydrophobic group.

[0131] It is well known to the skilled person that a wide selection of hydrophobic groups exists and that their detailed structures are not always of critical importance. Thus, any hydrophobic group, not itself susceptible to degradation in aqueous solution, creating an amphiphilic compound when attached to the hydrophilic moiety may be utilized in the present invention. As non-limiting examples, the hydrophobic moiety or moieties may independently be a straight-chain,

branched-chain or cyclic, saturated or unsaturated, optionally substituted, aliphatic group; an optionally substituted aromatic group; an optionally substituted hydrophobic polyoxyalkylene group, such as an optionally substituted polyoxypropylene group; an optionally substituted perfluoroalkyl group; an optionally substituted polysiloxane group; a lignin or rosin derivative; or a combination thereof.

5 **[0132]** As used herein, the term "substituted", in relation to the hydrophobic moiety or moieties, relates to the substitution of an organic group with any substituents not changing the hydrophobic nature of said moiety or the amphiphilic nature of the compound.

10 **[0133]** The hydrophobic moiety or moieties is/are preferably independently selected from a straight-chain, branched-chain or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic group; an unsubstituted or substituted aromatic group; an unsubstituted or substituted hydrophobic polyoxyalkylene group; an unsubstituted or substituted perfluoroalkyl group; an unsubstituted or substituted polysiloxane group; a lignin or rosin derivative; and any combination thereof. More preferably, the hydrophobic moiety or moieties is/are independently selected from a straight-chain or branched-chain, saturated or unsaturated, optionally substituted C₁-C₃₀ alkyl, preferably C₃-C₂₂ alkyl and most preferably the hydrophobic residue comprises at least one aromatic ring system.

15 **[0134]** Suitable compounds which may be used as surfactants in accordance with the present invention are disclosed in WO2005/105963 starting on page 6 up to and including page 12, to which reference is made here for further details.

20 **[0135]** Two examples of particularly preferred surfactants which may be used in the dispersions in accordance with the present invention are 3-oxo-5-phenyl pentanoic acid and benzoyl acetic acid, of which the latter has proven advantageous for certain preferred metal-based materials, namely for metal oxide compounds, especially for mixed oxides of indium and tin which find frequent use in the manufacture of transparent films in organic electronic devices.

25 **[0136]** In the invented dispersion, the amount of surfactant can vary to a large extent. On one hand, the weight of the surfactant, based on the weight of the fluid dispersing medium, is advantageously of at least 2 wt. %. It is preferably of at least 5 wt. %, possibly of at least 10 wt. % or of at least 15 wt. %, based on the weight of the fluid dispersing medium. On the other hand, the weight of the surfactant, based on the weight of the fluid dispersing medium, is advantageously of at most 50 wt. %. It is preferably of at most 35 wt. %, possibly of at most 30 wt. % or of at most 15 wt. %, based on the weight of the fluid dispersing medium.

30 **[0137]** The dispersion in accordance with the present invention comprise a fluid dispersing medium as component c). The term fluid, as generally understood, encompasses liquid and gaseous dispersing media. Preferably, the dispersing medium in the dispersion of the present invention is a liquid dispersing medium as described now in more details.

35 **[0138]** The liquid dispersing medium comprises advantageously one or more than one organic liquid(s) and is preferably capable of dissolving the surfactant used as component b) in the invented dispersion in the amount used so that there is no significant amount of dispersed, undissolved surfactant in the final dispersion which is visible.

40 **[0139]** The liquid dispersing medium may consist essentially of or may consist of one or more than one organic liquid(s). Alternatively, the fluid dispersing medium c) may be contain water as additional component besides the organic liquid(s). The skilled person will select the suitable liquid dispersing medium based on the requirements of the specific application case.

45 **[0140]** Without being bound thereto, the organic liquid may be chosen from linear, branched or cyclic aliphatic or aromatic hydrocarbons e.g. pentane, hexane, heptane, 2,2,4-trimethyl pentane, cyclopentane, cyclohexane, cycloheptane, benzene, toluene or xylene, from carboxylic acids and their esters such as acetic acid, ethyl acetate and butyl acetate, alcohols such as ethanol, 1-propanol, 2-propanol, 2-isopropoxy ethanol or 1-butanol, ethers such as tert.-butyl methyl ether, diethyl ether, diisopropyl ether, halogenated hydrocarbons such as carbon tetrachloride, chloroform, dichloromethane, 1,2 dichloro ethane or trichloro ethylene, ketones such as acetone, methyl ethyl ketone or N-methylpyrrolidone or dimethylformamide, dimethyl sulfoxide, 1-4 dioxane and mixtures thereof. The mixture ratio, if more than one organic liquid is used, is not subject to a particular limitation and the skilled person will adjust the mixture ratio in accordance with the specific application case.

50 **[0141]** Tetrahydrofuran, methyl ethyl ketone, 1-methyl-2-pyrrolidone, isopropanol and 2-isopropoxy ethanol and mixtures thereof, optionally mixed with water, have shown advantageous results in certain cases, notably when indium tin oxide is the metal-based material.

55 **[0142]** The dispersion in accordance with the present invention can be obtained by processes known to the skilled person for the manufacture of dispersion.

[0143] A general procedure for the preparation of nanoparticle dispersion is to weigh in the desired amount of metal-based material in a beaker in a fume hood. In another beaker the dispersing medium, here a liquid dispersing medium, and the surfactant are weighed in. The surfactant and the liquid dispersing medium may then be homogenized by hand mixing followed by stirring with a magnetic stirrer until the surfactant is fully dissolved. Then, particles of the metal-based material are added into the solution thus obtained gradually while stirring for about 30 min. Sometimes stirring can be prolonged for about 60 minutes to ensure the formation of a homogenous surfactant - dispersing medium - metal-based material suspension.

[0144] In some cases it has proved to be advantageous to subject the product thus obtained to an ultrasonic treatment

for a period of from 5 to 60 minutes.

[0145] The dispersion in accordance with the present invention are advantageously used notably for all kinds of functional films, e.g. transparent and conductive, or opaque and insulating films, which may be deposited on solid substrates or in bulk form through methods based on using dispersions. The dispersion in accordance with the present invention is preferably used notably for the manufacture of an ink suitable for being deposited into a functional film.

[0146] Accordingly, the dispersion in accordance with the present invention is notably suitable for the deposition of semiconductive, antistatic or dissipative films on solid substrates, for the deposition of insulating films on solid substrates, for the deposition of optically transparent, hazy or opaque films on solid substrates, for preparing luminescent films on solid substrates, for preparing pigment-based films on solid substrates or for preparing metal-based material catalysts in a bulk form or as films on solid substrates.

[0147] Furthermore, the dispersion in accordance with the present invention is also particularly suited for preparing a polymer - metal-based material composite.

[0148] The advantage of the invented dispersion for use in respective applications is the easy removability of the surfactant from the final product after deposition or processing into a bulk material. If such a final product is used as pigment, catalyst, luminescent material, ionic conductor or the like, the presence of residual surfactant in the film or other shaped article is usually detrimental and removal thereof is desired.

[0149] Especially in cases where temperature labile substrates are used on which the films are deposited (such as e.g. polymers or the like), removal of the surfactant as far as possible poses a challenge.

[0150] Thus, in accordance with the present invention, the film is preferably deposited on a solid substrate which may have a 1D, 2D or 3D structure. The substrate may be porous or have a smooth surface without pores, depending on the targeted application.

[0151] Without being limited to any specific type of substrate material, metals, glass, ceramic materials, paper and hybrid materials may be mentioned here as suitable substrate material. The skilled person will select the suitable substrate material in accordance with the final use.

[0152] Another embodiment of the present invention relates to the use of the dispersion in accordance with the present invention for the deposition of a conductive film on a solid substrate, in particular on a substrate having a deformation temperature of 400°C or less, particularly preferred on a polymeric substrate having a deformation temperature of 400°C or less.

[0153] The term "deformation temperature", as used herein, denotes the temperature above which the substrate undergoes a dimensional deformation under a specified load as defined in ASTM D648 or ISO 75. ASTM D 648 specifies two different loads thereby yielding two values for the material tested. For the purpose of the present invention, the deformation temperature denotes the value at a load of 0.455 MPa, i.e. at the lower weight specified in ASTM D 648.

[0154] Still another embodiment of the present invention relates to the manufacture of conductive films on a substrate having a temperature of deformation of less than 400 °C comprising

- a) providing the substrate,
- b) depositing an invented dispersion as above defined on the surface of the substrate and
- c) thereafter removing the surfactant by thermodecomposition at a temperature below the deformation temperature of the substrate.

EXAMPLES

Synthesis of benzoyl acetic acid

[0155] Benzoyl acetic acid was synthesized according to the procedure published WO 2010/120232 via saponification of ethyl benzoyl acetate.

[0156] 1000 ml of 0.2 mol/l solution of ethyl benzoyl acetate (90%, Sigma Aldrich) in 0.5 mol/l NaOH (aq.) was prepared and stirred for 24 hours at room temperature, to obtain sodium benzoyl acetate. This solution was neutralized with 2.0 mol/l HCl to pH below 2, whereby benzoyl acetic acid precipitated. The solid product was separated from the aqueous solution by filtration, and the filtrate was washed with a small portion of distilled water passed through the filter. The obtained product was thereafter dried in open air without further purification. The product was stored in a refrigerator at a temperature of 4°C for further use.

General method for preparation of the dispersions

[0157] The desired amount of indium tin oxide (ITO) nanoparticles (metal oxide a), comprising 90% In₂O₃ and 10 % SnO₂) was weighed in a beaker in a fume hood. In another beaker the surfactant b) (benzoyl acetic acid) and dispersing medium c) were weighed in. The surfactant and the dispersing medium were homogenized by hand mixing followed by

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stirring with magnetic stirrer until the benzoyl acetic acid was completely dissolved. Then, the ITO nanoparticles were added into the above solution gradually while stirring for about 30 min. In some cases stirring was prolonged for about 60 minutes to ensure that a homogenous stabilizer-organic liquid-nanoparticle suspension was obtained. This was due to solubility difference of benzoyl acetic acid in different dispersing mediums tested.

[0158] Thereafter, the suspension was moved to a glass beaker and a 13 mm Vibracell sonicator tip was immersed into the suspension and the suspension was sonicated for about 7 min in an ice bath with a power setting of 30% on the VC750 sonicator. (Pulse mode was not used).

[0159] Thereafter, the suspension was removed from the sonicator and stirred with a magnetic stirrer for another 30 min.

[0160] To avoid overheating and thermal decomposition of benzoyl acetic acid, half of the amount of surfactant was added before the sonication and the other half of surfactant was added after finishing the sonication.

[0161] **Examples 1 to 5** - Dispersions with 2 wt. % ITO, based on the weight of the dispersing medium, and 1 wt. % benzoyl acetic acid, based on weight of the dispersing medium.

[0162] The dispersions prepared are summarized in Table 1.

Table 1

Ex.	Nature of the dispersing medium	Amount of dispersing medium (g)	Amount BA in (g)	Amount of ITO (g)
1	THF	10	0,10	0,20
2	MEK	10	0,10	0,20
3	NMP	10	0,10	0,20
4	2-IPE	10	0,10	0,20
5	IPA	10	0,10	0,20

THF: Tetrahydrofuran, MEK: Methyl-ethyl-ketone, NMP: N-Methyl-2-pyrrolidone, 2-IPE: 2-Isopropoxy ethanol, IPA: 2-Hydroxypropane, BA: Benzoyl acetic acid

[0163] The dispersions showed a certain stability after 30 min but settled down after 4 days.

Examples 6 to 8

[0164] Example 1 was repeated with THF, 2-IPA and IPE as liquid dispersing medium and increasing the amount of BA to 5 wt. % (0.5 g) and the amount of ITO to 10 wt. % (1 g)

[0165] No visible phase separation was obtained after 3-4 days. Dynamic light scattering (DLS) measurement using Nanosizer (Malvern Instrument) was carried out with these dispersions to analyze the particle size distribution. The evaluation was done by the method provided by the manufacturer of the instrumentation.

[0166] The Z-average particle size as defined in ISO 13321 and ISO 22412 was determined. The Z-Average size or Z-Average mean used in dynamic light scattering is a parameter also known as the cumulants mean. It is the primary and most stable parameter obtainable by DLS. ISO 22412 defines this value as the harmonic intensity averaged particle diameter.

[0167] The Z-average particle sizes were 210 nm for IPE, 228 nm for THF and 166nm for IPA dispersion, which is a clear indication that benzoyl acetic acid is able to stabilize ITO nanoparticles in these liquid dispersing media without significant agglomeration of the nanoparticles.

Examples 9 to 14

[0168] Dispersions with even higher amounts of ITO and benzoyl acetic acid as surfactant were prepared using the general method described above. The compositions are shown in Table 2.

Table 2

Ex.	Nature of the dispersing medium	Amount of dispersing medium (g)	Amount BA in g	Amount of ITO (g)
9	IPA	10	0,76	2.0
10	IPA	10	0.78*	5.0
11	2-IPE	10	1.52	2.0
12	2-IPE	10	1.55	5.0

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(continued)

Ex.	Nature of the dispersing medium	Amount of dispersing medium (g)	Amount BA in g	Amount of ITO (g)
13	THF	10	1.54	2.0
14	THF	10	1.49	5.0
* Limitation of solubility of BA in the dispersing medium				

[0169] The dispersion showed a good stability for more than 10 days with THF overall showing the best results. The ITO nanoparticles were well dispersed and aggregate size (determined by scanning electron microscopy) was less than 300 nm, i.e. the particles were still nanoparticulate.

[0170] **Examples 15 to 20** - Dispersions were prepared in accordance with Table 3 using THF as dispersing medium

Table 3

Ex.	Amount THF (g)	Amount of surfactant (g)	Amount of ITO (g)	Concentration ITO wt. %
15	8.4	1.2	2.4	20
16	3	3.0	6.0	50
17C	8.4	1.2	2.4	20
18C	3.0	3.0	6.0	50
19C	9.6	0	2.4	20
20C	6	0	6.0	50

[0171] Examples 15 to 16 comprise benzoyl acetic acid in accordance with the present invention, whereas examples 17C to 20C are comparative examples comprising [(2-(2-methoxyethoxy)ethoxy)acetic acid (MEA) as surfactant (Examples 17C and 18C) and no surfactant (Examples 19C and 20C).

[0172] The samples of Examples 15 to 18 comprising a surfactant showed much better dispersion stability than those of Examples 19 and 20. To investigate the quality of the dispersions in terms of particle size of the dispersed particles over time, the samples of Examples 13 to 20 were analyzed using DLS as described hereinbefore. In this context, the samples were diluted as detailed hereinafter.

[0173] The concentrated sample was shaken by hand strongly to dissolve all the particles collected on the bottom of the vial during the storage time. 2 droplets of the 20% concentrated suspension were diluted in 20ml of the liquid dispersing medium in a glass vial and the vial was shaken to dissolve the material and get a translucent sample. In case of 50% concentrated solution, only 1 droplet was used. All the measurement was done at 25°C, refractive index of ITO and dispersant was assumed to be 2,0 and 1,409, respectively, and viscosity of the THF was set to 0,4549.

[0174] The results of the particle size measurements are given in Table 4.

Table 4

Examples-Samples of surfactant		Zeta average particle size (nm)			
		Start	1 day	1 week	1 month
19C	No surfactant	479	1569	2174	1236
20C	No surfactant	1214	3186	3405	1635
13	BA	147			171
15	BA	169	198	194	197
14	BA	194			187
16	BA	272	231	226	206
17C	MEA	271	225	234	174
18C	MEA	174	154	154	146

[0175] Figure 1 shows a graphical representation of the results obtained for the dispersions. All dispersions were

prepared with THF as dispersing medium.

[0176] The bars for the individual dispersions represent from left to right for each dispersion the values at the start, after 1 day, after 1 week and after 1 month.

[0177] From Table 4 and Figure 1 one can see easily that without any stabilizer added, particle size was very large from the start and grow bigger and bigger over time.

[0178] In the case of using BA as a stabilizer, particle size was dramatically reduced from the start, the size being even smaller than for the reference sample in the case of 15,20 and 30% ITO, and continuing to be stable over time, with no dramatic size increase being visible. In the case of MEA-stabilized ITO nanoparticles also in THF, a similar trend can be seen.

[0179] Transmission electron microscopy measurements show that aggregation of the ITO nanoparticles is prohibited with BA as well as with MEA.

[0180] By TEM, it could also be confirmed that ITO nanoparticles are in most cases, single crystalline nanoparticles of 20-30 nm. From high resolution TEM image of ITO nanoparticles, a superstructure that has d-spacing much larger than normal d-spacing in ITO crystals was observed in some of the samples. Thus, overall, BA and MEA seem to be suitable to stabilize nanoparticulate ITO dispersions in THF and to avoid aggregation of the nanoparticles.

[0181] In order to see the decomposition of the different stabilizers both stabilizers and dispersions were characterized by DSC (Differential Scanning Calorimeter) and TGA (Thermo Gravimetric Analysis).

[0182] The experiments were performed using an initial temperature of 25°C, a final temperature of 550°C and a temperature gradient of 5°C/min. Nitrogen was used as gas at a rate of 20 ml/min.

[0183] The results are shown in Figures 2 to 4.

[0184] Figure 2 shows the TGA and DSC of the surfactants BA and MEA as such;

[0185] Figure 3 shows the results for dispersions with 20 wt. % ITO and

[0186] Figure 4 shows the result for the dispersions with 50 wt. % ITO.

[0187] In Figures 2, 3 and 4, the capital letters A and A' represent BA respectively the dispersions comprising BA, whereas B and B' represent MEA respectively the dispersions comprising MEA.

[0188] From Figure 2, one can clearly see that there is a shift in decomposition temperature for the different surfactants, and indeed BA decomposes at lower temperature than the MEA. The same is true for both 20 wt. % and 50 wt. % dispersions of ITO stabilized in THF, as can be seen from Figures 3 and 4.

[0189] From Figure 3 and Figure 4 one can see the same trend. That is, the surfactant decomposes at low temperature in the case of BA stabilized ITO nanoparticles, while decomposition of MEA occurs at much higher temperatures in the case of MEA stabilized ITO nanoparticles in THF dispersions.

[0190] Thus, BA offers the same dispersion quality and stabilization but has the important advantage of easy removability at lower temperatures compared to MEA.

Claims

1. Dispersion comprising

a) solid particles comprising at least one metal element in elemental form and/or at least one metal compound of at least one metal element, wherein the metal element is selected from (i) elements of group IA except hydrogen, (ii) elements of group IIA, (iii) elements of group IIIA, (iv) elements of group IVA except carbon, (v) arsenic, antimony, bismuth, tellurium, polonium and astatine, (vi) elements of groups IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIIIB, (vii) lanthanides, (viii) actinides and (ix) mixtures thereof,

b) at least one surfactant comprising a β -keto carboxylic acid group, and
c) a fluid dispersing medium.

2. Dispersion in accordance with claim 1, wherein the surfactant comprises a hydrophobic moiety attached to the β -keto carboxylic acid group via a bond from a carbon or an oxygen atom of the hydrophobic moiety to a carbon atom of the β -keto carboxylic acid group.

3. Dispersion in accordance with claim 2, wherein the hydrophobic moiety is attached through a carbon atom of the hydrophobic group to the β -carbon atom of the β -keto carboxylic acid group.

4. Dispersion in accordance with claim 2 or 3, wherein the hydrophobic group is selected from a straight-chain, branched-chain or cyclic, saturated or unsaturated, substituted or unsubstituted aliphatic group; an unsubstituted or substituted aromatic group; an unsubstituted or substituted hydrophobic polyoxyalkylene group; an unsubstituted or substituted perfluoroalkyl group; an unsubstituted or substituted polysiloxane group; a lignin or rosin derivative; and any com-

ination thereof.

5. Dispersion in accordance with claim 1, wherein the surfactant is benzoyl acetic acid.

5 6. Dispersion in accordance with any one of the preceding claims, wherein the solid particles comprise at least one metal element in elemental form.

7. Dispersion in accordance with any one of the preceding claims, wherein the solid particles comprise at least one metal compound.

10 8. Dispersion in accordance with claim 7, wherein the metal compound belongs to at least one class of compounds chosen from the class of metal boride compounds, the class of metal carbide compounds, the class of metal pnictide compounds, the class of metal oxide compounds and the class of metal chalcogenide compounds.

15 9. Dispersion in accordance with claim 8, wherein the metal compound is a metal oxide compound.

10. Dispersion in accordance with claim 9, wherein the metal oxide compound is a mixed oxide of indium and tin.

20 11. Dispersion in accordance with any one of the preceding claims, wherein the solid particles have an average particle diameter of at most 300 nm.

12. Dispersion in accordance with any one of the preceding claims, wherein the fluid dispersing medium is a liquid dispersing medium comprising one or more than one organic liquid(s).

25 13. Dispersion in accordance with claim 12, wherein the organic liquid is chosen from methyl ethyl ketone, 1-methyl-2-pyrrolidone, isopropanol, 2-isopropoxy ethanol, tetrahydrofuran and mixtures thereof.

30 14. Use of the dispersion in accordance with any one of the preceding claims for depositing a functional film on a solid substrate wherein the solid substrate has a temperature of deformation of 400 °C or less.

15. Process for the manufacture of a conductive film on a substrate having a temperature of deformation of less than 400 °C comprising

a) providing the substrate,

35 b) depositing the dispersion in accordance with any of claims 1 to 13 on the substrate, and

c) removing the surfactant by thermodecomposition at a temperature below the deformation temperature of the substrate.

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Figure 1

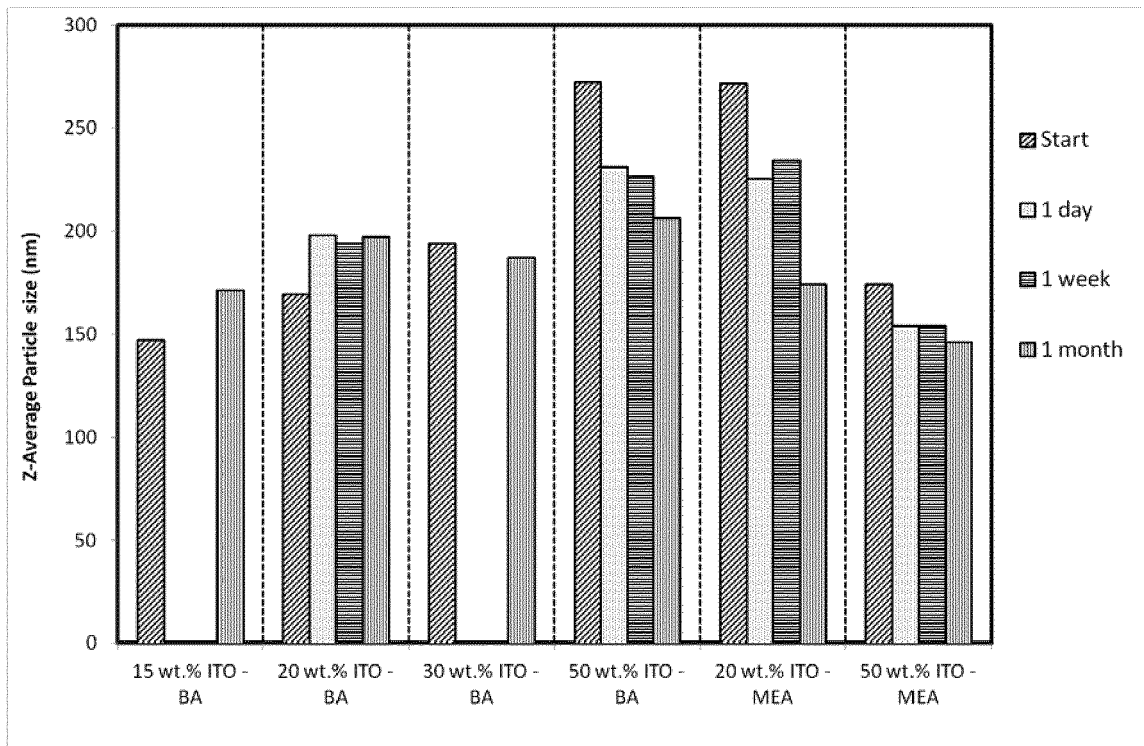


Figure 2

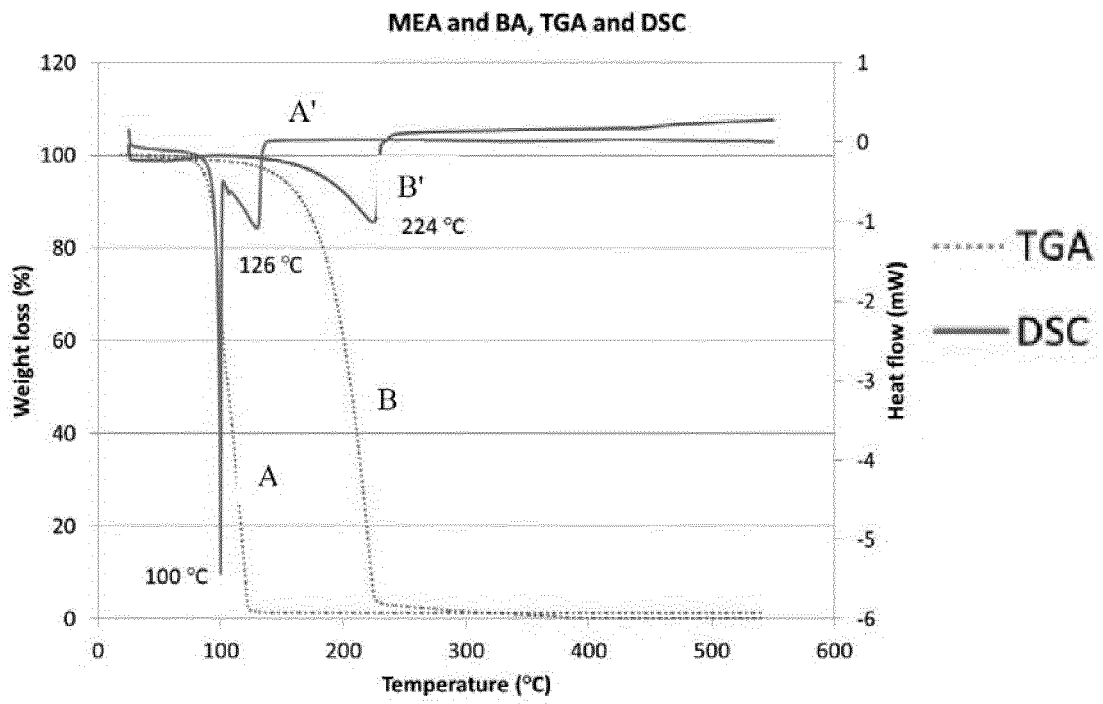


Figure 3

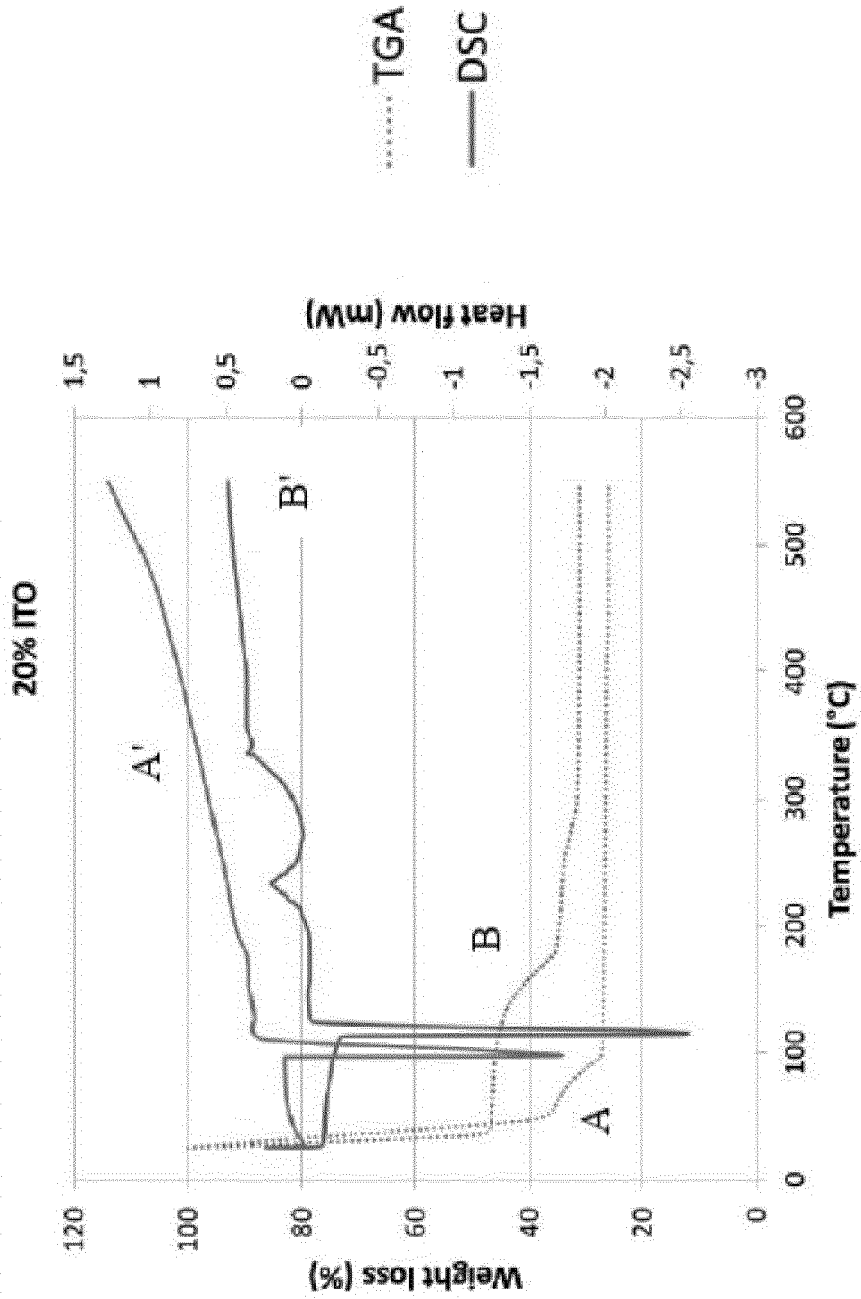
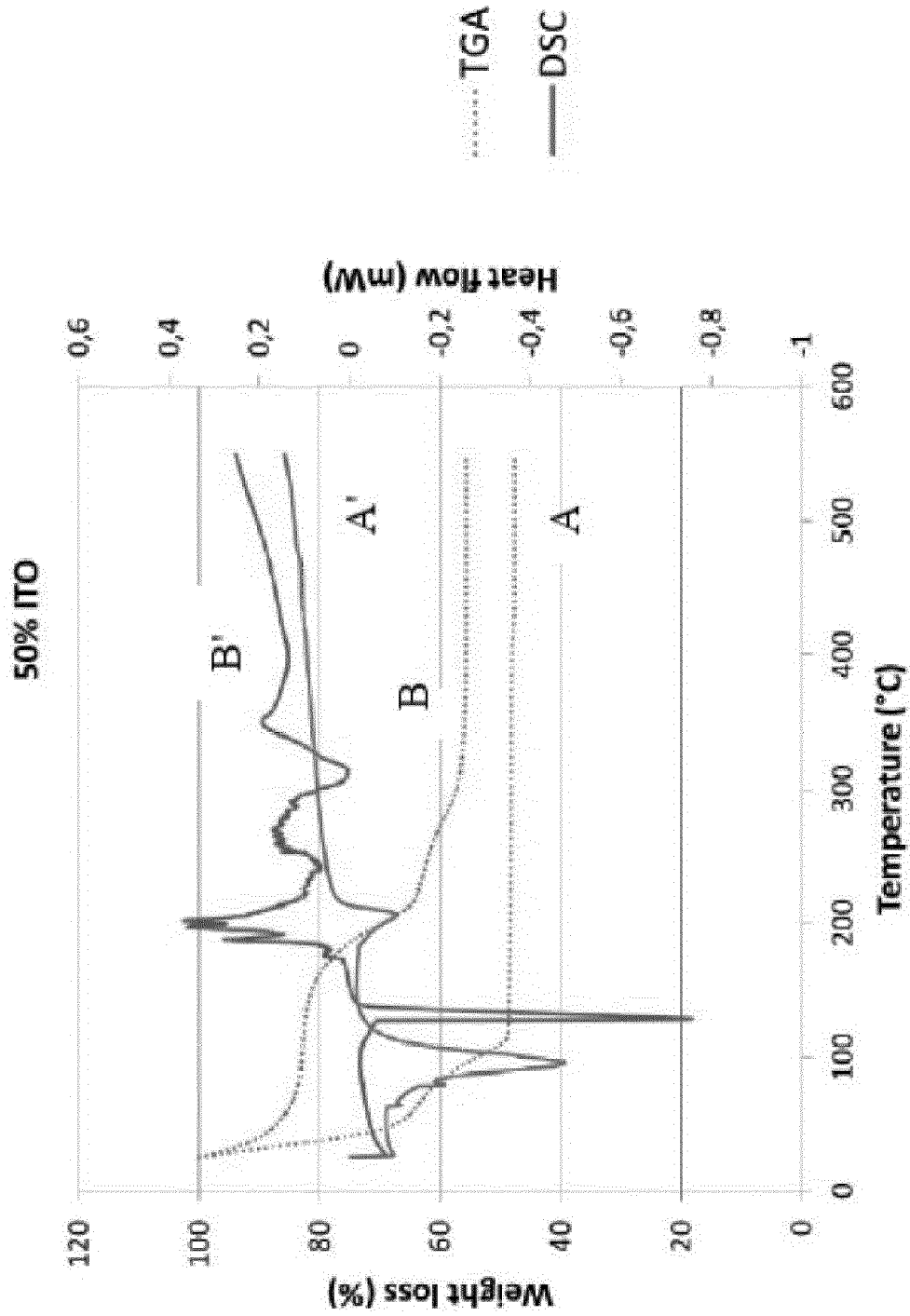


Figure 4





EUROPEAN SEARCH REPORT

Application Number
EP 15 20 2586

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	EP 0 524 630 A2 (MATSUSHITA ELECTRIC IND CO LTD [JP]) 27 January 1993 (1993-01-27) * abstract * * claims 13,15,30,34,35,40,41 * -----	1-13	INV. B22F1/00 C23C18/12 H01B1/22
X	DATABASE WPI Week 201570 Thomson Scientific, London, GB; AN 2015-598808 XP002757484, & WO 2015/146409 A1 (SUMITOMO RIKO CO LTD) 1 October 2015 (2015-10-01) * abstract *	1-9,11, 12,14,15	
X	US 2005/250861 A1 (ANDERSSON MARTIN [SE]) 10 November 2005 (2005-11-10) * abstract * * claims 13,15,30,34,35,40,41 * -----	1-5,12, 13	
A	EP 1 765 965 A1 (YKI YTKEMISKA INST AB [SE]) 28 March 2007 (2007-03-28) * the whole document * -----	1-5,12, 13	TECHNICAL FIELDS SEARCHED (IPC) B22F C23C H01B
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 May 2016	Examiner Riederer, Florian
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 15 20 2586

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0524630 A2	27-01-1993	DE 69223186 D1	02-01-1998
		DE 69223186 T2	12-03-1998
		EP 0524630 A2	27-01-1993
		US 5578248 A	26-11-1996
		US 5998011 A	07-12-1999

WO 2015146409 A1	01-10-2015	JP 5847225 B2	20-01-2016
		JP 2015187931 A	29-10-2015
		WO 2015146409 A1	01-10-2015

US 2005250861 A1	10-11-2005	NONE	

EP 1765965 A1	28-03-2007	DK 1765965 T3	24-09-2012
		EP 1765965 A1	28-03-2007
		ES 2390461 T3	13-11-2012
		PL 1765965 T3	30-11-2012
		PT 1765965 E	03-10-2012
		US 2008051471 A1	28-02-2008
		WO 2005105963 A1	10-11-2005

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 524630 A [0012]
- WO 2005105963 A [0013] [0134]
- WO 2010071641 A [0014]
- WO 2010120232 A [0155]