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(71) **Applicant**: **ENI S.P.A.** [IT/IT]; Piazzale E.mattei, 1, 00144 Roma (IT).

(72) **Inventors**: **RAMELLO, Stefano**; Via Alfieri 15/d, I - 28100 Novara (IT). **BUZZONI, Roberto**; Via Dante Alighieri, 14, I - 10034 Chivasso (TO) (IT).

(74) **Agent**: **MAURO, Marina**; Murgitroyd & company, Piazza Borromeo 12, 20123 Milano (IT).

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(54) **Title**: METHOD FOR MEASURING THE ADHESION OF COATINGS TO SUBSTRATES

(57) **Abstract**: The invention relates to a method for determining the adhesion of a coating to a substrate. In particular, the method is applicable to coatings based on metal oxides. Said method comprises: a) dipping in a liquid the surface on which the oxide is deposited, b) subjecting the liquid to stirring, c) recovering the surface on which the oxide is deposited and drying it, d) obtaining an image of the surface on which the oxide is deposited, e) measuring the percentage surface coverage of the oxide using an image analysis software that is applied to the image obtained in step (d), where said percentage corresponds to the oxide's adhesion to the surface.

Method for measuring the adhesion of coatings to substrates

Description

The present invention relates to a method for measuring the adhesion of a coating to a substrate. In particular, the method is applicable to coatings based on metal oxides.

The introduction of quality control has played a decisive role in industry worldwide, and where these systems have been introduced the quality and service life of products have been substantially increased. However, a problem which is still of major significance is that of further improving the quality control on a product or material by identifying novel measurement methods which are as simple and economical as possible.

In particular, it is of industrial interest to identify methods for evaluating the level of adhesion of coatings to substrates, since high adhesion brings about significant improvements in the performance of the composite in question. As things stand, it may be found extremely difficult to compare data obtained by different techniques, and even when a single method is considered, significant confusion and discrepancy may arise when the data are interpreted: for example in the scratch test, which is well known to the person skilled in the art and has numerous variants, for example ASTM D6677-07, ASTM D2197-10, D3359-09, it is known that the process may be affected by adhesion losses within the coating layer. Phenomena of this type are for example described in Bull, S.J., Rickerby, D.S., Matthews, A., Leyland, A., Pace, A.R., and Valli, J., Surf. Coat. Technol. 36, 1988, p. 503 and in Perry, A. J., Surf. Eng. 2, 1986, p. 183. Further, the test has to provide quantitative or semi-quantitative results, and be clearly linked to one or more properties of the composite material (Sauders, S.R. and Vetters, H.R., *Thin Solid Films,* 299, 1997, pp. 82-87).

In particular, the problem of identifying a method for measuring the adhesion of coatings to supports is of major significance in photovoltaic devices for converting energy from light radiation into electrical energy. The growing need for energy is driving research towards the study of new alternatives to the traditional sources, oil, gas, carbon and nuclear. In particular, a subject of growing importance is the conversion of solar energy into electricity by exploiting novel photovoltaic technology. Photovoltaic silicon cells are developing towards second-generation technology, such as the thin layer and radiation concentration: at any rate, these technologies are still expensive, and second-generation technologies are not sufficiently efficient at present.

The search for viable alternative technologies has led, in particular in the last decade, to the development of the so-called third-generation technology of photovoltaic cells: this definition includes both photovoltaic cells based on other semiconductors, such as metal selenides and tellurides, and in particular so-called organic photovoltaic cells such as Grätzel cells or "dye-sensitised solar cells" DSSCs, or other types or organic and/or polymer cells such as "bulk hetero junctions" BHJs. DSSCs operate by a photoelectrochemical mechanism. The absorption of light and the separation of charges (electrons and holes) take place separately.

The first step is promoted by a layer of dye, or photosensitiser, which interacts, in terms of electron transfer, with the surface of nanometre-scale particles of titanium dioxide as a semiconductor, deposited on a transparent, conductive glass. Upon absorbing the radiation, the photosensitiser generates an excited state, raising an electron from the ground state (HOMO) to the first available unoccupied orbital (LUMO), from which, if the energy levels are compatible, a charge transfer may take place to the conduction band of the titanium oxide, on the surface of which the photosensitiser is anchored via acid groups (generally carboxyl groups) present in the molecule. Subsequently, the electron migrates from the conduction band of the titanium dioxide to the electrode (conductive glass). Simultaneously, a positive charge (hole) is transferred from the photosensitiser, in the oxidised form thereof, to a mediator electrolyte, which transports the positive charge to the counter-electrode. These cells are promising because of the low cost due to the simplicity of manufacture and the high efficiency, which currently reaches approximately 11% on small, laboratory-scale cells, this percentage being based on the entire solar spectrum. Ideally, the absorption of the photosensitiser should overlap as much as possible with the solar emission spectrum; in this context, various transition metal complexes and organic dyes have been studied to rationalize the properties and behaviour thereof using advanced quantum-mechanical calculations.

More specifically, DSSCs comprise the following elements:

- the anode, formed by a transparent support coated with a thin layer of transparent conductive oxide,
- a layer or TiO_2 deposited on the anode,
- a photoactive layer, formed by a photosensitiser anchored to the TiO_2, which may be organic or organometallic,
- the cathode, which is preferably metal (platinum is most common), but may also be formed of various carbon-based materials (graphite).

The anode is a transparent support coated with a thin layer of transparent conductive oxide, it being possible for said transparent support to be rigid, in which case it is suitable to use glass or quartz, or flexible, in which case it is suitable to use composites based on plastic polymers or metal foils.

The composites based on plastic polymers may for example be polyethylene terephthalate coated with ITO (indium tin oxide) (PET/ITO) and polyethylene naphthenate coated with ITO (PEN/ITO), as described for example in Dye Sensitized Solar Cells, eds. K. Kalyanasundram, EPFL Press, distributed by CRCC Press, 2010, p. 22. The main advantages of this type of substrate are the reduced weight, the flexibility and the simple scale-up to industrial-scale print processes, such as roll-to-roll.

As regards the third type of substrate, metal foils may for example be made of titanium, aluminium or stainless steel. Metal foils have the same advantages as polymer-based substrates, aside from the transparency, and may therefore only be used on one side of the cell, whilst it is necessary for the other side to be formed of transparent material so as to allow light to enter the device. Preferably, the conductive substrate used is a conductive TOC glass (Transparent Conducting Oxide-glass), conductive glass meaning a structure in which a transparent glass substrate is coated with a likewise transparent conductive oxide. The requirements for the TCO substrate are low electrical resistance of the oxide layer and high transparency towards solar radiation in the visible-NIR range. The transparent conductive oxide may be of a thickness between 40 and 250 nm, and may for example be tin-doped indium oxide (ITO), aluminium-doped zinc oxide (AZO), gallium-doped zinc oxide (GZO), or fluorine-doped tin oxide (FTO). The preferred TCO substrate to which to apply the method of the present invention is FTO.

The methods for depositing the conductive oxide on the support are well known to the person skilled in the art and are for example described in I.A. Rauf, J. Applied Physics, Volume 79, P4057 (1996).

TiO_2 may in turn be deposited on the conductive support by various techniques, such as doctor blade coating, spray coating or screen printing.

In the above-described sector, the literature demonstrates a glaring absence of methods for measuring the adhesion of coatings to supports in the case of metal oxides deposited on transparent supports for use, in photovoltaic devices, for converting energy from light radiation into electrical energy. Although it is noted that one of the basic aspects determining the performance of the DSSC is the formulation of the paste used for depositing the nanocrystalline TiO_2 film and the resulting level of adhesion of the TiO_2 to the support after calcination, consideration is merely given to the effect of the physical features of the deposited TiO_2, such as surface area, roughness, pore size and film thickness, on the performance of the device under lighting conditions, in particular the energy conversion efficiency of the cell, but the effect of the formulation of the pastes on the level of adhesion of the TiO_2 layer to the support is not taken into account (Suresh Kumar Dhungel, Jesse G. Park, “Optimization of paste formulation for TiO_2 nanoparticles with wide range of size distribution for its application in dye sensitized solar cells", Renewable Energy, 35, 12, December 2010, 2776-2780, http://dx.doi.org/10.1016/j.renene.2010. 04.031). The same authors recognize how the properties of the layer (or series of layers) of TiO_2 are mainly controlled via the film preparation process, but do not consider the aspect of the adhesion of the TiO_2 to the support and the relevant consequences for the durability of the device. Mention is made of the various procedures conventionally used for depositing TiO_2 monolayers or double/triple/quadruple layers of TiO_2 (multilayers) from various TiO_2 precursors, as well as the various deposition techniques (U. Opara Krašovec, M. Berginc, M. Hočevar, M. Topic, "Unique TiO_2 paste for high efficiency dye-sensitized solar cells", Solar Energy Materials & Solar Cells, 93 2009, pp. 379-381). Whilst it is recognized that it is essential to identify a preparation technique which can be adopted in industrial conditions for DSSC application, once again the aspect of the adhesion of the material is not considered.

Many articles have taken into consideration the preliminary treatments of the support, which, according to the teachings in the scientific literature, is first treated with an aqueous $TiCl_4$ solution with the aim of producing a thin, compact TiO_2 layer and ensuring good mechanical contact between the successive layers of TiO_2 and the conductive substrate. Nevertheless, the nature of the layer is merely hypothesised, and the quality of the adhesion is not considered, much less measured. Therefore, it is noted that good adhesion to the support is necessary, but again only the electrical conductivity of the device is taken into consideration, and not other physical features such as adhesion of the TiO_2 layers to the substrate and the durability of the device.

Some researchers, in view of the complexity of the process for depositing multiple TiO_2 layers, have set themselves the goal of identifying new formulations for depositing the first layer of TiO_2 on the conductive support. For example, some researchers have compared the "standard" TiO_2 paste, with terpineole and methyl cellulose added, with the paste based on the so-called Pechini method (M. Hočevar, M. Berginc, U. Opara Krašovec, M. Topič, "Development of TiO_2 pastes modified with Pechini sol-gel method for high efficiency dye-sensitized solar cell", Journal of Sol-Gel Science and Technology, 48, 2008, 156-162). In a subsequent article, a further improvement in the formulation of the TiO_2 paste formed by the Pechini method is found upon changing the molar ratio between some reagents and the titanium precursor (U. Opara Krašovec, M. Berginc, M. Hočevar, M. Topič, "Unique TiO_2 paste for high efficiency dye-sensitized solar cells", Solar Energy Materials & Solar Cells, 93 2009, pp. 379-381, doi:10.1016/j.solmat.2008.11.012).

Other improvements have been proposed in which the content of the polyethylene glycol (PEG), another additive commonly used in the TiO_2 paste formulation, is varied (Chen-

Hsin Yang and Shao-Hong Liao, “Hydrothermal Processed TiO_2 Nanoparticles for Optimization in Dye-Sensitized Solar Cells Using Statistical Experimental Strategies”, ECS Transactions, 19, 32, 3-20 2009, doi: 10.1149/1.3268158). Finally, another problem has been investigated, namely the formulation of TiO_2 pastes suitable for providing homogeneous, i.e. crack-free surfaces, but again the results are stated merely on the basis of subjective visual comparison by the researcher (Sarker S., Nath NC, Rahman M.M., Lim S.S., Ahammad A.J., Choi W.Y., Lee J.J., “TiO_2 paste formulation for crack-free mesoporous nanocrystalline film of dye-sensitized solar cells”, J. Nanosci. Nanotechnol. 2012, 12, 7, 5361-6).

Whilst pursuing the same object, to formulate TiO_2 pastes suitable for providing homogeneous (crack-free) surfaces, other researchers have compared pastes produced using commercial TiO_2 powders with TiO_2 prepared via sol-gel (Sasipriya Kathirvel, Huei-Siou Chen, Chaochin Su, Hsiue-Hsyan Wang, Chung-Yen Li, and Wen-Ren Li, “Preparation of Smooth Surface TiO2 Photoanode for High Energy Conversion Efficiency in Dye-Sensitized Solar Cells”, Journal of Nanomaterials, 2013, Article ID 367510, 8 pages, http://dx.doi.org/10.1155/2013/367510).

In said article, it is observed that in general the TiO_2 films are deposited on the support using commercial TiO_2 powders, or reproductions thereof, with some exceptions: for example, S. Ito et al. studied various methods of homogenising commercial TiO_2’s, by grinding in a mortar or using a ball mill, for preparing the pastes for depositing on the substrate (S. Ito, K. Takahashi, S. I. Yusa, T. Imamura, and K. Tanimoto, “Effects of homogenization scheme of TiO_2 screen-printing paste for dye-sensitized solar cells,” International Journal of Photoenergy, 2012, Article ID 405642, 7 pages). Lee et al. studied the variations in the surface morphology of the TiO_2 film based on the percentage of polyethylene glycol (PEG) in the pastes (K.-M. Lee, V. Suryanarayanan, and K.-C. Ho, “The influence of surface morphology of TiO_2 coating on the performance of dye-sensitized solar cells,” Solar Energy Materials and Solar Cells, 90, 15, 2398–2404, 2006). In a series of experiments, Dhungel and Park studied the morphology of the TiO_2 films in the pastes (S. K. Dhungel and J. G. Park, “Optimization of paste formulation for TiO_2 nanoparticles with wide range of size distribution for its application in dye sensitized solar cells,” Renewable Energy, 35, 12, 2776–2780, 2010). Finally, Jeong et al. compared the morphology of the TiO_2 films obtained using terpineole as a film dispersant with TiO_2 films obtained from Dyesol commercial pastes (N. C. Jeong, O. K. Farha, and J. T. Hupp, “A convenient route to high area, nanoparticulate TiO_2 photoelectrodes suitable for high-efficiency energy conversion in dye-sensitized solar cells,” Langmuir, 27, 5, 1996–1999, 2011). However, although the morphological aspect and physical features of the TiO_2 film are examined more closely, none of these articles consider the aspect of the adhesion of the material to the support.

Only one recent article, Lee et al., *Langmuir*, 2008, 24, 13225, qualitatively evaluates the adhesion level, by scratching the oxide layer with the tip of a pencil. In a volume dedicated to the study of oxides deposited on FTO glasses for photovoltaic applications, *Dye Sensitized Solar Cells*, eds. K. Kalyanasundram, EPFL Press, distributed by CRCC Press, 2010, the matter is not actually addressed, and brief mention is merely made of the above-cited Kalyanasundram article. Nevertheless, the authors confirm, on p. 224, that to obtain an acceptable service life of the photovoltaic cell the stability has to be determined in four respects: the level of adhesion of the oxides to the FTO glass, and the assembly of the cell, of the module and of the complete system.

In relation to the aspects of adhesion discussed above, a simple, economical method has now been found which makes it possible to evaluate and measure the adhesion of coatings to substrates, said evaluation also being quantitative.

The present invention therefore relates to a method for determining the adhesion of an oxide deposited in a uniform layer on a surface which comprises:

a) dipping in a liquid the surface on which the oxide is deposited,
b) subjecting the liquid to stirring,
c) recovering the surface on which the oxide is deposited and drying it,
d) obtaining an image of the surface on which the oxide is deposited,
e) measuring the percentage surface coverage of the oxide using an image analysis software that is applied to the image obtained in step (d), where said percentage corresponds to the oxide’s adhesion to the surface.

It is understood that before any test the percentage surface coverage of the oxide, measured by the same procedure, is 100%.

The liquid used in the method according to the invention may, for example, be selected from water, heptane, acetonitrile, oxygenated solvents and mixtures thereof of any desired composition. Of the oxygenated solvents, alcohols, in particular ethanol, ketones, in particular acetone, ethers, in particular tetrahydrofuran, and esters, in particular ethyl acetate, may for example be employed.

It is a preferred aspect of the present invention to use water.

The stirring may be carried out by any known means suitable for bringing about mechanical action of the liquid on the surface covered by the oxide. For example, said stirring may be carried out mechanically or electromagnetically.

The stirring speed should preferably be such as not to require excessively long times, in terms of an application, to bring about the formation of surface regions not covered by the oxide: the stirring speed should thus preferably be such as not to require more than 4 hours for step (b). Further, the stirring speed should not be such as to form within the sample a cone of solvent-free space, which would make it impossible to wet the actual sample, invalidating the method. Preferably, a stirring speed between 600 and 1100 rpm is used, even more preferably between 700 and 900 rpm.

The oxide deposited on a surface, the adhesion of which can be evaluated using the method of the present invention, may be any desired metal oxide supported on a surface, and is preferably selected from titanium oxide TiO_2, zinc oxide ZnO, niobium oxide Nb_2O_5 and titanates of general formula $MTiO_3$, where M is selected from Ca, Mg and Sr.

The surface is preferably selected from glasses, composites based on plastic polymers or metal foils.

The composites based on plastic polymers may for example be polyethylene terephthalate or polyethylene naphthenate.

The metal foils may for example be made of titanium, aluminium or stainless steel.

Preferably, the method can be applied to conductive glasses, particularly TOC conductive glass (Transparent Conducting Oxide-glass), conductive glass meaning a structure in which a transparent glass substrate is covered with a conductive oxide. The requirements for the TCO substrate are low electrical resistance of the oxide layer and high transparency towards solar radiation in the visible-NIR range. The transparent conductive oxide may be of a thickness between 40 and 250 nm, and may for example be tin-doped indium oxide (ITO), aluminium-doped zinc oxide (AZO), gallium-doped zinc oxide (GZO), or fluorine-doped tin oxide (FTO). ITO or FTO surfaces are preferred for the present invention. Even more preferably, the surface used in the method of the present invention on which the metal oxide is deposited is FTO.

The analysis method of the present invention, for evaluating the adhesion, is applied to metal oxides deposited on surfaces, regardless of the method of depositing the oxide on the surface. In particular, the method may be used to determine the adhesion of an oxide deposited in a uniform layer on a surface when this deposition has been carried out by any of the methods known to the person skilled in the art. The drying may be carried out using any known method, for example leaving the sample in the air for a period varying from 12 to 24 hours, or placing it in an oven at a temperature of between 50 °C and 120 °C for periods of between 1 and 3 hours.

After drying, the oxide deposited on the surface is evaluated by obtaining an image: said image may be obtained using any software and apparatus suitable for this purpose. Said apparatuses and softwares are commercially available. The images may for example originate from microphotography or from interfaces connected to digital optical microscopy devices as well as to LM, SEM, TEM equipment. For the purposes of the present invention, a digital optical microscope is preferably used along with image acquisition software. For example, the Dino-Lite Pro microscope from AnMo Electronics Corporation may be used, and the image may be obtained for example using the software provided with said instrument, DinoCapture version 2.0 from AnMo Electronics Corporation.

Once the image has been obtained, it is analysed to evaluate the percentage surface coverage: said evaluation is carried out using image analysis technology. The analysis may be carried out using any software known to the person skilled in the art for this use. For example, it is possible to use the colour recognition capability of a software suitable for dividing the digital image into a series of pixels, each provided with the colour and size information thereof. This technique makes it possible to assess surfaces rapidly with high precision, and in particular it will be possible to calculate the left-over white area, in other words the surface covered with oxide.

Said technique is for example described in R. Lee, B. Poürdeyhímí, C. Hazzard, J. Summerville, Analysis of coatings appearance and durability testing induced surface defects using image capture/processing/analysis, *Revista de metalurgia*, Vol Extr. (2003) 206-212; or in J. Grande, Crack Characterization Using Image Analysis, Microsc Microanal 11 (Suppl 2), 2005.

Suitable softwares for this purpose are for example:

- Visilog V6-Xpert from Noesis, part of the FEI Company group,
- IMAGIN from Metkon; SmartView from Gruppo Fluke,
- Image Pro Plus from Media Cybernetics, Inc., version 7.0.

It is understood that before any test the percentage surface coverage of the oxide, measured by the same procedure, is 100%.

A level of adhesion is associated with the percentage coverage using the following table:

Adhesion level	Description
10	The surface covered after treatment is between 95% and 100% The oxide is extremely difficult to remove
8	The surface covered after treatment is between 90% and 95% The oxide is difficult to remove
6	The surface covered after treatment is between 80% and 90% The oxide is fairly difficult to remove
4	The surface covered after treatment is between 70% and 80% The oxide is not difficult to remove

2	The surface covered after treatment is between 60% and 70% The oxide is easily removed
0	The surface covered after treatment is between 50% and 60% The oxide is removed in part when barely placed in contact with the liquid

Using the method of the present invention, by comparison with the known art, it becomes possible to carry out rapid screenings of multiple samples for the purpose of identifying and eliminating those which are more unstable or brittle. The comparison has to be made between samples to which the same method has been applied while using the same conditions: liquid, stirring speed, stirring duration, apparatus and software.

In particular, since the measurement is quantitative, it is possible to establish an adhesion quality scale within a group of samples: the comparison between each of these data and the value of a corresponding feature, for example the energy yield, makes it possible to select a compromise between durability and efficiency, by thus identifying the most advantageous sample in terms of industrial implementation of the cell.

Accordingly, the invention relates in particular to a method for identifying, among a plurality of oxides deposited in uniform layers on surfaces, the one with the best characteristic of adhesion, said method comprising:

a) dipping in a liquid the surface on which the oxide is deposited,
b) subjecting the liquid to stirring,
c) recovering the surface on which the oxide is deposited and drying it,
d) obtaining an image of the surface on which the oxide is deposited,
e) measuring the percentage surface coverage of the oxide using an image analysis software that is applied to the image obtained in step (d), where said percentage corresponds to the oxide's adhesion to the surface,
f) repeating the steps a) to e) for each of the oxides deposited on a surface,
g) comparing the results obtained in step (e) for each of the oxides deposited on a surface and choosing the oxide that shows the lowest percentage of surface not covered.

The above method may be applied to a group of samples of oxides deposited on surfaces which differ in the type or surface used or in the method of applying the oxide, or else, within the same method, for evaluating the impact of varying a preparation parameter.

For the purpose of better understanding the present invention and for putting it into practice, some illustrative, non-limiting examples are given in the following.

Example 1 – Preparing paste A

A procedure analogous with that described in G.P. Smestad, Solar Energy Materials and Solar Cells, 55, 1998, 157-178 is followed. In particular, a suspension of TiO_2 is prepared by gradually adding 20 ml nitric acid HNO_3 to 12 g commercially available TiO_2 powder (P25, Degussa) in a suitable container whilst grinding using a pestle. 1 ml dilute acid solution (pH = 3-4 in deionised water) is added once the preceding adding and mixing operation has produced a homogeneous, lump-free paste in the container. The paste obtained is then spread (doctor blade technique) on a conductive FTO glass (Hartford Glass Co., TEC 8, with a thickness of 2.3 mm and a resistance of 6-9 Ω/cm^2), previously washed using water and ethanol. The glass was cut to dimensions of 5 × 7 cm. A voltmeter is used to check which side of the glass is conductive. Four pieces of adhesive tape (Scotch, 3M) are applied to the face of the conductive glass sheet to mask a 5 mm strip on three of the four edges, and a 25 mm strip is masked on the fourth side, the upper side. The tape forms a 40-50 μm mould in which part of the TiO_2 suspension is deposited: three drops of the TiO_2 paste are distributed on the free surface of the support, then a glass rod is slid over the glass to spread and distribute the material (doctor blade technique). The TiO_2 film is subsequently left to dry in air for 1 min. The tape is subsequently carefully removed, and the glass with TiO_2 is first placed in an oven and dried for 30 min at 120 °C, and then calcined in a furnace at 450 °C for a further 60 min. At the end, the glass slide is kept in air for the test.

Example 2 – Preparing paste B

A procedure analogous with that described in A. Kay, M. Graetzel, J. Phys. Chem., 97, 1993, 627 is followed.

In particular, a TiO_2 suspension is prepared as follows: a solution of 0.2 ml acetyl acetone and 1 ml water is added to 12 g commercially TiO_2 powder (P25, Degussa) in a suitable container whilst grinding using a pestle. A further 19 ml water are then added, in increments of 1 ml, whilst continuing to mix in the container. 1 ml aqueous acetyl acetone solution is added once the preceding adding and mixing operation has produced a homogeneous, lump-free paste in the container.

The paste obtained is then spread (doctor blade technique) on a conductive FTO glass (Hartford Glass Co., TEC 8, with a thickness of 2.3 mm and a resistance of 6-9 Ω/cm^2), previously washed using water and ethanol. The glass was cut to dimensions of 5 × 7 cm. A voltmeter is used to check which side of the glass is conductive. Four pieces of adhesive tape (Scotch, 3M) are applied to the face of the conductive glass sheet to mask a 5 mm strip on three of the four edges, and a 25 mm strip is masked on the fourth side, the upper side. The tape forms a 40-50 μm mould in which part of the TiO_2 suspension is deposited. More specifically, three drops of the TiO_2 paste are distributed on the free surface of the support, then a glass rod is slid over the glass to spread and distribute the material (doctor blade technique). The TiO_2 film is subsequently left to dry in the air for 1 min. The tape is subsequently carefully removed, and the glass with TiO_2 is first placed in an oven and dried for 30 min at 120 °C, and then calcined in a furnace at 450 °C for a further 60 min. At the end, the glass slide is kept in air for the test.

Example 3 – Preparing paste C

A procedure analogous with that described in S. Lunphut and S. Santhaveesuk, Journal of Material Science and Applied Energy, 2, 1, 2013, 22-24 is followed. In particular, a suspension of TiO_2 is prepared by gradually adding 20 ml nitric acid HNO_3 to 12 g commercially available TiO_2 powder (P25, Degussa) in a suitable container whilst grinding using a pestle. 1 ml dilute acid solution (pH = 3-4 in deionised water) is added once the preceding adding and mixing operation has produced a homogeneous, lump-free paste in the container. Finally, 3 drops of Triton X-100 surfactant are added.

The paste obtained is then spread (doctor blade technique) on a conductive FTO glass (Hartford Glass Co., TEC 8, with a thickness of 2.3 mm and a resistance of 6-9 Ω/cm^2), previously washed using water and ethanol. The glass was cut to dimensions of 5 × 7 cm. A voltmeter is used to check which side of the glass is conductive. Four pieces of adhesive tape (Scotch, 3M) are applied to the face of the conductive glass sheet to mask a 5 mm strip on three of the four edges, and a 25 mm strip is masked on the fourth side, the upper side. The tape forms a 40-50 µm mould in which part of the TiO_2 suspension is deposited. More specifically, three drops of the TiO_2 paste are distributed on the free surface of the support, then a glass rod is slid over the glass to spread and distribute the material (doctor blade technique). The TiO_2 film is subsequently left to dry in air for 1 min. The tape is subsequently carefully removed, and the glass with TiO_2 is first placed in an oven and dried for 30 min at 120 °C, and then calcined in a furnace at 450 °C for a further 60 min. At the end, the glass slide is kept in air for the test.

Example 4 – Preparation of paste D

A procedure analogous with that described in D.S. Tsoukleris, T. Maggos, C. Vassilakos, P. Falaras, Catalysis Today, 129, 2007, 96–101 is followed. In particular, a suspension of TiO_2 is prepared as follows: a 10% acetyl acetone solution (2.3 ml) is added to 0.5 g commercially available TiO_2 powder (P25, Degussa) in a suitable container whilst grinding using a pestle. A further 1.5 ml water and 3 drops of Triton X-100 surfactant are added, whist continuing to mix in the container for a total of 60 min, until a homogeneous, lump-free paste is obtained.

The paste obtained is then spread (doctor blade technique) on a conductive FTO glass (Hartford Glass Co., TEC 8, with a thickness of 2.3 mm and a resistance of 6-9 Ω/cm^2), previously washed using water and ethanol. The glass was cut to dimensions of 5 × 7 cm. A voltmeter is used to check which side of the glass is conductive. Four pieces of adhesive tape (Scotch, 3M) are applied to the face of the conductive glass sheet to mask a 5 mm strip on three of the four edges, and a 25 mm strip is masked on the fourth side, the upper side. The tape forms a 40-50 μm mould in which part of the TiO_2 suspension is deposited. More specifically, three drops of the TiO_2 paste are distributed on the free surface of the support, then a glass rod is slid over the glass to spread and distribute the material (doctor blade technique). The TiO_2 film is subsequently left to dry in air for 1 min. The tape is subsequently carefully removed, and the glass with TiO_2 is first placed in an oven and dried for 30 min at 120 °C, and then calcined in a furnace at 450 °C for a further 60 min. At the end, the glass slide is kept in air for the test.

Example 5 – Preparation of paste E

A procedure based on that described in D.S. Tsoukleris, T. Maggos, C. Vassilakos, P. Falaras, Catalysis Today, 129, 2007, 96–101 is followed. A suspension of TiO_2 is prepared as follows: 5 g commercially available TiO_2 (P25, Degussa), 5 g ethyl cellulose (Aldrich) and 15 g α-terpineole (Aldrich) are introduced into a suitable container. Mixing is carried out in the container until a homogeneous, lump-free paste is obtained.

The paste obtained is then spread (doctor blade technique) on a conductive FTO glass (Hartford Glass Co., TEC 8, with a thickness of 2.3 mm and a resistance of 6-9 Ω/cm^2), previously washed using water and ethanol. The glass was cut to dimensions of 5 × 7 cm. A voltmeter is used to check which side of the glass is conductive. Four pieces of adhesive tape (Scotch, 3M) are applied to the face of the conductive glass sheet to mask a 5 mm strip on three of the four edges, and a 25 mm strip is masked on the fourth side, the upper side. The tape forms a 40-50 μm mould in which part of the TiO_2 suspension is deposited. More specifically, three drops of the TiO_2 paste are distributed on the free surface of the support, then a glass rod is slid over the glass to spread and distribute the material (doctor blade technique). The TiO_2 film is subsequently left to dry in air for 1 min. The tape is subsequently carefully removed, and the glass with TiO_2 is first placed in an oven and dried for 30 min at 120 °C, and then calcined in a furnace at 450 °C for a further 60 min. At the end, the glass slide is kept in air for the test.

Example 6 – Preparation of paste F

A procedure based on that described in Ito, S., Chen, P., Comte, P., Nazeeruddin, M. K., Liska, P., Péchy, P. and Grtzel, M. (2007), Fabrication of screen-printing pastes from TiO_2 powders for dye-sensitised solar cells. Prog. Photovolt: Res. Appl., 15: 603–612. doi: 10.1002/pip.768 is followed.

A suspension of TiO_2 is prepared as follows: 6 g commercially available TiO_2 (P25, Degussa) and 1 ml acetic acid are introduced into a suitable container. This is followed by five additions of 1 ml H_2O and six additions of 2.5 ml ethanol. After each addition, stirring is carried out in the container until a homogeneous, lump-free paste is obtained (approximately 5 min). The paste is transferred into a beaked with 100 ml ethanol. The suspension is kept under agitation using a magnetic stirrer. A series of 30 sonications are carried out (Vibra cell 72408, Bioblock scientific), each of 2 seconds followed by 2 seconds of rest. 20 g a-terpineole are added, then the above-described sonication procedure is repeated. Finally, 30 g 10% w/w aqueous methyl cellulose solution are added, and then the above-described sonication procedure is repeated. The suspension is transferred into a rotary evaporator and the ethanol is removed by evaporation. The paste obtained is then spread (doctor blade technique) on a conductive FTO glass (Hartford Glass Co., TEC 8, with a thickness of 2.3 mm and a resistance of 6-9 Ω/cm^2), previously washed using water and ethanol. The glass was cut to dimensions of 5 × 7 cm. A voltmeter is used to check which side of the glass is conductive. Four pieces of adhesive tape (Scotch, 3M) are applied to the face of the conductive glass sheet to mask a 5 mm strip on three of the four edges, and a 25 mm strip is masked on the fourth side, the upper side. The tape forms a 40-50 μm mould in which part of the TiO_2 suspension is deposited. More specifically, three drops of the TiO_2 paste are distributed on the free surface of the support, then a glass rod is slid over the glass to spread and distribute the material (doctor blade technique). The TiO_2 film is subsequently left to dry in air for 1 min. The tape is subsequently carefully removed, and the glass with TiO_2 is first placed in an oven and dried for 30 min at 120 °C, and then calcined in a furnace at 450 °C for a further 60 min. At the end, the glass slide is kept in air for the test.

Example 7 – Test

A slide prepared as described in Example 1 is dipped in water and subjected to stirring (850 rpm) for 15 minutes. The slide is recovered and left to dry in air for 15 hours. The surface on which the oxide is deposited is photographed using the Dino-Lite Pro microscope from AnMo Electronics Corporation with DinoCapture version 2.0 software from AnMo Electronics Corporation. Then, the image is processed and analysed using Image Pro Plus software from Media Cybernetics, Inc., version 7.0, to measure the percentage of surface still covered with oxide. The following result is obtained:

Surface covered: 85%

Adhesion level: 6

Example 8 – Test

A slide prepared as described in Example 2 is dipped in water and subjected to stirring (850 rpm) for 15 minutes. The slide is recovered and left to dry in air for 15 hours. The surface on which the oxide is deposited is photographed using the Dino-Lite Pro microscope from AnMo Electronics Corporation with DinoCapture version 2.0 software from AnMo Electronics Corporation. Then, the image is processed and analysed using Image Pro Plus software from Media Cybernetics, Inc., version 7.0, to measure the percentage of surface still covered with oxide. The following result is obtained:

Surface covered: 81%

Adhesion level: 6

Example 9 – Test

A slide prepared as described in Example 3 is dipped in water and subjected to stirring (850 rpm) for 15 minutes. The slide is recovered and left to dry in air for 15 hours. The surface on which the oxide is deposited is photographed using the Dino-Lite Pro microscope from AnMo Electronics Corporation with DinoCapture version 2.0 software from AnMo Electronics Corporation. Then, the image is processed and analysed using Image Pro Plus software from Media Cybernetics, Inc., version 7.0, to measure the percentage of surface still covered with oxide. The following result is obtained:

Surface covered (%): 98

Adhesion level: 10

Example 10 – Test

A slide prepared as described in Example 4 is dipped in water and subjected to stirring (850 rpm) for 15 minutes. The slide is recovered and left to dry in air for 15 h. The surface on which the oxide is deposited is photographed using the Dino-Lite Pro microscope from AnMo Electronics Corporation with DinoCapture version 2.0 software from AnMo Electronics Corporation. Then, the image is processed and analysed using Image Pro Plus software from Media Cybernetics, Inc., version 7.0, to measure the percentage of surface still covered with oxide. The following result is obtained:

Surface covered (%): 94

Adhesion level: 8

Example 11 – Test

A slide prepared as described in Example 5 is dipped in water and subjected to stirring (850 rpm) for 15 minutes. The slide is recovered and left to dry in air for 15 h. The surface on which the oxide is deposited is photographed using the Dino-Lite Pro microscope from AnMo Electronics Corporation with DinoCapture version 2.0 software from AnMo Electronics Corporation. Then, the image is processed and analysed using Image Pro Plus software from Media Cybernetics, Inc., version 7.0, to measure the percentage of surface still covered with oxide.

The following result is obtained:

Surface covered (%): 100

Adhesion level: 10

Example 12 – Test

A slide prepared as described in Example 6 is dipped in water and subjected to stirring (850 rpm) for 15 minutes. The slide is recovered and left to dry in air for 15 h. The surface on which the oxide is deposited is photographed using the Dino-Lite Pro microscope from AnMo Electronics Corporation with DinoCapture version 2.0 software from AnMo Electronics Corporation. Then, the image is processed and analysed using Image Pro Plus software from Media Cybernetics, Inc., version 7.0, to measure the percentage of surface still covered with oxide.

The following result is obtained:

Surface covered (%): 87

Adhesion level: 6

Example 13 – Test

Example 7 is repeated using a stirring time of 4 hours. The following result is obtained:

Surface covered (%): 71

Adhesion level: 4

Example 14 – Test

Example 8 is repeated using a stirring time of 4 hours. The following result is obtained:

Surface covered (%): 71

Adhesion level: 4

Example 15 – Test

Example 9 is repeated using a stirring time of 4 hours. The following result is obtained:

Surface covered (%): 87

Adhesion level: 6

Example 16 – Test

Example 10 is repeated using a stirring time of 4 hours. The following result is obtained:

Surface covered (%): 76

Adhesion level: 4

Example 17 – Test

Example 11 is repeated using a stirring time of 4 hours. The following result is obtained:

Surface covered (%): 96

Adhesion level: 10

Claims

1. Method for determining the adhesion of an oxide deposited in a uniform layer on a surface which comprises:
    a) dipping in a liquid the surface on which the oxide is deposited,
    b) subjecting the liquid to stirring,
    c) recovering the surface on which the oxide is deposited and drying it,
    d) obtaining an image of the surface on which the oxide is deposited,
    e) measuring the percentage surface coverage of the oxide using an image analysis software that is applied to the image obtained in step (d), where said percentage corresponds to the oxide's adhesion to the surface.
2. The method in accordance with claim 1 wherein the metal oxide is selected from TiO_2, ZnO, Nb_2O_5 and $MTiO_3$, where M is selected from Ca, Mg and Sr.
3. The method in accordance with claim 1 wherein the surface on which the oxide is deposited is selected from glass, composites containing plastic polymers and metal foils.
4. The method in accordance with claim 3 wherein the glass is coated with a conductive oxide.
5. The method in accordance with claim 1 wherein the liquid is selected from water, heptane, acetonitrile, oxygenated solvents and mixtures thereof.
6. The method in accordance with claim 1 wherein the stirring speed is between 600 and 1100 rpm.
7. The method in accordance with claim 6 wherein the stirring speed is between 700 and 900 rpm.
8. The method in accordance with claim 1 wherein the image is obtained using an electronic microscope with image acquisition software.
9. The method in accordance with claim 1 wherein, in step (e), the measurement of the surface not covered with oxide is identified by an image analysis software.
10. Method in accordance with one or more of the preceding claims for identifying, among a plurality of oxides deposited in a uniform layer on surfaces, the one with the best characteristic of adhesion, wherein said method comprises:
    a) dipping in a liquid the surface on which the oxide is deposited,
    b) subjecting the liquid to stirring,
    c) recovering the surface on which the oxide is deposited and drying it,
    d) obtaining an image of the surface on which the oxide is deposited,
    e) measuring the percentage surface coverage of the oxide using an image

analysis software that is applied to the image obtained in step (d), where said percentage corresponds to the oxide's adhesion to the surface,

f) repeating the steps a) to e) for each of the oxides deposited on a surface,

g) comparing the results obtained in step (e) for each of the oxides deposited on a surface and choosing the oxide that shows the lowest percentage of surface not covered.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/065420

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N19/04
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)
G01N H01G H01L

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FAKHOURI H ET AL: "Highly efficient photocatalytic TiOcoatings deposited by open air atmospheric pressure plasma jet with aerosolized TTIP precursor", JOURNAL OF PHYSICS D: APPLIED PHYSICS, INSTITUTE OF PHYSICS PUBLISHING LTD, GB, vol. 47, no. 26, 5 June 2014 (2014-06-05), page 265301, XP020266388, ISSN: 0022-3727, DOI: 10.1088/0022-3727/47/26/265301 [retrieved on 2014-06-05] the whole document ----- -/--	1-10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"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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Date of the actual completion of the international search	Date of mailing of the international search report
29 July 2015	07/08/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zwerger, Markus

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/065420

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/065420

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