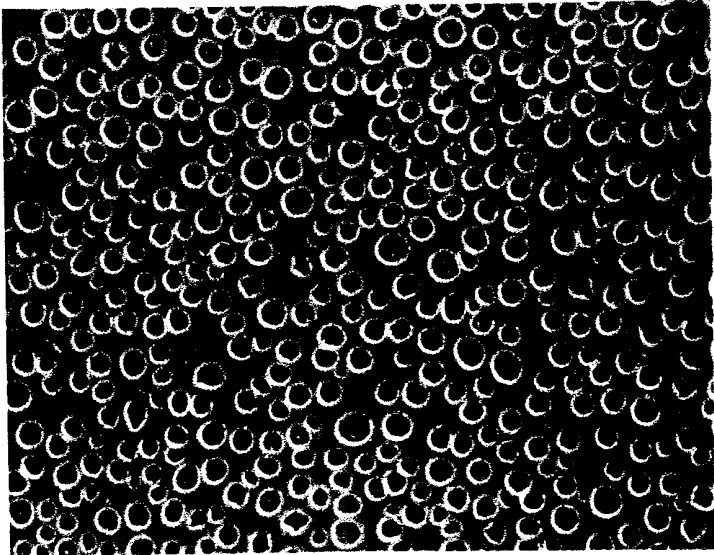


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(54) Title: TITANIUM OXIDE LAYER  (57) Abstract Porous titanium oxide layer and method of making same. The layer can be used in photochemical cells.		

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TITANIUM OXIDE LAYER

Field of the Invention

5 The present invention relates to titanium oxide layer. The present invention also relates to the use of titanium oxide in photochemical cells and components thereof.

Background of the Invention

10 There is significant interest in protecting the environment (e.g., preventing global warming caused by carbon dioxide). There is also interest in better utilization of non-fossil energy sources (e.g., sunlight). Some current methods for converting sunlight into electrical energy include the use of so-called silicone solar cell devices.

15 Nature, Vol. 353, pp. 737-40, 1991, reports a photochemical cell that includes an optically transparent film of titanium oxide particles made from colloidal sol. The cell is said to exhibit commercially realistic energy-conversion efficiency.

20 Methods of making titanium oxide film are also reported, for example, in, Chem. Matter by V. Shklover et al., Vol. 9, pp. 430-39, 1997 and Japanese Unexamined Patent Publication (Kokai) No. 8-99041, published April 16, 1996. Such methods include preparing a sol containing fine particles of titanium oxide formed by hydrolysis of a titanium alkoxide (e.g., titanium isopropoxide). The sol was then heated and calcined at a temperature of 600-700°C. It is also known, for example, that titanium oxide film can be made from a paste of ultra-fine titanium oxide fine particles suspended in liquid medium.

25 Referring again to Kokai No. 8-99041, such publication reports a titanium oxide film used as a photocatalyst wherein the titanium oxide film was prepared from a sol formed by hydrolysis of a titanium alkoxide together with polyethylene glycol. The sol was calcined at a temperature of 600-700°C to provide a porous titanium oxide film. Further, it is reported that the pore size and density can be adjusted based on the molecular weight and amount of the polyethylene glycol used. It is also reported that a transparent sol of titanium oxide can be obtained by adding a hydrolysis inhibitor (e.g., alcoholamines, glycols, amides, or diketones) during hydrolysis of the titanium alkoxide.

30

The preparation of titanium oxide layers from sols typically involves complicated steps, wherein if a low yield is obtained with any one step, the effect is to reduce the amount of material available for the next step, and hence to reduce the yield for the overall process. For example, in preparing a titanium oxide paste, the titanium oxide particles are dispersed in a solvent as uniformly as possible while grinding agglomerated titanium oxide fine particles. With regard to the method involving hydrolyzing a titanium alkoxide to form fine titanium oxide particles, the calcining step is controlled to grow the desired (fine) particles size.

When a porous titanium oxide film is used as a constituent element of a photochemical cell, the porous titanium oxide film is generally supported by a substrate of glass and electrically connected to a transparent electrode member of ITO (indium tin oxide) or SnO_2 (tin oxide). If the porous titanium oxide film is prepared by heating and calcining a sol, such as described in Kokai 8-99041, the substrate and/or electrode member may be adversely affected (e.g., the substrate or member may deform or change in chemical composition).

Summary of the Invention

The present invention provides a method of producing a titanium oxide layer, comprising:

- coating a solution prepared by combining
 - at least one titanium alkoxide,
 - solvent,
 - at least one polyether having a number average molecular weight of about 2,000 to about 20,000, and
 - at least one reaction inhibitor for inhibiting hydrolysis of the titanium alkoxide, wherein the at least one reaction inhibitor is selected from the group consisting of alcoholamines, glycols, amides, diketones, and combinations thereof,
- onto a surface of a substrate; and
- calcining the coated solution at a temperature ranging from about 450°C up to 600°C

to provide a porous (i.e., has an interconnected pore structure with an average pore diameter preferably in the range from about 10 nm to about 400 nm; more preferably, in the range from about 60 nm to about 200 nm; most preferably, about 60 nm) titanium oxide layer that includes titanium oxide having an anatase crystalline structure.

5 In another aspect, the present invention provides a porous titanium oxide layer formed upon calcination a titanium oxide precursor material at a temperature titanium oxide, wherein the porous titanium oxide layer includes titanium oxide having an anatase crystalline structure, wherein the average pore size (and typically the pore size distribution) can be controlled, and wherein the titanium oxide precursor material is derived from a
10 solution prepared by combining

at least one titanium alkoxide,
solvent,

at least one polyether having a number average molecular weight of about
2,000 to about 20,000, and

15 at least one reaction inhibitor for inhibiting hydrolysis of the titanium alkoxide, wherein the at least one reaction inhibitor is selected from the group consisting of alcoholamines, glycols, amides, diketones, and combinations thereof.

In yet another aspect, the present invention provides an article including a
20 porous titanium oxide layer, the article comprising a substrate having at least one surface and a porous titanium oxide layer thereon, wherein the porous titanium oxide layer includes titanium oxide having an anatase crystalline structure and wherein the porous titanium oxide layer is formed by calcining a titanium oxide precursor material at a temperature ranging from about 450°C up to 600°C to provide the porous titanium oxide layer, the
25 titanium oxide precursor material being derived from a solution prepared by combining

at least one titanium alkoxide,
solvent,

at least one polyether having a number average molecular weight of about
2,000 to about 20,000, and

30 at least one reaction inhibitor for inhibiting hydrolysis of the titanium alkoxide, wherein the at least one reaction inhibitor is selected from

the group consisting of alcoholamines, glycols, amides, diketones, and combinations thereof.

In yet another aspect, the present invention provides a photochemical cell comprising a plurality of constitutional element, wherein at least one of the constitutional elements includes a porous titanium oxide layer thereon, wherein the porous titanium oxide layer includes titanium oxide having an anatase crystalline structure, and wherein the porous titanium oxide layer is formed by calcining a titanium oxide precursor material at a temperature ranging from about 450°C up to 600°C to provide the porous titanium oxide layer, the titanium oxide precursor material being derived from a solution prepared by combining

at least one titanium alkoxide,
solvent,

at least one polyether having a number average molecular weight of about 2,000 to about 20,000, and

at least one reaction inhibitor for inhibiting hydrolysis of the titanium alkoxide, wherein the at least one reaction inhibitor is selected from the group consisting of alcoholamines, glycols, amides, diketones, and combinations thereof.

The porous structure of the titanium oxide layer according to the present invention is capable of being made at a relatively low temperature (i.e., below 600°C), and with good product yields as compared, for example, to conventional process that include heat treatment above 600°C. Although not wanting to be bound by theory, it is believed that the use of the polyether makes it possible to make the titanium oxide layer with a calcining temperature that is below 600°C.

One preferred use of titanium oxide layer according to the present invention is a cathode electrode in an electrochemical solar cell. An important aspect for the preferred operation of such a cell is the amount of sensitizing dye that can be incorporated into the titanium oxide layer. Titanium oxide layers according to the present invention offer a number of advantages over titanium oxide layers prepared conventional sol-gel or colloidal methods. The porous structures of the latter titanium oxide layers tend to be relatively dense. Typically, it is more difficult for the sensitizing dye to penetrate into a

dense porous structure than it is to penetrate into a porous structure that is less dense. Hence, the dye-sensitizer tends to be absorbed near the surface of the titanium oxide layer, but does not tend to be significantly absorbed deeper into the layer. By contrast, the porous structures of the titanium oxide layers according to the present invention are less
5 dense and have larger pore sizes. Increasing the amount of sensitizing dye incorporated into the titanium oxide layer is desired because it tends to lead to an increase in the amount of photoelectric current.

Preferably, and typically, the pore structure of titanium oxide layers according to the present invention are such openings at one major surface of the layer
10 extend to the opposed major surface. In another aspect, multi-layers of titanium oxide layer according to the present invention may be used to increase the amount of photo-sensitizer available in an electrochemical solar cell application.

Brief Description of the Drawing

15 FIG. 1 is an electron photomicrograph showing a porous structure of a titanium oxide layer made by a method according to the present invention.

FIG. 2 is a graph showing a relationship between the amount (in grams) of polyethylene glycol and the volume fraction (%) of pores in the TiO_2 layer.

20 FIG. 3 is a graph showing a relationship between the molecular weight of polyethylene glycol and the diameter (in nanometers) of pores in the TiO_2 layer.

Detailed Description

A titanium alkoxide solution is typically prepared by adding titanium alkoxide to a solvent (i.e., a solvent to the titanium alkoxide) such as alcohol (e.g.,
25 methanol, isopropyl alcohol, etc.). Preferred titanium alkoxides include titanium tetraisopropoxide, titanium tetrabutoxide, and titanium tetraethoxide. Suitable titanium alkoxide, such as titanium tetraisopropoxide, are commercially available, for example, from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Although the titanium alkoxide content can vary, for example, according to the desired results, the titanium alkoxide
30 content is preferably about 5-20% by weight, based on the total weight of the solution.

Suitable polyethers for carrying out the present invention include polyethylene glycol and polypropylene glycol. Suitable polyethers are commercially available, for example, from Wako Pure Chemical Industries, Ltd. Preferably, the alcohol solution contains about 0.1-2% by weight polyethers, based on the total weight of the solution.

Suitable reaction inhibitors for carrying out the present invention include alcoholamines (e.g., monoethanolamine, diethanolamine, and triethanolamine), amides (e.g., formamide, dimethylamide, and acetylamine), diketones (e.g., acetylacetone), and glycols (e.g., ethylene glycol and diethylene glycol). Suitable reaction inhibitors are commercially available, for example, from Wako Pure Chemical Industries, Ltd. The desired amount of reaction inhibitor is typically dependent on the amount of the titanium alkoxide, the degree of hydrolysis of the titanium alkoxide, and effectiveness of the reaction inhibitors in inhibiting hydrolysis. Typically it is preferable to have a 1:1 molar ratio of reaction inhibitor to titanium alkoxide.

The substrate onto to which titanium oxide layer according to the present invention is applied (e.g., coated) is selected based on the desired use of the resulting article or device, as well as on its capability with the process and materials used to make the layer. Suitable substrate materials typically include alumina, diamond, graphite, titanium nitride, silicon carbide, aluminum nitride, and glass. A preferred substrate material for some applications are those made of soda-lime glass, wherein the glass preferably has a softening below 600°C, but does not exhibit substantial deformation until heated to a temperature above 630°C.

The titanium alkoxide solution can be applied to a substrate using conventional techniques such as spin coating, dip coating, or spraying. The (wet) thickness of the coated solution is typically about 0.05-10 micrometer.

If titanium oxide layer according to the present invention is to be used as a constituent element of an electrode of a photochemical cell, a transparent electrode member of indium tin oxide (ITO) or tin oxide (SnO_2) is preferably disposed between a transparent substrate (e.g., a glass substrate) and the titanium oxide layer.

The coated solution (and substrate) is heated and calcined (e.g., in an oven) at a temperature(s) of about 450°C or more, but less than 600°C (i.e., the temperature

range is from 450°C, up to 600°C), preferably a temperature(s) in the range from range from about 450°C to about 500°C. The resulting titanium oxide layer is porous. Preferably, titanium oxide layer according to the present invention includes pores in the range from about 10-400 nanometers. Pores less than about 10 nanometers tend to make it difficult for a sensitizing dye or electrolyte to penetrate very deeply into the layer. Pores greater than about 400 nanometers tend to lead to an undesirably low surface area for the titanium oxide material. In another aspect, the titanium oxide layer according to the present invention preferably has a density of 10-80% of theoretical density.

The present invention allows porous titanium oxide layers to be formed on substrates at relatively low temperatures, and thus tends to reduce thermal degradation and warpage of the substrate, as well as to other components (e.g., electrode elements) that may be present.

Titanium oxide layers according to the present invention typically exhibit good weather resistance and durability, as well as nontoxicity. Titanium oxide layers according to the present invention are useful for example, in making the electrode of the photochemical cell, as a photocatalyst, or as a coating material. In addition, ground titanium oxide (i.e., in powder form) according to the present invention may be useful in cosmetic applications and in tooth paste.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

Examples

Example 1

Example 1 was prepared by adding 15 grams of titanium tetraisopropoxide (obtained from Wako Pure Chemical Industries, Ltd. Of Osaka, Japan) to 100 ml of ethanol, while stirring the ethanol, followed by the addition of 5 grams of triethanolamine (a reaction inhibitor; obtained from Wako Pure Chemical Industries, Ltd.), and 0.5 gram of polyethylene glycol.

The resulting solution was coated onto a soda-glass substrate having an indium tin oxide (ITO) coating thereon (obtained from Nippon Plate Glass Co. of Japan under the trade designation "ITO SUBSTRATE") using a conventional spin coating technique to provide a layer having a coating thickness of 0.08 micrometer. The layer-coated substrate was placed in an oven, heated to 450°C, and calcined at that temperature for 60 minutes to provide a titanium oxide layer on the substrate.

Examples 2 and 3 were prepared as described for Example 1 except the amount of polyethylene glycol added was 0.75 gram and 1 gram, respectively.

The resulting (calcined) layer for Example 2 was examined using scanning electron microscopy (SEM). Referring to FIG. 1, pores are evident in the titanium oxide layer. The size of the pores was measured by using an interatomic force microscope (AFM), and determined to be have an average pore diameter of about 60 nanometers. Further, the size of the titanium oxide particles in the layer was determined to have an average particle diameter of about 30 nanometers. The size of the pores in the Example 1 and 3 (calcined) layers were about the same as those for the Example 2 (calcined) layer. Further, the volume fraction of pores for each of Examples 1, 2, and 3 was also determined by using the interatomic force microscope.

Referring to FIG. 2, the occupation ratio for each of these examples is plotted as a function of the amount of polyethylene glycol used to prepare the ethanol-based solutions. These results indicate that the number of pores, per unit volume, formed in the (calcined) titanium oxide layer can be controlled or adjusted based upon the relative amount of polyethylene glycol used to make the ethanol-based solution. Further, these examples show that a suitable calcining temperature for this process can be at least as low as 450°C.

Examples 4-6

Examples 4, 5, and 6 were prepared as described for Example 1 except the number average molecular weight of the polyethylene glycol was 2000, 7500, and 20000, respectively (obtained from Wako Pure Chemical Industries, Ltd. under the trade designation "POLYETHYLENE GLYCOL 2000", "POLYETHYLENE GLYCOL 6000", and "POLYETHYLENE GLYCOL 20000", respectively).

The surfaces of the resulting titanium oxide layers were examined as described for Example 2. The average pore diameter for Example 4 was the same as that for Example 1. Referring to FIG. 3, the average pore diameter for each of Examples 4, 5, and 6 are plotted as the molecular weight of the respective polyethylene glycol used to make the (calcined) layer. The average pore size increased as the molecular weight of polyethylene glycol increased.

Comparative Example

A Comparative Example was prepared as described for Example 1 except that no polyethylene glycol was used. The surface of the resulting titanium oxide layer was examined as described for Example 2. The average pore diameter was lower than the resolution capability of the AFM (i.e., less than 10 nanometers).

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What is claimed is:

1. A method of producing a titanium oxide layer, comprising:
coating a solution prepared by combining
5 at least one titanium alkoxide,
solvent,
at least one polyether having a number average molecular weight of
about 2,000 to about 20,000, and
at least one reaction inhibitor for inhibiting hydrolysis of said
10 titanium alkoxide, wherein said at least one reaction
inhibitor is selected from the group consisting of
alcoholamines, glycols, amides, diketones, and combinations
thereof,
onto a surface of a substrate; and
15 calcining the coated solution at a temperature ranging from about 450°C up
to 600°C to provide a porous titanium oxide layer that includes titanium oxide having an
anatase crystalline structure.
2. The method according to claim 1 wherein pores in said titanium
20 oxide layer have an average diameter in the range from about 10 nm to about 400 nm.
3. The method according to claim 2 wherein the calcining temperature
is in the range from about 450°C to about 500°C.
- 25 4. The method according to claim 2,
wherein the titanium alkoxides is selected from the group consisting
of titanium tetraisopropoxide, titanium tetrabutoxide, titanium tetraethoxide, and
combinations thereof,
wherein the solvent is selected from the group consisting of
30 methanol, isopropyl alcohol, and combinations thereof,

wherein the polyether is selected from the group consisting of polyethylene glycol, polypropylene glycol, and combinations thereof, and wherein the reaction inhibitor is selected from the group consisting of alcoholamines, amides, diketones, and glycols, and combinations thereof.

5

5. The method according to claim 2,

wherein the titanium alkoxides is selected from the group consisting of titanium tetraisopropoxide, titanium tetrabutoxide, titanium tetraethoxide, and combinations thereof,

10

wherein the solvent is selected from the group consisting of methanol, isopropyl alcohol, and mixtures thereof,

wherein the polyether is selected from the group consisting of polyethylene glycol, polypropylene glycol, and mixtures thereof, and

15

wherein the reaction inhibitor is selected from the group consisting of monoethanolamine, diethanolamine, and triethanolamine', formamide, dimethylamide, and acetylamine, acetylacetone, ethylene glycol and diethylene glycol, and combinations thereof.

20

6. The method according to claim 2 wherein said solution contains about 5-20% by weight of said titanium alkoxide, and about 0.1-2% by weight of said polyethers, based on the total weight of the solution

25

7. The method according to claim 6 wherein the molar ratio of said reaction inhibitor to said titanium alkoxide is 1:1.

8. The method according to claim 2 wherein the molar ratio of said reaction inhibitor to said titanium alkoxide is 1:1.

30

9. A porous titanium oxide layer made according to the method of claim 2.

10. An article comprising a substrate having at least one surface and a porous titanium oxide layer made by the method according to claim 2 thereon.

5 11. A photochemical cell comprising a plurality of constitutional element, wherein at least one of said constitutional elements includes a porous titanium oxide layer made according to the method of claim 2 thereon.

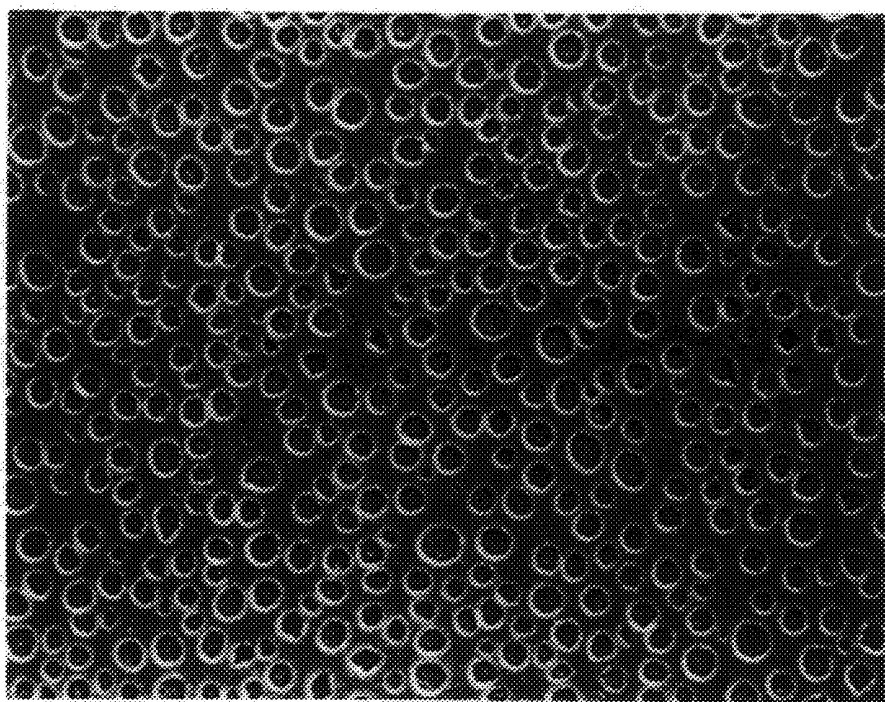


FIG. 1

2/2

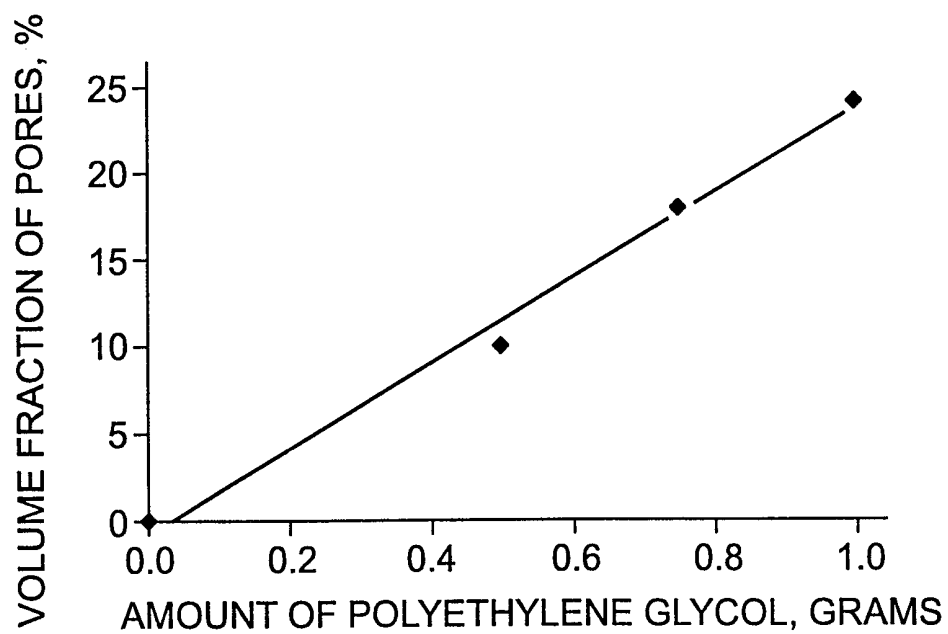


FIG. 2

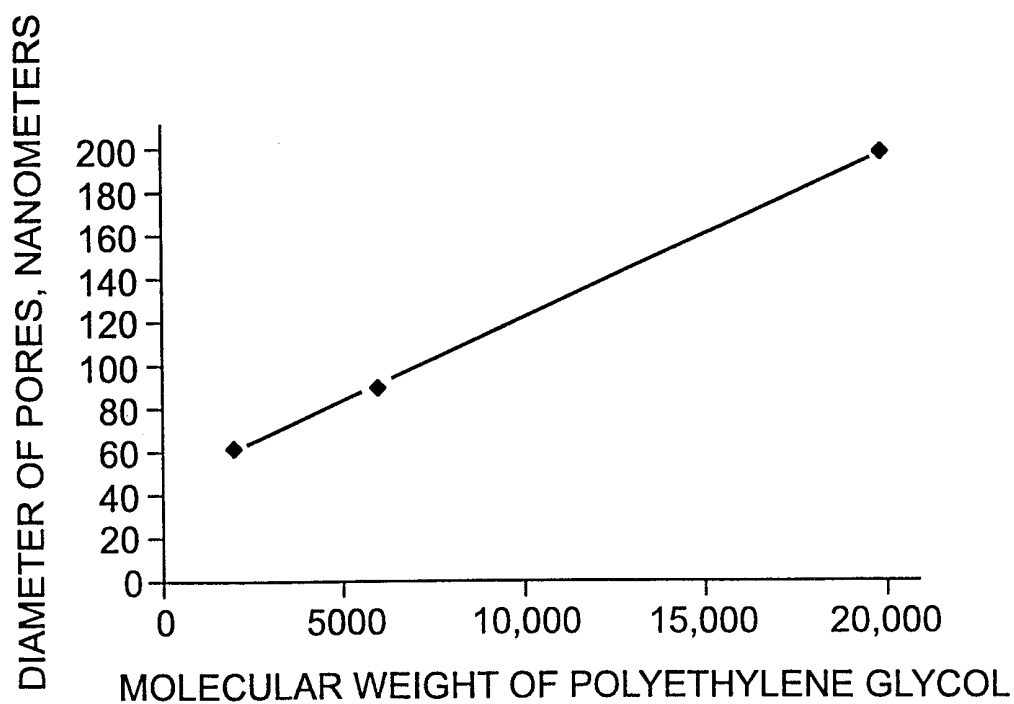


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No.
PC1/US 99/12018

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01G23/047 H01G9/20

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)
IPC 6 C01G H01G C01B

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KATO K ET AL: "Roles of polyethylene glycol in evolution of nanostructure in TiO2 coatings" THIN SOLID FILMS, vol. 298, no. 1-2, 20 April 1997 (1997-04-20), page 76-82 XP004085114 ISSN: 0040-6090 the whole document	1-6,9,10
A	K.KATO: "morphology of thin anatase coatings..." JOURNAL OF MATERIALS SCIENCE, vol. 30, 1995, pages 837-841, XP002114811 the whole document	1

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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Date of the actual completion of the international search

9 September 1999

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