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(54) TUMBLING-ENHANCED PROCESS FOR PREPARING ASSEMBLED FILMS ON WOVEN AND NON-WOVEN TEXTILES, TISSUES, OR PERMEABLE SOFT OBJECTS

(57) The present invention relates to a process according to a process for preparing a film on a substrate comprising the steps of:
- setting a permeable substrate in a rotative drum,
- rotating the drum, and
- spraying at least a first liquid containing an adsorbing or chemisorbing component(s) (LCACC) and at least a second LCACC onto the substrate,

wherein at least a first LCACC and/or at least a second LCACC is sprayed onto the substrate while the drum is rotated thereby sequentially depositing the first LCACC and the second LCACC to form a layer pair and preferably repeating said spraying to deposit several layer pairs

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Description

[0001] The present invention relates to a process for preparing assembled films on permeable soft objects, in particular for accelerating the deposition of Layer-by-Layer (LbL) films on permeable soft objects and applications thereof. The present invention also relates to material comprising textile substrate, said textile substrate being coated by one or more layer pairs of at least a first LCACC and a second LCACC forming a layer pair

[0002] The consecutive LbL deposition is well known since about 25 years (Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials, 2nd Edition (Eds: Decher, G. and Schlenoff, J. B.), Wiley-VCH: Weinheim, 2012, US 5208111). However, the LbL deposition on the surface of soft permeable objects is hampered by the fact that those objects retain substantial amounts of liquid when taken out of the "deposition solution", thus rendering rinsing or the deposition of a following layer very difficult. The removal of liquid from the pores is essential for the LbL assembly:

- to permit liquid accessibility to the object surface including pores ;
- to avoid contamination of the rinsing solutions ;
- to avoid dilution of the liquid containing an adsorbing or a chemisorbing component(s) (LCACC) by the liquid present in the pores ;
- to avoid contamination of LCACC and of the growing surface by complexation or reaction between molecules present in the pores and oppositely charged molecules used for the next layer.

[0003] For such applications the LbL process can be seen as a multiple impregnation of the same object with different components. Unlike conventional impregnation, LbL impregnation does not remove the previously deposited matter in a further impregnation step. The same holds in a similar way for simultaneous spraying and mixed forms of both.

LbL known processes and associated drawbacks

[0004] The surface of the object to be coated must be brought in contact with the liquid containing the material to be deposited. There are several ways to wet surfaces with liquids: dipping, spraying, doctor blading, ...

[0005] There is thus a need for a process for preparing films by LbL deposition having one or more of the following technical advantages:

- a reduced deposition time,
- rapid accumulation of coated material on the textile (> 10% weight in few minutes)
- adjustable quantity, quality, homogenity, uniformity and roughness,
- being suitable for all kind of materials that can be placed in the centrifuge drum, notably permeable materials such as for example a textile material, and allowing a sufficient drainage of the liquid with which the material has been impregnated or in contact during the different steps of the process,
- being suitable for large surfaces (restricted by the size of the centrifuge drum), and
- being achievable in a continuous way, i.e. consisting in one continuous step, or a sequence of several different discontinuous steps.

Aims of the invention

[0006] The present invention aims to solve the technical problem of providing a process for preparing a film by LbL deposition with a very important time saving (up to 99.5% compared to known dipping processes) and at low cost.

[0007] The present invention aims notably to solve the technical problem of providing a process for preparing a film by LbL deposition having a sufficient thickness, a good homogeneity, and a good shape-fitting of the substrate on which it is deposited.

[0008] The present invention aims notably to solve the technical problem of providing a process for preparing a film by LbL deposition on a microporous object, notably a textile, with a very important time saving (up to 99.5% compared to known dipping processes), a low cost, a high consistency, and notably a better than required homogeneity and uniformity.

[0009] The present invention aims more specifically to solve the technical problem of providing a process for preparing a photocatalytic film by LbL deposition on a permeable substrate, notably a textile, with a very important time saving (up to 99.5% compared to known processes), a low cost, a high consistency, and notably a better than required homogeneity and uniformity.

Detailed description of the invention

[0010] The present inventors have discovered a process for preparing films in particular by LbL deposition overcoming one or more, preferably all, of the above-described technical problems.

[0011] The present invention relates to a process for preparing a film on a substrate comprising the steps of:

- setting a permeable substrate in a rotative drum,
- rotating the drum, and
- spraying at least a first liquid containing an adsorbing or chemisorbing component(s) (LCACC) and at least a second LCACC onto the substrate,

wherein at least a first LCACC and/or at least a second LCACC is sprayed onto the substrate while the drum is rotated thereby sequentially or simultaneously depositing the first LCACC and the second LCACC to form a layer pair and preferably repeating said spraying to deposit several layer pairs.

[0012] One important technical advantage of the present invention is the fast removal of the liquid from the pores already during the spray-wetting of the textile or permeable material to be coated. This leads to a significant speed-up of the deposition process especially for multimaterial coatings since there is no need to change the baths while depositing, rinsing, depositing and so forth.

[0013] The process according to the present invention may also be called a tumbling-enhanced process. In general, in such a process there is a competition between adjustable parameters such as the time of passage of liquid through the textile, the kinetics of adsorption on textiles and the kinetics of precipitation onto textiles which whose balance depends on the deposition method (alternate or simultaneaous spray-assisted assembly) and conditions: longer spraying time especially in combination with a rinsing step favor adsorption, shorter spraying times, especially without rinsing step or simultaneous spraying (M. Lefort, G. Popa, E. Seyrek, R. Szamocki, O. Felix, J. Hemmerle, L. Vidal, J. C. Voegel, F. Boulmedais, G. Decher, and P. Schaaf, Angew. Chemie - Int. Ed., vol. 49, no. 52, pp. 10110-10113, 2010.) favor precipitation. Similarly, the rotation speed of the drum favors adsorption or mixing. The details depend on the requirements of the specific application.

[0014] Actually, the classic impregnation is not a layer formation. The impregnation agent contained in the liquid stays in the textile during drying which must not be forced by excessive tumbling.

[0015] An impregnating machine for textile materials is already known according to ES 2005932 (Bit Maquina S.A.). The machine consists of a centrifuge with a rotating drum operated by a hydraulic motor, and with perforated side-walls. A textile material is settled in the drum which has a cover with one centrally-mounted head spraying the impregnating liquid. The head is fed with one impregnating liquid by a pump from a separate supply tank, which has a return pipe from the centrifuge, forming a closed cycle. This machine is thus specifically designed for spraying not more than one liquid solution onto a material, which results in a "dried-onto" deposit typically much thicker than an adsorbed film and which is easily rinsed away. As a consequence, this machine is not suitable for the preparation of films by LbL deposition. Moreover, it was unpredictable whether such impregnating technique could provide a proper coated substrate using LbL deposition. In particular, it was unpredictable whether the drainage of liquid by centrifugal forces would be suited for a successful LbL deposition.

[0016] On the contrary, the present invention allows to prepare films by LbL deposition:

- with a reduced deposition time,
- with a high consistency of LbL films,
- rapid accumulation of coated material on the textile (which can be > 10% weight in few minutes for some embodiments),
- resulting in adjustable/good quality, homogeneous and uniform LbL films,
- suitable for all kind of materials permeable to liquid, for example woven or non-woven tissues and objects with continuous pores, and notably porous materials such as for example textile materials, and allowing a sufficient drainage of the liquid in which the material has been in contact with during the different steps of the process,
- suitable for large surfaces, and
- achievable in a continuous way or a sequence of several discontinuous steps.

[0017] In the present invention, LbL means Layer-by-Layer and relates to the Layer-by-Layer deposition. A LbL film means a film obtained by Layer-by-Layer deposition and comprising layers assembled by non covalent (electrostatic interactions, hydrogen bonding, Van der Waals interactions and/or hydrophobic interactions) and/or covalent bonds. In one specific embodiment, LbL film comprises alternating layers of oppositely charged molecules, which are polyionic materials (polyanions or polycations), such as for example polyelectrolytes, polymers, particles, proteins, DNA, etc.

[0018] In the present invention, a drum means a hollow cylinder that could be rotated, the internal surface of it being the inner wall and the outside surface of it being the outside wall. The hollow cylinder presents a permeable wall.

[0019] Here, the term porous objects refers to objects that are permeable to liquid.

[0020] LbL technique has been used worldwide for several applications (flame retardant, antibacterial, ...). Several LbL-based products are already on the market.

[0021] Photocatalysis is a chemical reaction which is driven by the illumination of a chemical moiety, the photocatalyst, by ultraviolet, visible or infrared radiation. The photocatalyst absorbs the light and it is involved in the transformation of the reaction partners. A photocatalyst is a catalyst thus able to produce, upon absorption of light, chemical transformations of the reaction partners.

[0022] A permeable substrate is a substrate permeable to a liquid, in particular to a liquid which may penetrate to the opposite side of the substrate. The permeable substrate includes, among others, textile, membrane and fabric, and web.

[0023] Preferably the substrate is permeable to water or any liquid solution. In one embodiment, a permeable substrate comprises pores: it is a porous material.

[0024] In one specific embodiment, the substrate is a textile, a paper, a fleece, a sponge with continuous pores, a tissue or a fabric.

[0025] In one embodiment, the substrate comprises or consists of a non-woven textile.

[0026] In one embodiment, the substrate comprises or consists of a woven textile.

[0027] In one embodiment, the substrate is cleaned and/or activated before the process for preparing a film.

[0028] Typically, the substrate is a textile.

[0029] In one embodiment, the substrate surface is activated before the spraying step.

[0030] In one embodiment, the spraying comprises or consists of alternate spraying of the first LCACC and of the second LCACC. Such an embodiment may possibly comprise the steps of depositing a liquid and draining the liquid for each sprayed solution (first LCACC, second LCACC, rinsing). Thus, the method or process can be considered as a cyclic process where one cycle corresponds to the deposition of one layer pair. Typically, the maximum thickness per layer is limited to a plateau and the film growth depends on the number of spray cycles.

[0031] The deposition is not necessary repeated with identical layer pairs of the first LCACC and the second LCACC. In one embodiment, the alternating layer pairs are identical. In one embodiment, the alternating layer pairs are different.

[0032] In one embodiment, the resulting film comprises or consists of 2 to 12 layer pairs.

[0033] In one embodiment, the resulting film comprises or consists of 13 to 50 layer pairs.

[0034] In one embodiment, the resulting film comprises or consists of 51 to 500 layer pairs.

[0035] Advantageously, said first LCACC comprises a first ionic species and said second layer-forming comprises a second ionic species, wherein the charge of the first and second ionic species are opposite.

[0036] The LCACCs are prepared according to the art such that the LCACCs can be easily sprayed.

[0037] LCACCs are typically solutions or colloid suspensions or dispersions. Typically, in one embodiment, each layer is formed by the components in solution or in suspension/dispersion through regular adsorption on the substrate. In other words, in one embodiment, each layers is typically formed by deposition of the components of the LCACC that are retained on the substrate after centrifugation.

[0038] In one embodiment, the first LCACC and the second LCACC comprise advantageously different components. Advantageously, the invention controls cross-contamination and dilution of LCACC. The removal of the previous liquid will accelerate the contact with the next liquid.

[0039] Advantageously, the invention controls contamination of the growing surface.

[0040] In one specific embodiment, one of the at least two LCACC comprises a chemical species to be deposited by LbL, wherein the concentration of said species is between 0.01 g/L and the limit of solubility of said species, typically from 0.01 to 50 g/L.

[0041] In one embodiment, one of the at least two LCACC comprises a polyelectrolyte.

[0042] In one embodiment, the first LCACC comprises a polyelectrolyte cation and the second LCACC comprises a polyelectrolyte anion.

[0043] one embodiment, the first LCACC comprises a polyelectrolyte anion and the second LCACC comprises a polyelectrolyte cation.

[0044] In one embodiment, one of the at least two LCACC comprises a polyelectrolyte solution which is selected from the group consisting of aminoethylaminopropyl-methylsiloxane-dimethylsiloxane copolymer, poly(sodium 4-styrenesulfonate) (PSS), ammonium acryloyl-dimethyltaurate-carboxyethyl-acrylate copolymer, poly(allylamine hydrochloride) (PAH), poly(dimethyldiallylammonium chloride) (PDDA), polyethylene imine (PEI) and their mixtures.

[0045] In one preferred embodiment, one of the at least two LCACC comprises a polyelectrolyte solution which is selected from the group consisting of poly(allylamine hydrochloride) (PAH), poly(dimethyldiallylammonium chloride) (PDDA) and their mixtures.

[0046] In one embodiment, the concentration of the polyelectrolyte is comprised between 0,1 to 20 g/L, preferably 0,5 to 10 g/L, more preferably 0,5 to 2 g/L.

[0047] In one embodiment, one of the at least two LCACC comprises a metal selected from the group consisting in

Ti, W, Zn, Sn, Zr, Fe and their mixtures.

[0048] In one embodiment, one of the at least two LCACC comprises a metal oxide.

[0049] In one embodiment, one of the at least two LCACC comprises a metal oxide, wherein the metal is selected from the group consisting in Ti, W, Zn, Sn, Zr, Fe and their mixtures, and/or a metal hydroxyde, wherein the metal is selected from the group consisting in Ti, W, Zn, Sn, Zr, Fe and their mixtures.

[0050] In one embodiment, one of the at least two LCACC comprises a metal oxide selected from the group of TiO_2, WO_3, ZnO, Ga_2O_3, SnO, ZrO_2, Fe_2O_3, metal chalcogenides like ZnTe, ZnS, ZnSe, CdSe, CdS, CdTe and their mixtures.

[0051] In one embodiment, one of the at least two LCACC comprises a photocatalyst.

[0052] In one embodiment, one of the at least two LCACC comprises TiO_2.

[0053] Advantageously, one of the at least two ionic solutions comprises at least one metal oxide nanoparticles.

[0054] In one embodiment, said metal oxide is titanium dioxide.

[0055] In one embodiment, one of the at least two LCACC comprises rutile and/or anatase TiO_2. Rutile or anatase refers to the crystalline phase of TiO_2,

[0056] In one specific embodiment, one of the at least two LCACC comprises a TiO_2 which is a mixture of rutile and anatase.

[0057] In one specific embodiment, one of the at least two LCACC is a dispersion of TiO_2, which is prepared by sonication of a TiO_2 powder in water.

[0058] In one specific embodiment, one of the at least two LCACC is a dispersion of TiO_2, wherein the TiO_2 particles have an average size of less than 100 nm, preferably less than 50 nm, more preferably less than 30 nm.

[0059] Advantageously, the highest concentration of TiO_2 in the dispersion allows a faster deposition.
In one specific embodiment, one of the at least two LCACC is a dispersion of TiO_2, wherein the concentration is between 0.01 to 50 g/L, preferably between 1 to 50 g/L.

[0060] In one specific embodiment, one of the at least two LCACC is a dispersion of TiO_2, wherein the concentration is between 0.01 to 50 g/L, preferably between 10 to 50 g/L, more preferably between 1 to 50 g/L and having a pH of 8 to 14. At this pH-value, the TiO_2 particles are thus negatively charged.

[0061] The resulting film is a multicomponent film.

[0062] In one specific embodiment, the resulting film comprises or consists of a layer of TiO_2/PDDA, for example obtained by simultaneous spraying of a PDDA polyelectrolyte solution and a TiO_2 dispersion.

[0063] In one specific embodiment, the resulting film comprises or consists of a layer of TiO_2/PAH, for example obtained by simultaneous spraying of a PAH polyelectrolyte solution and a TiO_2 dispersion.

[0064] In one specific embodiment, the resulting film comprises or consists of one or more, preferably from 5 to 40, preferably from 2 to 30 layer pairs of (TiO_2/PDDA, for example obtained by alternate spraying of a PDDA polyelectrolyte solution and a TiO_2 dispersion.

[0065] In one specific embodiment, the resulting film comprises or consists of one or more, preferably from 5 to 40, preferably from 2 to 30 layer pairs of (TiO_2/PAH), for example obtained by alternate spraying of a PAH polyelectrolyte solution and a TiO_2 dispersion.

[0066] In one specific embodiment, the resulting film comprises or consists of one or more, preferably from 5 to 40, preferably from 2 to 30 layer pairs of (TiO_2/PDDA), for example obtained by alternate spraying of a PDDA polyelectrolyte solution and a TiO_2 dispersion.

[0067] In one specific embodiment, the resulting film comprises or consists of one or more, preferably from 5 to 40, preferably from 2 to 30 layer pairs of (TiO_2/PAH), for example obtained by alternate spraying of a PAH polyelectrolyte solution and a TiO_2 dispersion.

[0068] In one embodiment, the resulting film further comprises a first layer of poly(ethylene imine) coating on the substrate.

[0069] In one embodiment, the resulting film has photocatalytic properties.

[0070] In one embodiment, the resulting film comprises or consists of TiO_2 with other materials. For example, the resulting film comprises or consists of a multifunctional coating combining for example self-decontaminating, flame-retardant or superhydrophobic properties.

[0071] In one embodiment, the resulting film further comprises a protective epoxy resin layer on top of it.

[0072] Such epoxy resin layer can be thin (1 to 100 nm). It improves the mechanical stability and the durability of the film against abrasion and washing. For resulting films having photocatalytic properties, the epoxy resin layer improves the mechanical stability and the durability of the film against abrasion and against washing, advantageously without decreasing the photocatalytic activity.

[0073] Of particular interest are water-soluble epoxy resins.

[0074] In one embodiment, said protective epoxy resin layer on top of the resulting film consists of or comprises a layer of epoxy resin poly[(o-cresyl glycidyl ether)-coformaldehyde] (Cresol Novolac Epoxy Resin also called CNER) and branched PEI as a hardener assembled through the formation of covalent bonds.

[0075] In one specific embodiment, said protective epoxy resin layer on top of the resulting film consists of or comprises a $(CNER/PEI)_3$ film.

[0076] The resulting film results in a mass increment of the substrate after deposition of said resulting film.

[0077] In one embodiment, said mass increment is superior to 0.5%.

[0078] In one embodiment, said mass increment is superior to 1%.

[0079] In one embodiment, said mass increment is superior to 2%.

[0080] In one embodiment, said mass increment is superior to 3%.

[0081] In one embodiment, said mass increment is superior to 4%.

[0082] In one embodiment, said mass increment is superior to 5%.

[0083] In one embodiment, said mass increment is superior to 7%.

[0084] Figure 1 is a scheme of the device for the process of the invention.

[0085] As a rotating device, a centrifuge (1) can be used.

In order to build-up films the substrate is set into the centrifuge drum (10). The substrate (20) is placed on the inner wall (2) of the drum (10). The wall of the drum is perforated with holes (13) in order to evacuate the sprayed liquids.

[0086] The drum is rotating around a vertical axis (30). The distance between the substrate (or the inner wall of the drum) and this axis has a constant value during the rotation of the drum.

[0087] While rotating, LCACC are sprayed alternatively (quasi-continuously) or continuously using Airbrush nozzles (40,41) onto the substrate (which is preferably on the inner wall of the drum).

[0088] The rotating device is equipped with at least two nozzles spraying the at least two LCACC. The nozzles are connected with an automated spraying device. The nozzles have a fixed position (they are not rotating).

As the device is fully automated, it allows controlling precisely the air pressure/flow and flow rate of solution delivered to each spray nozzle. Moreover, the distance spray nozzles/substrate and tilt angle can be easily adjusted.

[0089] In one embodiment, the flow rate value is comprised between, preferably, more preferably 1 mL/min and 15 mL/min.

[0090] In one embodiment, the air pressure value is comprised between, preferably, more preferably 7 L/min and 10 mL/min.

[0091] In one embodiment, the spraying time for one layer is comprised between preferably, more preferably 15 to 45 s.

[0092] In one embodiment, a drying step may be applied between each layer deposition which corresponds simply to a centrifugation of the substrate, preferably for 60 s. The drying time is defined as the time during which the coated sample is rotating in the centrifuge without any additional action. During this time the majority of the sprayed liquid is removed from the permeable material, such as a textile material for example, by the centrifugal force.

[0093] In one embodiment, a rinsing step may be applied after the deposition of the one or more layers, preferably between each layer if several layers are present. A rinsing step may be performed by spraying water from a nozzle in order to rinse the layer and thereby remove or limit unwanted components on the deposited layer.

[0094] When a rinsing step and/or a drying step is performed after the deposition of two layers, preferably between each layer, the LCACCs are thus sprayed alternatively (the deposition is said to be *"quasi-continuous"*).

[0095] In one embodiment, LCACCs are sprayed simultaneously (from separate spraying devices) with no rinsing or drying step in between (the deposition is said to be *"continuous").*

[0096] In one embodiment, the process for preparing a film on a substrate further comprises a step of depositing an epoxy resin layer on top of the last LCACC sprayed. Typically, the deposition of the epoxy film is not carried out using a rotative drum of the invention, notably as it requires the use of an organic solvent for the preparation of the epoxy solution. The epoxy resin layer can be deposited according to a method known in the art.

[0097] Preferably, said process further comprises a rinsing step between two layer depositions, preferably between each layer deposition.

[0098] Preferably, said process further comprises a drying step between two layer depositions, preferably between each layer deposition.

[0099] The substrate size may be as large as the drum dimensions.

[0100] In one embodiment, the rotational speed is comprised between 500 to 5000 rpm, preferably 1500 to 3000 rpm. In one embodiment, the rotational speed is comprised between 500 to 5000 rpm, preferably 1500 to 3000 rpm and the drum diameter is comprised between 5 and 300 cm, preferably 16.5 cm.

[0101] This set-up allows simultaneously the impregnation of the substrate and the drainage of liquid by centrifugal forces suited for LbL deposition. This step is essential for the LbL assembly in order to avoid complexation between molecules present in the pores and oppositely charged molecules used for the same or next layer.

[0102] The process consists in one cycle per layer: the substrate is set into the drum and the process for preparing the LbL film is directly started.

[0103] In one embodiment, the cycle per layer comprises:

- rotating the substrate;
- exposing the substrate to liquid;

- waiting time (exposition may or may not continue and/or rotation may or may not continue);
- removing liquid from pores (exposition may or may not continue);
- stopping the exposition to liquid;
- stopping rotation.

[0104] If several layers are formed, these successive steps are repeated. In such case the step of stopping the rotation of the drum is preferably performed only at the last cycle.

[0105] Preferably, components with long adsorption times, i.e. superior to 5 min, should not be sprayed or should be sprayed at very low rotation speed for a short time (e.g. 10 s), followed by putting the drum to rest for the time of adsorption (e.g. 1 h), the object must stay wet, spin-up again and then rinsed.

[0106] Preferably, if the components have long adsorption times they cannot be deposited in optimal regular way, because the coating would be rinsed and centrifuged away before adsorbing on the substrate. That is why the invention relates to another embodiment, wherein:

1. LCACC is distributed on the substrate in the centrifuge;
2. Centrifuge is switched off so the LCACC can adsorb on substrate;
3. Centrifuge is turned on again and the substrate is rinsed;
4. Deposition of next layer can begin if an additional layer has to be deposited.

[0107] The invention also relates to a material comprising a film coated substrate obtained according to the process according to the present invention.

[0108] The invention also relates to a material comprising textile substrate, said textile substrate being coated by one or more layer comprising said first LCACC and second LCACC. Typically a layer pair is formed at least by a first LCACC and a second LCACC. In one embodiment, layer pairs in a material are not formed by the same combination of LCACC.

[0109] The material of the invention may be prepared according to all variants, embodiments, including preferred and advantageous embodiments relating to the process of the invention. Accordingly, the material of the invention is also defined by the features implied by the process of the invention.

[0110] The resulting film can have photocatalytic, flame-retardant, self-cleaning, self-decontaminating, heat and electrical conductivity, UV-blocking and/or antimicrobial properties. Photocatalysis includes a large variety of reactions like partial or total oxidations, hydrogen transfer, dehydrogenation and may be applied in water purification treatment as well as in degradation of gas pollutants. The resulting film brings photocatalytic properties on a textile substrate.

Brief description of the figures

[0111]

Figure 1 is a scheme of the device for the process.

Figure 2 are SEM micrographs of bare polyester (left) and LbL modified polyesters prepared by dipping (middle) and according to the invention (right) observed at different magnifications.

Figure 3 represents the variations of deposited mass during the deposition of $(P25/PDDA)_n$ films on textiles as a function of the number of deposition steps and the concentration of PDDA.

Figure 4 shows the variations of deposited mass during the deposition of $(P25/PDDA)_n$ and $(S5\text{-}300B/PDDA)_n$ films on textiles as a function of the number of deposition steps and various TiO_2 concentrations.

Figure 5 shows the variations of deposited mass during the deposition of $(P25/PDDA)_{20}$ on textiles as a function of the concentration of TiO_2 dispersion.

Figure 6 shows the evolution of mass increment of polyester fabrics coated by continuous spraying of P25 at a concentration of 2.5 g/L and PDDA as a function of the spraying time.

Figure 7 shows the evolution of mass increment of polyester fabrics coated by continuous spraying of P25 at a concentration of 25 g/L and PDDA as a function of the spraying time.

Examples

Preliminary remarks:

[0112] Milli-Q water is an ultrapure water with a resistivity of 18.2 MΩ.cm, obtained by purification with a Milli-Q gradient system (Millipore, Molsheim, France).

[0113] TBAOH means tetrabutylammonium hydroxide.

[0114] PDDA means poly(dimethyldiallylammonium chloride).

[0115] PAH means poly(allylamine hydrochloride).

[0116] Textiles in the examples are woven textiles.

Example 1: Process for preparing a film by LbL deposition according to the invention using three LCACCs:

[0117]

1. LCACC 1 : Polyethylene imine solution (only used as first layer on the substrate)
2. LCACC 2 : TiO_2 dispersion
3. LCACC 3 : Poly(dimethyldiallylammonium chloride) solution
4. Substrate : Cotton fabric

- Materials:

1. LCACC 1: Polyethylene imine solution

Preparation of polyethylene imine solution

[0118] Polyethylene imine (PEI) was dissolved in Milli-Q water to obtain a PEI solution with a concentration of 1 g/L.

2. LCACC 2: TiO_2 dispersion

Preparation of TiO_2 dispersion

[0119] Dispersions of TiO_2 were prepared from titania powders (TiO_2 P25, Degussa-Evonik). To prepare dispersion from powder, TiO_2 powder was added to 40 mL of Milli-Q water at pH = 11 (adjusted by TBAOH) while stirring. After 2 hours of stirring, the titania suspension was sonicated by a tip sonicator for 25 min with a total energy of 600 kJ (Bioblock Scientific vibracell 75042). The sonication leads to disaggregation of titania particles. Subsequently suspension was cooled down to the room temperature. As hydroxide ions present in TBAOH solution adsorb on titania nanoparticles surface during stirring and sonication, pH was readjusted to around 9.5. To get rid of aggregates which were not destroyed during sonication, a centrifugation was applied, 15 min at 5000 rpm (4000 g). At the end of the process obtained dispersion had a milky white color and a concentration of about 25 g/L.

[0120] For LbL deposition, TiO_2 dispersion was diluted to a concentration of 2.5 g/L. The dilution was performed by mixing mother dispersion with Milli-Q water previously adjusted at pH 9.5 (to avoid re-agglomeration of titania nanoparticles).

3. LCACC 3: Poly(dimethyldiallylammonium chloride) solution

Preparation of poly(dimethyldiallylammonium chloride) solution

[0121] Poly(dimethyldiallylammonium chloride) was dissolved in Milli-Q water to obtain a concentration of 1 g/L. The pH of the poly(dimethyldiallylammonium chloride) solution was then adjusted to 9.5 with TBAOH, the pH used for titania dispersion.

4. Substrate

[0122] The substrate is a cotton fabric (textile).

[0123] First the cotton fabrics were cut into 5 x 10 cm and cleaned.

[0124] To clean and activate the textile the following procedure was used:

Cleaning and activating procedure for cotton fabrics

[0125] In order to clean cotton fabrics, they were immersed for 24 hours in 5% solution of anionic surfactant (Hellmanex III®) and stirred using a magnetic stirrer. Because cellulose fibres existing in cotton tissues contains hydroxyl functional groups of the β-1,4-linked glucose monomers, phosphates and anionic tenside components were not only cleaning cotton fabrics but also activating them by generating negative charges. So further activation processes were not required. After such procedure cotton fabrics were intensively rinsed with Milli-Q water, water:ethanol 1:1 mixture and Milli-Q water again. Subsequently cotton fabrics were dried for 4h in 60°C and cooled to room temperature.

- Process:

[0126] Firstly the substrates were coated by one PEI layer using the dipping procedure. The cleaned substrates were dipped for 20 min in 1 g/L PEI solution followed by 3 rinsing steps in Milli-Q water for 3 min respectively.

[0127] Then, as a rotating device, a centrifuge was used. In order to build-up films, the pieces of textile were placed into the centrifuge drum (into the inner wall of the drum). While rotating, solutions and suspensions were sprayed alternatively by airbrush nozzles to the interior of centrifuge (inner wall of the drum). Titania and polyelectrolyte nozzles were placed respectively at 12 cm and 10 cm from the fabric with an angle of 35° toward the inner wall of the rotating drum.

[0128] To control the spraying parameters as the flow rate and the air pressure, nozzles were connected to an automated spraying device. The used flow rate was 13 mL/min for titania suspension, polyelectrolyte solution and water used for rinsing. The applied air flow was 8 L/min for titania suspension and polyelectrolyte solution and 9 L/min for the water used for rinsing. The spraying time was set for 30 s for each component as well as for rinsing. Optionally, between each layer deposition, a drying step may be applied which is simply centrifugation of textile for 60 s.
The rotational speed of the centrifuge was 2600 rpm during the process.
The diameter of the rotating drum was 16.5 cm.

[0129] The spraying sequence was thus the following:

1. The first layer sprayed on PEI pre-coated substrate was the TiO_2 dispersion.
2. Spraying water for rinsing.
3. Spraying the polyelectrolyte solution.
4. Spraying water for rinsing.

A first layer pair was formed after this first sequence. The sequence was repeated to obtain the deposition of a film composed of 10 layer pairs on the PEI pre-coated substrate.
A $PEI(TiO_2/PDDA)_{10}$ film was deposited on the substrate.

Example 2: Process for preparing a film by LbL deposition according to the invention using three LCACCs :

[0130]

1. LCACC 1 : Polyethylene imine solution (only used as first layer)
2. LCACC 2 : TiO_2 dispersion
3. LCACC 3 : Poly(allylamine hydrochloride) solution
4. Substrate : Cotton fabric (textile)

- **Materials:**

[0131] The same materials were used as in example 1 except for:

LCACC 3 : Poly(allylamine hydrochloride) solution

Preparation of Poly(allylamine hydrochloride) solution

[0132] Poly(allylamine hydrochloride) was dissolved in Milli-Q water at a concentration of 1 g/L.

- Process:

[0133] The same process as in example 1 was performed to prepare a textile coated with 10 layer pairs of LbL deposited.

[0134] A $PEI(TiO_2/PAH)_{10}$ film was deposited on the substrate.

Example 3: Process for preparing a film by Layer-by-Layer (LbL) deposition according to the invention using three LCACC :

[0135]

1. LCACC 1 : Polyethylene imine solution (only used as first layer)
2. LCACC 2 : TiO_2 dispersion
3. LCACC 3 : Poly(dimethyldiallylammonium chloride) solution

4. Substrate : Polyester fabrics

-Materials:

[0136] The same materials were used as in example 1 except for the substrate which was polyester fabrics (textile).
[0137] First the polyester fabrics were cut into 5 x 10 cm and cleaned.
To clean and activate the textile the following procedure was used:

Cleaning and activating procedure for polyester fabrics

[0138] For cleaning polyester fabrics the same procedure as used for cleaning cotton fabrics was followed. However to generate the charge on the fibres, oxygen plasma activation was applied. Textiles after cleaning and drying were put into plasma cleaner. Activation of a surface by plasma is known by the person skilled in the art. Such procedures were able to generate negative charge on polyester fabrics without making any serious damages to it.

- Process:

[0139] The same process as in example 1 was used.
[0140] A PEI(TiO_2/PDDA)$_{10}$ film was deposited on the substrate.

Example 4: Process for preparing a film by LbL deposition according to the invention using three LCACCs :

[0141]

1. LCACC 1 : Polyethylene imine solution (only used as first layer)
2. LCACC 2 : TiO_2 dispersion
3. LCACC 3 : Poly(allylamine hydrochloride) solution
4. Substrate : Polyester fabrics

- Materials:

[0142] The same materials were used as in example 2 except for the substrate which was polyester fabric (textile).
[0143] First the polyester fabrics were cut into 5 x 10 cm and cleaned.
[0144] To clean and activate the textile the procedure used in example 3 was applied.

- Process:

[0145] The same process as in example 1 was used.
[0146] A PEI(TiO_2/PAH)$_{10}$ film was deposited on the substrate.

Example 5 (comparative to example 1): Process for preparing a film by LbL deposition by a dipping process using :

[0147]

1. LCACC 1 : Polyethylene imine solution (only used as first layer on the substrate)
2. LCACC 2 : TiO_2 dispersion
3. LCACC 3 : Poly(dimethyldiallylammonium chloride) solution
4. Substrate : Cotton fabric (textile)

- Materials:

[0148] The same materials were used as in example 1.

- Process

[0149] The following process was used:

Layer-by-Layer assembly by dipping

[0150] Firstly, the substrate was coated by one PEI layer using the dipping procedure.
The cleaned substrates were dipped for 20 min in 1 g/L PEI solution followed by 3 rinsing steps in Milli-Q water for 3 min respectively.
After drying the substrate was dipped alternatively in a TiO_2 dispersion and in a polyelectrolyte solution for 20 min followed by 3 rinsing steps in Milli-Q water at a pH value adjusted to the pH of the titania dispersion (9.5). Thus a layer pair (TiO_2/polyelectrolyte) is deposited on the substrate. The repetition of this procedure leads to build-up of a multilayer film.

[0151] The dipping sequence is the following (after coating the textile with a PEI layer):

1. The first layer was obtained by dipping the substrate in the TiO_2 dispersion,
2. Then the substrate was dipped 3 times 3 min in water for rinsing,
3. The second layer was obtained by dipping the substrate in the polyelectrolyte solution.
4. The substrate was dipped 3 times 3 min in water for rinsing.

[0152] A first layer pair is formed after this first sequence. The sequence is repeated to obtain the deposition of a film composed of 10 layer pairs on the PEI pre-coated substrate.
A PEI(TiO_2/PDDA)$_{10}$ film was deposited on the substrate.

Example 6 (comparative to example 3): Process for preparing a film by LbL deposition by a dipping process using :

[0153]

1. LCACC 1 : Polyethylene imine solution (only used as first layer on the substrate)
2. LCACC 2 : TiO_2 dispersion
3. LCACC 3 : Poly(dimethyldiallylammonium chloride) solution
4. Substrate : Polyester fabric (textile)

- Materials:

[0154] The same materials were used as in example 3.

- Process

[0155] The same process as in example 5 (dipping process) was used.

[0156] A PEI(TiO_2/PDDA)$_{10}$ film was deposited on the substrate.

Example 7: Film characterizations

Gravimetric determination of adsorbed mass

[0157] Weighing of textiles in examples 1, 3, 5 and 6 was performed before and after performing the LbL deposition process in order to determine the gained mass after film deposition. For the quantitative determination of adsorbed quantities of adsorbing species the gravimetric procedure must account for residual solvent. For the case of TiO_2 deposition the following procedure was applied:
Textiles after cleaning (before LbL deposition) or after film deposition were dried in oven 3h at 60 °C, then were put in a desiccator containing a saturated solution of magnesium chloride (constant humidity = 33%) and kept there for around 24 h. The gravimetric measurements were performed always 10 s after taking the piece of fabric from the desiccator. A balance with a precision of 0.01 mg was used to perform the measurements. The results can be found in Table 1.

Table 1

	Average mass increment for LbL assembly according to the process of the invention	Average mass increment for LbL assembly according to the dipping process
Substrate : cotton fabric	10,85 % (Example 1)	2,1 % (Comp. example 5)

(continued)

	Average mass increment for LbL assembly according to the process of the invention	Average mass increment for LbL assembly according to the dipping process
Substrate : polyester fabric	6,4 % (Example 3)	2,4 % (Comp. example 6)
Estimation of the time required for film deposition	10 min	620 min

[0158] These experiments show that a higher mass increment is obtained for films prepared by a process according to the invention in substantially less time than those built by a dipping process.

[0159] Additional analyses were performed:

X-ray diffraction analysis:

[0160] The presence of TiO_2 particles in the coating was demonstrated by X-ray diffraction.

[0161] A qualitative analysis of the relative intensities of rutile and anatase TiO_2 indicates that the deposited films of examples 1 to 6 are mainly composed of anatase TiO_2, this is in agreement with the TiO_2 P25 powder composition certified by the manufacturer.

X-ray photoelectron spectroscopy

[0162] Based on the XPS results, the presence of TiO_2 nanoparticles in the LbL films deposited in examples 1 to 6 was confirmed.

Scanning and transmission electron microscopy

[0163] To get information about the quality of coatings and their morphology, bare polyester and modified polyesters prepared according to examples 3 and 6 were analyzed using scanning (SEM) electron microscopy (Figure 2).

[0164] Bare polyester is a woven textile composed of fibers showing a smooth surface and no visible defects (Figure 2, left column). The LbL deposition of a $(P25/PDDA)_{10}$ film by dipping or according to the process of the present invention on polyester fibers leads to the formation of an homogeneous rougher surface (Figure 2, middle and right columns).

[0165] This indicates that the film deposition could be achieved using both techniques as confirmed previously by XRD and XPS.

However, compared to dipping, the coating performed by the process according to the present invention is smoother and without any cracks.

Photocatalytic activity

[0166] The photocatalytic activity of the samples was demonstrated according to the following procedure:

> Methylene blue was deposited on the textile pieces obtained according to examples 1 to 6 by dipping a 1 cm^2 polyester fabric into a methylene blue solution at 10^{-3} mol/L for one minute. After drying the textiles were illuminated by a "solar glo" lamp at a distance of 20 cm (received power of 310 $\mu W/cm^2$). While almost no degradation of methylene blue was observed for bare polyester after one hour of illumination, a complete degradation of methylene blue is obtained within 1 hour of illumination for a sample coated by five layer pairs and ten layer pairs, and within 15 minutes for the sample coated by 20 layer pairs. The faster degradation of methylene blue on impregnated LbL modified textiles comes from the proximity between the dye and the catalyst generated by the process according to the invention. Therefore, the textiles according to the present invention present a photocatalytic activity.

Example 8: influence of the polyelectrolyte concentration on the build-up of $(P25/PDDA)_n$ films on textiles prepared according to the process of the invention

[0167] $(P25/PDDA)_n$ films on textiles were prepared according to the process of the invention with the following parameters:

Rotational speed of centrifuge: 2600 rpm
Concentration of TiO_2 dispersions: 2.5 g/L

Other deposition parameters as well as the deposition sequence of one layer pair are indicated in Table 2.

Table 2

Step number	Sprayed solution / drying	Flow rate [mL/min]	Air flow [L/min]	Time [s]
1	TiO_2 dispersion	13	8	30
2	Rinsing solution	13	9	30
3	Drying	-	-	60
4	Polyetectrolyte solution	13	8	30
5	Rinsing solution	13	9	30
6	Drying	-	-	60

[0168] To study the influence of the polyelectrolyte concentration on the build-up of $(P25/PDDA)_n$ films, PDDA solutions at concentrations of 10 g/L, 1 g/L, and 0.1 g/L were prepared.

[0169] Figure 3 shows the results.

[0170] A regular growth was observed for all PDDA concentrations. PDDA at a concentration of 1 g/L leads to the highest growth rate, and the mass increment reaches a value of 4.3% after 50 deposition steps. Use of PDDA at a concentration of 0.1 g/L shows a lower growth rate compared to 1 g/L and the mass increment reaches a value of 2.9% for 50 deposition steps. Surprisingly, the lowest growth rate was observed for a PDDA concentration of 10 g/L and the mass increment reaches a value of 1.8% for 50 deposition steps.

Example 9: influence of the TiO_2 concentration on the build-up of $(TiO_2/PDDA)_n$ films on textiles prepared according to the process of the invention

[0171] $(P25/PDDA)_n$ films on textiles were prepared according to the process of the invention with the following parameters:

Rotational speed of centrifuge: 2600 rpm
Concentration of polyelectrolyte: 1 g/L

[0172] Other deposition parameters as well as the deposition sequence of one layer pair are given in Table 2 of example 8.

[0173] The deposition of TiO_2-based LbL films on textiles with different concentrations of titanium dioxide nanoparticles (5, 10, and 25 g/L of P25 and around 200 g/L of S5-300B) was studied. P25 titanium dioxide was provided free of charge by Degussa-Evonik® (Germany) as a fine powder. S5-300B is an alkaline commercially available dispersion of nano-anatase TiO_2 from Cristal Global®.

[0174] The results are showed on Figure 4.

On the Figure 4 it is possible to observe a high influence of the TiO_2 concentration on the film build-up. A regular growth is observed for all TiO_2 concentrations while the growth rate increases by increasing the nanoparticle concentration. For a film built with the highest P25 concentration (25 g/L) it was possible to reach a mass increment of 23% only after 20 deposition steps. In the case of the commercially available dispersion S5-300B the mass increment corresponds approximately to 50% of the textiles for 20 depositions steps.

By plotting the dependence of the mass increment as a function of the P25 concentration (Figure 5) for a film composed of 20 layer pairs, a linear growth was observed.

To conclude, the concentration of polyelectrolyte and TiO_2 strongly influences the build-up of films. These results clearly demonstrate that thick coatings can be prepared in a short amount of time for commercially available dispersion: 50% of mass increment can be reached after only 20 min of deposition. Such growth rate is currently unreachable using any other known deposition method and can be of great interest for industrial applications.

Example 10: Growth behavior of $(TiO_2/PDDA)_n$ films on textiles prepared according to the process of the invention - continuous deposition process

[0175] The quasi-continuous tumbling-enhanced LbL deposition can be further advanced to lead to the continuous tumbling-enhanced assembly of interacting species where 2 or more interacting species are sprayed continuously onto the textile substrate instead of bringing the two interacting species into contact step-by-step.
In addition, this technique leads to the formation of non-stratified films in contrast to films prepared by quasi-continuous tumbling-enhanced LbL assembly. This method has been used to fabricate TiO_2-based coating on textiles and compared with the results obtained by quasi-continuous tumbling-enhanced LbL assembly.

[0176] $(P25/PDDA)_n$ films on textiles were prepared according to the process of the invention with the following parameters:

Rotational speed of centrifuge: 2600 rpm
Concentration of TiO_2 dispersions: 2.5 g/L
Concentration of polyelectrolyte: 1 g/L

Other deposition parameters are given hereafter:

The TiO_2 dispersion and polyelectrolyte solution are sprayed simultaneously at a liquid flow rate of 13 mL/min and an air flow of 8 L/min.

[0177] Figure 6 shows the build-up of $(P25/PDDA)_n$ films by continuous spraying on textiles with a P25 concentration of 2.5 g/L. This film grows regularly as a function of the spraying time.

[0178] LbL films assembled by continuous deposition follow a similar growth as films prepared by quasi-continuous deposition. Nevertheless, continuous spraying requires more time to reach similar mass increment (2500 s against 600s for a mass increment of roughly 1.6%). Moreover, continuous spraying consumes higher amounts of solution than quasi-continuous tumbling-enhanced LbL assembly.

[0179] Figure 7 shows the evolution of mass increment of polyester fabrics coated by continuous spraying of P25 at a concentration of 25 g/L and PDDA as a function of the spraying time.

Claims

1. A process for preparing a film on a substrate comprising the steps of:

- setting a permeable substrate in a rotative drum,
- rotating the drum, and
- spraying at least a first liquid containing an adsorbing or chemisorbing component(s) (LCACC) and at least a second LCACC onto the substrate,

wherein at least a first LCACC and/or at least a second LCACC is sprayed onto the substrate while the drum is rotated thereby sequentially depositing the first LCACC and the second LCACC thereby forming a layer comprising said first LCACC and second LCACC.

2. The process according to claim 1, wherein the spraying comprises or consists of alternative spraying of the first LCACC and of the second LCACC, thereby forming a layer pair comprising said first LCACC and second LCACC, and preferably repeating said spraying to deposit several layer pairs.

3. The process according to claim 1, wherein the spraying comprises or consists of simultaneous spraying of the first LCACC and of the second LCACC.

4. The process according to any of claims 1 to 3, wherein said first LCACC comprises a first ionic species and said second layer-forming comprises a second ionic species, wherein the charge of the first and second ionic species are opposite.

5. The process according to any of claims 1 to 4, wherein the substrate is a textile, a paper, a fleece, a sponge with continuous pores, a tissue or a fabric.

6. The process according to any of claims 1 to 5, wherein the substrate surface is activated before the spraying step.

7. The process according to any of claims 1 to 6, wherein one of the at least two ionic solutions comprises at least one metal oxide nanoparticles.

8. The process according to claim 7, wherein said metal oxide is titanium dioxide.

9. The process according to any of claims 1 to 8, wherein said process further comprises a step of depositing an epoxy resin layer on top of the last LCACC sprayed.

10. The process according to any of claims 1 to 9 wherein said process further comprises a rinsing step between each layer deposition.

11. The process according to any of claims 1 to 10 wherein said process further comprises a drying step between each layer deposition.

12. A material comprising a film coated substrate obtained according to the process of any of claims 1 to 11.

13. A material comprising textile substrate, said textile substrate being coated by one or more layer pairs of at least a first LCACC and a second LCACC forming a layer pair.

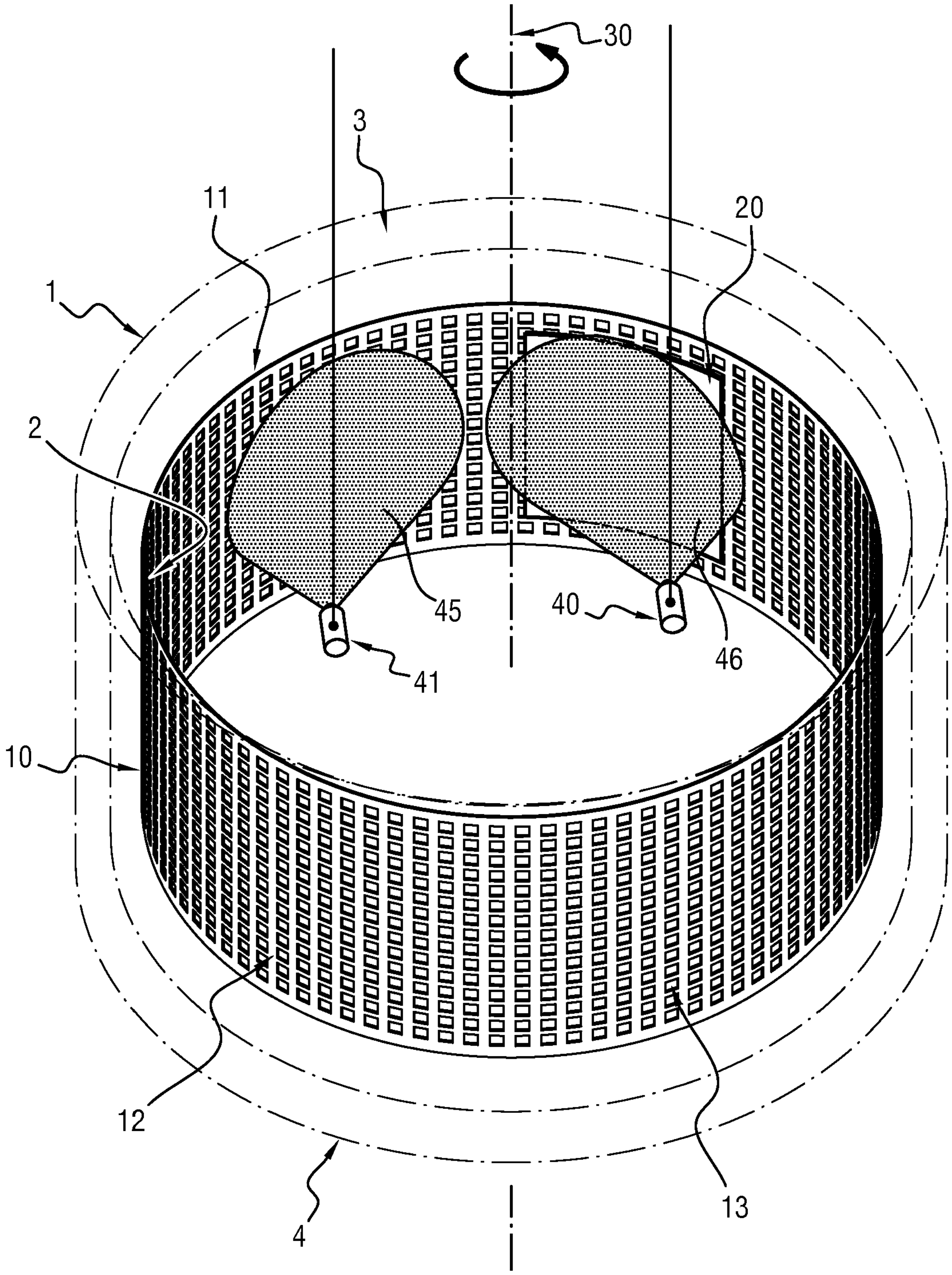

FIG.1

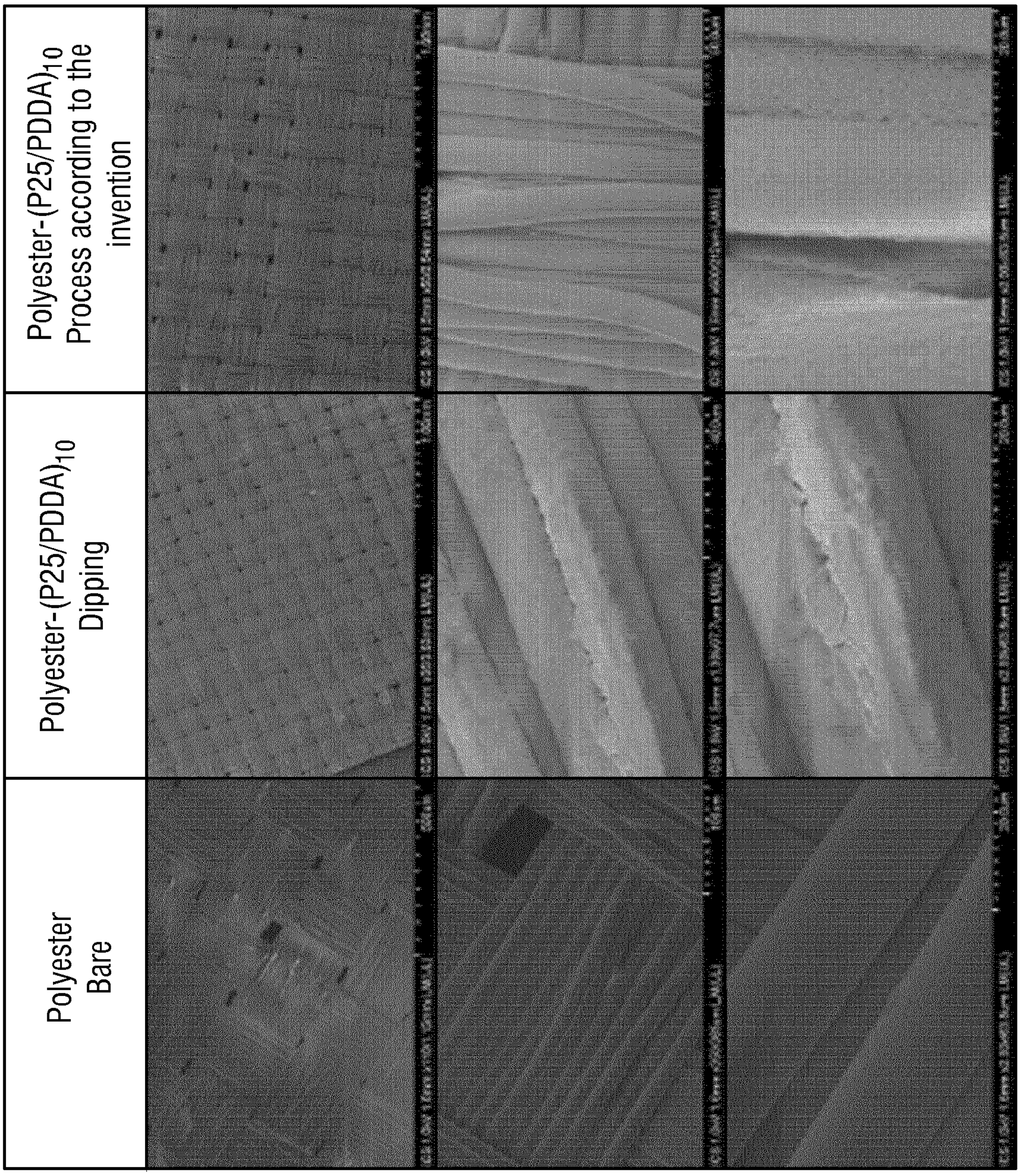
Polyester
Bare
Polyester-(P25/PDDA)$_{10}$
Dipping
Polyester-(P25/PDDA)$_{10}$
Process according to the invention

FIG.2

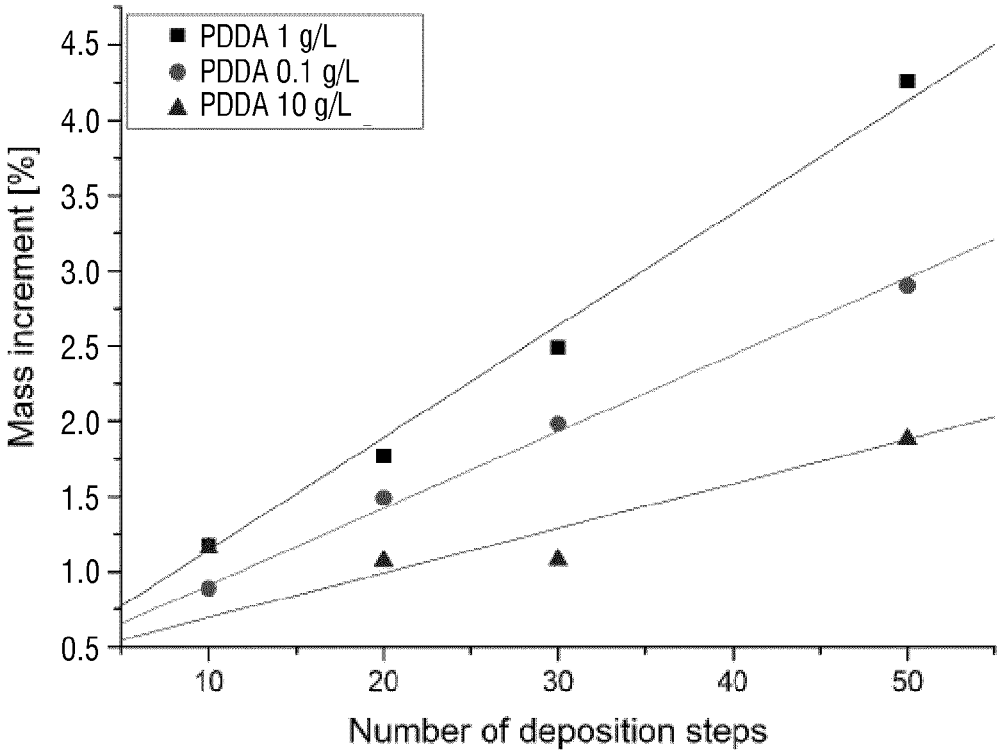
■ PDDA 1 g/L
● PDDA 0.1 g/L
▲ PDDA 10 g/L
Mass increment [%]
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10
20
30
40
50
Number of deposition steps

FIG.3

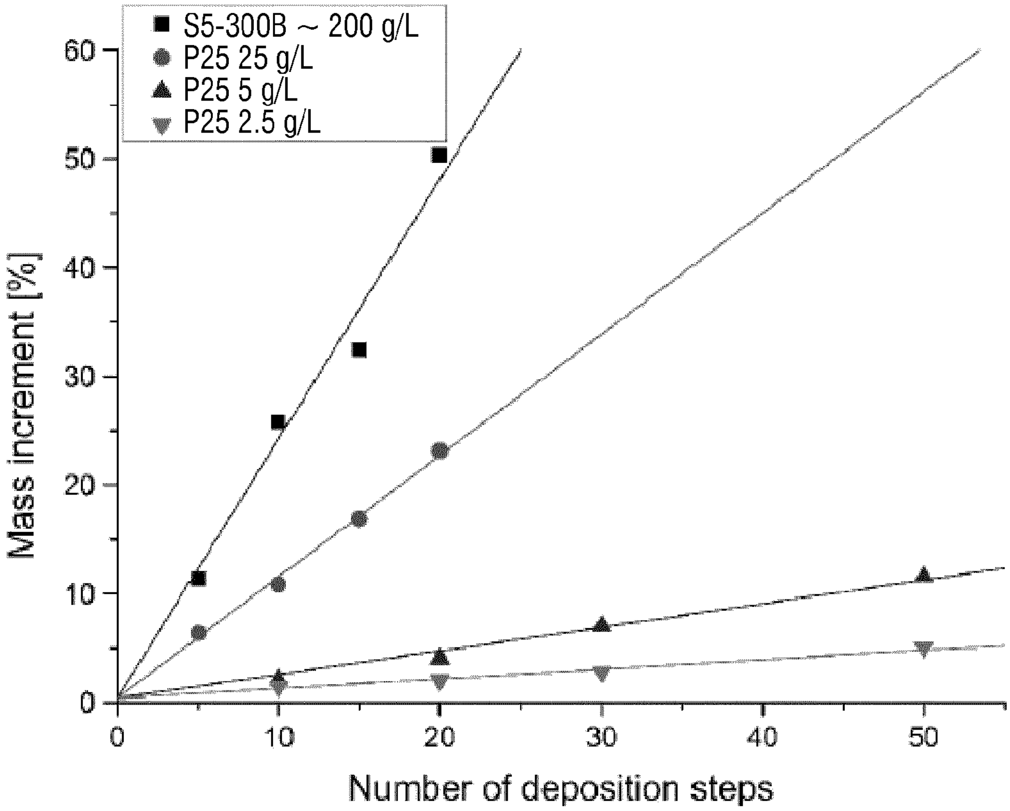
■ S5-300B ~ 200 g/L
● P25 25 g/L
▲ P25 5 g/L
▼ P25 2.5 g/L
Mass increment [%]
60
50
40
30
20
10
0
0
10
20
30
40
50
Number of deposition steps

FIG.4

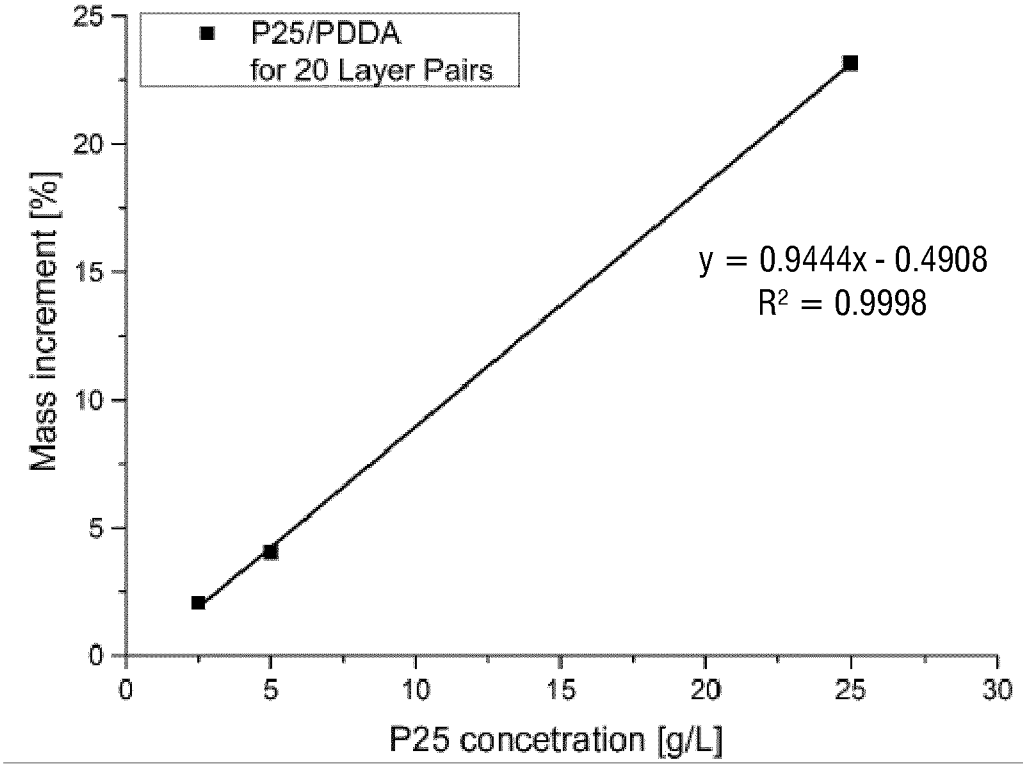
■ P25/PDDA
for 20 Layer Pairs
y = 0.9444x - 0.4908
R² = 0.9998
Mass increment [%]
P25 concetration [g/L]
0
5
10
15
20
25
30

FIG.5

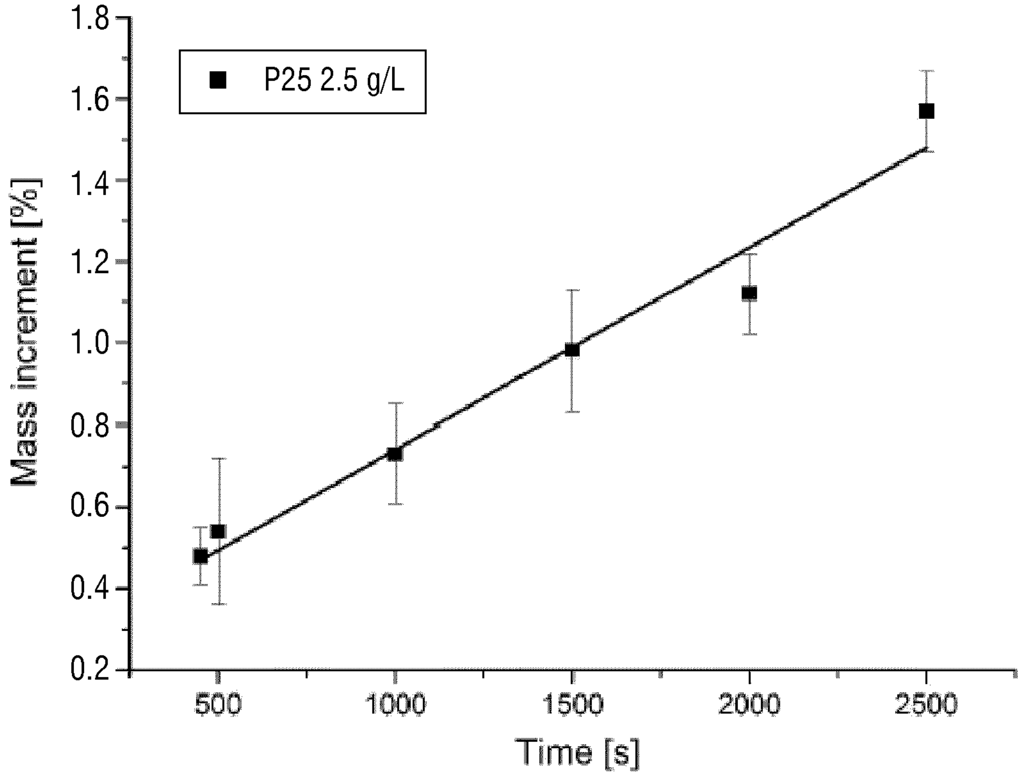
■ P25 2.5 g/L
Mass increment [%]
Time [s]
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
500
1000
1500
2000
2500

FIG.6

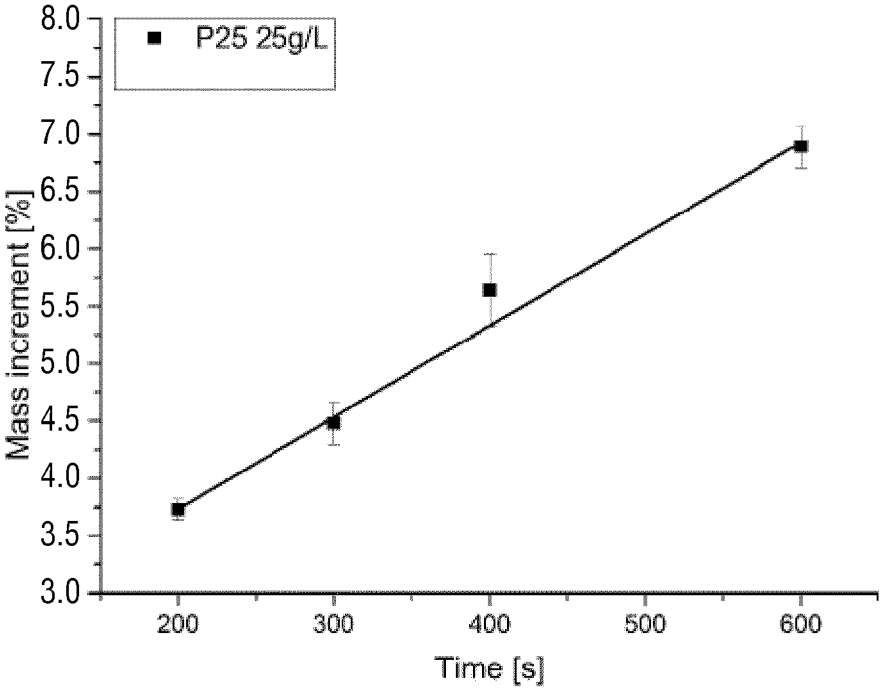
P25 25g/L
Mass increment [%]
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
200
300
400
500
600
Time [s]

FIG.7

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EUROPEAN SEARCH REPORT

Application Number
EP 17 30 6822

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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