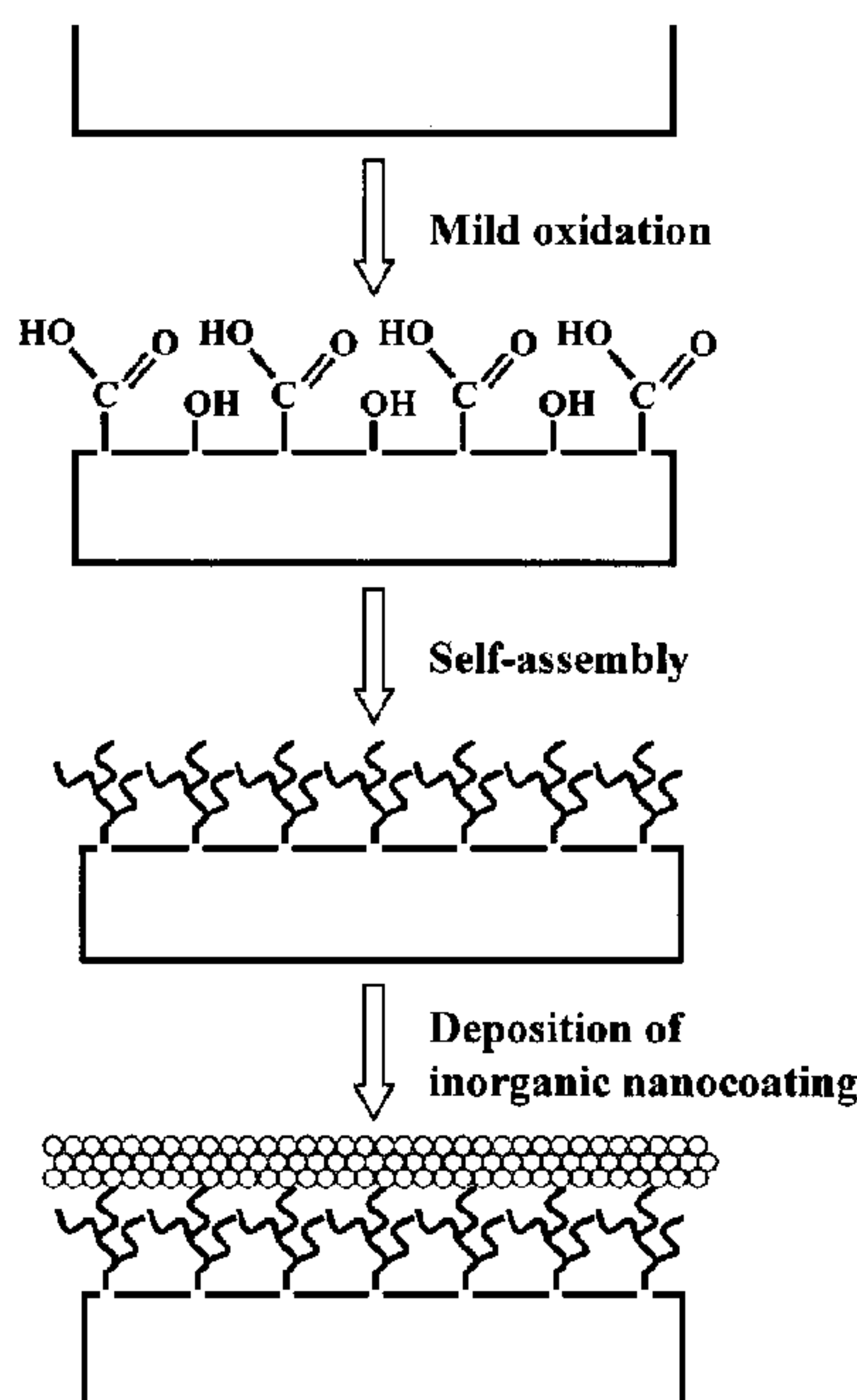




(86) Date de dépôt PCT/PCT Filing Date: 2010/12/15
 (87) Date publication PCT/PCT Publication Date: 2011/06/30
 (45) Date de délivrance/Issue Date: 2018/02/06
 (85) Entrée phase nationale/National Entry: 2012/06/21
 (86) N° demande PCT/PCT Application No.: IB 2010/003246
 (87) N° publication PCT/PCT Publication No.: 2011/077211
 (30) Priorité/Priority: 2009/12/23 (EP09380197)

(51) Cl.Int./Int.Cl. *C09D 5/00* (2006.01)
 (72) Inventeurs/Inventors:
 SCHONEVELD, ERIK, ES;
 SANCHIS BRINES, FRANCISCO, ES;
 ORTEGA MURGUIALDAY, AMAYA, ES;
 GOMEZ CORDON, JULIO, ES;
 LORENTE AROCA, MA DOLORES, ES;
 CORDERO ETCHABERRY, DIANA, ES
 (73) Propriétaire/Owner:
 SILICALIA, SL, ES
 (74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : COMPOSITION POUR REVETEMENT
 (54) Title: COMPOSITION FOR COATING



(57) **Abrégé/Abstract:**

The method consists of the formation of a layer over a stone substrate to increase its hardness, chemical resistance, wear and scratch resistance, comprising applying on the substrate a coating matrix incorporating an organic material and fillers including inorganic nanoparticles and/or microparticles; chemically binding said matrix to the substrate, by a self-assembly process and/or a binding process by covalent bonding, electrostatic bonding, van der Waals bonding or hydrogen bonds; and finally drying said matrix. The mentioned organic material is selected from organosilanes, organophosphates, polycarboxylic compounds, compounds based on triazine heterocycles and said nanoparticles are nanoparticles of oxides, carbides, borides, nitrides of metals or of semimetals.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
30 June 2011 (30.06.2011)(10) International Publication Number
WO 2011/077211 A1(51) International Patent Classification:
C09D 5/00 (2006.01)(21) International Application Number:
PCT/IB2010/003246(22) International Filing Date:
15 December 2010 (15.12.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09380197 23 December 2009 (23.12.2009) EP(71) Applicant (for all designated States except US): **SILICALIA, SL** [ES/ES]; C/ Grabador Esteve, 8, E-46004 Valencia (ES).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SCHONEVELD, Erik** [NL/ES]; Silicalia, SL, C/ Grabador Esteve, 8, E-46004 Valencia (ES). **SANCHIS BRINES, Francisco** [ES/ES]; Silicalia, SL, C/ Grabador Esteve, 8, E-46004Valencia (ES). **ORTEGA MURGUIALDAY, Amaya** [ES/ES]; Silicalia, SL, C/ Grabador Esteve, 8, E-46004 Valencia (ES). **GÓMEZ CORDÓN, Julio** [ES/ES]; Silicalia, SL, C/ Grabador Esteve, 8, E-46004 Valencia (ES). **LORENTE AROCA, Ma, Dolores** [ES/ES]; Silicalia, SL, C/ Grabador Esteve, 8, E-46004 Valencia (ES). **CORDERO ETCHABERRY, Diana** [ES/ES]; Silicalia, SL, C/ Grabador Esteve, 8, E-46004 Valencia (ES).(74) Agent: **TORNER LASALLE, Elisabet**; Gran Via de les Corts Catalanes, 669 bis, 1r. 2a., E-08013 Barcelona (ES).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD,

[Continued on next page]

(54) Title: COMPOSITION FOR COATING

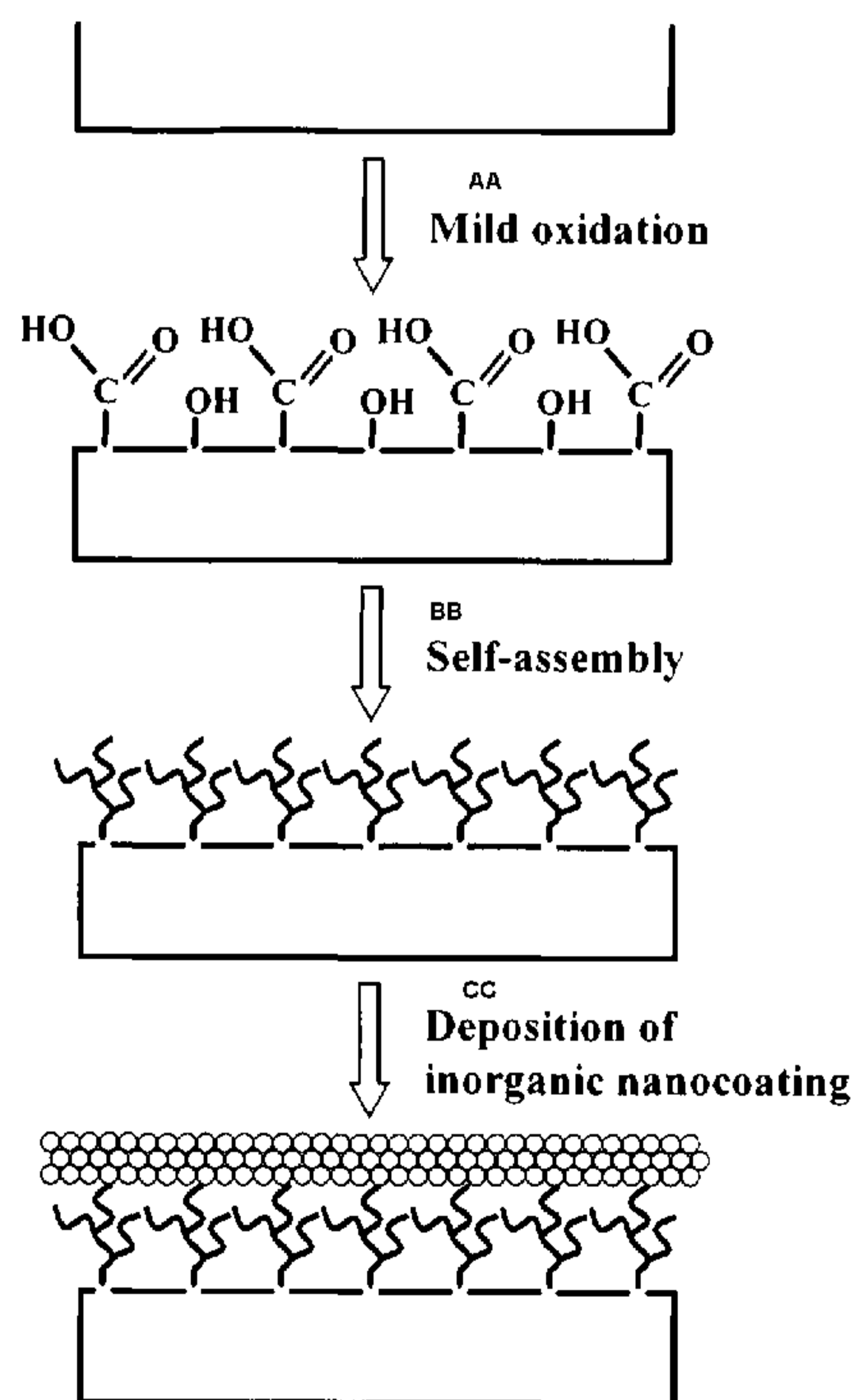


FIG. 6

(57) Abstract: The method consists of the formation of a layer over a stone substrate to increase its hardness, chemical resistance, wear and scratch resistance, comprising applying on the substrate a coating matrix incorporating an organic material and fillers including inorganic nanoparticles and/or microparticles; chemically binding said matrix to the substrate, by a self-assembly process and/or a binding process by covalent bonding, electrostatic bonding, van der Waals bonding or hydrogen bonds; and finally drying said matrix. The mentioned organic material is selected from organosilanes, organophosphates, polycarboxylic compounds, compounds based on triazine heterocycles and said nanoparticles are nanoparticles of oxides, carbides, borides, nitrides of metals or of semimetals.

WO 2011/077211 A1 

SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

COMPOSITION FOR COATING

Field of the Art

5 The present invention relates, in a first aspect, to a method for coating a stone substrate, the latter being understood in this description as a natural marble or a stone aggregate comprising calcareous materials and/or dolomitic limestones agglomerated by means of a binder, the method providing a coating layer which increases the hardness, increases chemical resistance, wear and scratch resistance of said stone substrate. The coating of this invention improves the stability of
10 the surface against the etching by chemical products and reduces stains.

 The process of the invention allows both increasing the service life, in optimal conditions, of stone substrates such as an artificial marble slab, and considerably extending the scope of use of such products (given the indicated resistance of the exposed surface to multiple factors) as well as reducing the number of scratched or defective pieces during the handling,
15 transport and installation.

 The method of said first aspect of the invention provides a coating based on self-assembly technology which allows connecting materials with nanostructures.

 A second aspect of the invention concerns to an element in the form of a board made of stone material incorporating a coating formed according to the proposed method.

20 In a third aspect the invention supplies a composition for coating an element in the form of a board made of stone material, the composition comprising a first organosilane material and inorganic nanoparticles and/or microparticles bound in a matrix by means of a self-assembly process.

Prior State of the Art

25 In the current process for obtaining artificial marble slabs, mixtures of marble aggregates with perfectly controlled granulometry which represent more than 90% of the composition of the material are used. Thermosetting resins, previously conditioned with catalysts and accelerants, are generally used as a binder element of the fillers. Due to the petrographic nature of the minerals used and the intrinsic properties of the polyester resins, artificial marble pavings have a
30 low chemical resistance, wears and scratches occurring which reduce the service life of the substrate. Scratch and wear resistance can be related to the hardness of the material or resistance presented by a material upon being scratched by another one which is defined as the Mohs scratch and abrasion resistance of the material. This condition is one of the main drawbacks of Marble type stone substrates, both of natural and agglomerate marble.

35 Traditional transparent coatings based on silicones or other polymers have a good resistance against isolated impacts or aggressions, but have a low resistance when they are subjected to constant stresses, such as the passage areas, due to the low abrasion and scratch resistance of the products based on silicones and plastics.

 There are different technologies to solve said drawback. Fillers (wollastonite, nanoclays)
40 slip agents or additives based on silicone are generally used in bulk. These techniques are only

valid for applications with low wear requirements. When greater wear resistances are required technologies of coatings of resins with inorganic fillers and laminates are used. But this solution generates a surface with a plastic visual appearance which is poorly appreciated in the market of high end decoration products.

5 The use of coatings is one of the most advanced technologies. Coatings are generally applied to protect, improve or decorate different products. However, there is a low adhesion between the coating and the polymer material due to the low polarity of the latter. The way to increase this adhesion generally involves increasing the surface energy of the plastic through different methods: exposure to high energy sources such as flame, corona, plasma and UV
10 radiation treatment. Generally, it is easier for a surface with high surface energy to be "wet" by the coating, therefore it will be easier to paint the substrate and the adhesion between both phases will be improved. Nevertheless, there are still drawbacks when using these methods, mainly due to environmental reasons, to the fact that they are slow and not very uniform processes, in addition to the existence of limitations due to the fact that these materials are not
15 very heat-stable.

 Special coating processes such as Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), and Wet Deposition Coating (or sol-gel), are well known technologies to deposit inorganic coatings (SiO_2 , carbides, nitrides, metal oxides,...) on different substrates including plastics. However, on plastic materials this type of technology
20 has certain limitations such as its high cost, low deposition speed, high energy consumption and toxic gas production, among others.

 Patent US5751018 discloses a method comprising applying a semiconductor layer, by means of a SAM process, on an inorganic substrate. In particular, it proposes covalently binding bridging moieties, through a first functional group, to the surface of the inorganic
25 substrate and, by means of its other functional group, to semiconductor nanocrystals, also covalently. The teachings of this patent are not applicable to a coating for stone substrates, since neither the nature of said substrate nor the demands of the coating are considered.

 Application WO2004094303A2 proposes joining two articles by means of nanofibers, wherein for an embodiment, one of the articles is made of stone. In its specification it is
30 indicated that a SAM process in collaboration with microcontact printing techniques to construct the nanofibers can be used for this joining.

Application EP1802455A2 proposes applying an aluminum phosphate coating to a substrate. In its specification it is indicated that such coating, among others, supplies a greater hardness. It is also indicated that an additional coating layer, "overcoating", can be applied to said coating by means of a self-assembly monolayer or SAM process. Such additional layer
5 can include organic molecules or polymers, coatings based on silane, as well as the proposed aluminum phosphate material itself. It is also indicated that the proposed coating can have organic or inorganic additives, such as metal ions such as silicon, iron, zinc and manganese or a mixture thereof, as well as nanocrystalline zinc, titanium oxides or a mixture thereof.

Application WO2006/042116 relates to aluminium phosphate compositions for
10 coating a metal or plastic substrate.

Application WO2009/032988 discloses a composition having a small amount of hydrophobic particles dispersed in water. Said composition can be applied on glass, painted surfaces, steel, alloy, plastic and ceramic surfaces in order to produce a self-cleaning surface, which is difficult to wet.

Application WO2008/085350 proposes an electrically conductive coating composition including carbon nanotubes dispersed in a solvent which may be applied to a surface to form a thin film which is resistively heatable. This coating composition is particularly useful on aircraft or other substrate surfaces to prevent the formation of ice or to melt ice.

Application WO2007/102960 discloses a hydrophobic self-cleaning coating
20 composition that can be applied onto a surface of plastic, metal, glass, ceramic fiberglass in order to form thereon a wet and dirty repellent coating.

Application EP1832629 discloses an anti-corrosive coating with self-healing properties comprising corrosion inhibiting pigment that comprises nanoreservoirs of corrosion inhibitor. This coating is applied by layer-by-layer deposition and provides smart release of
25 the corrosion inhibitor in function of an external stimulus, such as change of pH, humidity, light, electromagnetic fields.

Application WO2006/008739 relates to coating metal surfaces, such as metal implants, with biomolecules that provide a substrate for the growth of a protective cell layer.

Application EP 2085442 proposes the use of fluorine-containing organosilane
30 compositions for treating substrates to improve their water-repellency and oil-repellency. These organosilane compositions have a very low fluorine content and a very low amount of

active ingredients.

Application WO2006/010663 relates to the treatment of the surface of natural stones by means of a sol-gel method to seal the pores of the substrate surface in such a manner that the coating allows the escape of water vapor from the pores, while prevents water containing
5 solvents to enter into the pores. The described scaling matrix is able to enter into the pores but does not form a film on the remaining part of the surface. Therefore, the proposed matrix material is not a coating because it does not form a layer on the substrate.

Given the insufficiencies in the mentioned prior state of the art relating to the protection of a stone substrate, a novel coating has been developed in which a high-resistance
10 chemical bond which is covalent, electrostatic, by van der Waals forces, etc., is produced between a stone substrate comprising an aggregate of calcareous materials and/or dolomitic limestones and the transparent coating, reaching resistances similar to quartz slabs with a visual appearance of stone.

Description of the Invention

15 The invention provides a method for coating a stone substrate by means of the formation thereon of a coating layer to increase the hardness, wear and scratch resistance of said substrate. The proposed coating also makes the surface more resistant to etching and staining.

The mentioned stone substrate is based, for a preferred embodiment, on a mixture of
20 stone aggregates with calcareous materials and/or dolomitic limestones, agglomerated by means of a binder.

Accordingly, there is described a method for coating a stone type substrate, said substrate being based on a mixture of stone aggregates with calcareous materials and/or dolomitic limestones agglomerated by means of a first binder, said method comprising the
25 formation of a layer over said substrate to increase its hardness, chemical resistance, wear and scratch resistance, said method being characterized in that it comprises the following steps: applying on said substrate a coating matrix incorporating at least one organic material that is selected from organosilanes, organophosphonates, polycarboxylic compounds, compounds based on triazine heterocycles and fillers including inorganic nanoparticles and/or
30 microparticles; chemically binding said matrix to the substrate by means of conducting a self assembly process and/or by means of a binding process by covalent bonding, electrostatic

- 4A -

bonding, van der Waals bonding or hydrogen bonds; and drying said matrix, wherein said organic material, which is at least one in number, and/or said nanoparticles and/or microparticles are functionalized with molecules with at least one of the following groups: Si-OH, SiOR (R= organic compound) or Si-Cl, aldehyde or ketone or COOH, NH₂, phosphates, phosphonates, sulfonates, sulfates, or the combination thereof and wherein said nanoparticles and microparticles are selected from the group including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, n-Na₂SiO₃ or a combination thereof, to form a three-dimensional lattice, which is bound to the substrate by chemical bonds encapsulating different nanoparticles and/or microparticles.

Thus, the method of this invention consists of the formulation of nanostructured coatings by means of a self-assembly process from organic and inorganic precursors with the ability to form a three-dimensional lattice, which is firmly bound to the substrate by chemical bonds encapsulating different nanoparticles and/or microparticles and obtaining coatings with high abrasion and scratch resistance.

In relation to the organic material, it is selected, according to an embodiment, from organosilanes, organophosphates, polycarboxylic compounds, compounds based on triazine heterocycles and said nanoparticles are nanoparticles of oxides, carbides, borides, nitrides of metals or semimetals, selected from the group including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, n-Na₂SiO₃ or a combination thereof functionalized with the components of said nanoparticles and/or microparticles.

The coating matrix further comprises an organic or inorganic binder and an organic or inorganic solvent.

Said binder is particularly a thermosetting aqueous-based polymer and said solvent is an aqueous or alcoholic medium and said thermosetting polymer is based on triazine heterocycles, such as methoxylated melamine.

In relation to the methodology for applying the coating matrix, it is performed by means of a co-deposition of organic material and nanoparticles and/or microparticles.

- 4B -

For the purpose of accelerating a dehydration process of free functional groups and improving the cross-linking thereof during the drying of the mentioned matrix, the method further comprises a controlled heat application to the coated substrate.

In a second aspect, there is described a board made of stone material, comprising a natural calcareous substrate or a stone agglomerate incorporating calcareous materials and/or dolomitic limestones with a coating layer formed according to the method described above.

According to an embodiment, the agglomerate of the substrate of the board made of stone material proposed by the second aspect of the invention comprises powder of calcareous and/or dolomitic materials and a binder resin.

For another embodiment, the mentioned coating layer comprises inorganic micro- and/or nanoparticles with great hardness trapped in the mentioned matrix, of at least one material of the group of materials including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, $n\text{-Na}_2\text{SiO}_3$ or a combination thereof.

In a third aspect, there is also described a composition for coating an element in the form of a board made of stone type substrate, said substrate being based on a mixture of stone aggregates with calcareous materials and/or dolomitic limestones agglomerated by means of a first binder, characterized in that said composition comprises at least one organic material selected from organosilanes, organophosphonates, polycarboxylic compounds, compounds based on triazine heterocycles and fillers including inorganic nanoparticles and/or microparticles; wherein said organic material and said inorganic nanoparticles and microparticles are functionalized with molecules having at least one of the following groups: Si-OH, SiOR (R= organic compound) or Si-Cl, aldehyde or ketone or COOH, NH₂, phosphates, phosphonates, sulfonates, sulfates and wherein said nanoparticles and microparticles are selected from the group including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, $n\text{-Na}_2\text{SiO}_3$, or a combination thereof; being bound in a matrix by means of conducting a self-assembly process and/or other chemical bonding or electrostatic or chemical interaction processes.

- 4C -

The composition described above also comprises, for an embodiment, an aqueous-based organic binder, an aqueous, alcoholic, hydroalcoholic solvent and a reaction accelerator.

In relation to the mentioned first organosilane material, it is, for a preferred embodiment, an organofunctionalized silane selected from the group of materials including: 5 TEOS (tetraethyl orthosilicate), gamma-methacryloxypropyltrimethoxysilane, BTSE (1,2-bis triethoxysilyl)ethane, hexadecyltrimethoxysilane, (3-glycidoxypropyltrimethoxysilane), dichlorodiphenylsilane, dichlorodimethylsilane; organophosphonates, polycarboxylic compounds, compounds based on triazine heterocycles or an organic material having triazine 10 groups selected from 1,3,5-triazine or having free amino groups, selecting diamino-PEG from this group. In addition, the mentioned nanoparticles and microparticles are selected from the group of materials including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, n-Na₂SiO₃, or a combination thereof.

15 The composition proposed by the third aspect of the invention contemplates that, according to a preferred embodiment, the nano- and microparticles forming it, jointly or alternatively, are functionalized with phosphonates, amino, aldehyde, sulfonates, sulfates, carboxyl groups or organosilanes.

Various embodiments of the claimed invention relate to a method for coating a stone 20 type substrate, said substrate being based on a mixture of stone aggregates with calcareous materials and/or dolomitic limestones agglomerated by means of a first binder, said method comprising the formation of a coating layer over said substrate to increase its hardness, chemical resistance, wear and scratch resistance, said formulation of a coating layer being characterized in that it comprises the steps: applying on said substrate a coating matrix 25 incorporating at least one organic material that is selected from organosilanes, organophosphonates, polycarboxylic compounds, compounds based on triazine heterocycles and fillers including inorganic nanoparticles and/or microparticles; chemically binding said matrix to the substrate by means of conducting a self assembly process and/or by means of a binding process by covalent bonding, electrostatic bonding, van der Waals bonding or 30 hydrogen bonds; and drying said coating matrix, wherein said organic material, which is at least one in number, and/or said nanoparticles and/or microparticles are functionalized with

- 4D -

molecules with at least one of the following groups: Si-OH, Si-Cl or SiOR wherein R is an organic compound, aldehyde or ketone or COOH, NH₂, phosphates, phosphonates, sulfonates, sulfates, or the combination thereof and wherein said nanoparticles and microparticles are selected from the group including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, n-Na₂SiO₃, and combinations thereof, to form a three-dimensional lattice, which is bound to the substrate by chemical bonds encapsulating different nanoparticles and/or microparticles.

Various embodiments of the claimed invention relate to a composition for coating an element in the form of a board made of stone type substrate, said substrate being based on a mixture of stone aggregates with calcareous materials and/or dolomitic limestones agglomerated by means of a first binder, characterized in that said composition comprises at least one organic material selected from organosilanes, organophosphonates, polycarboxylic compounds, compounds based on triazine heterocycles and fillers including inorganic nanoparticles and/or inorganic microparticles; wherein said organic material and said inorganic nanoparticles and microparticles are functionalized with molecules having at least one of the following groups: Si-OH, Si-Cl or SiOR wherein R is an organic compound, aldehyde or ketone or COOH, NH₂, phosphates, phosphonates, sulfonates, sulfates and wherein said nanoparticles and microparticles are selected from the group including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, n-Na₂SiO₃, and combinations thereof; being bound in a matrix by means of conducting a self-assembly process and/or other chemical bonding or electrostatic or chemical interaction processes.

- 5 -

In relation to the organic binder, a thermosetting polymer with reactive functional groups is used.

The previous and other advantages and features will be more fully understood from the following detailed description of several embodiments with reference to the attached drawings, which must be taken as a non-limiting illustration.

Brief Description of the Drawings

In said drawings:

Figure 1 schematically shows the self-assembly process on the substrate, this layer is formed from a hydroalcoholic organosilane solution. The cross-linking due to the dehydration of SiOH...HOSi units and which give rise to Si-O-Si bonds, occurs after a heat treatment at low temperatures;

Figure 2 shows a nanoparticle the structure of which is formed by 2 units, a core of a composition and an outer part of a different composition; an onion type nanoparticle;

Figure 3 shows a thin self-assembled layer on the surface of the substrate in which octanuclear Si₄O₄ units are shown;

Figure 4 shows other example of functionalization of surfaces and self-assembly based on the use of amino and aldehyde functional groups.

Figure 5 shows an example in which molecules with aldehyde functional groups and triazines for the self-assembly process are used. The incorporation of triazines allows creating three-dimensional lattices.

Figure 6 schematically shows a self-assembly process on a substrate according to the principles of this invention: mild oxidation of the surface, self-assembly and deposition of the nanocomposite. This process can occur in 3 steps, in two steps and even in a single step.

Figure 7 shows the incorporation of silanols in the matrix due to a spontaneous self-assembly. In this process the dehydration and formation of the bond occurs.

Figure 8 shows in its top part a coating structure according to the invention with microparticles only, whereas in the bottom part a structure in which microparticles and nanoparticles are combined is depicted.

Detailed Description of Several Embodiments

The invention provides a coating with high hardness based on nanofillers and/or microfillers together with a TEOS, silane bond matrix etc.

The invention proposes the formulation of a hard coating based on the dispersion of said nanofillers and/or microfillers in an alcoholic or hydroalcoholic aqueous solvent which allows increasing the surface hardness of a stone substrate by more than 2 or 3 points in the Mohs scale.

Said development consists of a matrix of multifunctional molecules wherein one of the functional groups is capable of self-assembling or covalently bonding, thus being molecules with at least one of the following groups: Si-O (R= organic compound) or Si-Cl, aldehyde or ketone, CO or COOH, phosphates, sulfates, or the combination of one of these groups such as thiolphosphate, which will produce a three-dimensional lattice due to a spontaneous self-

assembly. Some of the used molecules are: thiols, alkoxy silanes, carboxylic acids, alkoxy metalates and phosphonic acids.

The second functional group is a group capable of initiating the polymerization of monomers in a controlled manner.

5 Some of the functional molecules used are: Tetraethyl orthosilicate, bis-1,2 (triethoxysilyl)ethane, 3-glycidoxypropyltrimethoxysilane, gamma-aminopropylsilane, dichlorodimethylsilane, bis-dichloromethylphenylsilane, hexadecyltrimethoxysilane,...

10 To favor the adhesion with the substrate of the fillers, the aqueous/hydroalcoholic medium can be acidified by means of adding acetic, hydrochloric, tartaric, ethylenediaminetetraacetic, etc., type acid which favor the self-assembly by means of creating silanol, carboxyl or phosphonate groups.

The micro and nanoparticles finally selected are stable in aqueous medium and/or colloidal solution and are added during the oligomerization of the developed molecule, thus allowing a good control of the percentage of nanofillers with additives.

15 The choice of the used fillers was made based on the composition, structure, size and cost thereof. Some of the fillers considered are:

Alumina (Al_2O_3)

Boron carbide (B_4C)

Boron nitride (BN)

20 Silicates

Glass microspheres

Silicon carbide (SiC)

Silica (SiO_2)

Quartz

25 Copper oxide (CuO)

Micro- and nanofibers

30 To promote the molecular cross-linking between the surface of the stone substrate and the multifunctional nanostructured coating, a self-assembly (SAM) technology is used which allows creating strong bonds disregarding the polarity of the surfaces to be bound, furthermore maintaining the appearance of the original piece.

The self-assembly technology is based on the fact that the surface of some materials can be modified through a surface activation, which could consist of a moderate oxidation thereof, and/or of a chemical functionalization process using molecules capable of self-assembling.

35 This new technique provides an effective bond between the surface of the material and the coating of micro- and nanoparticles, due to the possibility of forming a molecular cross-linking in the surface while the appearance of the original piece is maintained.

This molecular anchoring process involves three steps: activation, self-assembly and co-deposition of micro- and nanoparticles. These three steps can be performed in a single step: activation, self-assembly and co-deposition of micro- and nanoparticles as is detailed in Figure 6,

when the molecules responsible for the activation and for creating three-dimensional lattices on the surface of the substrate and the micro- and nanofillers are in the same composition.

The first step involves an activation in moderate conditions of the surface of the substrate to be treated for the purpose of functionalizing it, creating optimal functional groups for the self-assembly of organic molecules in the surface thereof, for increasing the potentiality of said surface to give rise to self-assembly reactions.

The carboxyl and hydroxyl groups formed during the activation process (first step) provide the active sites so that the molecules are self-assembled with the suitable functional groups (second step). In said second step the self-assembly technique based on the formation of covalent bonds and other weaker interactions such as electrostatic or van der Waals interactions between the functional groups of the surface of the activated substrate and bi- or multifunctional organic molecules is applied. Thus, stable molecules chemically bound to the surface of the piece must be spontaneously produced.

In the third step, the co-deposition of inorganic micro- and nanoparticles with high hardness (SiC, BN, SiO₂, TiO₂, ZrO₂, quartz, alumina, B₄C, etc..) occurs on the surface of the substrate to obtain a high quality coating. The micro- and/or nanoparticles are trapped in the lattice which said molecules are capable of forming, maximizing the matrix-particle interaction. The self-assembled molecules are bound to the surface by means of a chemical adsorption process (the binding of the adsorbate to the solid surface by forces where their energy levels are close to those of the chemical bonds) providing an effective binding between the substrate and the molecules.

These three phases can be reduced to a single one, to that end it is necessary to use in the same formulation the hard micro- and nanoparticles of the third phase and which will be co-deposited in the coating together with the molecules capable of functionalizing the surface of the substrate and creating three-dimensional lattices by means of self-assembly.

A hard, transparent coating is obtained with a binding by means of chemical or electrostatic interactions or bonds, which have a high abrasion resistance, maintaining mechanical properties.

Using this technology, from organic and inorganic precursors with the ability to form a three-dimensional lattice, different micro- and/or nanoparticles are encapsulated.

The incorporation in the matrix of multifunctional molecules with at least one of the following groups: Si-O or Si-Cl, CO or COOH, amine, carbonyl, free aldehyde groups, carboxyl, phosphates, sulfates, or the combination of one of these groups such as thiolphosphate produces a three-dimensional lattice due to a spontaneous self-assembly as is shown in Figure 7 (for the case of silanol groups).

With reference to the figures of the drawings, it must be emphasized that when the marble surface, formed mainly from crystalline structures of metal carbonates, the major one being calcium carbonate, is treated with compounds such as organosilanes, phosphonates, thiols, compounds with amino, aldehydes or carboxyl groups, a deposition of thin layers occurs on the XCO₃ units, giving rise to -O-X-O-Si type bonds, for the case of organosilanes.

- 8 -

For this type of material, silicon compounds form Si-O-Si-O type bonds, thus forming three-dimensional structures with excellent adherence to the marble substrate.

If a hydroalcoholic-based solution of organosilanes is heat-treated at low temperatures, it gives rise to a dehydration of the silanol units which change from Si-OH to Si-O-Si type groups (with or without an organic chain), allowing a cross-linking between layers (Figure 1).

According to the silane molecule used (BTSE; TEOS, GLYMO, etc...), the structure of the nanoparticle can be formed by octanuclear units (SiO)₄ (Figure 3), onion type (Figure 2), etc... These silicon oxide (SiO) nanoparticles created "in situ" are deposited on the surface of the substrate and, by means of a self-assembly process, are chemically bound to the surface.

Another example of functionalization of surfaces and self-assembly is the reaction between bi- or multifunctional aldehydes and surfaces chemically modified with amine groups. In this case, reactions of self-assembly will occur between the amine functional groups and the aldehyde groups (Figure 4). When molecules with aldehyde functional groups are used to give self-assembly reactions, different types of agents can be used which allow creating three-dimensional lattices by means of reaction with free aldehyde or hydroxyl groups. These molecules must have at least 3 free amino groups as for example melamine, tri- or tetraamines, etc. (Figure 5).

Micro- and/or nanoparticles with a high hardness will be incorporated to the formulation to increase the hardness and wear resistance of the coating even more. Some nanostructured coatings are approximately three times more resistant than the coatings commonly used and last 40% more. With this method the nanoparticles can be directly applied to the surface of the coating and the final cost can be significantly reduced. Furthermore, the possibility of achieving a customized thickness from a nanolayer to microns contributes to a cost reduction.

The developed product consists of a novel coating with thicknesses between 100 nanometers and 500 microns formed by the co-deposition by means of the self-assembly of micro- and nanoparticles with high hardness, using to that end an organic or organometallic matrix with the capacity to give self-assembly reactions both on the surface of the substrate and between the components of the formulation, allowing the formation of three-dimensional lattices.

Until the optimal formulation of the coating was achieved, different types of functional molecules, solvents, as well as fillers varied in chemical composition, structural composition as well as particle size were tested.

The application parameters (layer thickness, drying temperatures,...), treatment forms (immersion, gun spraying, ...), etc....also influence the qualitative result and final behavior of the coating.

All these factors affect the hydrophobicity of the coating, the surface tension generated, the correct cross-linking of the molecules, the more or less transparent appearance, bubble generation, the loss of adhesion causing for example afterwards a sticky surface, cracking, etc....

Therefore, the right combination of the correct binding agents, the activation of the suitable solvent medium, the optimal fillers, as well as the application method and some specific application parameters, finally lead to obtaining an effective and chemically stable coating.

- 9 -

Several Examples of implementation of the invention are detailed below by way of a non-limiting illustration.

EXAMPLE 1:

1 ml of hydrochloric acid is added to a magnetically stirred ethanol/water (80 ml ethanol; 20 ml H₂O) hydroalcoholic solution. 55 ml of TEOS (tetraethyl orthosilicate) and 23 ml of GLYMO (3-glycidoxypropyltrimethoxysilane) are added. The solution is left stirring for 10 minutes and 5.4 g of alpha-silicon carbide with a particle size of 80 nm are added. The mixture is left stirring for 5 minutes and is applied on the surface of the artificial marble slabs.

It is left to dry in an oven at 120°C for 25 minutes.

EXAMPLE 2:

1 ml of hydrochloric acid is added to a magnetically stirred ethanol/water (80 ml ethanol; 20 ml H₂O) hydroalcoholic solution. 40 ml of TEOS (tetraethyl orthosilicate) and 40 ml of GLYMO (3-glycidoxypropyltrimethoxysilane) are added. The solution is left stirring for 10 minutes and 5.4 g of alpha-silicon carbide with a particle size of 1 micron are added. The mixture is left stirring for 5 minutes and is applied on the surface of the artificial marble slabs.

It is left to dry in an oven at 85°C for 45 minutes

EXAMPLE 3:

The artificial marble slab (substrate) is introduced in an aqueous solution of HCl at 3.5% by volume for 40 seconds at 25°C. The substrate is washed with water 3 times and the substrate is left to dry.

1 ml of hydrochloric acid is added to a magnetically stirred ethanol/water (80 ml ethanol; 20 ml H₂O) hydroalcoholic solution. 25 ml of TEOS (tetraethyl orthosilicate) and 55 ml of GLYMO (3-glycidoxypropyltrimethoxysilane) are added. The solution is left stirring for 10 minutes and 4.4 g of alpha-silicon carbide with a particle size of 1 micron and 1 g of alpha-silicon carbide with a particle size of 80 nm are added. The mixture is left stirring for 5 minutes and is applied on the substrate.

It is left to dry in an oven at 85°C for 45 minutes

EXAMPLE 4:

The artificial marble slab (substrate) is introduced in an aqueous solution of HCl at 3.5% by volume for 40 seconds at 25°C. The substrate is washed with water 3 times and the substrate is left to dry.

1 ml of hydrochloric acid is added to a magnetically stirred ethanol/water (80 ml ethanol; 20 ml H₂O) hydroalcoholic solution. 55 ml of TEOS (tetraethyl orthosilicate) and 25 ml of GLYMO (3-glycidoxypropyltrimethoxysilane) are added. The solution is left stirring for 10 minutes and 25 g of silica with a particle size of 6 microns are added. The mixture is left stirring for 5 minutes and is applied on the substrate.

It is left to dry in an oven at 85°C for 45 minutes

By combining the new hard coating based on micro- and/or nanofillers and a formulated silane (or phosphonates) bond matrix and this binding technique with the substrate:

- A stable coating on the substrate has been achieved.

- 10 -

- Increasing the hardness of the substrate has been achieved.
- Improving the scratch resistance of the substrate has been achieved.
- The adherence of the coating to the substrate has been improved since a chemical bond between the coating and the polyester resin has been created.
- 5 - The chemical resistance and resistance to detergents of the test pieces have been improved.
- Working at low temperature has been achieved.
- Work is carried out in a medium with low toxicity since the solvent used is an aqueous or hydroalcoholic medium, thus preventing harmful volatile emissions and without risk of
- 10 irritation or other health risks for the person handling the solution.

EXAMPLE 5: Etching test.

Some marble pieces are polished and an etching and staining test is subsequently performed therein comparing with non-polished pieces. The result is that the polished pieces have been out of coating and are easily attacked by the hydrochloric acid.

- 15 The areas where it is observed that there is coating remain without alteration. In this case, the achieved hardness reaches 6 in the Mohs scale compared to 3 of the untreated piece. A certain splitting is seen but no scratch is observed nor does loss of material occur.

- 20 When hydrochloric acid and lye are poured, bubbling does not occur and no reaction occurs until several hours have elapsed. In contrast, an untreated piece is etched straightaway and the marble is immediately consumed.

The method of the invention allows achieving the following specific objectives:

- Improvement of the behavior against abrasion without altering the original appearance of the substrate.
- It does not affect other properties of the end product (bending, impact resistance, processability, physical characteristics, mechanical properties, etc.)
- 25 - With this new treatment, a stable coating is formed which is long-lasting, mainly due to the high adherence on the substrate which is generated by means of the formation of robust interactions of electrostatic, covalent type, etc., between the coating and the substrate.
- 30 - It works in a broad range of stone substrates based on a mixture of stone aggregates agglomerated by means of an organic binder. The binder used as a binding agent of the stone material being able to be both thermosetting and thermoplastic. The nature of the mineral varies according to the petrographic origin of the chosen natural stone (marble, limestone, quartz, granite, etc....)
- 35 - It prevents agglomeration problems when working in bulk.
- It reduces the generation of waste after the production process: decrease of the rejection of scratched pieces.
- The additional costs of the end product are minimum.
- There are no environmental risks or health risks since they are treatments based on
- 40 volatile-free solvents.

- 11 -

- Upon working at low temperature it is possible to have pieces without apparent degradation, unlike what can occur with more aggressive deposition systems such as those of plasma or corona.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for coating a stone type substrate, said substrate being based on a mixture of stone aggregates with calcareous materials and/or dolomitic limestones agglomerated by means of a first binder, said method comprising the formation of a coating layer over said substrate to increase its hardness, chemical resistance, wear and scratch resistance, said formulation of a coating layer being characterized in that it comprises the steps:
- applying on said substrate a coating matrix incorporating at least one organic material that is selected from organosilanes, organophosphonates, polycarboxylic compounds, compounds based on triazine heterocycles and fillers including inorganic nanoparticles and/or microparticles;
- chemically binding said matrix to the substrate by means of conducting a self assembly process and/or by means of a binding process by covalent bonding, electrostatic bonding, van der Waals bonding or hydrogen bonds; and
- drying said coating matrix,
- wherein said organic material, which is at least one in number, and/or said nanoparticles and/or microparticles are functionalized with molecules with at least one of the following groups: Si-OH, Si-Cl or SiOR wherein R is an organic compound, aldehyde or ketone or COOH, NH₂, phosphates, phosphonates, sulfonates, sulfates, or the combination thereof and wherein said nanoparticles and microparticles are selected from the group including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, n-Na₂SiO₃, and combinations thereof,
- to form a three-dimensional lattice, which is bound to the substrate by chemical bonds encapsulating different nanoparticles and/or microparticles.
2. The method according to claim 1, characterized in that said coating matrix comprises a thermosetting aqueous-based polymer as a binder and an aqueous, or alcoholic or hydroalcoholic solvent and a reaction accelerator.

3. The method according to claim 2, characterized in that said thermosetting polymer is a triazine heterocycle.

4. The method according to any one of claims 1 to 3, characterized in that said application on the substrate of said coating matrix is performed by means of a co-deposition
5 of organic material and nanoparticles and/or microparticles.

5. The method according to any one of claims 1 to 4, characterized in that said drying of the matrix comprises the step of applying heat to the coated substrate to accelerate a dehydration process of the free functional groups and improve the cross-linking thereof.

6. A board made of stone material, comprising a natural calcareous substrate or a
10 stone agglomerate incorporating calcareous materials and/or dolomitic limestones with a coating layer formed according to the method according to any one of claims of 1 to 5.

7. The board according to claim 6, characterized in that said coating layer has a thickness within the range of 100 nanometers to 500 microns.

8. The board according to claim 6 or 7, characterized in that said coating layer
15 comprises inorganic microparticles and/or inorganic nanoparticles with high hardness of at least one material selected from: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, $n\text{-Na}_2\text{SiO}_3$, and combinations thereof.

9. A composition for coating an element in the form of a board made of stone
20 type substrate, said substrate being based on a mixture of stone aggregates with calcareous materials and/or dolomitic limestones agglomerated by means of a first binder, characterized in that said composition comprises at least one organic material selected from organosilanes, organophosphonates, polycarboxylic compounds, compounds based on triazine heterocycles, and fillers including inorganic nanoparticles and/or inorganic microparticles;

25 wherein said organic material and said inorganic nanoparticles and microparticles are functionalized with molecules having at least one of the following groups: Si-OH, Si-Cl or SiOR wherein R is an organic compound, aldehyde or ketone or COOH, NH_2 , phosphates, phosphonates, sulfonates, sulfates and wherein said nanoparticles and microparticles are selected from the group including: alumina, boron carbide, boron nitride, silicates, glass
30 microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell

particles, $n\text{-Na}_2\text{SiO}_3$, and combinations thereof; being bound in a matrix by means of conducting a self-assembly process and/or other chemical bonding or electrostatic or chemical interaction processes.

10. The composition according to claim 9, comprising an aqueous-based organic
5 binder material, an aqueous, alcoholic, hydroalcoholic solvent and a reaction accelerator.

11. The composition according to claim 9 or 10, characterized in that said organosilane material is an organofunctionalized silane selected from the group of materials including: TEOS (tetraethyl orthosilicate), gamma-methacryloxypropyltrimethoxysilane, BTSE (1,2-bis (triethoxysilyl)ethane, hexadecyltrimethoxysilane, 3-
10 glycidoxypropyltrimethoxysilane, dichloro(diphenyl)silane, dichlorodimethylsilane; organophosphonates, polycarboxylic compounds, and compounds based on triazine heterocycles or an organic material having triazine groups selected from 1,3,5-triazine or having free amino groups, selecting diamino-PEG from this group, and wherein said inorganic nanoparticles and inorganic microparticles are selected from the group of materials
15 including: alumina, boron carbide, boron nitride, silicates, glass microspheres, silicon carbide, silica, quartz, copper oxide, micro- and nanofibers, core-shell particles, $n\text{-Na}_2\text{SiO}_3$, and combinations thereof.

12. The composition according to claim 11, characterized in that said nano- and microparticles are functionalized with phosphonates, amino, aldehyde, sulfonates, sulfates,
20 carboxyl groups or organosilanes.

13. The composition according to any one of claims 9 to 12, characterized in that the organic binder is a thermosetting polymer with reactive functional groups.

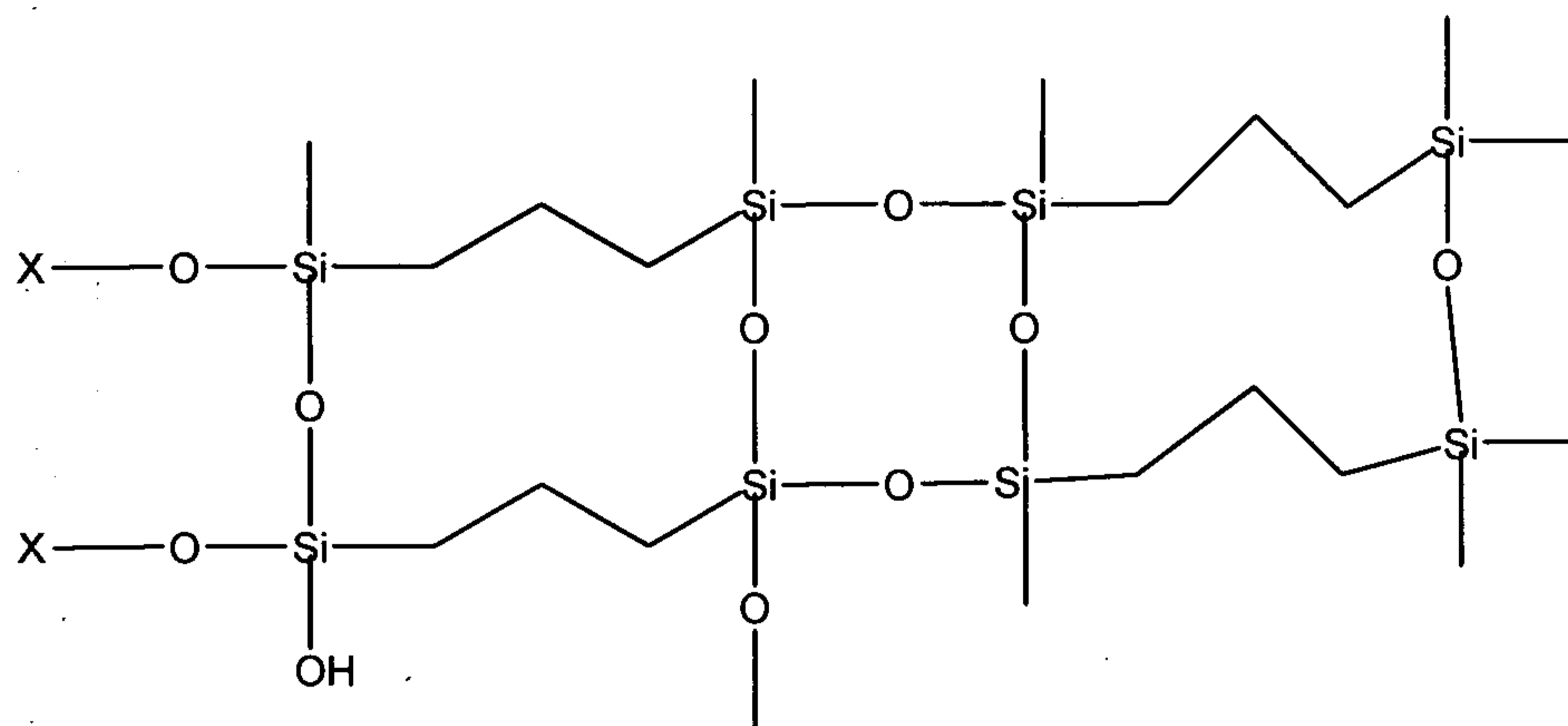


FIG. 1

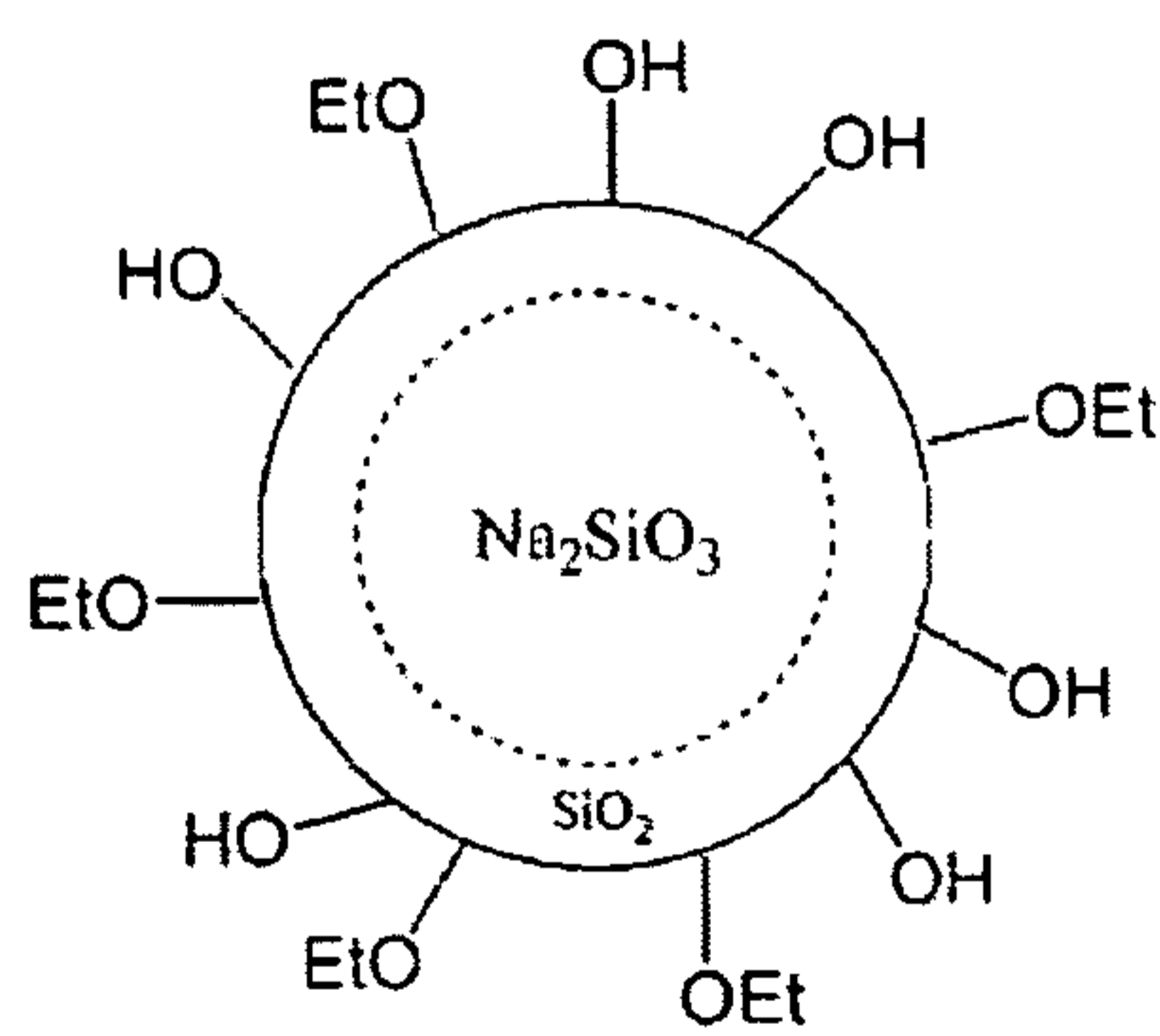


FIG. 2

2/5

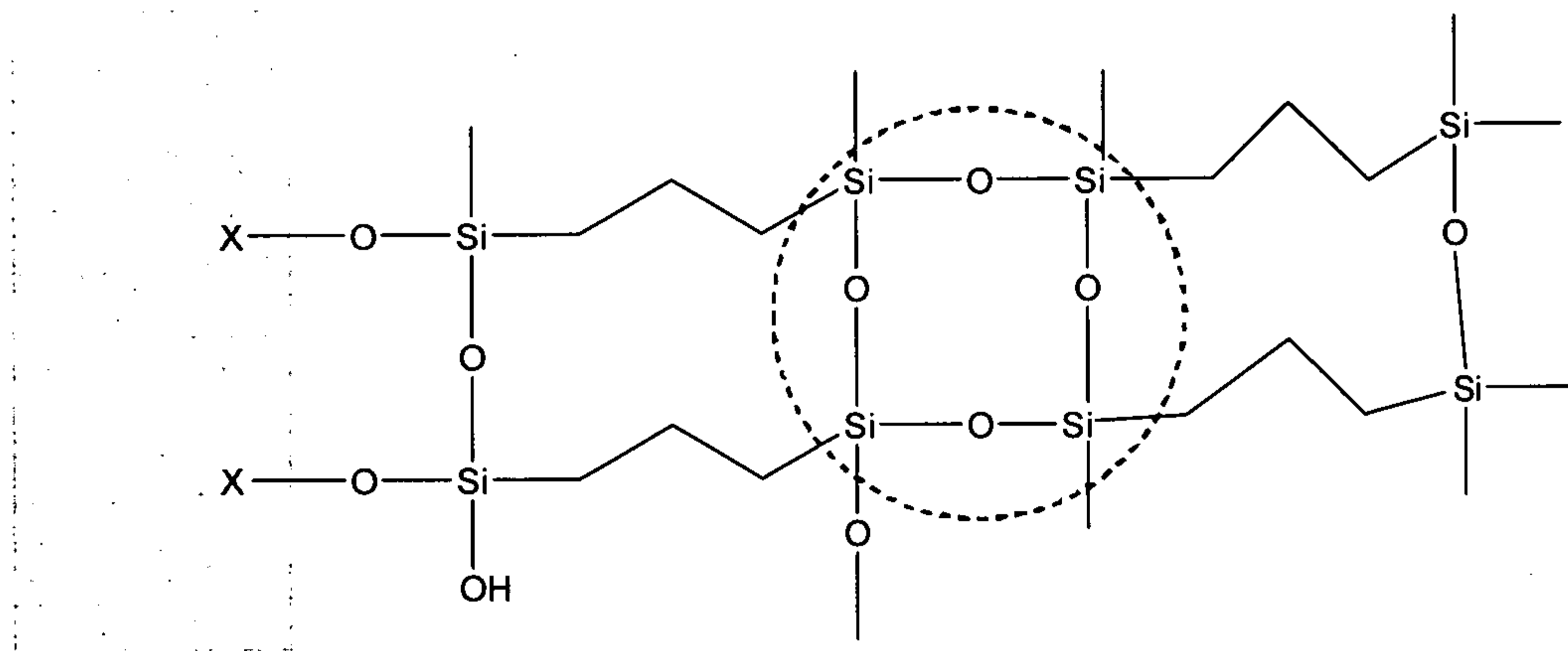


FIG. 3

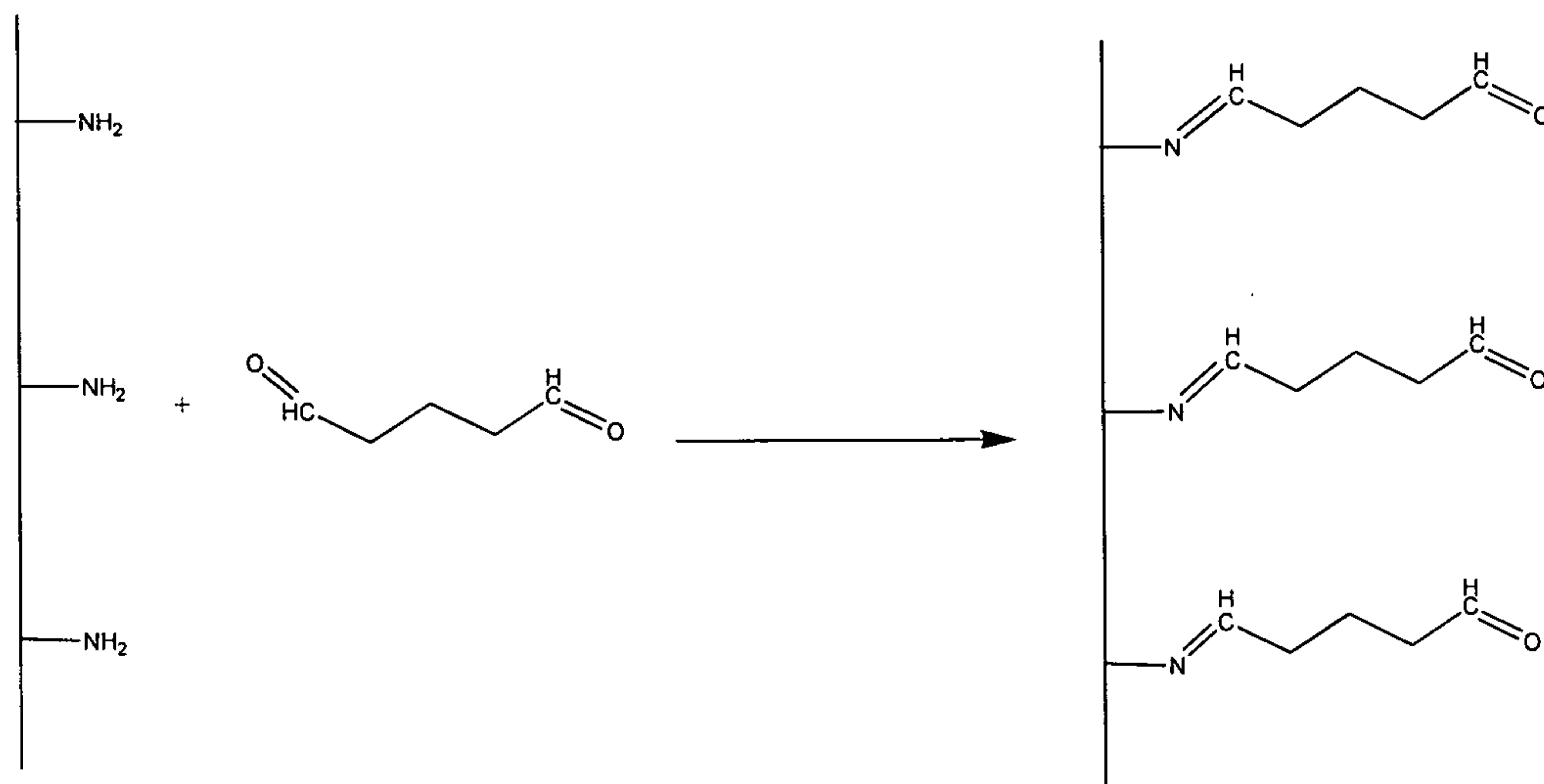


FIG. 4

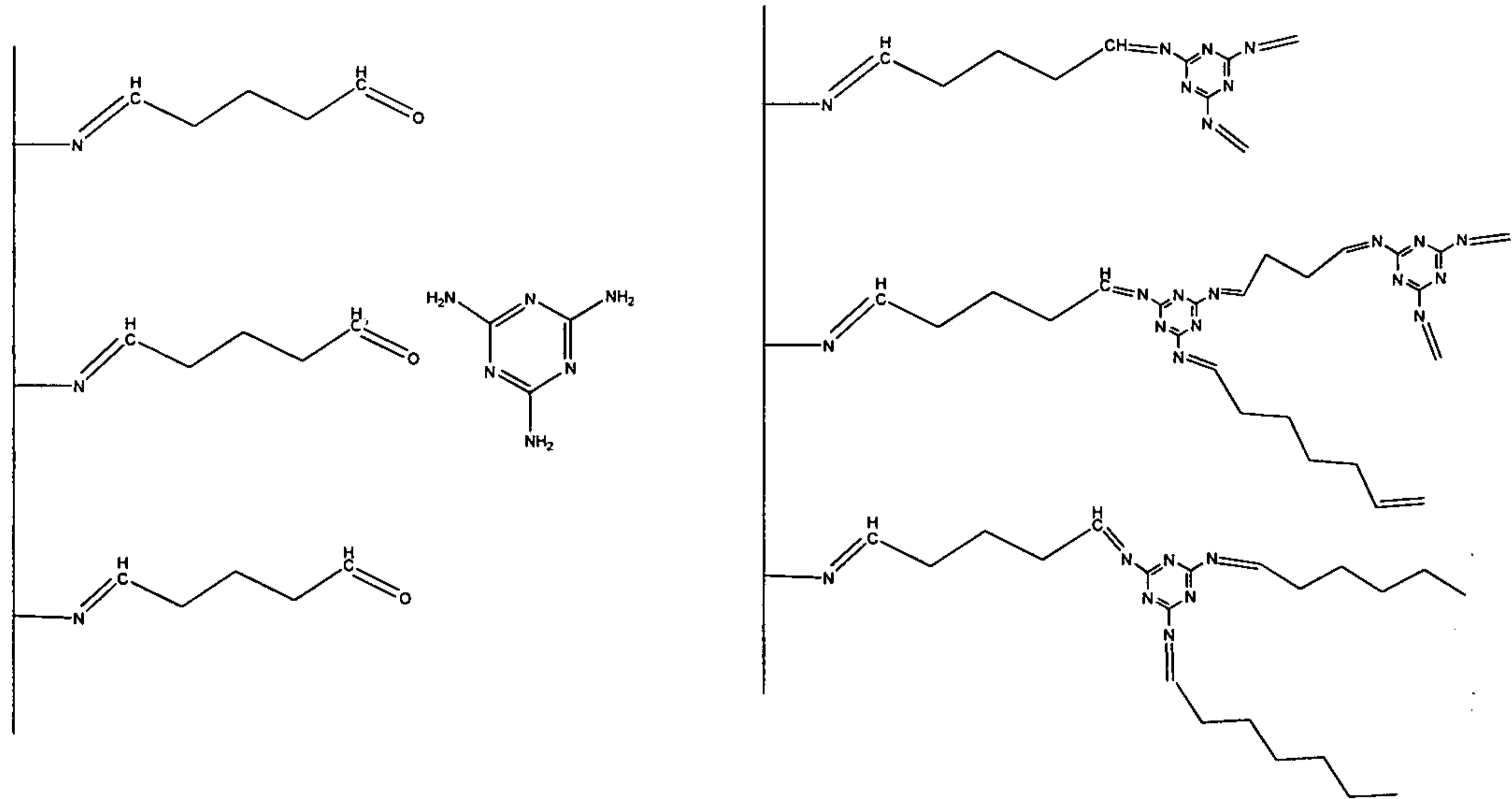


FIG. 5

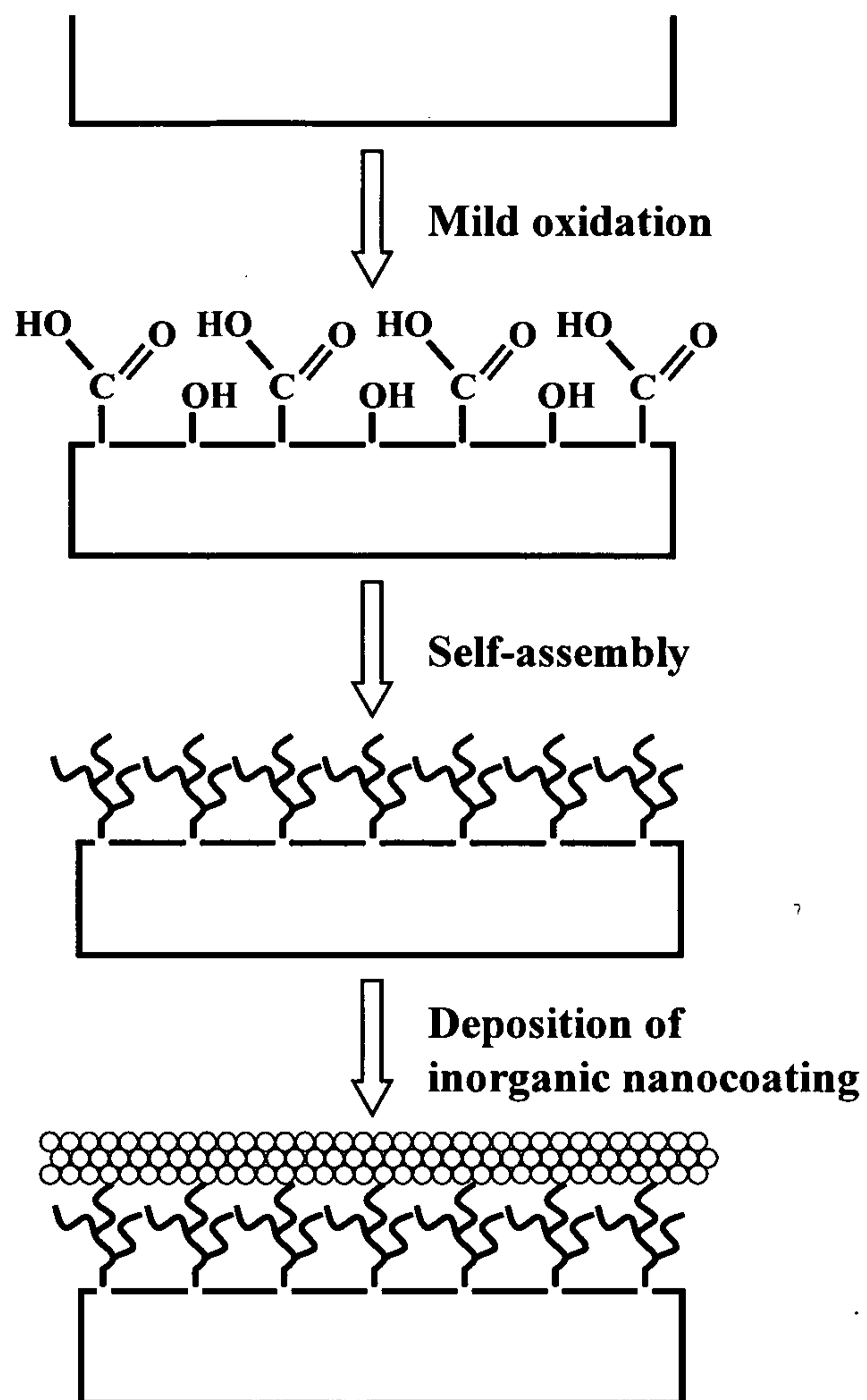


FIG. 6

5/5

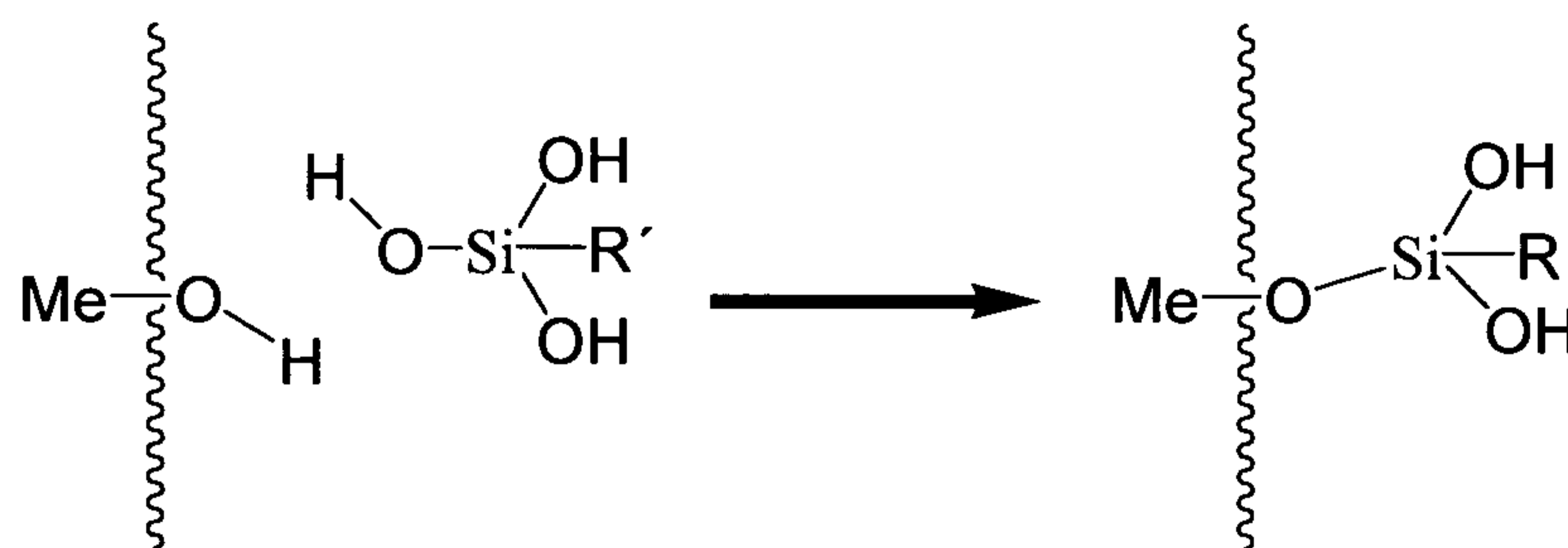
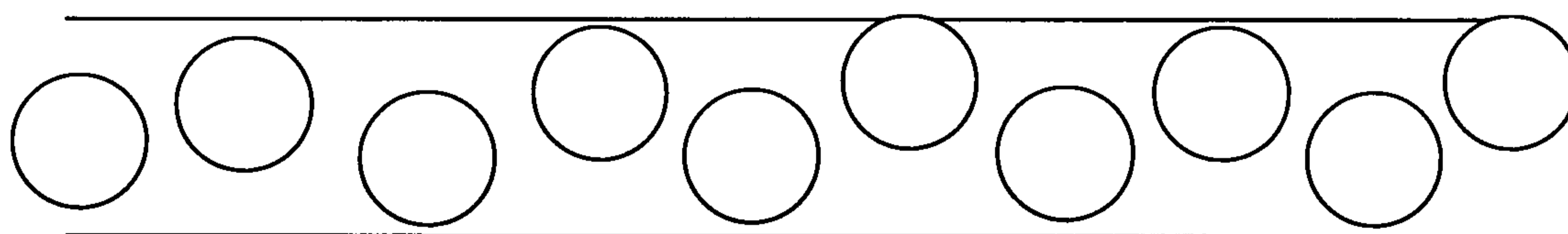


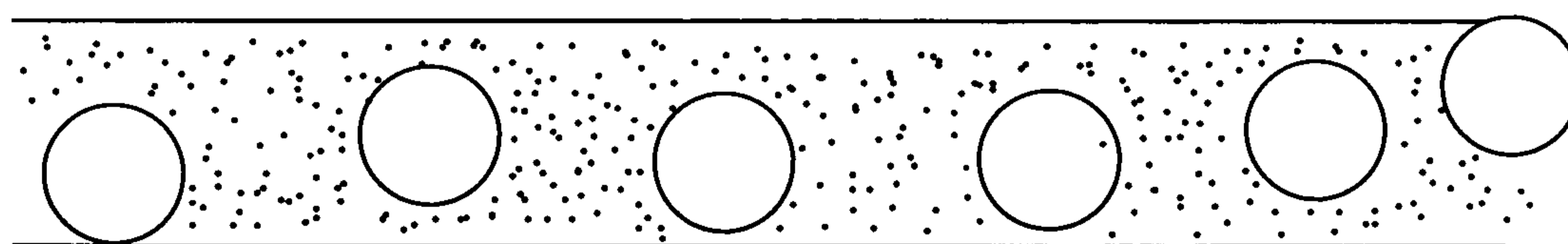
FIG. 7

Microcomposite



SUBSTRATE

Micro & nanocomposite



SUBSTRATE

FIG. 8

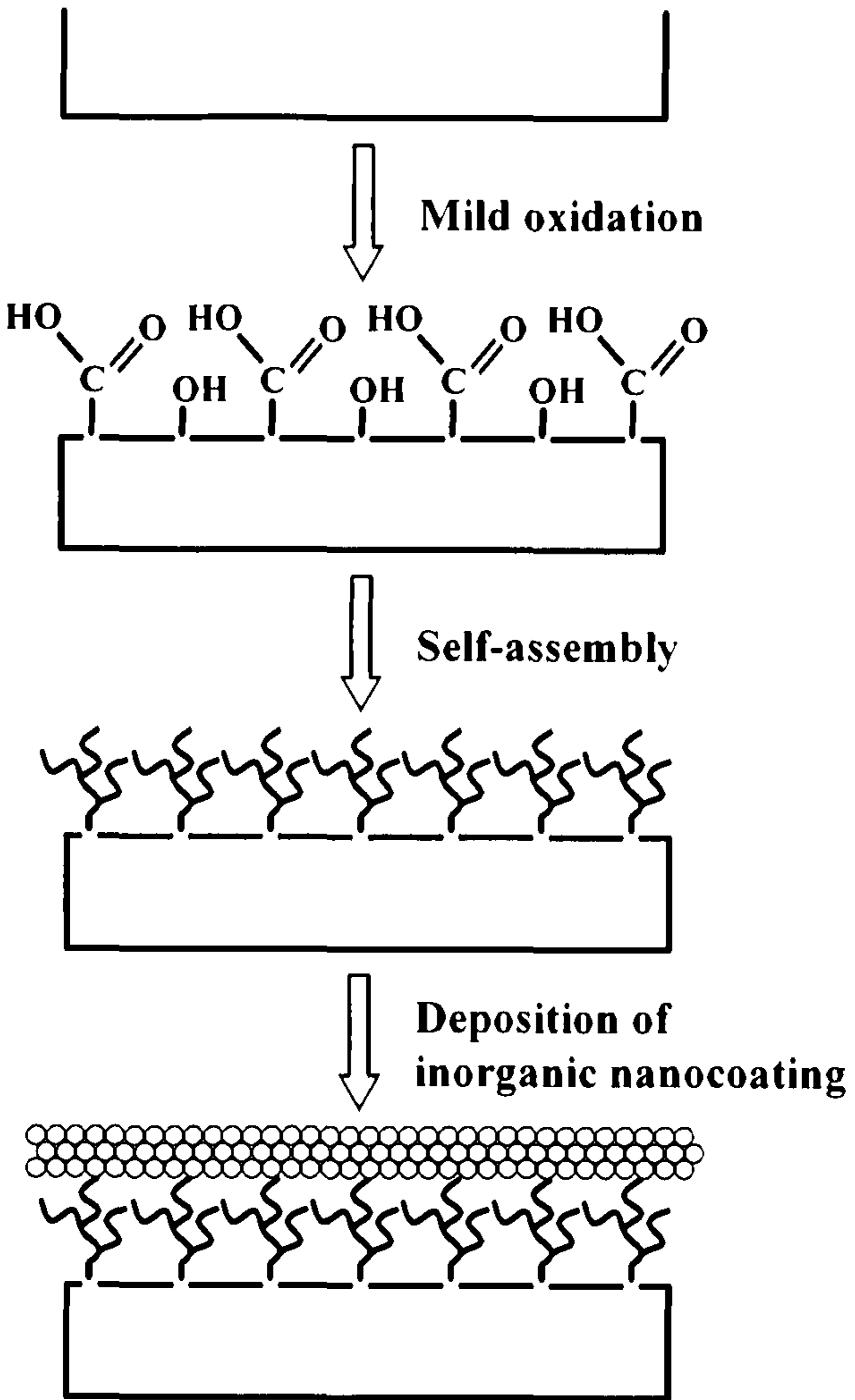


FIG. 6