US 20110168558A1

(19) **United States**

(12) **Patent Application Publication**

Fransaer et al.

(10) **Pub. No.: US 2011/0168558 A1**

(43) **Pub. Date: Jul. 14, 2011**

(54) **AQUEOUS ELECTROPHORETIC DEPOSITION**

(76) Inventors: **Jan Fransaer**, Leefdaal (BE); **Bram Neirinck**, Izogem (BE); **Omer Van Der Biest**, Herent (BE); **Jozef Vleugels**, Olen (BE)

(21) Appl. No.: **13/121,096**

(22) PCT Filed: **Sep. 25, 2009**

(86) PCT No.: **PCT/EP2009/062472**

§ 371 (c)(1),
(2), (4) Date: **Mar. 25, 2011**

Related U.S. Application Data

(60) Provisional application No. 61/194,316, filed on Sep. 26, 2008, provisional application No. 61/195,392, filed on Oct. 6, 2008.

(30) **Foreign Application Priority Data**

Oct. 8, 2008 (GB) 0818403.8

Publication Classification

(51) **Int. Cl.**
C25D 13/04 (2006.01)
C25D 13/00 (2006.01)

(52) **U.S. Cl.** **204/477**

(57) **ABSTRACT**

From an environmental, safety and economic perspective water should be the solvent of choice for electrophoretic deposition under industrial circumstances. However, because of the electrolytic decomposition of water, the majority of EPD is carried out in non-aqueous solvents.

Approaches of the art for aqueous deposition involve the separation of the reaction and deposition front by means of a membrane, the use of palladium electrodes to absorb the formed hydrogen, addition of chemicals to suppress the electrolysis reaction, or lowering voltages below the threshold for water electrolysis. With the first two solutions, the production of coatings is impractical since the deposit is not formed on the electrode, or the electrode material is not suitable since the substrate is usually prescribed by the application. The use of specialty chemicals is expensive and difficult to control. Low voltages have been used to form high quality deposits from aqueous systems but they display very low deposition rates, which are not attractive from an economical perspective.

Present invention provides a system and a means for which high voltages can be used in the electrophoretic deposition from aqueous suspensions without decomposition of water at satisfying deposition rates. It shows that the deposits obtained show a high green density with excellent surface quality.

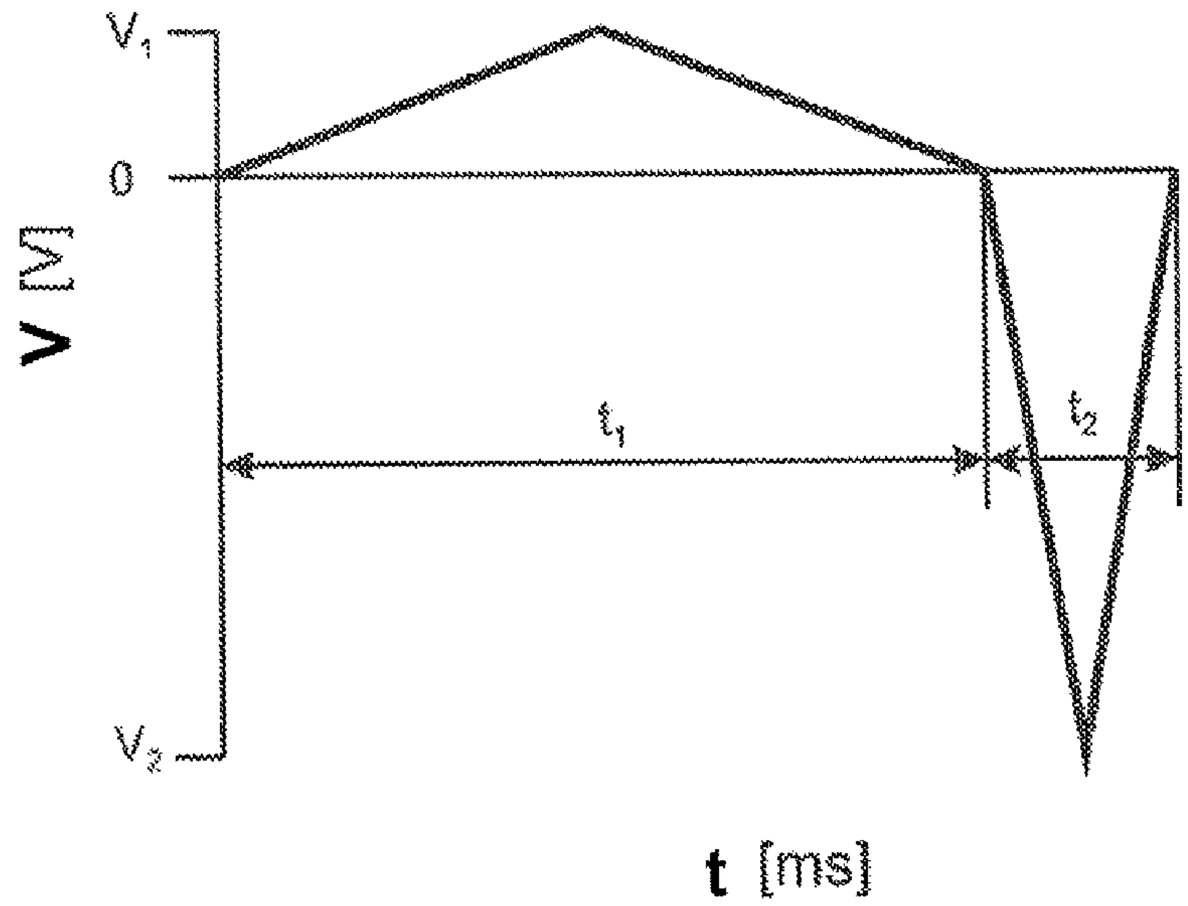

Figure 1

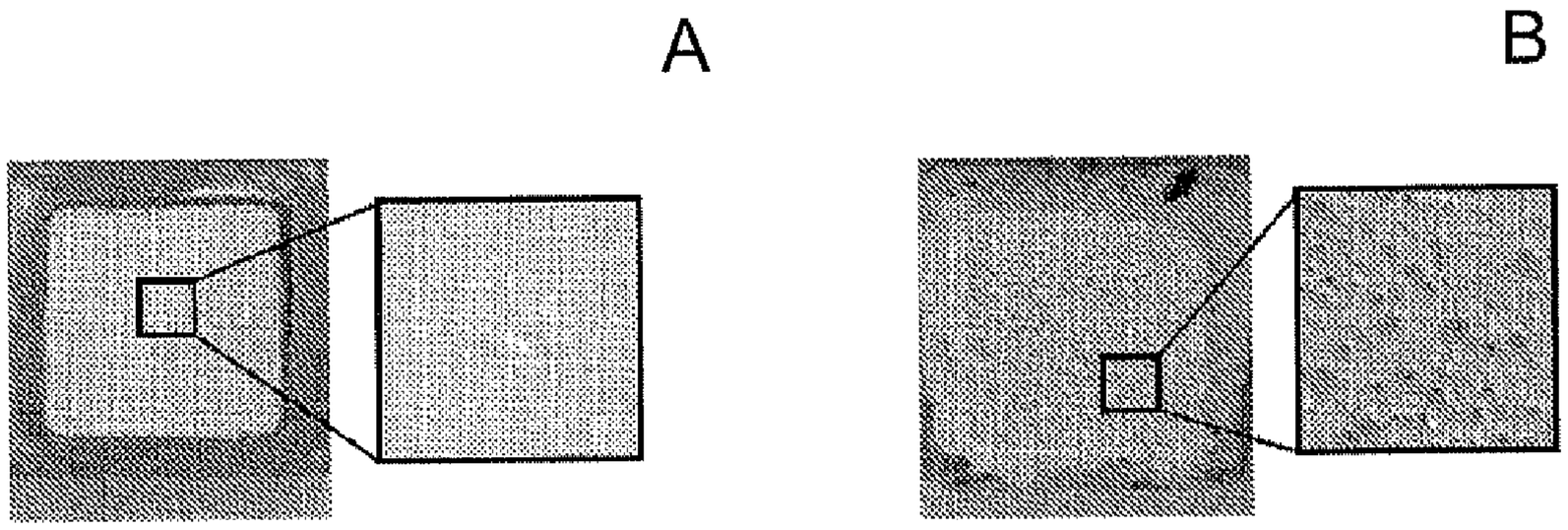

Figure 2

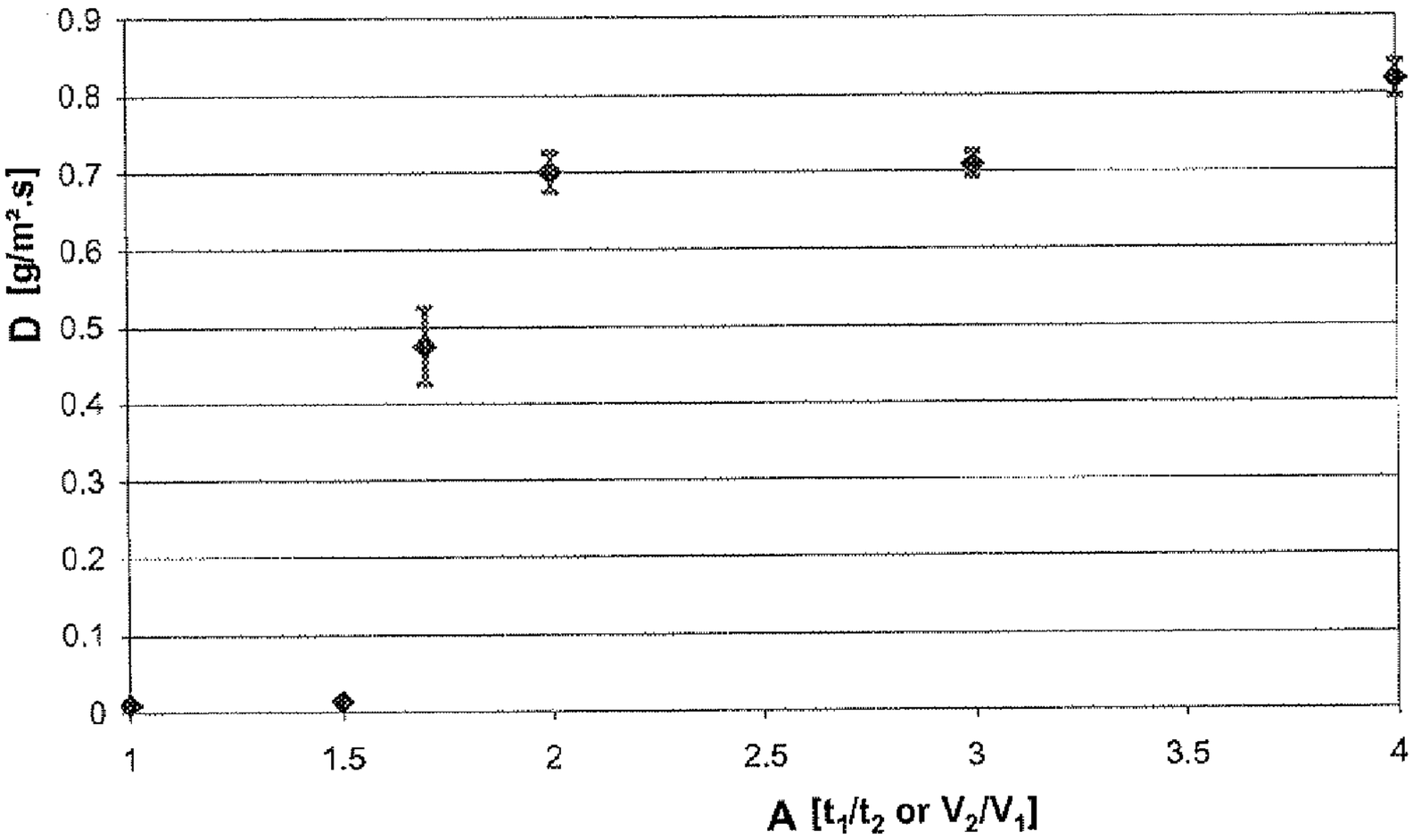

Figure 3

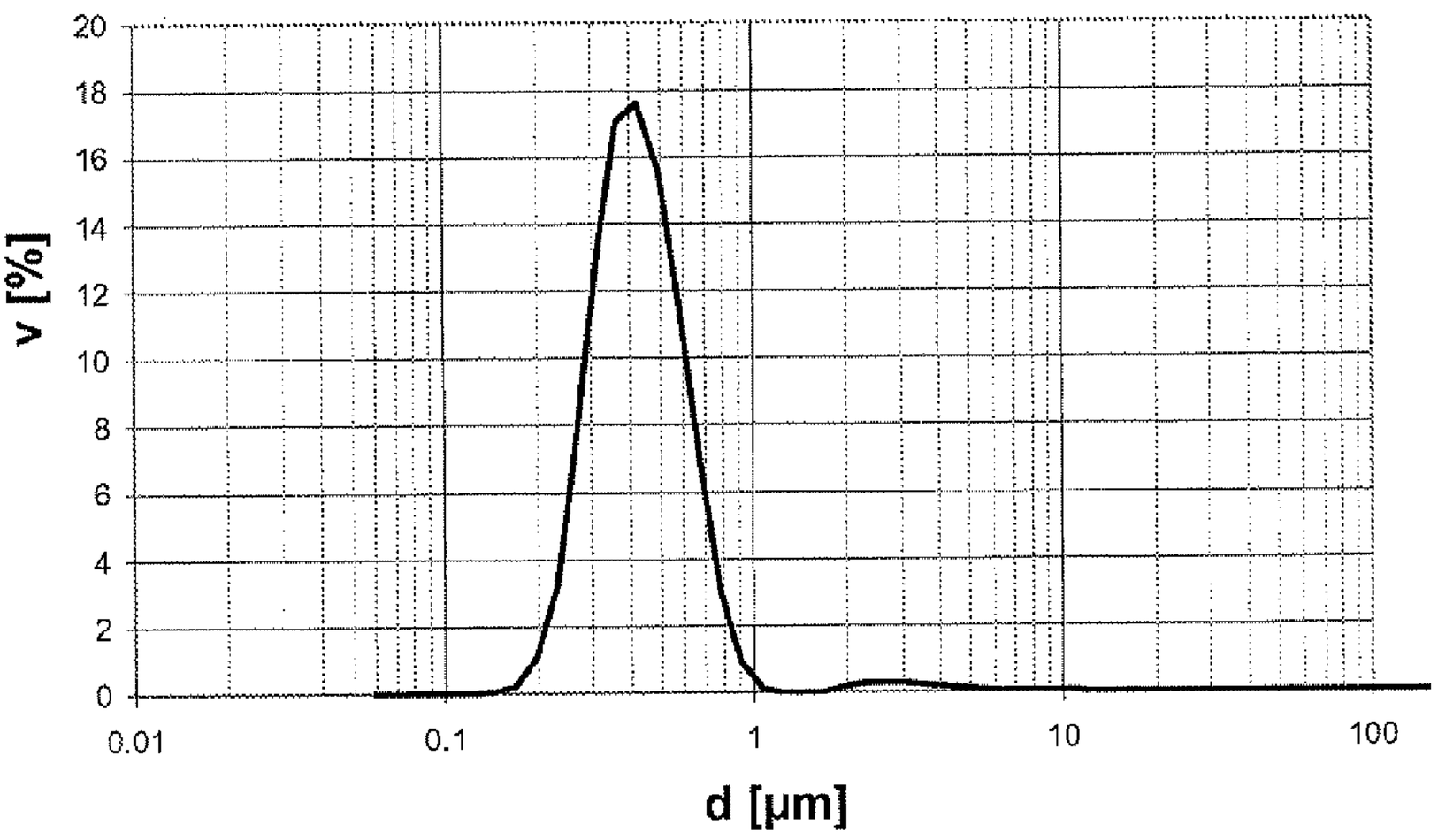

Figure 4

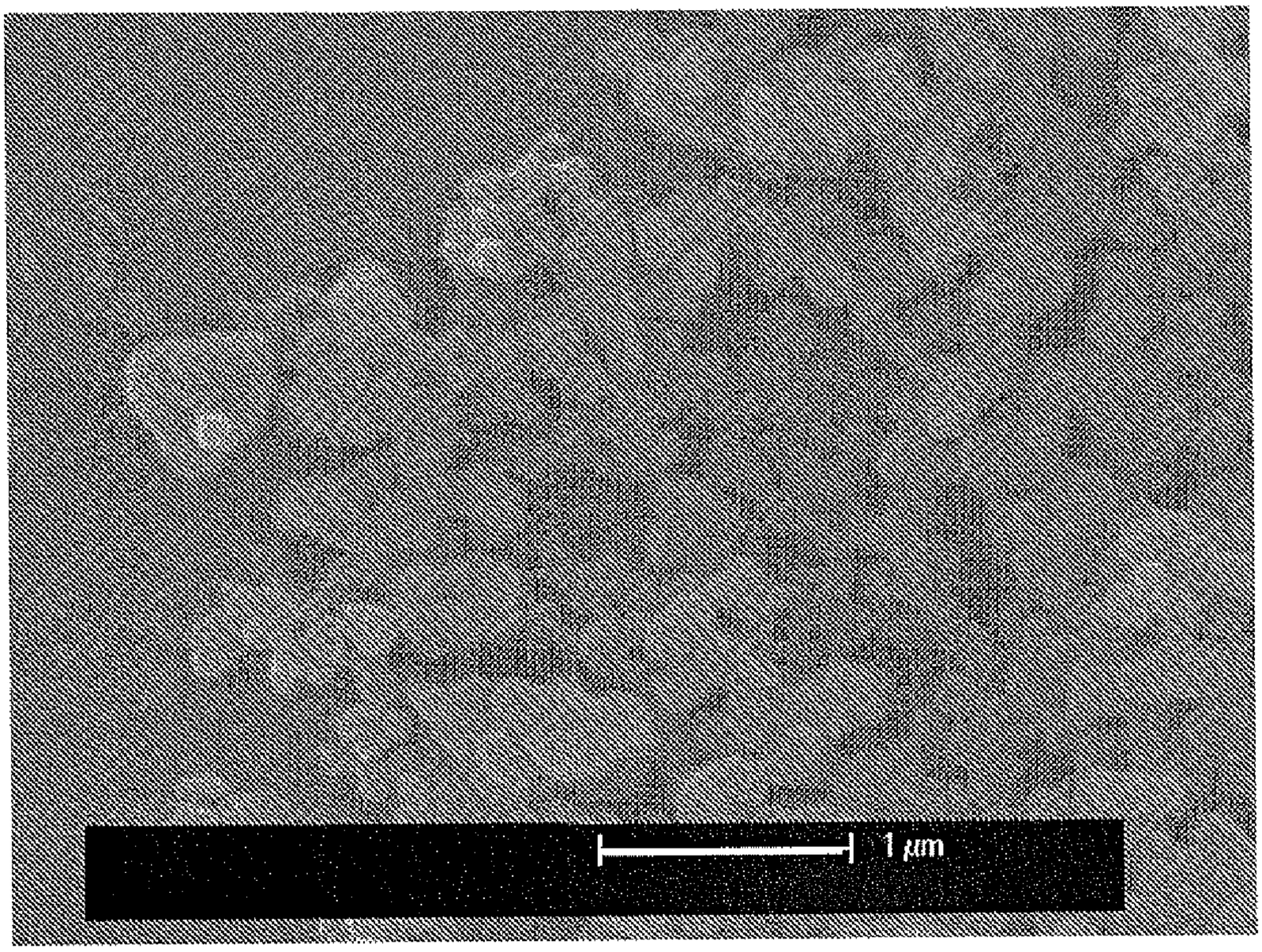

Figure 5

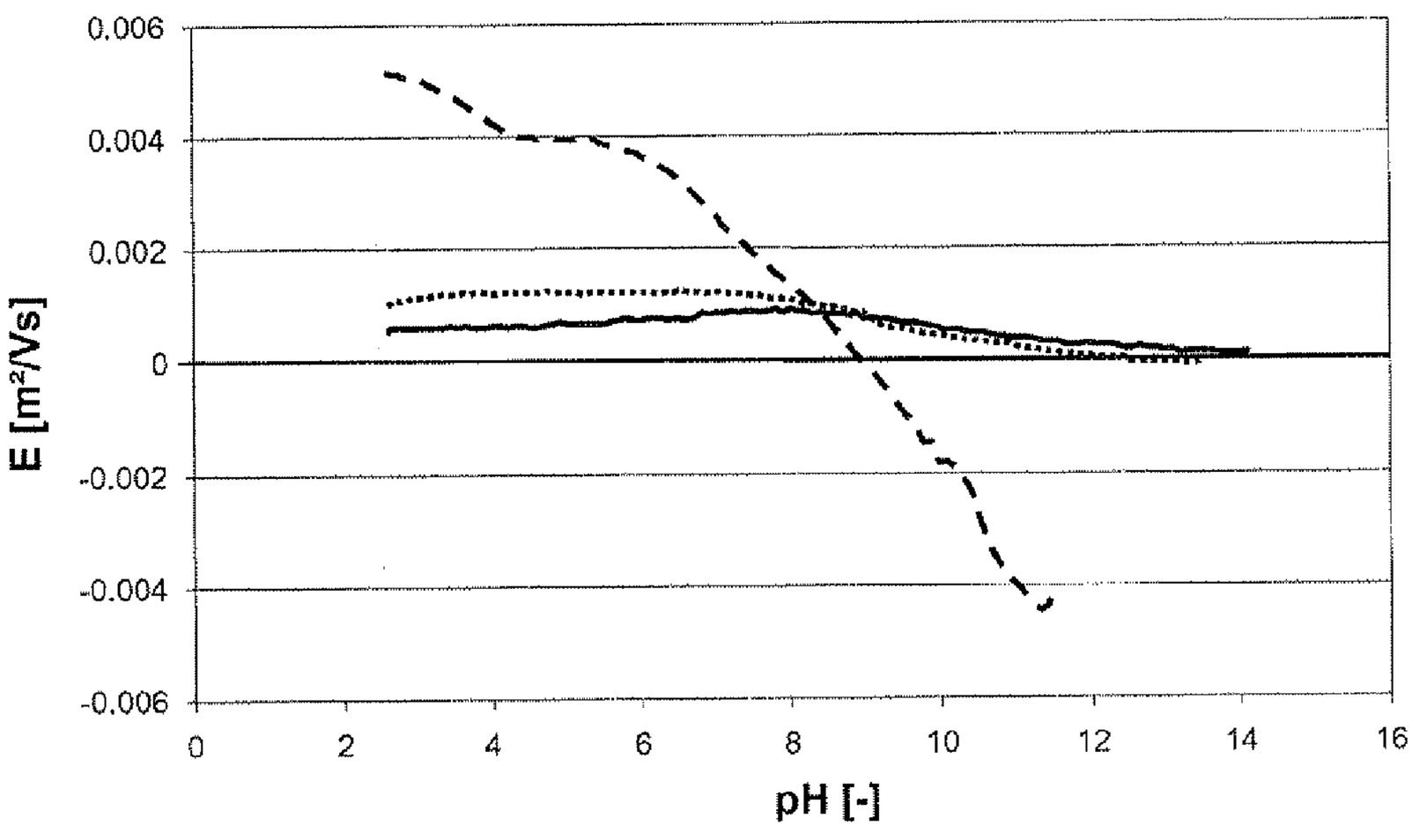

Figure 6

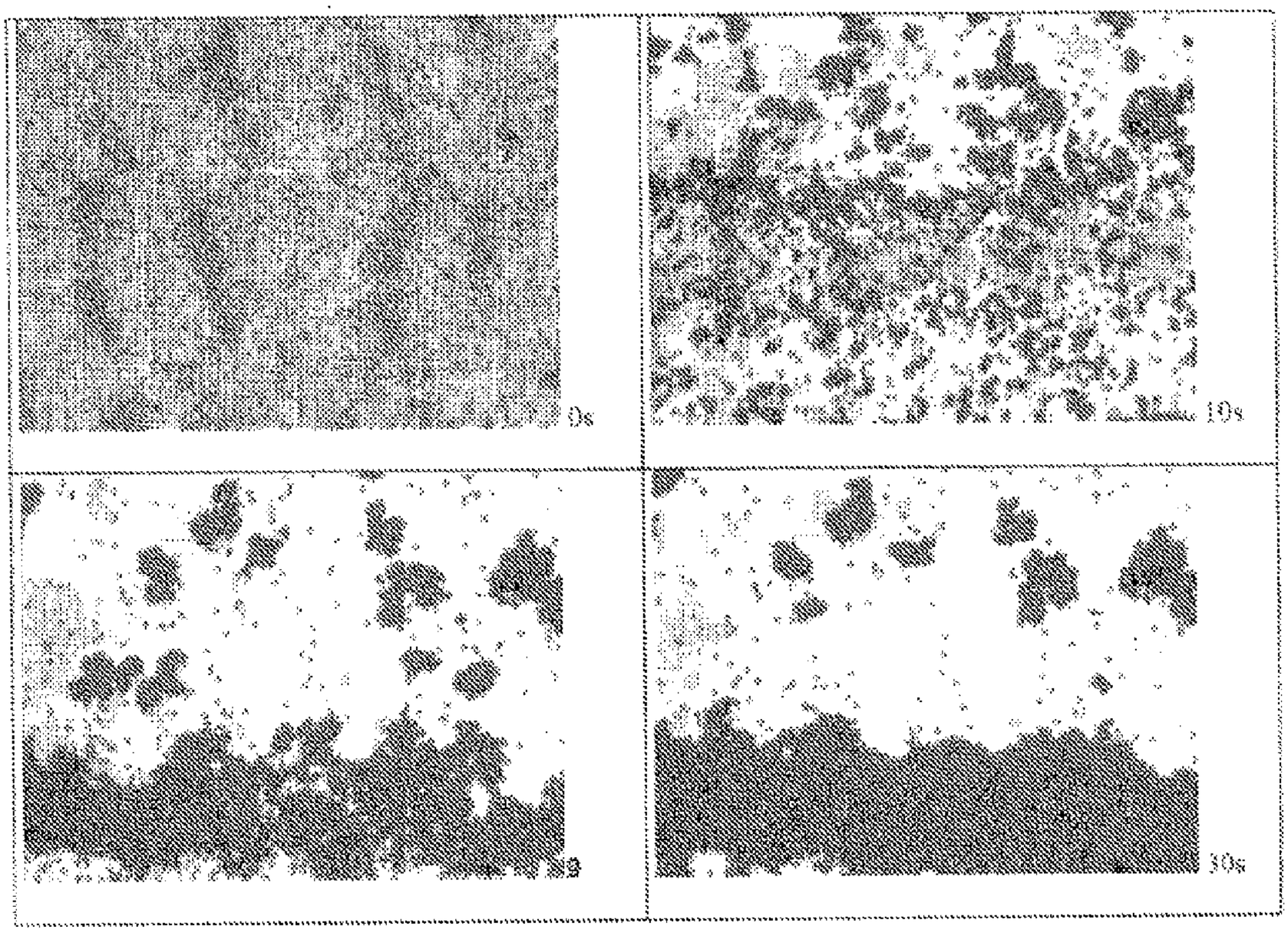

Figure 7

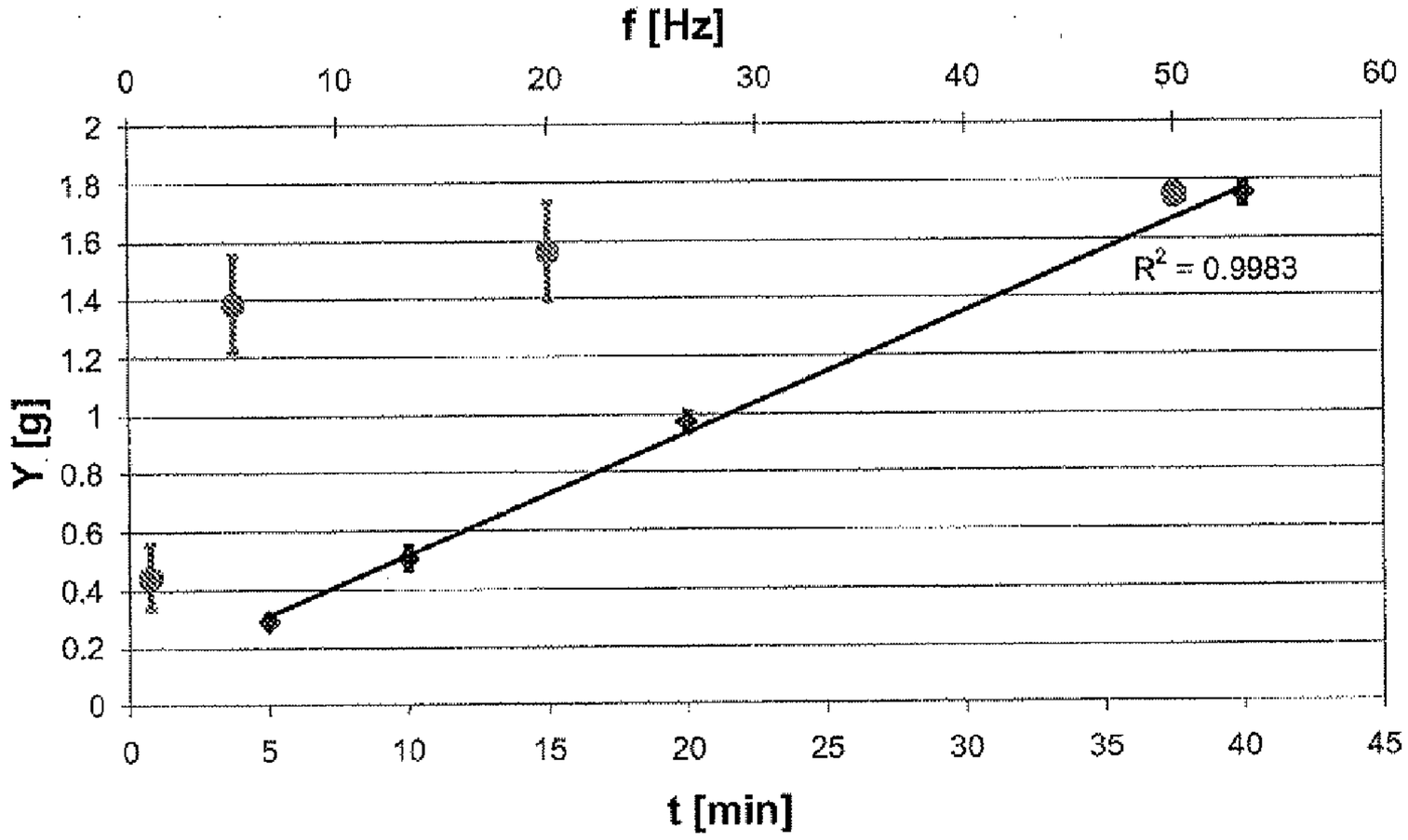

Figure 8

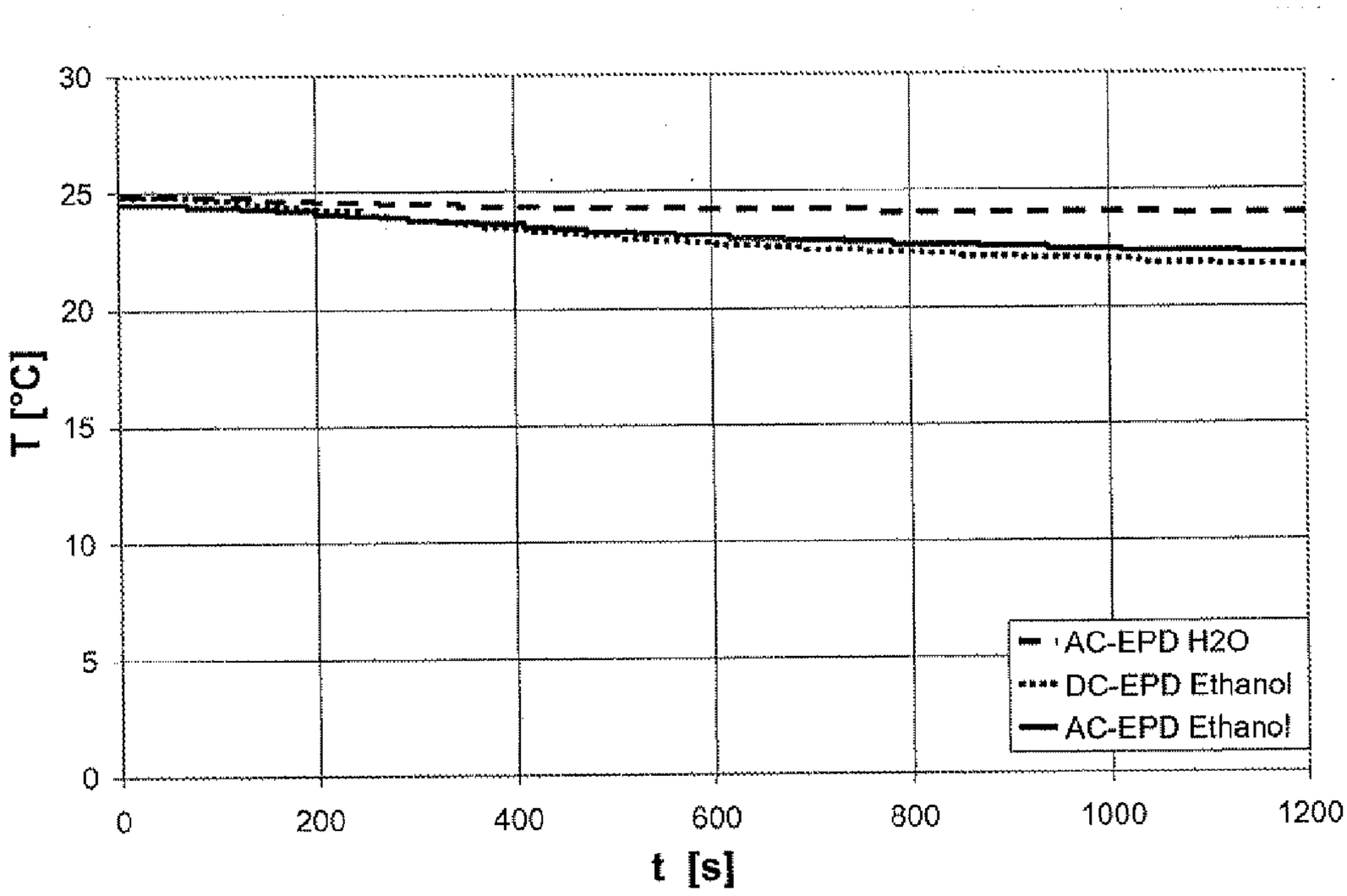

Figure 9

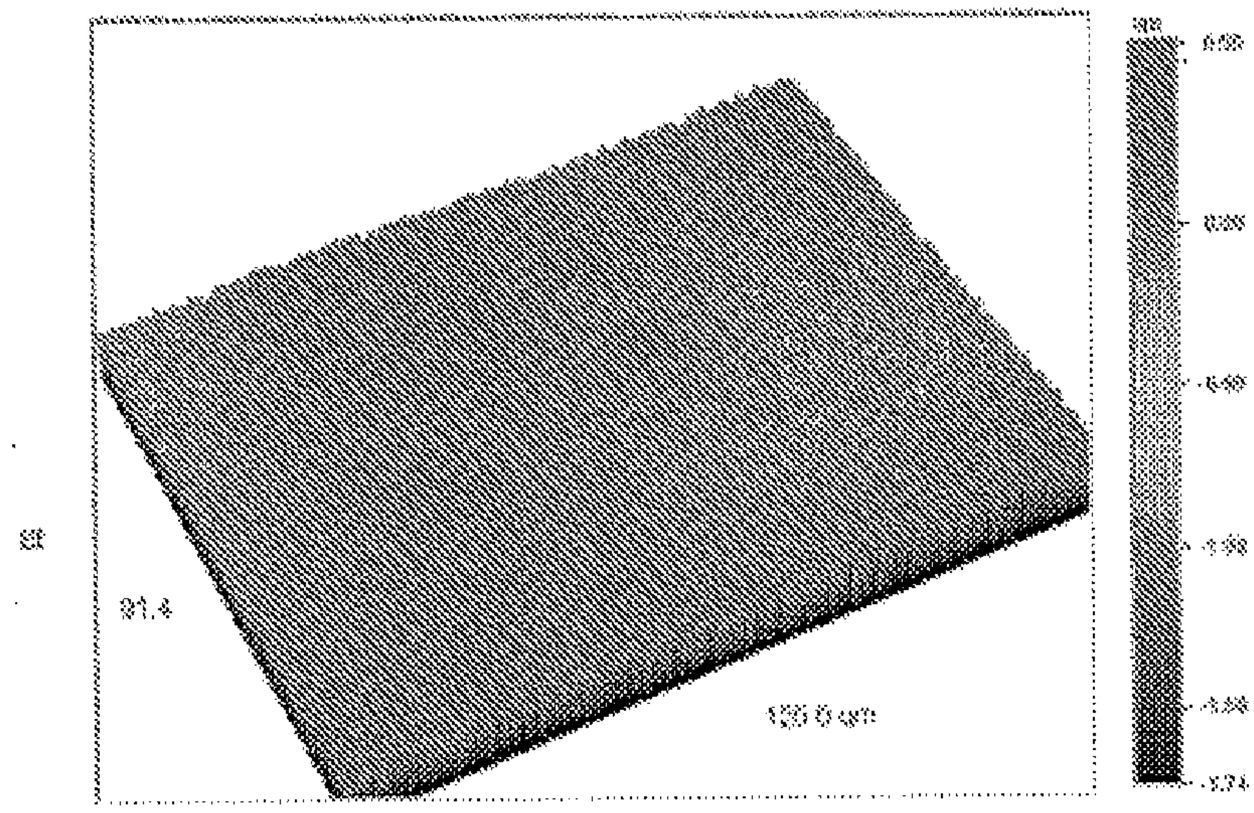

Figure 10

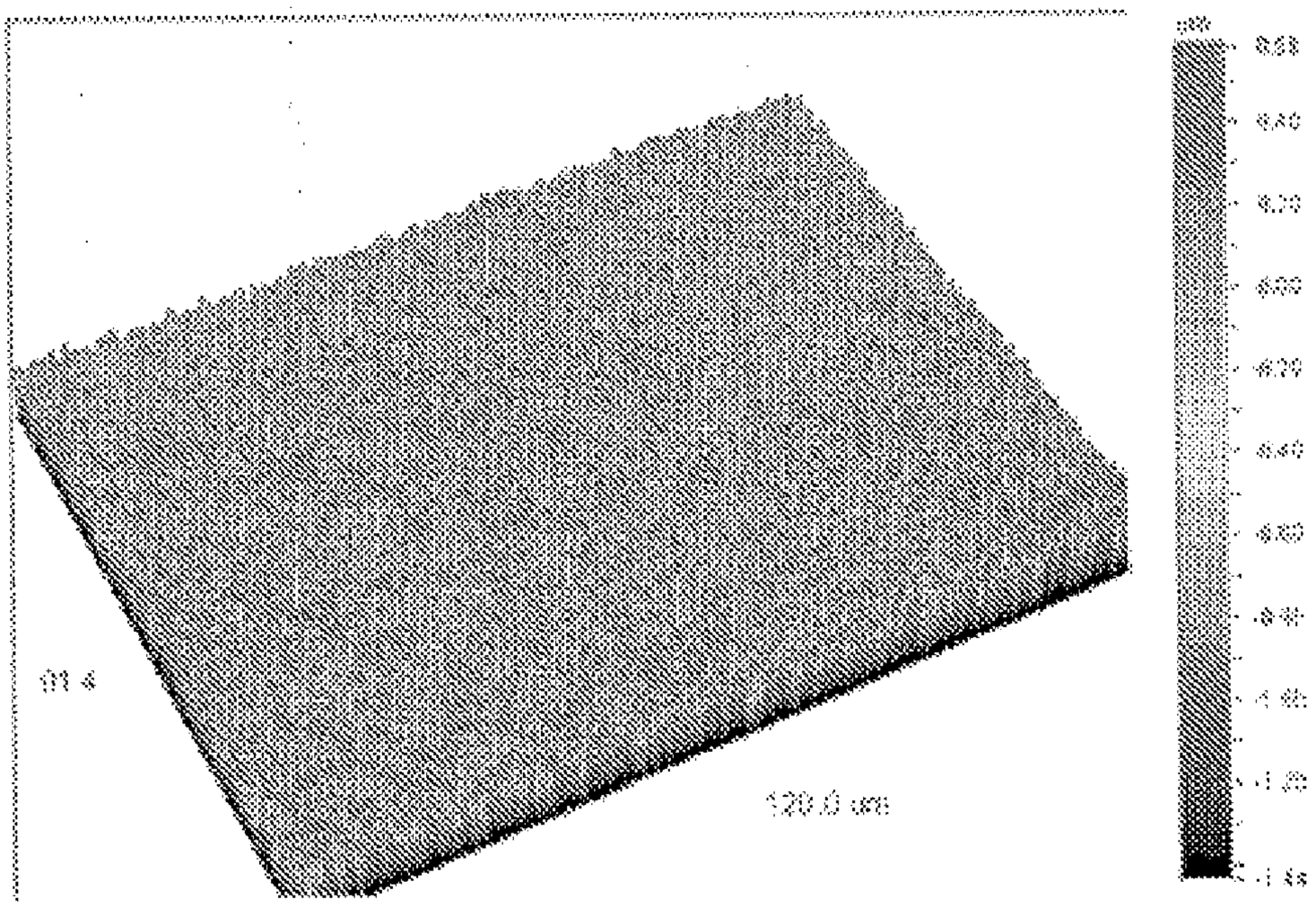

Figure 11

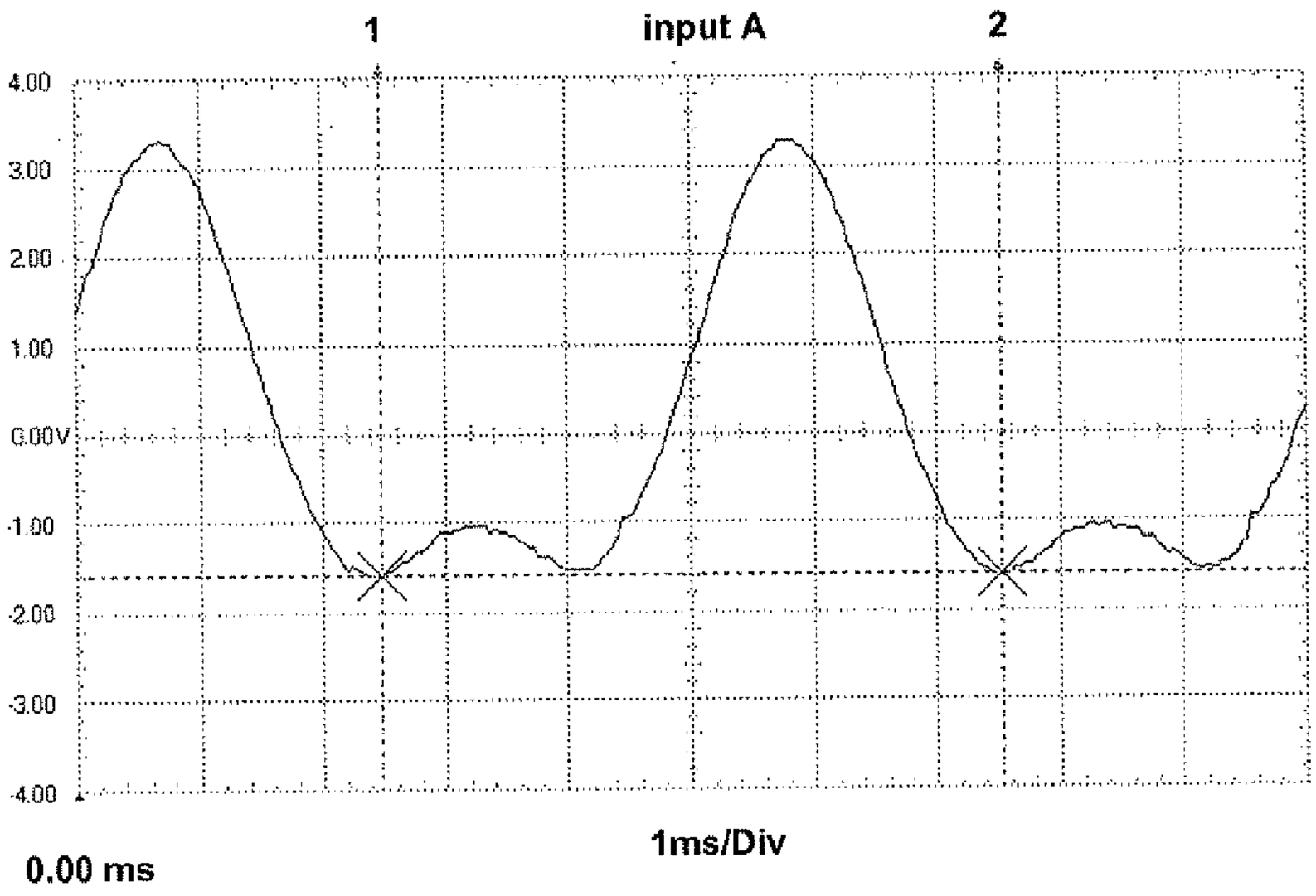

Figure 12

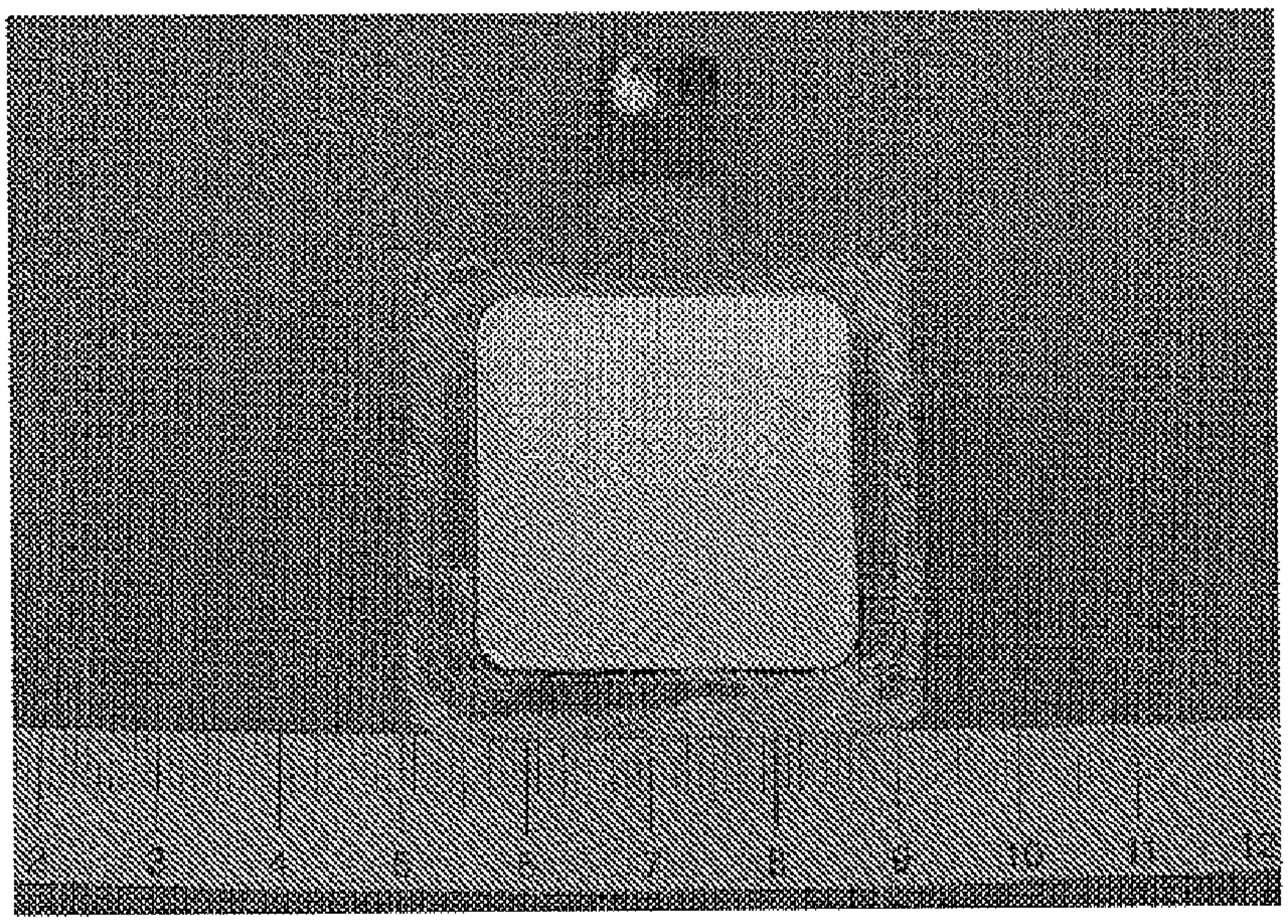

Figure 13

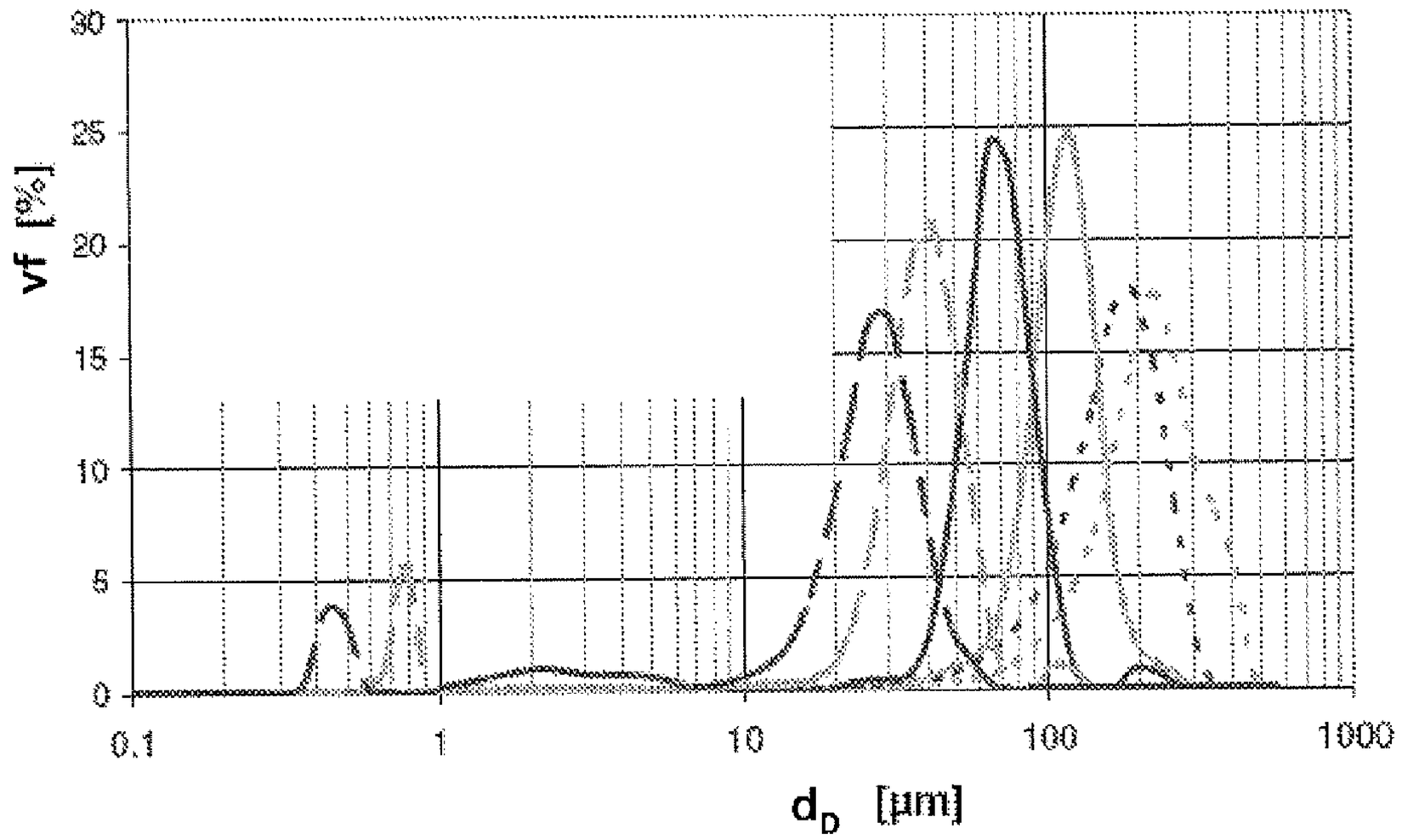

Figure 14

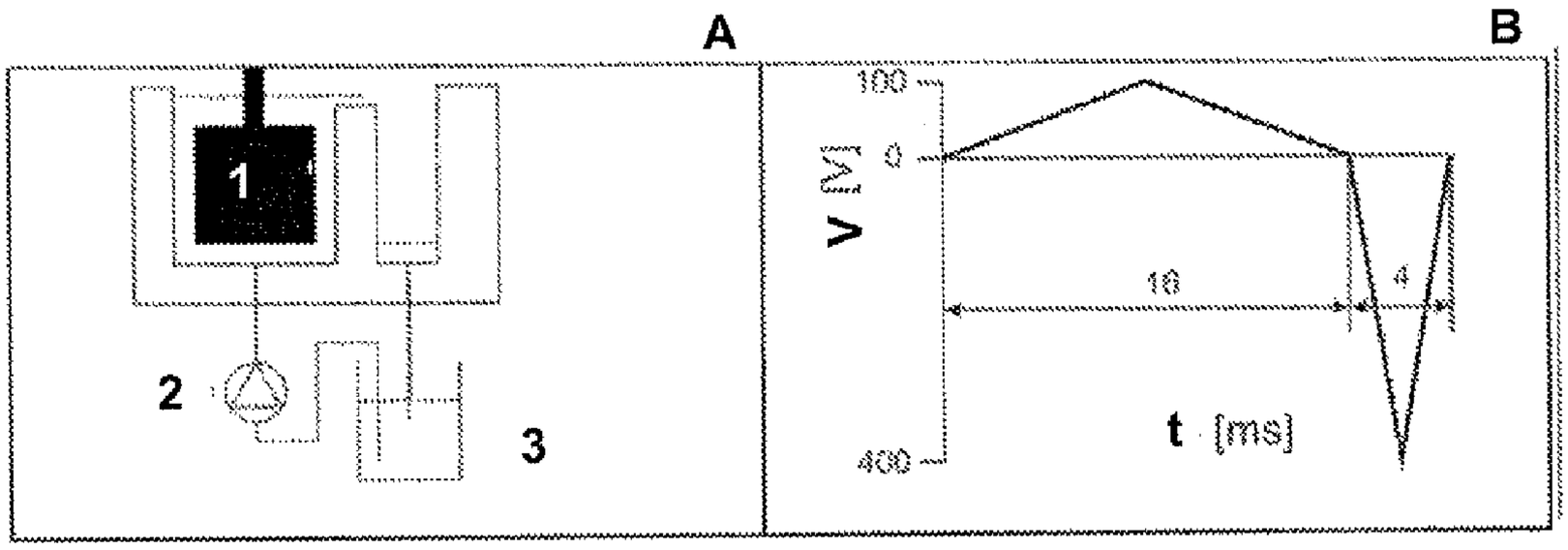

Figure 15

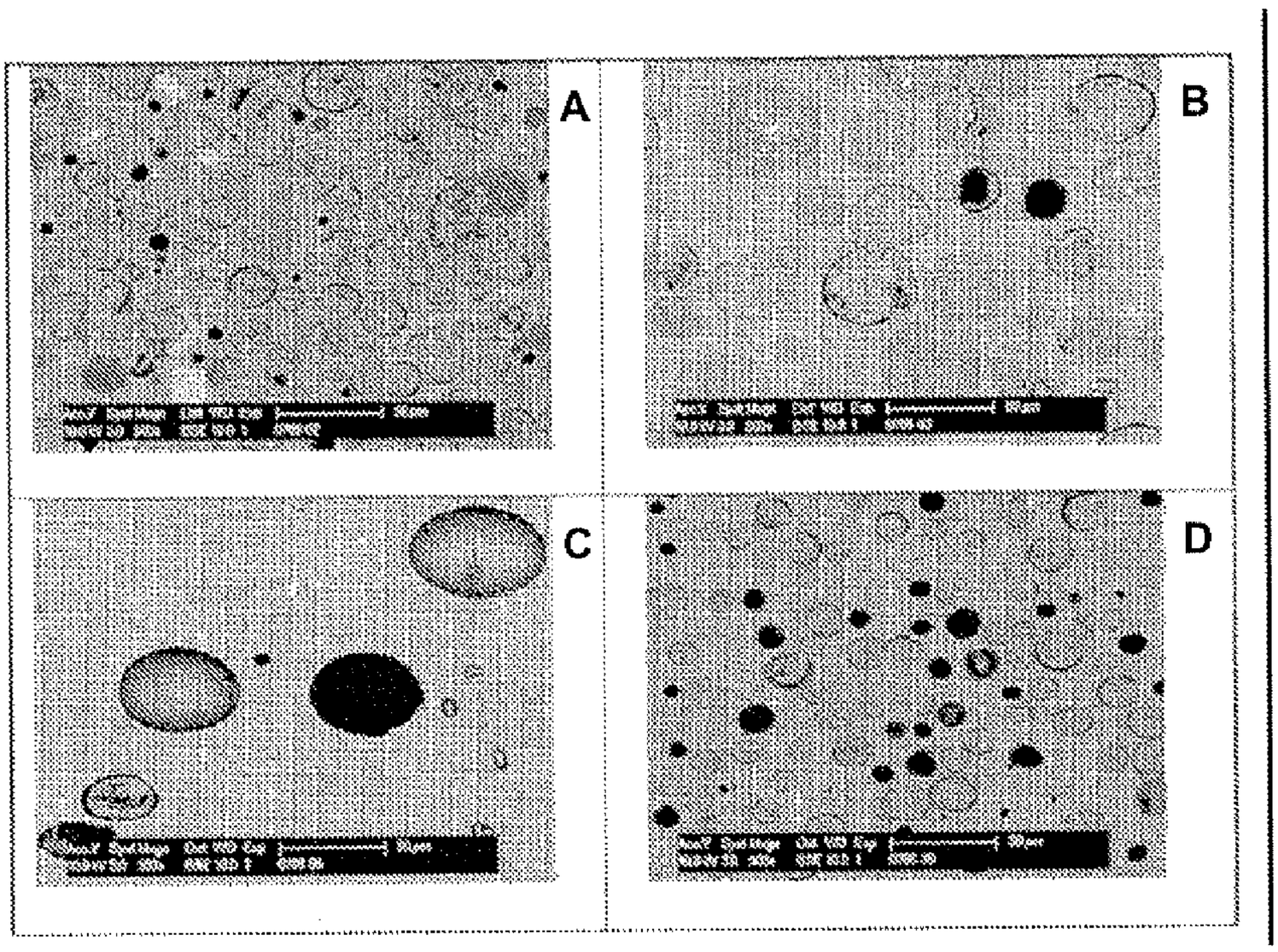

Figure 16

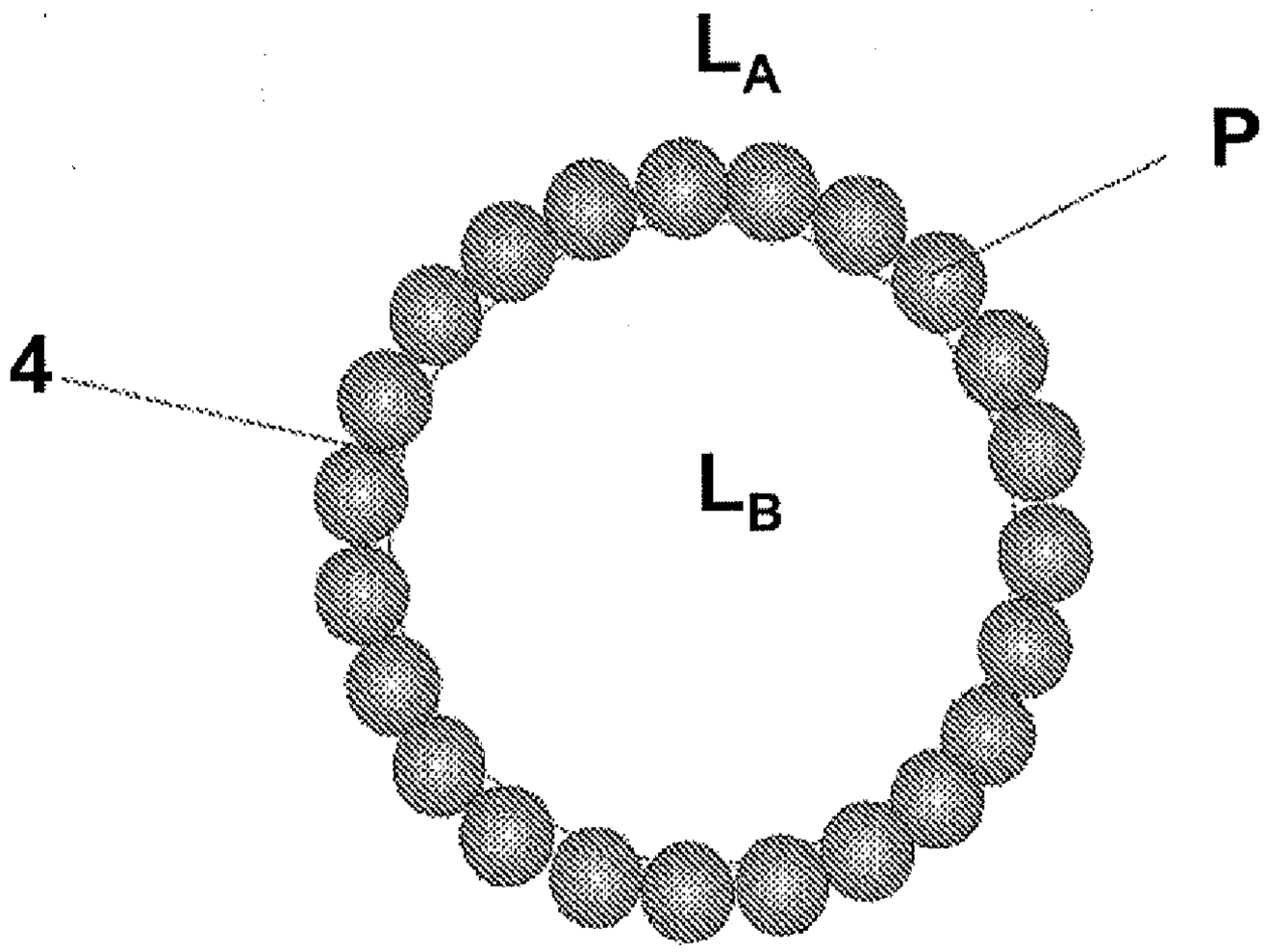

Figure 17

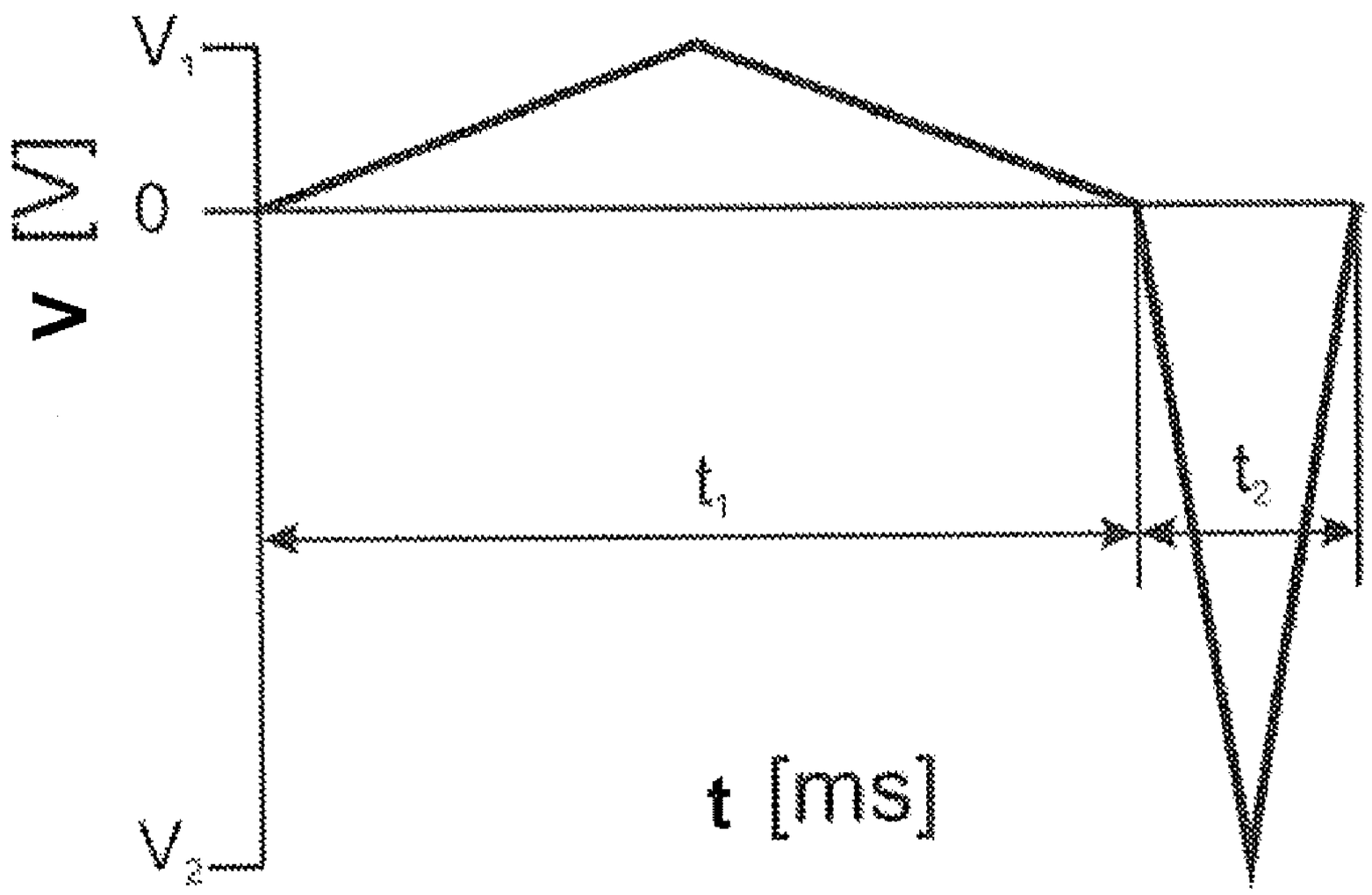

Figure 18

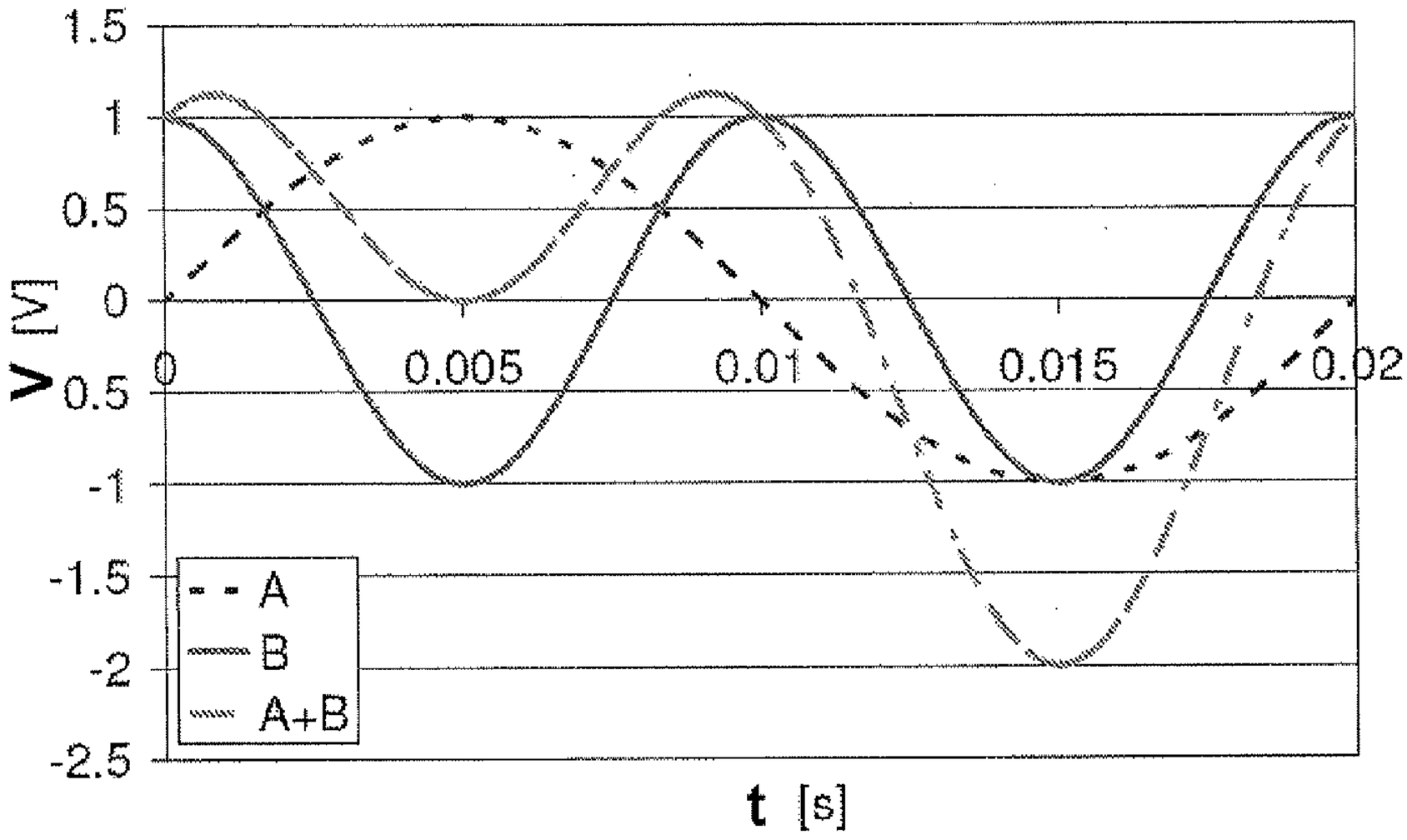

Figure 19

AQUEOUS ELECTROPHORETIC DEPOSITION

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates generally to the process of the deposition of 1) colloidal particles suspended in an aqueous medium or in an aqueous medium slurry or 2) organic or metallo-organic molecules dissolved in an aqueous medium, (preferably concentrated systems and most preferably highly concentrated systems) under the influence of an electric field onto an electrode or porous substrate placed in front of an electrode.

[0002] More particularly the present invention relates to a controllable system and method for electrophoretic deposition in unbalanced AC electric fields (UAC-EPD) to form smooth deposits with no visible defects or to form a coating or a deposit.

BACKGROUND OF THE INVENTION

[0003] Electrophoretic deposition (EPD) is a colloidal processing technique in which a suspension or solution of charged particles or charged organic or metallo-organic molecules is placed in an electric field. The charged particles move towards one of the electrodes (electrophoresis) and subsequently form a deposit on this electrode (deposition) see VanderBiest, O. & Vandeperre, L. J. Electrophoretic deposition of materials. Annual reviews of material science 29, 327-352 (1999).

[0004] From environmental, economical and technical point of view water is the ideal solvent. Since water covers ⅔ of the earth's surface and its is involved in all biological processes in living cells and life on earth dependents on it; it is an ideal solvent for many natural molecules. Molecules that are charged or partially charged dissolve readily in water while molecules that do not have charges or partial charges on their surface do not mix readily with water. Demineralised water is non-toxic and can be produced at low cost in vast quantities. However these are not the most important advantages that water has to offer if we look at aqueous EPD from a technical point of view. Water has a higher dielectric constant than all of the other common solvents. This leads to higher an electrophoretic mobility, μ (m^2/Vs), and zeta potential. Since according to the basic principle of EPD, Hamaker's law (formula 2), the yield, Y (g), is proportional to this electrophoretic mobility, water has the potential of delivering higher yields for the same applied electric field, E (V/m), electrode area, S (m^2) and suspension solids concentration, C_s (g/m^3), than any other solvent.

$$Y = \int_{T1}^{T2} \mu E S C_s dt. \tag{2}$$

[0005] In addition water is the basic protonic solvent. The higher degree of dissociation ensures a more efficient charging of all pH sensitive particle surface groups and hence adds to the higher mobility in water at a given acid concentration. A final less obvious advantage of aqueous suspensions is the vast amount of knowledge on the behaviour of particles in aqueous media. Since water based systems are preferred in production environment most additives, such as binders and dispersants, have been optimized for water.

[0006] Water would therefore be the solvent of choice for electrophoretic deposition, but for the electrolytic decomposition of water. Most EPD is therefore carried out in non-aqueous solvents, direct current electrophoretic deposition from water being limited to low electric fields. Since the deposition rate depends directly on the strength of the applied, direct current EPD from water at low field is not attractive from an economical perspective. However, aqueous deposition has been studied by numerous researches and some solutions for the electrolysis problem have been published. J. Tabellion et al. in Materials Science volume 39, pages 803-811 (2004) proposed separating the reaction and deposition fronts; by means of a membrane; T. Uchikoski et al. in Journal of Materials Research volume 16, pages 321-324 (2001) proposed the use of palladium electrodes to absorb the hydrogen formed; Sakurada in Journal of the Ceramic Society of Japan volume 112, pages 156-155 (2004) proposed the addition of chemicals to suppress the electrolysis reaction; and R. C. Hayward et al. in Nature, volume 404, pages 56-59 (2000) and M. Bohmer in Langmuir, volume 12, pages 5747-5750 (1996) proposed lowering the voltages below the threshold for water electrolysis. With the first two solutions, the production of coatings is impractical because the deposit is not formed on the electrode, or the expensive electrode material is not suitable or economically infeasible as substrate material. The use of specialty chemicals is expensive, difficult to control and not ecological. R. C. Hayward et al. and M Bohmer have reported high quality deposits from aqueous systems at low voltages. However, despite the high quality of the deposits claimed using these techniques they display low deposition rates (e.g. 30 minutes to form a monolayer). Y. Hirata et al. in Journal of the Ceramic Society of Japan, volume 99, 108-113 (1991) reported the use of symmetric AC signals to form deposits by EPD from aqueous suspensions at high frequencies, but the deposition rate was extremely low and seemed to be controlled by the diffusion of alumina in the suspension.

[0007] WO 2004/052489A describes a method of attaching a nanostructure-containing material onto a sharp tip of an object, the method comprising: (i) forming a suspension of nanostructure-containing material in a liquid medium; (ii) immersing at least one electrode in the suspension; (iii) placing the sharp tip into the suspension; and (iv) applying a direct or alternating current to the immersed electrode and the sharp tip causing at least a portion of the nanostructure-containing material in the suspension to become attached to the object proximate at apex of the sharp tip. WO 2004/052489A discloses a dielectrophoresis method.

[0008] JP 52-056143A describes alternating current electrodeposition coating using an aqueous paint containing a salt of a purified polycarboxylic acid resin as binder.

[0009] DD 215338 A1 describes electrophoretic precipitation from a suspension using asymmetrical alternating voltage in which the negative portion is 1 to 25% of the maximum value of the positive voltage (by superimposing DC signal onto an AC signal) to improve coating e.g. of ceramic moulds. As a result unwanted electrochemical reactions were slowed down, yet not fully stopped. DD 215338A1 reported that the electrochemical dissolution of the electrodes was reduced

[0010] GB 253091A describes a method of depositing—organic material electrically on or in a fabric which comprises placing the fabric on the outer surface of a gas-permeable anode in contact with an aqueous electroconducting emulsion of the organic material to be deposited, passing a depositing

current through the emulsion and the anode and withdrawing the gas formed at the outer surface of the anode through the anode by causing a lower pressure to be exerted on its inner surface than on its outer surface. GB 253091A further stated that the current should preferably be an effectively unidirectional one, it may be a current of constant value, or a direct current of pulsating character and in some instances it is useful to employ an unbalanced alternating current, which is most conveniently obtained by superimposing an alternating current upon a direct current.

[0011] U.S. Pat. No. 1,589,327 describes a process of depositing a cellulosic compound on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting emulsion containing droplets of the cellulosic compound and passing a depositing electric current through said surface and emulsion. U.S. Pat. No. 1,589,327 further describes that for some purposes it may be convenient to employ a considerably unbalanced alternating current.

[0012] Thus, there is an urgent need in the art for EPD systems that allow the use of high voltage with high deposition rates in an aqueous (watery) medium and in particular of EPD systems with further reduced or completely halted gas bubble generation due to water electrolysis.

SUMMARY OF THE INVENTION

[0013] The present invention concerns an electrophoretic deposition (EPD) process in reduced or limited water electrolysis in an aqueous environment characterized in that the process involves subjecting positively or negatively charged or partially charged molecules or colloidal particles to an unbalanced alternating current (UAC) electric fields for depositing molecules or particles in aqueous medium from the aqueous medium onto an electrode or porous substrate placed in front of an electrode.

[0014] The controllable system and method for electrophoretic deposition in unbalanced AC electric fields (UAC-EPD) of present invention surprisingly allows the deposition of thin layers with an average thickness in the nanometer scale but also thick layers with an average thickness in the centimeter, millimeter or micrometer scale.

[0015] It is an object of present invention to deposit cationic polymers in smooth coatings from an aqueous medium onto anodes or porous substrate placed in front of an anode by subjecting them to unbalanced (asymmetric) alternating current (UAC) electric signals to reduce or prevent electrolysis of water in the aqueous medium.

[0016] It is also an object of present invention to deposit anionic polymers in smooth coatings from an aqueous medium onto cathodes or porous substrate placed in front of a cathode by subjecting them to unbalanced alternating current (UAC) electric signals to reduce or prevent electrolysis of water in the aqueous medium.

[0017] It is also an object of present invention to deposit charged microorganism and living cells or cell components in smooth coatings from an aqueous medium onto a conductive medium or electrode or porous substrate placed in front of an electrode by subjecting them to unbalanced alternating current (UAC) electric signals in which the amplitude differs significantly for the positive and negative part to reduce or prevent electrolysis of water in the aqueous medium.

[0018] It is also an object of present invention to deposited bioactive agents in thin coatings (nanometer scale average thickness) or in thick coatings (micrometer scale average thickness) from an aqueous medium onto a conductive medium or electrode or porous substrate placed in front of an electrode by subjecting them to unbalanced alternating current (UAC) electric to reduce or prevent electrolysis of water in the aqueous medium.

[0019] The present invention further concerns a system of high voltage EPD of colloidal particles suspended in an aqueous medium while the decomposition of water is suppressed below the point of gas bubble formation. The current problem in the art of high voltages water decomposition is solved by applying an unbalanced alternating electric field. Contrary to what one might expect, the particles form an adhering deposit on the selected electrodes (deposition electrodes), the experimental results of present invention clearly demonstrated that by present invention deposits with high green density (>60% in the case of monomodal spherical submicron Alumina particles) and smooth surface can be formed from aqueous suspensions.

[0020] These findings allow the replacement of volatile, expensive and environmentally unfriendly solvents (as currently used in the art) by an aqueous (watery) medium while a strong enough electric field can be applied in order to ensure a satisfying deposition rate. The overall yield is lower than we are accustomed from DC-EPD. On the other hand only a fraction of the time is used to deposit particles. Taking that into account, the yield in function of deposition time is larger than during DC-EPD.

[0021] Defect-free high density green deposits can be obtained from aqueous suspensions if the electrolysis of water is avoided. The quality of these deposits is equal or better than those produced in the past by conventional electrophoretic deposition from alcohol based suspensions. Furthermore the deposition mechanics still exhibit a linear increase of deposit yield and no self limiting behaviour was observed, suggesting the possibility of limitless thickness.

[0022] In accordance with the purpose of the invention, as embodied and broadly described herein, the invention is broadly drawn to an unbalanced AC electric fields (UAC-EPD) process for depositing amphoteric substance or self-charging compounds in aqueous solutions under the influence of an unbalanced AC electric field onto an electrode or porous substrate placed in front of an electrode or for depositing colloidal particles with an electric charge or that comprise charged metallo-organic molecules dissolved or suspended in an aqueous medium or an aqueous slurry. UAC-EPD is preferably carried out using concentrated systems and most preferably using highly concentrated systems. In diluted solutes or suspended systems, the particles can move independently from one another. In other words if one solute or particle moves due to the electric field it should not be influenced in its movement due to the presence of other particles or solutes. In concentrated suspensions or solutions individual particles or solutes experience influence from each other during movement. In highly concentrated systems the hydrodynamic diameters of the components, being either particles or solutes, overlap. The present invention is particularly suitable for molecules that readily mix in water as a suspension or a solution.

[0023] In one aspect of the invention, the electrophoretic deposition (EPD) process for depositing charged, partially charged or self-charging compounds or organic or metallo-organic molecules in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to

unbalanced alternating current (UAC) electric fields. These charged or self-charging compounds or molecules are solved in the aqueous medium or these charged or self-charging compounds or molecules are in colloidal particles. The charged or self-charging compounds or molecules can be in cells, cell organelles or cell components.

[0024] Yet another embodiment of present invention is an electrophoretic deposition (EPD) process for depositing charged metallo-organic molecules dissolved or suspended in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to an unbalanced AC-signal that has a voltage evolution of which the positive and negative amplitude differ in absolute value

[0025] Yet another embodiment of present invention is an electrophoretic deposition (EPD) process for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to an AC-signal of which the shape of the negative and positive signal part differ, preferably in amplitude and most preferably in both amplitude and duration and whereof the net resulting DC-signal of said unbalanced signal, obtained by calculating the voltage average over one period, is lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero.

[0026] Yet another embodiment of present invention is an electrophoretic deposition (EPD) process for depositing charged metallo-organic molecules dissolved or suspended in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to a signal in which the amplitude differs significantly for the positive and negative part, while maintaining a net integral over one period of lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero.

[0027] Yet another embodiment of present invention is an electrophoretic deposition (EPD) process for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to an UAC fields as depicted in FIG. **1**.

[0028] Yet another embodiment of present invention is an electrophoretic deposition (EPD) process for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to an unbalanced AC electric fields of one symmetrical sinus waves on top of another symmetrical sinus wave with an integral of lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero, over one time period

[0029] Yet another embodiment of present invention is an electrophoretic deposition (EPD) process for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to AC-fields that have an unbalanced form, yet yielding no net DC signal.

[0030] Yet another embodiment of present invention is an electrophoretic deposition (EPD) process for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode involves subjecting the molecules or colloidal particles to unbalanced AC electric fields that are composed of signals with different amplitudes for the negative and the positive part but with an integral of lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero, over one time period. It can be AC fields in which the amplitude and the duration of the negative and the positive part differ, but the overall integral over one period is lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero.

[0031] In still another aspect of the invention, unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention as described above is used to coat or paint a device or instrument for instance to coat a medical prostheses, an orthopaedic implant, dental endodontic or dental implant.

[0032] Another aspect of the invention is the use of unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention to remove said charged or self-charging compounds or molecules form an aqueous medium.

[0033] In a particular embodiment of present invention the unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention to produce a strong light-weight metals and alloys.

[0034] In yet another particular embodiment of present invention the unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention to produce a food or a feed.

[0035] Another aspect of the invention is the use of asymmetric alternating current electrophoretic deposition (UAC-EPD) of present invention to form smooth deposits with no visible defects or the use of asymmetric alternating current electrophoretic deposition (UAC-EPD) of any of present to form deposits with a smooth surface of a Ra of 10 to 50 μm, preferably a Ra of 10 to 10000 nm, more preferably a Ra of 10 to 500 nm, and most preferably a Ra of 10-200 nm. A further aspect is the realisation of a deposit with high green density >30%, preferably a deposit with high green density >50% or most preferably a deposit with high green density >60% produced by such process.

[0036] In still another aspect of the invention, unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention as described above is used to produce a device or instrument for instance to produce a medical prostheses, an orthopaedic implant, dental endodontic or dental implant.

[0037] Aspects of the present invention are realized by a coating process comprising the steps of: immersing an electrode or porous substrate placed in front of an electrode in an aqueous medium comprising charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles and subjecting said charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles in an aqueous medium to (asymmetric) unbalanced alternating current (UAC) electric fields, having a frequency and a positive and negative part each having an amplitude and a duration, to deposit electrophoretically said charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles onto said electrode or porous substrate placed in front of an electrode, characterised in that said amplitude of said unbalanced alternating current (UAC) electric field differs significantly for the positive and negative part, while maintaining a net integral of the applied signal over one period, i.e. average potential, is

lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero. An electrical field must be realised between the counter electrode and the electrode in the aqueous medium comprising charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles for electrophoretic deposition to occur. This can also be realised with the counter electrode outside the vessel containing the aqueous medium, if an electric field can still be realised between the counter electrode and the electrode in the medium.

[0038] Further aspects of the present invention are realized by the use of the above-mentioned coating process to form smooth deposits with no visible defects having a surface with a Ra of 10 to 50 μm, preferably a Ra of 10 to 10000 nm, more preferably a Ra of 10 to 500 nm, and most preferably a Ra of 10-200 nm.

[0039] Aspects of the present invention are also realized by a system for electrocoating a conductive substrate with organic or metallo-organic molecules or particles in which said system coats said conductive substrate with at least one layer or coating at a controllable average thickness in the nm or in the μm scale from a suspension in an aqueous working medium of one or more types of said organic or metallo-organic molecules or particles, wherein said system comprises a power supply connected to a signal generator to generate between a counter electrode and said conductive substrate, an unbalanced alternating current (AC) signal, said signal having a frequency and a positive and negative part each having an amplitude and a duration, in which said amplitudes for said positive and negative parts differ significantly, while maintaining a net integral of the applied voltage over one period, i.e. average potential, lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero, and furthermore said system comprises a control system connected to said signal generator for determining the frequency and amplitude of said unbalanced AC signal.

[0040] Particular and preferred aspects of the invention are set out in the accompanying independent and dependent claims. Features from the dependent claims may be combined with features of the independent claims and with features of other dependent claims as appropriate and not merely as explicitly set out in the claims.

[0041] Although there has been constant improvement, change and evolution of devices in this field, the present concepts are believed to represent substantial new and novel improvements, including departures from prior practices, resulting in the provision of more efficient, stable and reliable devices of this nature.

[0042] The above and other characteristics, features and advantages of the present invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention. This description is given for the sake of example only, without limiting the scope of the invention. The reference figures quoted below refer to the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0043] The present invention will become more fully understood from the detailed description given herein below and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, and wherein:

[0044] FIG. **1** is a schematic view showing one period of the applied unbalanced AC signal V is the voltage and t, the time.

[0045] FIG. **2** demonstrates α-Al_2O_3 Deposits formed using (a) 100 V DC for 1200 s or (b) a 50 Hz unbalanced AC field with V_1=100 V, V_2=−400V, t_1=16 ms, t_2=4 ms

[0046] FIG. **3**: is a schematic view of the deposition rate, D, of α-Al_2O_3 versus the asymmetry factor, A, of the applied signal. V_1, V_2, t_1, t_2 are defined in FIG. **1**. The suspension consisted of a 200 g/L SM8 in water containing 4.10-4 M HNO_3.

[0047] FIG. **4**: demonstrates the particle size distribution of SM8 powder measured by light scattering (Mastersizer micro+, Malvern) as volume, v, versus particle diameter, d.

[0048] FIG. **5**: is a micrograph of SM8 α-Al_2O_3 powder

[0049] FIG. **6**: demonstrates the electrophoretic mobility, E, of SM8 alumina as a function of operational pH for different solvent combinations: water (dashes), ethanol with 5 vol. % water (dots) and ethanol (full line)

[0050] FIG. **7**: shows the deposition of polystyrene particles from an isopropanol suspension in a 50 Hz unbalanced AC-field with an asymmetry factor of 4.

[0051] FIG. **8**: demonstrates the dependence of the deposition yield, Y, upon frequency, f, and time, t, for a 200 g/L Al_2O_3 (SM8, Baikowski) suspension containing 4 10^{-4}M HNO_3 in an unbalanced 500 V peak to peak field with an asymmetry factor of 4. Each experiment was repeated 3 times. The diamonds represent the time dependence at 50 Hz and the dots represent the frequency dependence after 40 minutes.

[0052] FIG. **9**: displays the temperature, T, as a function of time, t, during electrophoretic deposition for AC-EPD in water (dashes), AC-EPD in ethanol (full line) and DC-EPD in ethanol (dots).

[0053] FIG. **10**: provides a picture of the surface roughness of a deposit prepared by electrophoretic deposition of a 200 g/L SM8 ethanol suspension with 1 10^{-3} M HNO_3 and deposited at 200 V DC for 20 minutes

[0054] FIG. **11**: provides a picture of the surface roughness of a deposit prepared by electrophoretic deposition of a 200 g/L SM8 Water suspension with 4 10^{-4} M HNO_3 and deposited at 50 Hz 500 Vp-p for 20 minutes.

[0055] FIG. **12**: Example of an applied signal as measured during deposition (Fluke 97 scopemeter equipped with a voltage divider with a division factor of 100).

[0056] FIG. **13**: Example of α-alumina (SM8 grade, Baikowski) deposit made using the signal as shown in FIG. **12**.

[0057] FIG. **14**: provides the droplet size distribution as volume fraction, vf, versus droplet diameter, d_D, as measured using light scattering after 30 minutes stirring. All measured systems were prepared using 40 ml of aqueous suspension and 40 ml of cyclohexane, while the mass of stabilizing powder and the volume of charging agent (0.5M propionic acid) was varied: 0.1 g SM8/0.05 ml propionic acid (grey dashes with 2 peaks), 0.5 g SM8/0.1 ml propionic acid (black dashes with 2 peaks), 1 g SM8/0.1 ml propionic acid (grey line with a single peak), 2 g SM8/0.1 ml propionic acid (black line with a single peak), 5 g SM8/0.2 ml propionic acid (grey dash dot with a single peak) and 10 g SM8/0.4 ml propionic acid (black dash dot with a single peak).

[0058] FIG. **15**: Schematic representation of a) the EPD cell in which 1 is a deposition electrode, 2 is a pump and 3 is a suspension and emulsion reservoir and b) the applied unbal-

anced AC signal as a function of voltage, V, upon time, t, with an amplitude of 500 Vp-p and a frequency of 50 Hz.

[0059] FIG. **16**: Micrographs of polished cross-sections of Alumina grades A (a), B (b), C(c) and E (d) after sintering (see Table 1 and 2)

[0060] FIG. **17**: Solid particle stabilized emulsion droplet, where L_A is liquid A, L_B is liquid B, 4 is the inter-phase and P is a solid particle.

[0061] FIG. **18**: Typical example of an unbalanced AC-signal generated by a function generator as voltage, V, versus time, t, in ms. The ratios V**2**/V**1** and t**1**/t**2** are equal to ensure the elimination of a net DC-signal.

[0062] FIG. **19**: Unbalanced AC-signal as voltage, V, versus time, t, composed from two symmetrical sinus waves shifted 90° in phase and with a frequency ratio of 2.

DETAILED DESCRIPTION OF THE INVENTION

[0063] The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. The drawings described are only schematic and are non-limiting. In the drawings, the size of some of the elements may be exaggerated and not drawn on scale for illustrative purposes. The dimensions and the relative dimensions do not correspond to actual reductions to practice of the invention.

[0064] Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequence, either temporally, spatially, in ranking or in any other manner. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

[0065] Moreover, the terms top, bottom, over, under and the like in the description and the claims are used for descriptive purposes and not necessarily for describing relative positions. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other orientations than described or illustrated herein.

[0066] It is to be noticed that the term "comprising", used in the claims, should not be interpreted as being restricted to the means listed thereafter; it does not exclude other elements or steps. It is thus to be interpreted as specifying the presence of the stated features, integers, steps or components as referred to, but does not preclude the presence or addition of one or more other features, integers, steps or components, or groups thereof. Thus, the scope of the expression "a device comprising means A and B" should not be limited to devices consisting only of components A and B. It means that with respect to the present invention, the only relevant components of the device are A and B.

[0067] Similarly, it is to be noticed that the term "coupled", also used in the claims, should not be interpreted as being restricted to direct connections only. The terms "coupled" and "connected", along with their derivatives, may be used. It should be understood that these terms are not intended as synonyms for each other. Thus, the scope of the expression "a device A coupled to a device B" should not be limited to devices or systems wherein an output of device A is directly connected to an input of device B. It means that there exists a path between an output of A and an input of B which may be a path including other devices or means. "Coupled" may mean that two or more elements are either in direct physical or electrical contact, or that two or more elements are not in direct contact with each other but yet still co-operate or interact with each other.

[0068] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to one of ordinary skill in the art from this disclosure, in one or more embodiments.

[0069] Similarly it should be appreciated that in the description of exemplary embodiments of the invention, various features of the invention are sometimes grouped together in a single embodiment, figure, or description thereof for the purpose of streamlining the disclosure and aiding in the understanding of one or more of the various inventive aspects. This method of disclosure, however, is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the claims following the detailed description are hereby expressly incorporated into this detailed description, with each claim standing on its own as a separate embodiment of this invention.

[0070] Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For example, in the following claims, any of the claimed embodiments can be used in any combination.

[0071] Furthermore, some of the embodiments are described herein as a method or combination of elements of a method that can be implemented by a processor of a computer system or by other means of carrying out the function. Thus, a processor with the necessary instructions for carrying out such a method or element of a method forms a means for carrying out the method or element of a method. Furthermore, an element described herein of an apparatus embodiment is an example of a means for carrying out the function performed by the element for the purpose of carrying out the invention.

[0072] In the description provided herein, numerous specific details are set forth. However, it is understood that embodiments of the invention may be practiced without these specific details. In other instances, well-known methods, structures and techniques have not been shown in detail in order not to obscure an understanding of this description.

[0073] The following detailed description of the invention refers to the accompanying drawings. The same reference numbers in different drawings identify the same or similar elements. Also, the following detailed description does not limit the invention. Instead, the scope of the invention is defined by the appended claims and equivalents thereof.

[0074] Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the

detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

[0075] The following terms are provided solely to aid in the understanding of the invention.

DEFINITIONS

[0076] A molecule in the meaning of this invention is sufficiently stable group of at least two atoms in a definite arrangement held together by very strong chemical bonds, comprising the charged or self-charging molecules and the charged organic molecules and biomolecules.

[0077] The term "bio-active agent" as used herein broadly includes any compound, composition of matter, or mixture thereof, that has biological activity and can be delivered in the subject, preferably a mammal, to whom it is administered.

[0078] A biomolecule is any organic molecule that is produced by living organisms, including large polymeric molecules such as proteins, polysaccharides, and nucleic acids as well as small molecules such as primary metabolites, secondary metabolites, and natural products. As organic molecules, biomolecules comprise primarily carbon and hydrogen, nitrogen, and oxygen, and, to a smaller extent, phosphorus and sulphur. Other elements sometimes are incorporated but are much less common. Typical biomolecules are of the group of the nucleosides and nucleotides, the saccharides, lignin, lipids, amino acids, protein structures (for vitamins. A diverse range of biomolecules exist, including: small molecules (lipid, phospholipids, glycolipid, sterol, vitamin, hormone, neurotransmitter, carbohydrate, sugar, disaccharide) monomers (amino acids, nucleotides, monosaccharides), polymers (peptides, oligopeptides, polypeptides, proteins, nucleic acids, i.e. DNA, RNA oligosaccharides, polysaccharides (including cellulose) and lignin.

[0079] Nucleosides are molecules formed by attaching a nucleobase to a ribose ring. Examples of these include cytidine, uridine, adenosine, guanosine, thymidine and inosine. Nucleosides can be phosphorylated by specific kinases in the cell, producing nucleotides, which are the molecular building blocks of DNA (deoxyribonucleic acid) and RNA (ribonucleic acid). DNA or RNA has a negative charge.

[0080] Monosaccharides are the simplest form of carbohydrates with only one simple sugar. They essentially contain an aldehyde or ketone group in their structure. Examples of monosaccharide are the hexoses glucose, fructose, and galactose and pentoses, ribose, and deoxyribose Disaccharides are formed when two monosaccharides, or two single simple sugars, form a bond with removal of water. Examples of disaccharides include sucrose, maltose, and lactose.

[0081] Polysaccharides are polymerized monosaccharides, complex, carbohydrates. They have multiple simple sugars. Examples are starch, cellulose, and glycogen. They are generally large and often have a complex branched connectivity. Shorter polysaccharides, with 2-10 monomers, are called oligosaccharides. Lignin is a random polymer composed mainly of aromatic rings with short (up to three) aliphatic carbons chains connecting the rings. Lignin is the second most common biopolymer (after cellulose) and is one of the primary structural components of most plants. It contains subunits derived from p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol and is unusual among biomolecules in that it is racemic i.e. it is not optically active. The lack of optical activity is because the polymerization of lignin occurs via free radical coupling reactions in which there is no preference for either configuration at a chiral center.

[0082] Lipids are chiefly fatty acid esters, and are the basic building blocks of biological membranes. Another biological role is energy storage (e.g., triglycerides). Most lipids consist of a polar or hydrophilic head (typically glycerol) and one to three nonpolar or hydrophobic fatty acid tails, and therefore they are amphiphilic. For lipids present in biological membranes, the hydrophilic head is from one of three classes: Glycolipids, whose heads contain an oligosaccharide with 1-15 saccharide residues; Phospholipids, whose heads contain a positively charged group that is linked to the tail by a negatively charged phosphate group; and Sterols, whose heads contain a planar steroid ring, for example, cholesterol. Other lipids include prostaglandins and leukotrienes which are both 20-carbon fatty acyl units synthesized from arachidonic acid. They are also known as fatty acids

[0083] Fatty acids consist of unbranched chains of carbon atoms that are connected by single bonds alone (saturated fatty acids) or by both single and double bonds (unsaturated fatty acids). The chains are usually 14-24 carbon groups long, but it is always an even number.

[0084] Amino acids contain both amino and carboxylic acid functional groups. (In biochemistry, the term amino acid is used when referring to those amino acids in which the amino and carboxylate functionalities are attached to the same carbon, plus proline which is not actually an amino acid). Amino acids are the building blocks of long polymer chains. With 2-10 amino acids such chains are called peptides, with 10-100 they are often called polypeptides, and longer chains are known as proteins. These protein structures have many structural and enzymatic roles in organisms. There are twenty amino acids that are encoded by the standard genetic code, but there are more than 500 natural amino acids. When amino acids other than the set of twenty are observed in proteins, this is usually the result of modification after translation (protein synthesis). Only two amino acids other than the standard twenty are known to be incorporated into proteins during translation, in certain organisms: Selenocysteine is incorporated into some proteins at a UGA codon, which is normally a stop codon. Pyrrolysine is incorporated into some proteins at a UAG codon. For instance, in some methanogens in enzymes that are used to produce methane. Besides those used in protein synthesis, other biologically important amino acids include carnitine (used in lipid transport within a cell), ornithine, GABA and taurine. The particular series of amino acids that form a protein is known as that protein's primary structure. This sequence is determined by the genetic makeup of the individual. Proteins have several well-classified elements of local structure formed by intermolecular attraction, which forms the secondary structure of protein. They are broadly divided in two, alpha helix and beta sheet, also called beta pleated sheets. Alpha helices are formed of coiling of protein due to attraction between the amine group of one amino acid with the carboxylic acid group of another amino acid. The coil contains about 3.6 amino acids per turn and the alkyl group of amino acid lie outside the plane of coil. Beta pleated sheets are formed by strong continuous hydrogen bond over the length of protein chain. Bonding may be par-

allel or antiparallel in nature. Structurally, natural silk is formed of beta pleated sheets. Usually, a protein is formed by action of both these structures in variable ratios. Coiling may also be random. The overall 3D structure of a protein is termed its tertiary structure. It is formed as result of various forces like hydrogen bonding, disulphide bridges, hydrophobic interactions, hydrophilic interactions, van der Waals force etc. When two or more different polypeptide chains cluster to form a protein, quaternary structure of protein is formed. Quarternary structure is a unique attribute of polymeric and heteromeric proteins like haemoglobin, which consists of two alpha and two beta peptide chains. A vitamin is a compound that is generally not synthesized by a given organism but is nonetheless vital to its survival or health. These compounds must be absorbed, or eaten, but typically only in trace quantities.

Coating Process Using Unbalanced (Asymmetric) AC-Electrophoretic Deposition (UAC-EPD)

[0085] In theory water starts to decompose electrochemically at voltages above 1.24V [J. P. Hoare: *The electrochemistry of oxygen* (John Wiley & Sons Inc., New York 1968) or B. E. Conway: *Electrochemical data* (Elsevier publishing company, Amsterdam 1952)] However, surprisingly, in practice often potentials of 3-4V are needed before gas bubbles are formed. Nevertheless in most traditional EPD setups as well as in our experiments voltages are used that surpass this threshold more than a few times. Hence only the kinetics of the electrochemical system can be used to prevent electrolysis. This means that there must be a lower limit to the frequency above which no electrolysis occurs. In order to determine this lower limit the influence of frequency on the deposit quality and yield was measured (FIG. **8**).

[0086] Though the yield decreased appreciably at 1 Hz no bubble formation could be observed and the deposits were defect free. This does not mean that there is absolutely no electrolysis of water at this frequency, but that at least the reaction is slow enough to prevent the nucleation of bubbles. Next to the increase in yield the higher reproducibility of the experiments at higher frequencies was striking. Hence 50 Hz was chosen as the frequency to be used for all other tests.

[0087] In the past a decrease in deposition rate as the deposit grows has been noted in some systems. This behaviour was distinctively present when depositing from acidic ethanol suspensions. While this self limiting behaviour is unwished-for when producing thick deposits it can be useful if thin coatings are needed since it levels out the deposition rate over an entire electrode, no matter what the geometry is. This tendency to form layers of uniform thickness has been dubbed throwing power. The self limiting behaviour has been linked to the flow of ions trough the deposit. Either the build up of double layers in the deposit pores when using acidic ethanol systems or a depletion layer near the electrode hampers the free passage of ions. The result for both proposed mechanisms is an increased total cell resistance.

[0088] Because of the similarity between aqueous and ethanol based suspensions a second series of experiments was performed in which the deposit yield in function of time was recorded. These experiments showed that the yield increased linearly in function of time (which is in accordance with Hamaker's law). Hence up till 40 minutes of deposition no sign of self limiting behaviour could be observed. In theory this means that deposition is possible until the suspension runs out of particles.

[0089] Green density measurements were performed to give deeper insight in the deposit quality. If present, internal cavities caused by gas evolution should show in these values. And as expected a bigger difference was noted in the green density than in the visual appearance of the deposits. However, surprisingly the results show that the deposits made by UAC-EPD are denser than those typically obtained by DC-EPD from ethanol based suspensions (2). This not only means that there are no appreciable pores caused by gas evolution in the deposits made by AC-EPD of aqueous suspensions, but that the general packing is higher. Moreover the green density was higher than that of the reference samples produced by cold pressing and cold isostatic pressing (CIP'ing) (57.90±0.03%).

[0090] In a particular embodiment of present invention the frequency of said unbalanced signal or UAC lies between 0.1 Hz and 1 MHz, preferably between 1 Hz and 1 kHz and most preferably between 10 Hz and 200 Hz.

[0091] In a particular embodiment of present invention the frequency of said unbalanced signal or UAC has an applied signal strength lies between 1 V peak to peak and 10000V, preferably between 1V and 5000 V peak to peak, more preferably between 10V and 5000V peak to peak, most preferably between 10 V peak to peak and 2000V peak to peak and especially preferably between 50 V peak to peak and 1000 V peak to peak. The resulting electric field strength, calculated as the voltage over the interelectrode distance, lies between 100 V/m and 10^6 V/m, preferable between 1000 V/m and 10^5 V/m and most preferably between 2500 V/m and 25000 V/m.

[0092] The present invention solves the problems of high voltage EDP from water in the related art by method for electrophoretic deposition in unbalanced AC electric fields (UAC-EPD).

[0093] Unbalanced (asymmetric) AC electric fields (UAC) can be achieved by creating a signal in which the amplitude differs significantly for the positive and negative part, while maintaining a net integral over one period lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero. Such UAC fields as depicted in FIG. **1**. However the Unbalanced AC electric fields do not necessary need to have triangle form wave form. Alternatively one sinus waves on top of another sinus wave with an integral lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero, over one time period can be used and easily enforced without sudden changes

[0094] Such AC fields have an unbalanced form, yet yield no net DC signal. Alternatively such unbalanced AC electric fields can be described as an AC electric field that is composed of signals with different amplitudes for the negative and the positive part but with an integral lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero, over one time period. It can be AC fields in which the amplitude and the duration of the negative and the positive part differ, but the overall integral over one period is lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero.

[0095] The unbalanced AC-signal of present invention for depositing colloidal particles suspended in an aqueous medium or molecules in solution of an aqueous medium has a voltage evolution of which the positive and negative amplitude differ in absolute value. Yet over one period of the signal the net DC-voltage, calculated by integrating the voltage in function of time, is lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero. An

unbalanced AC-signal is a signal of which the shape of the negative and positive signal part differ, preferably in amplitude and most preferably in both amplitude and duration. However the net resulting DC-signal of said unbalanced signal, obtained by calculating the voltage average over one period, is lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero.

Wave Shapes of the UAC Signals EPD of Present Invention

Signal Shapes:

[0096] The unbalances can take different shapes such as triangle, sine; square or others.

[0097] A first and foremost option to generate unbalanced AC-signals is the use of a function generator. Any general shape of wave can be obtained in this manner. Care has to be taken to ensure that the voltage or current integral over one period is below the threshold for gas bubble evolution. In other words the absolute area below the positive end negative part of one signal period have to be of such size that the difference between them yields a absolute net voltage over one period smaller than 4V and preferably equal to zero. FIG. **18** shows a typical example of a wave composed of two triangles. Similar results can be obtained with block waves, trapezoidal waves or waves with rounded features. When utilizing amplifiers one must however take care that the wave offered to the amplifiers input is not distorted during amplification in such a manner that a net DC-signal is generated.

[0098] A second option is to compose an unbalanced AC-signal by superimposing two symmetrical signals, which are shifted in phase and have different frequencies, on one another. Since both original signals are symmetrical and have a net DC-value of zero the resulting composed signal also has a net DC-signal equal to zero (FIG. **19**)

[0099] For sinus waves this can be generalized by the following equations.

Signal 1: $E_1(t)=E_1\times\sin(\omega t)$

Signal 2: $E_2(t)=mE_2\times\sin(n\omega t+\phi)$

Composed signal: $E_{1+2}(t)=E_1\times\sin(\omega t)+mE_2\times\sin(n\omega t+\phi)$

[0100] With E_1 and E_2 the amplitudes of the original signals, ω the angular velocity, ϕ the phase shift and m and n two arbitrary multiplication factors of which n differs from 1. FIG. **19** shows an example in which $E_1=E_2=1$, $\omega=2\pi 50$, n=2 and $\phi=90°$ or $\pi/2$ radials.

Signal A: $E_A(t)=\sin(100\times\pi\times t)$

Signal B: $E_B(t)=\sin(200\times\pi\times t+\pi/2)$

Composed signal: $E_{A+B}(t)=\sin(100\times\pi\times t)+\sin(200\times\pi\times t+\pi/2)$

[0101] The amplitude of the negative peak is almost twice the size of the amplitude of the positive signal.

TABLE 3

yields of alumina (SM8 grade, Baikowski) deposit made using the signal as shown in FIG. 12	
10 g SM8	Yield = 0.698 g
0.1 ml 0.1M HNO_3	pH = 6.8
50 ml H_2O	500 V_{p-p} 50 Hz

TABLE 3-continued

yields of alumina (SM8 grade, Baikowski) deposit made using the signal as shown in FIG. 12	
10 g SM8	Yield = 0.772 g
0.1 ml 0.1M HNO_3	pH = 6.7
50 ml H_2O	500 V_{p-p} 500 Hz
10 g SM8	Yield = 0.786 g
0.1 ml 0.1M HNO_3	pH = 6.8
50 ml H_2O	500 V_{p-p} 200 Hz
10 g SM8	Yield = 0.675 g
0.1 ml 0.1M HNO_3	pH = 6.7
50 ml H_2O	500 V_{p-p} 20 Hz
10 g SM8	Yield = 0.804 g
0.1 ml 0.1M HNO_3	pH = 6.8
50 ml H_2O	500 V_{p-p} 100 Hz
10 g SM8	Yield = 0.818 g
0.1 ml 0.1M HNO_3	pH = 6.8
50 ml H_2O	500 V_{p-p} 50 Hz

[0102] UAC-EPD is an electrophoretic deposition or the process that colloidal particles suspended in a liquid medium or solved molecules in a liquid medium migrate and are deposited under the influence of the UAC fields onto an electrode or porous substrate placed in front of an electrode. Such UAC-EPD can include or can be used for electrocoating, cathodic electrodeposition, electrophoretic coating, or electrophoretic painting.

[0103] Examples of AC-fields that have an unbalanced form, yet yielding no net DC signal, are shown in FIG. **1**. The amplitude and duration of the negative and positive part differ, but the overall integral over one period is lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero. Electrophoretic deposition of α-Al_2O_3 powder in water using the unbalanced AC signal represented in FIG. **1**, resulted in smooth deposits with no visible defects. The surface quality of the deposits is comparable to that of deposits made from non-aqueous (ethanol, acetone) systems using a DC field. The deposits obtained from an aqueous suspension using a DC and unbalanced AC fields are compared in FIG. **2**, clearly revealing the effect of water electrolysis in case of the DC-electrical field, the AC-electrical field the superimposition of AC on DC field.

Charged, Partially Charged or Self-Charging Organic or Metallo-Organic Molecules or Colloidal Particles

[0104] The unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous onto an electrode or porous substrate placed in front of an electrode is particularly suitable for the deposition of inorganic substances such as hydroxides, oxides (including glasses), carbides, nitrites, borides, carbonates, carbonitrides, metals, phosphors, phosphates, hydrates, hydrides, fluorides, sulphides, sulphates, salts and apatites some of which can be bioactive or can be biocompatible.

[0105] The unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous medium onto an electrode or porous substrate placed in front of an electrode is particularly suitable for the deposition of organics such as monomers, precursors, hydrocarbons, functional hydrocarbons, macromolecules, oligosaccharides, polysaccharides, polymers (e.g. thermoplastic polymers, thermo curing polymers, biopoly-

mers, alginates, carrageen or other algae derived polymers, kollicoat IR, or resins, oligomers some of which can be bio-active and others biocompatible.

[0106] The unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous medium onto an electrode or porous substrate placed in front of an electrode is particularly suitable for the deposition of proteins (e.g. collagen), poly-nucleotides (e.g. DNA or RNA), sugars, fatty acids, amino acids, nucleotides.

[0107] The unbalanced alternating current electrophoretic deposition (UAC-EPD) of present invention for depositing charged or self-charging compounds or molecules in aqueous medium from the aqueous medium onto an electrode or porous substrate placed in front of an electrode is particularly suitable for the deposition of eukaryote or prokaryote cells. It can for instance be used for the deposition of amoeba, bacteria, yeast, plant cells, mammalian cells (e.g. human cells for instance osteoblasts) fungae, and of the organelles, cell components and macromolecules thereof. It is particularly interesting that these cells organelles, cell components and macromolecules thereof are bioactive.

[0108] Negatively charged molecules are present in biological systems. The "negatively charged molecules" are meant to include molecules such as nucleic acid molecules (e.g., RNA, DNA, oligonucleotides, mixed polymers, peptide nucleic acid, and the like), peptides (e.g., polyaminoacids, polypeptides, proteins and the like). Nucleotides, pharmaceutical and biological compositions have negatively charged groups that can ion-pair with the positively charged head group of the cationic lipids of the invention. The charge or isoelectric point (pI) can be changed. For example, the chemical conversion of surface carboxyl groups of antibodies to extended primary amino groups results in the cationization of the antibody. Nonglycolated Fab (pI>9.3), mildly cationic glyco-Fab (pI=7-9.3), mildly anionic glyco-Fab (pI=4.5-7) and strongly anionic glyco-Fab (pI<4.5) could be generated (*Cancer Res.* 59, pp. 422-430 *View Record in Scopus* Kobayashi et al. (1999)).

[0109] Food is made up of many different chemical components or parts, including vitamins, minerals, sugars, fibres, water, lipids, proteins and starches. In addition to these main nutrient components, many foods contain smaller amounts of biologically active chemicals. In plants, these are referred to as phytochemicals. Scientists can separate out all of these different components of foods. A food portion contains negatively charged molecules and positively charged molecules which by the present method of the invention can be deposited on a conductive substrate in a smooth coating and a desired thickness. Many food items contain anionic polymers.

[0110] Suitable cationic polymers are for instance selected from the group of cationic polyamines in particular, poly lysine (a polyamine that is almost completely protonated at physiological pH of 7.5), polyacrylamide, homopolymer of dimethyldiallyl ammonium chloride, 2-methacryloyloxyethyl trimethyl ammonium methosulfate, methacrylamido propyl trimethyl ammonium chloride, ethyleneimine, copolymers of acrylamide, cationic polyacrylic, dimethyldiallyl ammonium chloride, methacrylamido propyl trimethyl ammonium chloride, 2-methacryloyloxyethyl trimethyl ammonium methosulfate, C18 trimethyl ammonium chloride, C18(polyoxyethylene) methyl ammonium chloride, pDMAEMA [(poly(dimethylamino)ethyl methylacrylate], chitosan, Linear pEI, PVP, DEAE-dextran, Pll, comb-type copolymers (like pLL-gr-dextran and block copolymers (like the pEG-pLL block copolymer). Chitosan is one of a few natural cationic polysaccharides that are harmless, and it has several potential functions such as antimicrobial activity. The present invention can be used to make a coat or smooth objects of chitosan. Since the majority of the waterborne bacteria and viruses have a negative charge, positive charged cationic films produced by the unbalanced alternating current (UAC) electric signals method of present invention can be used to attract such and remove them.

[0111] Typical anionic polymers are the polymers of the group consisting of poly-L-glutamate, anionic acrylic polymers, hydrogels based on anionic urethane polyether-amine polyelectrolytes, polymers of anionic urethane, carbomer and polyvinyl acetate phthalate [PVAP], Eudragit S, Eudragit L 100-55, sodium carboxymethylcellulose, dextran sulfate and Nafion®-117. Hyaluronic acid (HA is the simplest glycosaminoglycan (a class of negatively charged polysaccharides). There are many natural anionic polymers that are obtainable by the purification method of Sainz-Serp, D; Wandrey, C: Minerva Biotechnol., 2005, p. 215-229. Anionic polymers inhibit fibrosis, scar formation and surgical adhesions and the present method is suitable for the formation of smooth coating of such anionic polymers on medical implants. hydrogels containing carboxylate anions such as copolymer of 2-hydroxyethyl methacrylate and sodium methacrylate, anionic polymers derived from L-tyrosine. Several negatively charged microorganisms responsible for plaque generation and the negatively charged films (for instance films of bis(naphthoxy)alkane sulfonates) have a mutual repulsion effect.

[0112] The majority of waterborne bacteria and viruses are negatively charged at a pH of about 6 to about 8. Polio virus has an isoelectric point at a pH of about 7 such that only at alkaline pH will the polio virus have a negative charge. The electrokinetic property of an intact cell generally dependents upon the surface property of cells.

[0113] The objects or coating produced by the process of present invention can comprise any bio-active compound that is suitable that is ionised, partially ionised or self charging of the various therapeutic classes of bio-active agents that can be administered while using the present dosage forms include, but are not limited to: analgesic agents; anesthetic agents; antiarthritic agents; respiratory drugs; anticancer agents; anticholinergics; anticonvulsants; antidepressants; antidiabetic agents; antidiarrheals; antihelminthics; antihistamines; antihyperlipidemic agents; antihypertensive agents; anti-infective agents such as antibiotics and antiviral agents; antiinflammatory agents; antimigraine preparations; antinauseants; antineoplastic agents; anti-Parkinson drugs; antipruritics; antipsychotics; antipyretics; antispasmodics; antitubercular agents; antiulcer agents and other gastrointestinally active agents; antiviral agents; anxiolytics; appetite suppressants; attention deficit disorder (ADD) and attention deficit hyperactivity disorder (ADHD) drugs; cardiovascular preparations including calcium channel blockers, CNS agents, and vasodilators; beta-blockers and antiarrhythmic agents; central nervous system stimulants; cough and cold preparations, including decongestants; diuretics; genetic materials; herbal remedies; hormonolytics; hypnotics; hypoglycemic agents; immuno-suppressive agents; leukotriene inhibitors; mitotic inhibitors; muscle relaxants; narcotic antagonists; nutritional agents, such as vitamins, essential amino acids and fatty

acids; parasympatholytics; peptide drugs; psychostimulants; sedatives; steroids; sympathomimetics; and tranquilizers.

[0114] Gastrointestinally active agents that can be used to be comprised in the objects or coatings according to the method of present invention include agents for inhibiting gastric acid secretion such as, but not limited to, the H2 receptor antagonists cimetidine, ranitidine, famotidine, and nizatidine, the H+ or K+-ATPase inhibitors (also referred to as "proton pump inhibitors") omeprazole and lansoprazole, and antacids such as, but not limited to, calcium carbonate, aluminum hydroxide and magnesium hydroxide. Also included within this general group are agents for treating infection with *Helicobacter pylori* (*H. pylori*) such as, but are not limited to, metronidazole, tinidazole, amoxicillin, clarithromycin, tetracycline, thiamphenicol and bismuth compounds (e.g. bismuth subcitrate and bismuth subsalicylate). Other gastrointestinally active agents that can be administered while using the present dosage forms include, but are not limited to, pentagastrin, carbenoxolone, sulfated polysaccharides such as sucralfate, prostaglandins such as misoprostol, and muscarinic antagonists such as pirenzepine and telenzepine. Additionally included are antidiarrheal agents, antiemetic agents and prokinetic agents such as, but are not limited to, ondansetron, granisetron, metoclopramide, chlorpromazine, perphenazine, prochlorperazine, promethazine, thiethyl-perazine, trifluprom azine, domperidone, trimethobenzamide, cisapride, motilin, loperamide, diphenoxylate and octreotide. Anti-microbial agents that can be used to be comprised in the objects or coatings according to the method of present invention include tetracycline antibiotics and related compounds (e.g. chlortetracycline, oxy-tetracycline, demeclocycline, methacycline, doxycycline, minocycline and roli-tetracycline); macrolide antibiotics such as, but not limited to, erythromycin, clarithromycin, and azithromycin; streptogramin antibiotics such as, but not limited to, quinupristin and dalfopristin; beta-lactam antibiotics, including penicillins (e.g., penicillin G, penicillin VK), antistaphylococcal penicillins (e.g. cloxacillin, dicloxacillin, nafcillin and oxacillin), extended spectrum penicillins (e.g. aminopenicillins such as ampicillin and amoxicillin, and antipseudomonal penicillins such as carbenicillin), cephalosporins (e.g. cefadroxil, cefepime, cephalexin, cefazolin, cefoxitin, cefotetan, cefuroxime, cefotaxime, ceftazidime and ceftriaxone) and carbapenems such as, but not limited to, imipenem, meropenem and aztreonam; aminoglycoside antibiotics such as, but not limited to, streptomycin, gentamicin, tobramycin, amikacin and neomycin; glycopeptide antibiotics such as teicoplanin; sulfonamide antibiotics such as, but not limited to, sulfacetamide, sulfabenzamide, sulfadiazine, sulfadoxine, sulfamerazine, sulfamethazine, sulfamethizole and sulfamethoxazole; quinolone antibiotics such as, but not limited to, ciprofloxacin, nalidixic acid and ofloxacin; anti-mycobacterials such as, but not limited to, isoniazid, rifampin, rifabutin, ethambutol, pyrazinamide, ethionamide, aminosalicylic and cycloserine; systemic antifungal agents such as, but not limited to, itraconazole, ketoconazole, fluconazole and amphotericin B; and miscellaneous antimicrobial agents such as, but not limited to, chloramphenicol, spectinomycin, polymyxin B (colistin), bacitracin, nitrofurantoin, methenamine mandelate and methenamine hippurate. Anti-diabetic agents that can be used to be comprised in the objects or coatings according to the method of present invention include, by way of example, acetohexamide, chlorpropamide, ciglitazone, gliclazide, glipizide, glucagon, glyburide, miglitol, pioglitazone, tolazamide, tolbutamide, triampterine, and troglitazone. Non-opioid analgesic agents that can be used to be comprised in the objects or coatings according to the method of present invention include, but are not limited to, apazone, etodolac, difenpiramide, indomethacin, meclofenamate, mefenamic acid, oxaprozin, phenylbutazone, piroxicam and tolmetin. Opioid analgesics that may be used in this invention include, but are not limited to, alfentanil, buprenorphine, butorphanol, codeine, drocode, fentanyl, hydrocodone, hydromorphone, levorphanol, meperidine, methadone, morphine, nalbuphine, oxycodone, oxymorphone, pentazocine, propoxyphene, sufentanil and tramadol. Anti-inflammatory agents that can be used to be comprised in the objects or coatings according to the method of present invention include non-steroidal anti-inflammatory agents, e.g. propionic acid derivatives such as, but not limited to, ketoprofen, flurbiprofen, ibuprofen, naproxen, fenoprofen, benoxaprofen, indoprofen, pirprofen, carprofen, oxaprozin, pranoprofen, suprofen, alminoprofen, butibufen, fenbufen, apazone, diclofenac, difenpiramide, diflunisal, etodolac, indomethacin, ketorolac, meclofenamate, nabumetone, phenylbutazone, piroxicam, sulindac and tolmetin. Suitable steroidal anti-inflammatory agents include, but are not limited to, hydrocortisone, hydrocortisone-21-monoesters (e.g. hydrocortisone-21-acetate, hydrocortisone-21-butyrate, hydrocortisone-21-propionate, hydrocortisone-21-valerate), hydrocortisone-17,21-diesters (e.g. hydrocortisone-17,21-diacetate, hydrocortisone-17-acetate-21-butyrate, hydrocortisone-17,21-dibutyrate), alclometasone, dexamethasone, flumethasone, prednisolone and methylprednisolone. Anti-convulsant agents that can be used to be comprised in the objects or coatings according to the method of present invention, by way of example, azetazolamide, carbamazepine, clonazepam, clorazepate, ethosuximide, ethotoin, felbamate, lamotrigine, mephenyloin, mephobarbital, phenyloin, phenobarbital, primidone, trimethadione, vigabatrin, topiramate, and benzodiazepines. CNS and respiratory stimulants that can be used to be comprised in the objects or coatings according to the method of present invention, but are not limited to, xanthines such as caffeine and theophylline; amphetamines such as amphetamine, benzphetamine hydrochloride, dextroamphetamine, dextroamphetamine sulfate, levamphetamine, levamphetamine hydrochloride, methamphetamine, and methamphetamine hydrochloride; and miscellaneous stimulants such as methylphenidate, methylphenidate hydro-chloride, modafinil, pemoline, sibutramine and sibutramine hydrochloride. Neuroleptic agents that can be used to be comprised in the objects or coatings according to the method of present invention include antidepressant drugs, antimanic drugs and antipsychotic agents. Suitable antidepressant drugs include:

(a) tricyclic antidepressants such as, but not limited to, amoxapine, amitriptyline, clomipramine, desipramine, doxepin, imipramine, maprotiline, nortriptyline, protriptyline and trimipramine,

(b) serotonin re-uptake inhibitors such as, but not limited to, citalopram, fluoxetine, fluvoxamine, paroxetine, sertraline and venlafaxine,

(c) monoamine oxidase inhibitors such as, but not limited to, phenelzine, tranylcypromine and (−)-selegiline, and

(d) other atypical antidepressants such as, but not limited to, nefazodone, trazodone and venlafaxine. Suitable anti-manic and anti-psychotic agents include:

(a) phenothiazines such as, but not limited to, acetophenazine, acetophenazine maleate, chlorpromazine, chlorpromazine hydrochloride, fluphenazine, fluphenazine hydro-chloride, fluphenazine enanthate, fluphenazine decanoate, mesoridazine, mesoridazine besylate, perphenazine, thioridazine, thioridazine hydrochloride, trifluoperazine, and trifluoperazine hydrochloride,

(b) thioxanthenes such as, but not limited to, chlorprothixene, thiothixene, and thiothixene hydrochloride, and

(c) other heterocyclic drugs such as, but not limited to, carbamazepine, clozapine, droperidol, haloperidol, haloperidol, decanoate, loxapine succinate, molindone, molindone hydrochloride, olanzapine, pimozide, quetiapine, risperidone and sertindole. Hypnotic agents and sedatives that can be used to be comprised in the objects or coatings according to the method of present invention include, but are not limited to, clomethiazole, ethinamate, etomidate, glutethimide, meprobamate, methyprylon, zolpidem and barbiturates (e.g. amobarbital, apropbarbital, butabarbital, butalbital, mephobarbital, methohexital, pentobarbital, phenobarbital, secobarbital and thiopental).

[0115] Anxiolytics and tranquilizers that can be used to be comprised in the objects or coatings according to the method of present invention include, but are not limited to, benzodiazepines (e.g. alprazolam, brotizolam, chlordiazepoxide, clobazam, clonazepam, clorazepate, demoxepam, diazepam, estazolam, flumazenil, flurazepam, halazepam, lorazepam, midazolam, nitrazepam, nordazepam, oxazepam, prazepam, quazepam, temazepam and triazolam), buspirone, chlordiazepoxide and droperidol. Anticancer and antineoplastic agents that can be used to be comprised in the objects or coatings according to the method of present invention, but are not limited to, paclitaxel, docetaxel, camptothecin and its analogues and derivatives (e.g. 9-aminocamptothecin, 9-nitrocamptothecin, 10-hydroxycamptothecin, irinotecan, topotecan and 20-O-β-glucopyranosyl camptothecin), taxanes (e.g. baccatins, cephalomannine and their derivatives), carboplatin, cisplatin, interferon-α 2A, interferon-α 2B, interferon-α N3 and other agents of the interferon family, levamisole, altretamine, cladribine, tretinoin, procarbazine, dacarbazine, gemcitabine, mitotane, asparaginase, porfimer, mesna, amifostine, mitotic inhibitors including podophyllotoxin derivatives such as, but not limited to, teniposide and etoposide, and vinca-alkaloids such as, but not limited to, vinorelbine, vincristine and vinblastine. Antihyperlipidemic or lipid-lowering or hyperlipidemic agents that can be used to be comprised in the objects or coatings according to the method of present invention, but are not limited to, HMG-CoA reductase inhibitors such as atorvastatin, simvastatin, pravastatin, lovastatin and cerivastatin, and other lipid-lowering agents such as, but not limited to, clofibrate, fenofibrate, gemfibrozil and tacrine. Anti-hypertensive agents that can be used to be comprised in the objects or coatings according to the method of present invention include, but are not limited to, arnlodipine, benazepril, darodipine, dilitazem, diazoxide, doxazosin, enalapril, eposartan, losartan, valsartan, felodipine, fenoldopam, fosinopril, guanabenz, guanadrel, guanethidine, guanfacine, hydralazine, metyrosine, minoxidil, nicardipine, nifedipine, nisoldipine, phenoxybenzamine, prazosin, quinapril, reserpine and terazosin. Cardiovascular preparations that can be used to be comprised in the objects or coatings according to the method of present invention include, by way of example, angiotensin converting enzyme (ACE) inhibitors such as, but not limited to, enalapril, 1-carboxymethyl-3-1-carboxy-3-phenyl-(1S)-propylamino-2,3,4,5-tetrahydro-1H-(3S)-1-benzazepine-2-one, 3-(5-amino-1-carboxy-1-S-pentyl)amino-2,3,4,5-tetrahydro-2-oxo-3-S-1-H-benza-zepine-1-acetic acid or 3-(1-ethoxycarbonyl-3-phenyl-(1S)-propylamino)-2,3,4,5-tetrahydro-2-oxo-(3S)-benzazepine-1-acetic acid monohydrochloride; cardiac glycosides such as, but not limited to, digoxin and digitoxin; inotropes such as amrinone and milrinone; calcium channel blockers such as, but not limited to, verapamil, nifedipine, nicardipene, felodipine, isradipine, nimodipine, bepridil, amlodipine and diltiazem; beta-blockers such as, but not limited to, atenolol, metoprolol; pindolol, propafenone, propranolol, esmolol, sotalol, timolol and acebutolol; antiarrhythmics such as, but not limited to, moricizine, ibutilide, procainamide, quinidine, disopyramide, lidocaine, phenyloin, tocainide, mexiletine, flecainide, encainide, bretylium and amiodarone; cardioprotective agents such as dexrazoxane and leucovorin; vasodilators such as nitroglycerin; and diuretic agents such as, but not limited to, hydrochlorothiazide, furosemide, bumetamide, ethacrynic acid, torsemide, azosemide, muzolimine, piretanide and tripamide. Anti-viral agents that can be used to be comprised in the objects or coatings according to the method of present invention include, but are not limited to, anti-herpes agents such as acyclovir, famciclovir, foscamet, ganciclovir, idoxuridine, sorivudine, trifluridine, valacyclovir and vidarabine; anti-retroviral agents such as didanosine, stavudine, zalcitabine, tenovovir and zidovudine; and other antiviral agents such as, but not limited to, amantadine, interferon-alpha, ribavirin and rimantadine. Sex steroids that can be used to be comprised in the objects or coatings according to the method of present invention include progestogens such as, but not limited to, acetoxypregnenolone, allylestrenol, anagestone acetate, chlormadinone acetate, cyproterone, cyproterone acetate, desogestrel, dihydrogesterone, dimethisterone, ethisterone (17α-ethinyl-testosterone), ethynodiol diacetate, fluorogestone acetate, gestadene, hydroxyprogesterone, hydroxyprogesterone acetate, hydroxyprogesterone caproate, hydroxymethylprogesterone, hydroxymethylprogesterone acetate, 3-ketodesogestrel, levonorgestrel, lynestrenol, medrogestone, medroxyprogesterone acetate, megestrol, megestrol acetate, melengestrol acetate, norethindrone, norethindrone acetate, norethisterone, norethisterone acetate, norethynodrel, norgestimate, norgestrel, norgestrienone, normethisterone and progesterone. Also included within this class are estrogens, e.g. β-estradiol (i.e. 1,3,5-estratriene-3,17β-diol, or 17β-estradiol) and its esters, including estradiol benzoate, valerate, cypionate, heptanoate, decanoate, acetate and diacetate; 17α-estradiol; ethinylestradiol (i.e. 17α-ethinylestradiol) and esters and ethers thereof, including ethinylestradiol-3-acetate and ethinylestradiol-3-benzoate; estriol and estriol succinate; polyestrol phosphate; estrone and its esters and derivatives, including estrone acetate, estrone sulfate, and piperazine estrone sulfate; quinestrol; mestranol; and conjugated equine estrogens. Androgenic agents, also included within the class of sex steroids, are drugs such as the naturally-occurring androgens androsterone, androsterone acetate, androsterone propionate, androsterone benzoate, androstenediol, androstenediol-3-acetate, androstenediol-17-acetate, androstenediol-3,17-diacetate, androstenediol-17-benzoate, androstenediol-3-acetate-17-benzoate, androstenedione, dehydroepiandrosterone (DHEA or prasterone), sodium dehydro-epiandrosterone sulfate, 4-dihydrotestosterone (DHT or stanolone), 5α-dihydrotest-

osterone, dromostanolone, dromostanolone propionate, ethylestrenol, nandrolone phenpropionate, nandrolone decanoate, nandrolone furylpropionate, nandrolone cyclohexanepropionate, nandrolone benzoate, nandrolone cyclohexanecarboxylate, oxandrolone, stanozolol and testosterone; pharmaceutically acceptable esters of testosterone and 4-dihydrotestosterone, typically esters formed from the hydroxyl group present at the C-17 position, including, but not limited to, the enanthate, propionate, cypionate, phenylacetate, acetate, isobutyrate, buciclate, heptanoate, decanoate, undecanoate, caprate and isocaprate esters; and pharmaceutically acceptable derivatives of testosterone such as, but not limited to, methyl testosterone, testolactone, oxymetholone and fluoxymesterone. Muscarinic receptor agonists that can be used to be comprised in the objects or coatings according to the method of present invention include, by way of example, choline esters such as, but not limited to, acetylcholine, methacholine, carbachol, bethanechol (carbamylmethylcholine), bethanechol chloride, cholinomimetic natural alkaloids and synthetic analogues thereof, including pilocarpine, muscarine, McN-A-343 and oxotremorine. Muscarinic receptor antagonists that may be used in this invention include belladonna alkaloids or semisynthetic or synthetic analogues thereof such as, but not limited to, atropine, scopolamine, homatropine, homatropine methyl bromide, ipratropium, methantheline, methscopolamine and tiotropium.

[0116] U.S. Pat. No. 5,145,684 discloses particles consisting essentially of 99.9 to 10% by weight of a crystalline drug substance having a solubility in water of less than 10 mg/ml, said drug substance having a non-crosslinked surface modifier adsorbed an the surface thereof in an amount of 0.1 to 90% by weight and sufficient to maintain an effective average particle size of less than about 400 nm. In particular it discloses a modified steroid A aqueous dispersion, comprising 5% steroid A, with a particle size distribution ranging from about 68 to 520 nm and a number average particle size of 204 nm. U.S. Pat. No. 5,503,723 discloses refining a nanoparticle dispersion by placing it between two electrodes and applying an electric field between said electrodes, wherein the dispersion consists essentially of particles of poorly soluble crystalline therapeutic or diagnostic agent, wherein 99% of the particles have a particle size below 400 nm and are associated with a surface modifier which is capable of stabilizing the nanoparticles. In particular, it describes a danazol dispersion wherein 10% of the particles are reduced in size down to 180 nm. U.S. Pat. No. 5,858,410 discloses a drug carrier, prepared using the jet stream principle and using surfactants such as Tween 80 and mannitol, comprising particles of a therapeutic agent which is insoluble, only sparingly soluble or moderately soluble in water, aqueous media and/or organic solvents, wherein the therapeutic agent has an average diameter below 1,000 nm and the proportion of particles larger than 5 μm in the total population is less than 0.1%. In particular, it describes aqueous nanosuspensions comprising 2-15% of a substituted pteridine and at least 0.1% Tween 80 wherein the average particle diameter is in a range from 200 to 800 nm. It also teaches that for special tetracaine compositions with a low (1%) drug concentration, nanosuspensions with an average particle size of 91 nm may be obtained. U.S. Pat. No. 5,922,355 discloses preparing microparticles of a water-insoluble or poorly soluble compound by, prior to or during reducing particle size (e.g. by sonication, homogenization, milling, microfluidization and precipitation, or recrystallization and antisolvent precipitation), mixing said particles with (a) a phospholipid and (b) at least one surfactant such that the concentration of phospholipid and surface modifier in the suspension or solid form is in the range of 0.1 to 50%, and thereafter applying energy to the mixture. It specifically describes drug formulations wherein the drug concentration is from 2 to 5%, wherein the mean particle size is between 35 and 98 nm and wherein there is no substantial variation in the mean particle size after one or more weeks storage of the formulations at 4° C. U.S. Pat. No. 6,221,400 discloses nanocrystalline formulations of HIV protease inhibitors wherein the average particle size is below 400 nm. It specifically describes nanoparticulate compositions of indinavir wherein the mean size of the nanoparticles is between 127 and 267 nm. International Patent application WO 02/055059 discloses methods involving both a water-miscible first solvent and an aqueous second solvent for preparing sub-micron sized particles of an organic compound. Using these methods, suspensions preparations wherein the average particle diameter is in the range from 180 to 700 nm. Thus a common feature of the prior art publications is that it is extremely difficult to obtain drug suspensions wherein the average particle size is within the nanometer range, preferably below 500 nm. This was apparently achieved only in very specific drugs, provided further that the drug concentration in the suspension is low, e.g. below 5% by weight. Because it is a sparingly water-soluble, normally crystalline active agent, itraconazole has attracted many attempts to improve its bioavailability. For instance, U.S. Pat. No. 6,346,533 discloses a method for obtaining itraconazole in an amorphous form exhibiting an improved bioavailability and having a particle diameter 0.5 to 10 μm. U.S. Pat. No. 6,497,905 discloses converting crystalline itraconazole into its amorphous form as a solid solution of a normally hydrophobic vehicle such as glyceryl monostearate, a monoglyceride, a diglyceride, a triglyceride, or a wax. This solid solution may be used as a component of a granular particle wherein itraconazole is present at about 5 to 60% by dry weight. Particle size of this granular particle is not specified. International Patent application WO 2004/043580 discloses an emulsification method comprising flowing, conducting or circulating a pre-mix of two or more immiscible liquids, said pre-mix preferably comprising at least a hydrophilic liquid and at least a lipophilic liquid, through one or more magnetic fields under conditions to emulsify the said pre-mix. Although emulsions prepared according to this method may be included into veterinary or pharmaceutical compositions, this document does not refer to the solubilization of poorly soluble drugs as such. US 2007/0082054, Particle size reduction of bioactive compounds, describes a method for reducing the average size of biologically active compound solid particles or agglomerates suspended in a liquid by flowing one or more times said liquid having biologically active compound solid particles or agglomerates suspended therein through one or more magnetic fields to reduce the average size of a substantial portion of the biologically active compound solid particles or agglomerates by at least 25%, wherein the linear flow rate of said liquid through each said magnetic field is between 0.25 and 25 m/s. These methods of particle size reduction can be used to reduce the average size of the particles in suspension and to improve the deposition of the reduced size colloidal particles suspended in an aqueous medium or in an aqueous medium slurry or the reduced size particles that stabilize an emulsion under the influence of an electric field onto an

electrode or porous substrate placed in front of an electrode whereby the electric fields involve unbalanced AC electric fields (UAC-EPD).

[0117] The material selected for coating are those upon which the molecules may be deposited via electrochemical deposition under an unbalanced alternating voltage. Suitable materials are electrically conductive, and may include metals (e.g., aluminum, antimony, cadmium, chromium, cobalt, copper, gold, iron, lead, magnesium, mercury, nickel, palladium, platinum, silver, tin, tungsten, zinc), metal alloys (steel, brass, bronze, etc.), semiconductors (e.g., silicon, gallium or germanium semiconductor materials), and/or conductive polymers (e.g., polypyrrole). The electrodes used in present invention can for instance comprise conductive polymers. Common classes of organic conductive polymers include poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, poly(aniline)s, poly(fluorene)s, poly(3-alkylthiophene)s, polytetrathiafulvalenes, polynaphthalenes, poly(p-phenylene sulfide), poly(para-phenylene vinylene)s, polyethelene terephthalate Dacron®, nylon, silk or other natural or synthetic polymeric material. Classically, these linear backbone polymers are known as polyacetylene, polyaniline, etc. "blacks" or "melanins".

EXAMPLES

[0118] The suspensions were prepared using fresh deionised water obtained from a commercial ion exchange setup (Sation Aqualab 50) and with an initial conductivity of 0.04 μS/cm. As powder SM8-grade α-alumina (Baikowski) was chosen and a constant concentration of 200 g/L was used for all experiments. The powder was charged by adjusting the pH below the IEP by means of nitric acid (Analytical reagent grade, 65%, Fluka) (Table 2). The IEP itself was determined by a potentiometric titration (Matec ESA 9800) (FIG. **6**) while the particle size was measured using light scattering (Malvern Mastersizer+) (FIG. **2**). In order to disperse the powder each suspension was agitated 15 minutes on a magnetic stirring plate, followed by an additional 15 minutes in an ultrasonic bath (Branson 2510).

[0119] Electrophoretic deposition was carried out in a teflon cell with two electrodes placed vertically at 3.5 cm distant from each other. The area available for deposition was 9 cm^2. The conductive polymer (carbon doped poly oxymethylene) deposition electrode was coated with graphite (NGS Dragon Seal Graphite) before deposition. Prior and after each experiment the temperature and conductivity (WTW inolab cond level 2) of the suspension is recorded (2). The signal (1) was generated using a function generator (HP 3314A) and amplified with an operational amplifier (Trek PZD 700 m/s). An amplitude of 500 volts peak to peak (V_{p-p}) and an asymmetry factor of 4 was used for all experiments. The deposits were consequently dried at room temperature for 24 hours. The yield was recorded by weighing the electrode prior to deposition and after drying. The green density of the samples produced using 40 minutes deposition time and a frequency of 5 Hz or higher was measured using the Archimedes principle. A lacquer with known density (Enthone B.V.) was applied to seal of the pores prior to submerging the samples. Before encapsulation any carbon transferred from the electrode to the deposit was removed. In addition three green density reference samples were produced by uniaxial cold-pressing SM8 powder into pellets, followed by CIP'ing (isostatic pressing) at 300 MPa. White light interferometry (Wyko NT3300, Veeco) was used to compare the deposit surface roughness of the produced samples with those produced by traditional EPD.

Deposit Characterization.

[0120] Visual inspection shows no sign of large defects such as gas bubbles breaking the surface of the deposits produced using the unbalanced AC-fields. The surface quality of the deposits is similar to those produced by EPD from ethanol-based suspensions using DC fields. White light interferometry confirms that the overall roughness is similar for samples produced using both techniques (R_a=±120 nm).

Example 1

Controllability of the Process

[0121] α-Al_2O_3 was deposited using the technology of present invention. The deposition rate of α-Al_2O_3 versus the symmetry of the applied signal V_1, V_2, t_1, t_2 (as defined in FIG. **1**). The suspension consisted of a 200 g/L SM8 in water containing 4.10^{-4} M HNO_3.

[0122] The more symmetric signals the smaller deposition rates observed. For instance symmetry of the signal was varied, by varying the height (amplitude) and width (pulse duration) of the triangular waves while maintaining a total period of 20 ms, a peak to peak height of 500 V and a net integral lower in absolute value than 4V, preferably lower than 1.24V and most preferably equal to zero, over one period. The asymmetry factor is determined as the ratio between the pulse heights, which is equal to the ratio of the pulse widths.

[0123] FIG. **3** shows that the deposition rate is zero when the applied field is symmetric (asymmetry factor equal to one) because no net electrophoresis occurs under the influence of symmetric AC fields. As the asymmetry factor increases the deposition rate increases as expected from equation (1). A threshold exists below which there is no deposition.

[0124] At higher asymmetry factors in FIG. **3** the average deposition rate during AC-EPD was lower than in DC-EPD. This is due to the fact that only a fraction of the time is used to drive the particles towards the deposition electrode. When taking this actual deposition time into account, the instantaneous deposition rate is higher than typically observed in ethanol (Anné, G., et al. *Journal of the American Ceramic Society* 89, 823-828 (2006)) When depositing Al2O3 from ethanol using a DC-field of 200 V, which is the average height of the high amplitude pulse used in the AC-EPD experiments with an asymmetry of 4, the deposition rate is 2.7 g/m2s. The deposition rate for the corresponding AC-field is 0.82 g/m2s but since deposition occurs during 1/5 of the time, the instantaneous deposition rate is 4.1 g/m2s.

[0125] In order to confirm the general nature of the method, conductive titanium diboride and negatively charged titanium dioxide powder were also deposited. The obtained deposits are of similar quality as those obtained with the non conductive positively charged alumina powder. No drying cracks were formed, which is typical for deposits with a high green density. The green density of the Al_2O_3 deposits obtained by AC-EPD is 60.6±0.9% (5 measurements, deposits made with 200 g/L Al_2O_3 (SM8, Baikowski) suspensions with 4 10^{-4}M HNO_3 and deposited with 500 V_{p-p} at 50 Hz). The green density of deposits made by DC-EPD from alcohol based suspensions using the same particles varies between 51 and 58% (Anné, G., et al. *Journal of the American Ceramic Society* 89, 823-828 (2006) and Anné, G., et al. *Journal of the*

European Ceramic Society 26, 3531-3537 (2006)). In comparison, SM8 grade Al_2O_3 samples isostatically pressed at 300 MPa have a green density of 57.9±0.03%, while the theoretical maximum density for a random stacking of monomodal spheres is 64% (German, R. M. *Metal Powders Industries Federation, Princeton, N.J.,* 1989 and To, L. T. & Stachurski, Z. H. *Journal of Non-Crystalline Solids* 333, 161-171 (2004)).

[0126] Present invention revealed that unbalanced AC-EPD allows the electrophoretic deposition from aqueous suspensions at high voltages. AC-EPD avoids the formation of gas bubbles on the electrode during electrophoresis from the electrolysis of water. Moreover, AC-EPD allows electrophoretic deposition from aqueous instead of organic solvent suspensions, which is strongly preferred from an environmental, safety and economic perspective, while maintaining the surface quality and processing rate of DC-EPD using organic solvents.

Example 2

Material and Methods

[0127] Fresh deionised water with an initial conductivity of 0.04 μS/cm and prepared with a commercial ion exchange setup (Sation Aqualab 50) was used for all suspensions. Commercially available α-Al_2O_3 (Baikowski grade SM8), TiB_2 (H.C.Starck grade F) and rutile TiO_2 (Kemira grade Rutilex) powders were used for experimentation. The TiO_2 was boiled and washed in a dialysis cell prior to use. No charging agent was added to the TiB_2 suspension while the TiO_2 was charged using KOH (Chem Lab 0.1 mol/l standard). HNO_3 (Fluky 65%) was used as a charging agent for the experiments with alumina. For each experiment a new suspension was prepared using 50 ml freshly prepared water and the indicated amount of powder and charging agent (Table 1). The suspensions were magnetically stirred for 15 minutes; followed by 15 minutes of treatment in an ultrasonic bath (Branson 2510), subsequently followed by 15 minutes of stirring on a magnetic plate. A programmable function generator (HP 3314A) was used to generate the unbalanced AC signal. A bipolar operational power supply and amplifier (Kepco BOP 1000M or Trek PZD 700 m/s) were used to amplify this by a factor of 100 or 200. The resulting signal, with a peak to peak amplitude of 500 V and a frequency of 1 to 50 Hz, was monitored with a digital oscilloscope (Fluke 97 50 MHz Scopemeter). One period of the signal is depicted in FIG. **1**. Deposition was carried out for 1200 s in a vertical cell equipped with conductive polymer (carbon doped poly oxy methylene (POM)) or stainless steel deposition electrodes and stainless steel counter electrodes with an electrode surface of 9 cm^2 and a separation distance of 3.5 cm. The deposition electrode is coated with graphite prior to deposition in order to ensure easy removal of the deposit after drying. The deposit is formed on the electrode that is negatively, respectively positively charged during the high amplitude section of the signal for the Al_2O_3, respectively TiB_2 and TiO_2 powder. The suspension conductivity and temperature was measured before each experiment (WTW inoLab Cond Level 2 equipped with a WTW LR 325/01 probe). All deposits were visually inspected for defects, and weighed in order to determine the yield. White light interferometry (Wyko NT3300, Veeco) was used to measure the deposit surface roughness. The green density as a percentage of the theoretical density was determined using the Archimedes method with ethanol as solvent and encapsulation with a lacquer with known dry density (Enthone B.V., The Netherlands). The green density of SM8 samples isostatically pressed into a cylindrical shape at 300 MPa was measured to be 57.90±0.03%.

[0128] Aluminium oxide (alumina or aloxite) is an amphoteric oxide of aluminium with the chemical formula Al_2O_3 that can react as either an acid or base. Other suitable amphoteric oxides that are suitable for the UAC-EPD present invention are the amphoterics comprising zinc, tin, lead, aluminium, and beryllium and amphoteric oxides of most metalloids (for instance Boron (B), zirconium (Zr), Silicon (Si), Germanium (Ge), Arsenic (As), Antimony (Sb), Tellurium (Te) and Polonium (Po)) and the amino acids, proteins, sugars, fatty acids or nulceotides which have amine and carboxylic acid groups or such amino acids and protein comprised in a suspended particles or a cell or a fragment or organelle thereof for instance a prokaryote cells such as cell of the bacteria or Archaea or an eukaryote cell such as the animals, plants, fungi, and protests cells.

[0129] The organelles, cell components or macromolecules of eukaryotic cells such as chloroplast (plastid), endoplasmic reticulum, Golgi apparatus, Mitochondrion, Vacuole, Nucleus, Organelle/Macromolecule, acrosome, autophagosome, centriole, cilium, glycosome, glyoxysome, hydrogenosome, lysosome, melanosome, mitosome, myofibril, nucleolus, parenthesome, peroxisome, ribosome or vesicle which have amine and carboxylic acid groups can be deposited by UAC-EPD.

[0130] Prokaryotic organelles, cell components and macromolecules such as carboxysome, chlorosome, flagellum, magnetosome, nucleoid, plasmid, ribosome or thylakoid which have amine and carboxylic acid groups can be deposited by UAC-EPD.

[0131] Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. It can be used as a pigment, it is then called titanium white, Pigment White 6, or CI 77891. Other oxides suitable for the UAC-EPD of present invention are titanium oxides in titanium alloyed with iron, aluminium, vanadium, molybdenum.

Example 3

Characterization

The Archimedes Method for Green Density Determination:

[0132] The green density is a value that relates to the particle packing in the formed object, and therefore is often used as a measure of the quality of the formed object. This value is traditionally stated as a percentage of the theoretical density of the material. For the measurement, the mass of the object is recorded. In order to include the interparticle porosity the object is coated with a lacquer that seals off this porosity, and after drying the mass of the coated object is registered as well. The volume of the coated object is measured by submerging it in a solvent of known density and measuring the buoyancy. The Archimedes principle is used to calculate the total volume of the coated object. From the weight difference before and after coating, the volume of the lacquer can be calculated and subtracted from the total volume. The density of the sealing lacquer is determined previously by coating a sub-

strate of known weight and density followed by measuring the volume of coating using the Archimedes method.

Powder Particle Information:

[0133] In order to assess particle packing in green structures data on the particle size distribution and particle morphology is needed. Hence for each powder used in experimentation the particles size is measured (FIG. **4**) and the morphology is visualized using electron microscopy (FIG. **5**). The used SM8 grade alumina depicts a mono modal particle size distribution. The SM8 powder has an irregular morphology which is closer to spherical particles than to platelets or needles.

Electrophoretic Mobility Dependence on Solvent System:

[0134] In order to illustrate the dependence of the electrophoretic mobility on the solvent system, potentiometric titrations were carried out and the electrophoretic mobility was measured as a function of the pH using the electro-acoustic technique (ESA 9800, Matec). For this, a 2.5 vol % SM8 alumina powder suspension was prepared by stirring and ultrasonification. An electrolyte background of 10-3 M KCl (1M KCl Titrimetric standard, Prolabo) was used. Prior to titration, the pH was adjusted to a base value by addition of KOH (for the aqueous suspension with 0.1M KOH titrimetric standard, Prolabo; for the ethanol based suspension with 0.1M KOH, Acros, in absolute ethanol, Prolabo). The suspensions were titrated with nitric acid (diluted in the solvent to 0.1M from 65% HNO3, Fluka).

[0135] The effectiveness of a solvent/powder combination for use in electrophoretic deposition is determined by this mobility—pH curve. Just as for the surface charge, powder particles often show a zero zeta potential value at a specific pH called the iso-electro point (IEP).

[0136] As is well known the pH is the negative logarithm of the activity of protons in a solvent. A direct consequence of this is that only protonic solvents can have a pH. Because the dissociation of the solvent itself plays an important role in the activity of the protons, pH scales depend on the solvent used, hence the term operational pH. For water, this scale conventionally ranges from 0 to 14, with a neutral pH value of 7. In comparison, the neutral pH in pure ethanol is 9.8, while the scale ranges from 0 to 19.6. Mixtures of both solvents will yield pH-scales located between both scales of the pure solvents. As a result of the above, the iso-electric point (IEP) will shift with the solvent used (FIG. **6**). Since the surface charge of most particles depends on the interaction with the solvent, specifically by interaction with the dissociated forms of the solvent, solvents that have a higher dissociation constant will facilitate the charging of the particles, in turn causing higher mobility and zeta potentials (FIG. **6**). Hence solvents with higher dissociation constants are preferentially used for the preparation of stable suspensions and EPD. Because most oxide powders contain hydrate water, unless they were specifically dried at high temperatures, water will always play a role in the charging of these particles even if no additional water has been introduced in the system.

Particle Clustering and Deposit Formation in AC Fields

[0137] The formation of almost perfectly stacked monolayers of particles has been observed in electrophoretic deposition. This effect has been attributed to electrohydrodynamic and electro-osmotic flow (EHF and BOF), which drive the particles together near and on the electrode. Since both flows are present in low frequency AC systems as well, these will play a role in the deposition of particles in AC-EPD. In order to confirm this, a flow cell was mounted on an optical microscope and the deposition of styrene particles in a 50 Hz unbalanced field was monitored (FIG. **7**).

Influence of Frequency and Amplitude:

[0138] 50 Hz is the maximum attainable frequency with a HP 3314A function generator for a programmed signal while maintaining sufficient resolution. Deposits were also made with 20, 5 and 1 Hz signals (FIG. **8**). The yield increases as the frequency increases but starts to level off above about 20 Hz. The reproducibility of the yield data is highest at 50 Hz. Hence this frequency was chosen for most experiments. At 1 Hz, the deposits were so thin that they warped during drying and cracked under their own weight. Despite of this, the deposits remain free of gas bubbles even at frequencies as low as 1 Hz and the high green density is maintained.

[0139] In DC-EPD, the field strength is increased to improve the deposition rate. However, too strong fields are known to yield unstable systems resulting in lower surface quality deposits. In order to investigate the influence of the field strength, the amplitude was increased to 750Vp-p during AC-EPD. Contrary to the expectation, the deposit yield decreased to 0.569 g over 40 minutes while employing this stronger field. At this point, the only explanation that can be offered is that the inverse field strength increases with the amplitude, causing resuspension of a larger fraction of the deposited particles reducing the overall deposition rate. A second but more obvious disadvantage of the higher applied voltage is that the current increases proportionally. The higher current leads to an increased temperature, which is detrimental for the deposition rate and deposit quality.

Deposition Yield in Function of Time:

[0140] DC-EPD from ethanol suspensions typically shows a self-limiting behavior when working under constant voltage conditions (Anné, G., et al. Journal of the American Ceramic Society 89, 823-828 (2006)). The possible reason for this behavior is the presence of thick double layers in the still porous deposit which hamper the free flow of ions. Since double layers are typically thinner in aqueous environment, the self-limiting behavior is unlikely to occur in water. Instead, the deposition rate remains constant and the yield increases linearly with time (FIG. **8**), suggesting the possibility of an unlimited deposit thickness.

Temperature Changes Due to the Applied Field:

[0141] Joule heat losses occurring in the suspension system are one of the main practical concerns when performing electrophoretic deposition, causing unstable suspensions and/or deposits of inferior quality. Typically, one tries to restrict the current flowing through a cell by using low conductivity systems or current controlled electrophoretic deposition. The same applies when using water in alternating fields for electrophoretic deposition. Hence care has been taken to monitor the suspension heating by measuring the suspension temperature before and after deposition.

[0142] For direct comparison between DC and AC-EPD, an additional set of experiments was performed. First 125 ml of a 200 g/L aqueous SMS suspension containing 4 10^{-4} M HNO3 was prepared using the experimental scheme

described in the main article. The initial conductivity Was measured to be 25.9 μS/cm. This suspension was placed in a horizontal EPD setup as described by Anné (Anné, G., et al. Journal of the American Ceramic Society 89, 823-828 (2006)). The suspension was recirculated through a stirred external vessel in which a combined conductivity and temperature probe was placed. This probe was used to log both temperature and conductivity simultaneously as a function of time. Finally a 50 Hz 500 Vp-p signal was applied for 20 minutes and a deposit was formed. Similarly 200 g/L SM8-ethanol suspensions were prepared. The conductivity of the ethanol suspensions was brought to 25 μS/cm using 0.1N HNO3 in ethanol. One suspension was subjected to 200 V DC while the other was deposited using the same unbalanced field as the aqueous suspension.

[0143] As shown in FIG. **9**, the temperature of all systems decreases as a function of time. The initial temperature of the suspensions is above room temperature due to the ultrasonification needed to disperse the particles. Because less heat is generated in the system than transported to the environment, the temperature gradually decreases. The slower reduction in temperature of the aqueous system is either due to a higher Joule heat generation in the suspension or a slower transport of heat to the environment. These experiments confirm previous measurements in a smaller vertical EPD cell, where temperature increases during EPD were limited. The temperature increase during 40 minutes deposition from a 200 g/L suspension containing 4 10^{-4}M HNO_3 utilizing a 1 to 50 Hz 500V_{p-p} signal never exceeded 5° C. Instead, an equilibrium was reached between the heat generated in the cell (in essence a square Teflon cup with 10 mm thick walls) and the heat transported towards the environment.

Deposit Surface Quality:

[0144] Smooth high quality layers are a hallmark feature attributed to coatings and objects produced by electrophoretic deposition. Hence any evolution in this field of research is only useful if it is able to deliver the same of even better surface quality. In order to check whether aqueous deposition using unbalanced AC-fields delivers deposits of at least the same surface quality as those produced by conventional EPD, surface roughness measurements using white light interferometry (Wyko NT3300, Veeco) were performed. As shown in FIG. **10** and FIG. **11**, there is no significant difference between the produced deposits. Both deposits have a R_a roughness of about 118 nm, which is roughly one fourth of the particle size. The deposited layers show no evidence of deposited agglomerates.

Example 4

On AAD-EPD of Emulsions Stabilized by Charged Solid Particles

[0145] UAC-EPD can be used to form deposits from emulsions stabilized by charged solid particles.

[0146] All emulsions were prepared with SM8-grade alumina (Baikowski), fresh deionized water and with an initial conductivity of 0.04 μS/cm obtained from a commercial ion exchange setup (Sation Aqualab 50) and cyclohexane (Analytical reagent grade, Prolabo). The exact compositions of the mixtures are given in Table 4. In a first step 2 suspensions are prepared by subsequently stirring for 15 minutes, followed by 15 minutes ultrasonification (Branson 2510) and an additional 15 minutes of stirring. During EPD, a 0.5 M propionic acid solution (Analytical reagent grade, Prolabo), and a 0.1 M nitric acid solution (Analytical reagent grade, 65%, Fluka) were used as charging agent as indicated in Table 4. In a second step the cyclohexane is added to the suspension containing the propionic acid and vigorously mixed for 30 minutes using a small size lab mixer (Lab egg, Ika). The size of the droplets is measured en shown in FIG. **14**. After this the second suspension is added to the emulsion and gently stirred to homogenise the suspension/emulsion mixture. The powder in this second suspension is intended to co-deposit with the droplets in order to form a solid structure in between the deposited cyclohexane. These mixtures are then placed in the cell used for electrophoretic deposition.

[0147] The EPD experiments were carried out in a cell with vertically placed electrodes with a separation distance of 3.5 cm and an effective area of 9 cm^2. The deposition electrode consists of a conductive polymer plate (carbon doped polyoxymethylene (POM)), while stainless steel is used as counter electrode. Prior to EPD, the polymer electrode was dip-coated with graphite (Dragon Seal Graphite, NGS) in order to ensure easy removal of the deposit. The emulsion/suspension system was recirculated using a peristaltic pump (Watson-Marlow 505 Du)

[0148] Electrophoretic deposition was performed using an unbalanced alternating signal with a frequency of 50 Hz and an amplitude of 500 V_{p-p} (FIG. **15***b*). This signal was applied using a function generator (HP 3314A) combined with an operational amplifier (Trek PZD 700 m/s). EPD was carried out during 20 minutes. The deposits were dried at room temperature for 24 hours. The yield was recorded by weighing the electrode prior to deposition and after drying. Finally, the deposits were consolidated by pressureless sintering in air at 1400° C. for 30 minutes, with a heating and cooling rate of 10° C./min (Nabertherm HT16/17).

[0149] Polished cross-sections of each sample, shown in FIG. **16**, were inspected using scanning electron microscopy (FEI XL30 FEG).

TABLE 4

Composition of the investigated mixtures

	Stabilized emulsion				Continuous phase suspension		
Experiment	V_{H2O} [ml]	$V_{Prop.\ acid}$ 0.5M [ml]	m_{SM8} [g]	$V_{Cyclohex}$ [ml]	V_{H2O} [ml]	V_{HNO3} 0.1M [ml]	m_{SM8} [g]
A	40	0.4	10	40	70	0.2	17.46
B	40	0.2	2	40	70	0.2	25.46
C	40	0.2	0.5	40	70	0.2	26.96
D	40	0.4	10	40	70	0.2	41.87
E	30	0.2	5	20	60	0.2	36.89

[0150] The present invention thus concerns the use of UAC-EPD to form deposits from emulsions stabilized by charged solid particles. The solid particle emulsions are obtainable by mixing at least two immiscible liquids to which solid particles or grains are added. When two immiscible liquids are brought together, an inter-phase area will be formed. By stirring the liquids, droplets are created increasing the inter-phase surface area. This is however an energetically unfavourable situation and the two phases will separate again when mixing is stopped. The droplets however can be partially or fully stabilized in the continuous phase by solid particles located at this inter-phase. Pickering first studied the principle of this stabi-

lization method and reported this in 1907 (Pickering, S. U., *Emulsions. J. Chem. Soc.* (London), 1907. 91: p. 2001-2021). In literature they are therefore often referred to as Pickering emulsions. The solid particles locate themselves at the inter-phase because of the difference in surface tension of the two liquids. Once located at this inter-phase the particle will remain there in a stable state. If enough particles are present, a hexagonal close packing (HCP) of solid particles can be achieved at the inter-phase. In this way, emulsion droplets can be stabilized with solid particles located at the inter-phase as shown in FIG. **17**. The amount and the size of the globules can be controlled by the amount of solid material added or the volume of emulsified liquid.

[0151] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

[0152] Several documents are cited throughout the text of this specification. Each of the documents herein (including any manufacturer's specifications, instructions etc.) are hereby incorporated by reference; however, there is no admission that any document cited is indeed prior art of the present invention.

TABLE 1

				Experimental data					
powder	electrode material	$C_{charging\ agent}$ [10^{-4} mol/l]	m_{powder} [g]	$\Lambda_{suspension}$ [μS/cm]	Time [min]	Amplitude [V_{p-p}]	Frequency [Hz]	Asymmetry [—]	yield [g]
Al_2O_3	polymer	—	5	10.88	20	500	50	4	0.51
Al_2O_3	stainless steel	—	5	9.79	20	500	50	4	0.57
Al_2O_3	polymer	2	5	14.12	20	500	50	4	0.82
Al_2O_3	stainless steel	2	5	14.88	20	500	50	4	0.79
Al_2O_3	polymer	2	10	25.30	20	500	50	4	1.57
Al_2O_3	polymer	4	10	24.3 ± 0.2^a	40	500	50	3	1.53 ± 0.04^a
Al_2O_3	polymer	4	10	24.5 ± 0.3^b	40	500	50	2	1.53 ± 0.05^b
Al_2O_3	polymer	4	10	24.3 ± 0.2^b	40	500	50	1.7	1.02 ± 0.11^b
Al_2O_3	polymer	4	10	24.6	40	500	50	1.5	0
Al_2O_3	polymer	4	10	24.6	40	500	50	1	0
Al_2O_3	polymer	—	10	9.60	20	500*	50	1	0
Al_2O_3	polymer	2	5	14.55	20	500*	50	1	0
Al_2O_3	polymer	4	10	25.4 ± 1.7^b	5	500	50	4	0.29 ± 0.01^b
Al_2O_3	polymer	4	10	24.4 ± 0.6^b	10	500	50	4	0.51 ± 0.04^b
Al_2O_3	polymer	4	10	24.5 ± 0.3^b	20	500	50	4	0.97 ± 0.04^b
Al_2O_3	polymer	4	10	25.2 ± 1.0^b	40	500	50	4	1.76 ± 0.04^b
Al_2O_3	polymer	4	10	22.5	40	750	50	4	0.57
Al_2O_3	polymer	4	10	22.9 ± 1.9^b	40	500	20	4	1.56 ± 0.17^b
Al_2O_3	polymer	4	10	23.8 ± 1.9^b	40	500	5	4	1.39 ± 0.17^b
Al_2O_3	polymer	4	10	23.6 ± 1.7^b	40	500	1	4	0.45 ± 0.11^b
Al_2O_3 Ethanol	polymer	10	10	6.94	20	200	0	—	2.92
TiB_2	polymer	—	5	50.10	20	500	50	4	0.62
TiO_2	polymer	4	5	25.50	20	500	50	4	0.63

[a,b]Average and standard deviation measured for 4^a and 3^b experiments.

TABLE 2

Summary of the used suspension compositions, deposition parameters and results. All AC-EPD experiments and density measurements were repeated 3 times.

Experiment	C_{HNO3} [10^{-4} mol/l]	$\Lambda_{suspension}$ [μS/cm]	Time [min]	Frequency [Hz]	Yield [g]	Green density [%]
A	4	23.6 ± 1.7	40	1	0.45 ± 0.11	/
B	4	23.8 ± 1.9	40	5	1.39 ± 0.17	60.35 ± 1.48
C	4	22.9 ± 1.9	40	20	1.56 ± 0.17	60.58 ± 1.16
D	4	25.2 ± 1.0	40	50	1.76 ± 0.04	60.28 ± 0.85
E	4	24.5 ± 0.3	20	50	0.97 ± 0.04	/
F	4	24.4 ± 0.6	10	50	0.51 ± 0.04	/
G	4	25.4 ± 1.7	5	50	0.29 ± 0.01	/
H*	10	6.94	20	0	2.92	57.78

*Control experiment performed using an absolute ethanol (Prolabo) based suspension and DC source. For this experiment a voltage of 200 V was applied.

1-53. (canceled)

54. A coating process comprising the steps of: immersing an electrode or porous substrate placed in front of an electrode in an aqueous medium comprising charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles and subjecting said charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles in an aqueous medium to (asymmetric) unbalanced alternating current (UAC) electric fields, having a frequency and a positive and negative part each having an amplitude and a duration, to deposit electrophoretically said charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles onto said electrode or porous substrate placed in front of an electrode, wherein said amplitude of said unbalanced alternating current (UAC) electric field differs significantly for the positive and negative part, while maintaining an applied signal whose net integral over one period, i.e. average potential, is lower in absolute value than 4V.

55. The coating process of claim **54**, wherein said duration of the negative and positive part of said UAC electric fields differ in addition to said amplitude of the negative and positive part of said UAC electric fields while the overall integral over one period, i.e. average potential, is lower in absolute value than 4V.

56. The coating process of claim **54**, wherein said charged or self-charging compounds or organic or metallo-organic molecules are dissolved in said aqueous medium.

57. The coating process of claim **54**, wherein the charged or self-charging compounds or organic or metallo-organic molecules are incorporated in colloidal particles in suspension in the aqueous medium or in an aqueous slurry.

58. The coating process of claim **54**, wherein the charged or self-charging compounds or organic or metallo-organic molecules are incorporated in charged or self-charging solid particles that stabilize an emulsion.

59. The coating process of claim **54**, wherein the charged or self-charging compounds or organic or metallo-organic molecules are in or from living or killed cells, cell organelles or cell components.

60. The coating process of claim **54**, wherein the charged compounds or organic or metallo-organic molecules are amino acids, nucleic acid molecules (e.g., RNA, DNA, oligonucleotides, polynucleotides, mixed polymers, peptide nucleic acid, and the like), peptides (e.g., polyaminoacids, polypeptides, proteins and the like).

61. The coating process of claim **54**, wherein the charged or self-charging compounds or organic or metallo-organic molecules are macromolecules.

62. The coating process of claim **54**, wherein the charged or self-charging compounds or organic or metallo-organic molecules are a bio-active agent.

63. A coating process comprising the steps of: immersing an electrode or porous substrate placed in front of an electrode in an aqueous medium comprising charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles and subjecting said charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles in an aqueous medium to (asymmetric) unbalanced alternating current (UAC) electric fields, having a frequency and a positive and negative part each having an amplitude and a duration, to deposit electrophoretically said charged, partially charged or self-charging organic or metallo-organic molecules or colloidal particles onto said electrode or porous substrate placed in front of an electrode, wherein said amplitude of said unbalanced alternating current (UAC) electric field differs significantly for the positive and negative part, while maintaining an applied signal whose net integral over one period, i.e. average potential, is lower in absolute value than 4V used to form smooth deposits with no visible defects having a surface with a Ra of 10 nm to 50 μm.

64. The coating process according to claim **63** to form a deposit with green density >30%.

65. The coating process according to claim **63** to produce a device, instrument, a medical prosthesis, an orthopaedic implant, dental endodontic or dental implant.

66. The coating process according to claim **63** to coat a medical prosthesis, an orthopaedic implant, dental endodontic or dental implant; or coat or paint a device or instrument.

67. The coating process according to claim **63** to immobilise charged or self-charging compounds or organic or metallo-organic molecules from an aqueous medium in a patterned structure on a substrate.

68. The coating process according to claim **63** to produce a food or feed.

69. The coating process according to claim **63** to produce a biocompatible implant.

70. The coating process according to claim **63** to form a deposit with an average thickness in the nm size range, in the micrometer scale, in the millimetre scale or in the centimetre scale.

71. The coating process according to claim **63** to coat components of a bioreactor.

72. The coating process according to claim **63** to produce monolithic objects, hollow objects, thin wall objects, membranes or wire for instance nanowires.

73. The coating process according to claim **63** to produce films of cationic or anionic polymers.

74. The coating process according to claim **63** to coat an implant, in particular an arterial or venal implant by a coating or layer with a compound selected from the group of consistence of polytetrafluoroethylene, polyethylene, polypropylene, polybutene, polyurethane, polyvinylpyrrolidone, polyethylene oxide, hyaluronic acid polymers, mixtures thereof and copolymers thereof.

75. The coating process according to claim **63** to coat a conductive substrate with organics such as monomers, precursors, hydrocarbons, functional hydrocarbons, macromolecules, oligosaccharides, polysaccharides, polymers (e.g. thermoplastic polymers, thermo curing polymers, biopolymers, alginates, carrageen or other algae derived polymers, kollicoat IR, or resins, oligomers some of which can be bioactive and others biocompatible.

* * * * *