

# Fabrication of titania dense layers by electrophoretic deposition in aqueous media

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## Abstract

Fabrication of titania dense layers by electrophoresis in aqueous media has been studied according to the suspension formulation. Stable titania suspensions with negatively charged particles are obtained by adding either the strong basis  $(C_2H_5)_4NOH$ , or the Tiron molecule or a salt of polymethacrylic acid. To prevent water electrolysis at the anode which is the collecting electrode, ethanol is added as cosolvent. A concentration of 10 vol% is sufficient to avoid gaseous emission at the anode and to keep a stable suspension suitable for electrophoretic deposition (EPD). The parameters influencing the deposit kinetic of particles are studied, such as the concentration of ethanol, of solid and of dispersant, and the current intensity applied. Finally, it is possible to fabricate layers with a relative density of 60% with a very narrow size distribution of pores.

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## 1. Introduction

Electrophoretic deposition (EPD) represents one of the colloidal forming routes in which consolidation is obtained via particle migration in response to an applied electric field. Under DC bias, charged colloidal particles move toward and deposit on an oppositely charged electrode to produce a consolidated layer or body. The formulation of stable suspensions is necessary to obtain dense green bodies with a homogeneous microstructure. A final sintering stage is essential to have a fully dense part. The thickness of the layer is flexible ranging from a few  $\mu m$  to a few mm depending on the amplitude of dc potential and its time of application. Another advantage is the feasibility to produce parts with complex shape and of constant thickness by adapting the geometry of the collecting electrode.<sup>1</sup> This process is much in use in industry and more particularly with systems using organic solvents rather than water.<sup>2,3</sup> Indeed, water electrolysis, which leads to a gaseous emission of either  $H_2$  or  $O_2$  at the collecting electrode, causes defects in the microstructure of the parts obtained.<sup>4,5</sup> Never-

theless, for obvious reasons of environment and cost, the use of aqueous systems is of increasing interest. The principle of electrophoresis supposes that the particles are electrically charged which is easier to obtain in a strongly dissociating solvent, such as water. Several ways exist to overcome the problems encountered due to water electrolysis: porous electrodes make it possible to catch bubbles within the deposit, but their use is suitable only for fabrication of monolithic objects and not for the coating of substrates<sup>6</sup>; water electrolysis can be reduced by controlling the intensity of the applied current but this implies quite a long deposition time.<sup>7</sup> Another way consists in modifying the suspension formulation<sup>8,9</sup> and this is the choice made in this study. In this context, we undertook to define powerful aqueous systems for the process of EPD by adapting their formulation. The basic assumption was to consider that the use of cosolvents could be beneficial. Indeed, experiments of voltamperometry revealed that the oxidation of ethanol occurs at a potential lower than that of water. Gaseous emission at the anode is then absent if the potential is lower than a critical value.

In this study, a titania powder, with rutile phase, has been chosen because this is a common pigment in the formulation of paints, deposited by electrophoresis and because

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potential applications are numerous. To disperse the TiO<sub>2</sub> powder, three ways which lead to different kind of surface modification, were used and we have preferred to create a negative repulsive potential between the particles because the anode then becomes the collecting electrode. The first one consists in adding a strong base (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH to ionize the hydroxyl surface groups. The second way consists in using an electrolyte, termed Tiron (OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(SO<sub>3</sub>Na)<sub>2</sub>. This compound which complexes the Ti<sup>4+</sup> ion in aqueous solution, is adsorbed on the rutile surface by forming an inner sphere complex by exchange of ligand with OH groups. The ionized sulfonate groups make it possible to create a negative surface charge producing a strong repulsive potential between the particles.<sup>10</sup> The third dispersant used is a sodium salt of polymethacrylic acid (PMANa) with carboxylate groups as ionizable functions. Being adsorbed on the particle surface, it allows a dispersion when carboxylate groups are ionized. Suspensions for EPD have a low solids content (<40 vol%), these three dispersants lead to the same quality of dispersion. The ethanol influence on the suspension stability has been studied and the results having been reported in another article.<sup>11</sup> It is to be recalled that the alcohol addition decreases the zeta potential of the particles and hence their mobility. In the same way the viscosity of the suspensions increases. Ethanol destabilizes the suspensions. Nevertheless, with an alcohol concentration of 10 vol%, which is sufficient to prevent the water electrolysis, the suspensions remain stable and the particles keep a sufficient mobility to allow deposit formation. This article presents the study of deposit formation by electrophoresis as a function of suspension formulation (solid content, composition of solvent, nature and concentration of the dispersant) and the current intensity. The adapted experiment made it possible to follow the in situ mass variation of the collecting electrode during the current application without the deposit having to be modified by a drying stage. To describe the basis for the kinetics of EPD, Hamaker<sup>12</sup> has proposed the following equation:

$$m = \frac{N_p \mu_p}{\sigma} I t, \quad (1)$$

derived by application of the mass conservation principle,  $N_p$  is the solid concentration;  $\mu_p$ , the particle mobility;  $I$ , the current intensity and  $\sigma$  the ionic conductivity of the solution. To observe a linear variation of  $m$  versus  $t$ , it is necessary to apply a constant intensity of current. With this technique of characterization, the parameters of the suspension formulation could be adjusted to allow a linear growth of the titania layers. Finally, the green layers were characterized with porosity measurements.

## 2. Experimental procedure

### 2.1. Starting materials

The powder (reference TRHP2) used in this study is purchased from Kerr McGee (USA). It is a rutile titanium dioxide

of high chemical purity (>99.7%). Concentration of Fe and S is lower than 10 ppm. Of particular interest is the fact that it has no organic coating. TRHP2 is free of agglomerates and displays a monomodal ( $d_{90}/d_{10}=2.8$ ), narrow particle size distribution with an average size of 0.4 μm. The specific surface area is equal to 7 m<sup>2</sup> g<sup>-1</sup> after being degassed at 300 °C for 2 h (N<sub>2</sub> BET) and the density is 4.2 g cm<sup>-3</sup>. A SEM picture of TRHP2 particles is shown in a previous article.<sup>11</sup> This powder is not self-dispersible in water and it flocculates immediately in aqueous suspension.

Dispersants are supplied by Aldrich. The strong base tetraethylammonium hydroxide (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH is a 35 wt% solution in water. Base addition ionizes hydroxyl surface groups and as the isoelectric point (IEP) of the powder is 5.6,<sup>11</sup> a high density of negative charge is expected. Moreover, with an organic basis, such as (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH, the cation considered as a breaker ion of the water network does not penetrate deeper in the compact layer at the solid solvent interface. The surface charge is not efficiently screened, and the amplitude of the interparticles potential is higher than with, for example, NaOH addition. (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH disperses efficiently TRHP2 powder from pH 8 for a concentration of 0.3 wt% of base added and for a solid loading of at least 50 vol%. Tiron, (OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(SO<sub>3</sub>Na)<sub>2</sub>, is a well known efficient dispersant of oxide powders. The role of each functional group grafted on the benzene ring has been determined to identify the dispersion mechanism.<sup>10</sup> All are essential for the dispersion. The molecule shows a strong affinity for the surface because it forms an inner sphere complex by ligand exchange via alcohol groups. This molecule is ionized in all the pH range and creates a negative surface charge via sulfonate groups. The pKa of the alcohol groups are 7.6 and 12.5. Tiron adsorption shifts the IEP of the suspension toward acidic values of pH and it has been also shown that around the IEP, the molecule can be considered as a bivalent anion and is adsorbed via SO<sub>3</sub><sup>-</sup> groups. This compound has been used to develop a new way of internal coagulation with alumina powder.<sup>13</sup> The optimal concentration of dispersant for TRHP2 powder ranges from 0.1 to 0.3 wt% of Tiron. With carboxylate groups, the sodium salt of polymethacrylic acid can be strongly adsorbed on the titania surface and under basic conditions, the polyelectrolyte is ionized and it creates a negative surface charge that permits the powder dispersion for an added concentration of 0.3 wt%. It is a 30 wt% solution in water (MW = 6500 (GPC),  $M_n = 4000$ ). Denatured ethyl alcohol is supplied by Prolabo and deionized water was used.

## 3. Methods

Electrophoretic mobility measurements of the titania particles in the various prepared slurries were measured using an electrokinetic sonic amplitude (ESA) measurement apparatus (Model ESA8000 Matec, Northborough, MA, USA). This technique and its operating principle have been described previously.<sup>11</sup> Measurements were carried out with slurries

containing a 3 vol% solid loading. The data recorded with the ESA analyser correspond to the measured ultrasonic signal converted to a voltage (ESA). According to the O'Brien model,<sup>14</sup> ESA voltages were converted to electrophoretic mobility with the following relationships:

$$\mu_p = \frac{ESA}{c\Delta\rho F} \quad (2)$$

where  $c$  is the velocity of sound in the suspension;  $\Delta\rho$ , the density difference between the solid and the liquid and  $\Phi=0.03$ , the concentration of solid in terms of volume fraction.

Electrophoretic depositions were performed in a 225 cm<sup>3</sup> Plexiglass cell with planar alumina electrodes (50.8 mm × 50.8 mm × 0.63 mm) which are covered by a 100 nm layer of an alloy (Au 80%/Pd 20%). The electrodes were fitted out in a Plexiglass matrix to keep constant the collecting area (15 cm<sup>2</sup>) and the distance between electrodes (2 cm). The electrodes were connected to a dc power supply (Keithley 237, Cleveland, USA) and to an electronic balance in order to measure the mass variation during and after the deposition. The accuracy of measurement is 0.001 g. Measurements of in situ mass are interesting because the method used does not disturb the deposit by a drying stage. But it is not the measurement of the absolute mass deposited but of the mass value modified by the Archimedes pressure. The powder mass deposited was measured after drying, which made it possible to follow the decrease of solid in the suspension during electrophoresis experiments.

The electrophoretic deposition procedure was as follows: a volume of 100 cm<sup>3</sup> of a dispersed suspension was poured into the cell. A dc power was applied for 10 min, the mass variations were measured for 10 min of deposition and for 10 min after, to test the layer adhesion. According to the suspension formulation, the goal of this first approach of EPD is to compare the influence of the ethanol concentration and of the method used to disperse titania particles on the deposition kinetics and on the layer adhesion. Criteria used are the linearity of the deposition kinetics and the weight loss after cutting the current versus time.

The porosimetry is a very effective analytical tool to evaluate the behavior of materials whose properties depend on the total volume of the pores and its size distribution. The apparatus (Autopore II 9215 of Micromeritics) is adapted for the study of any material whose pores size lies between 0.003 and 360 nm. The size of the penetrated pores is inversely proportional to the pressure applied to induce the mercury penetration in the sample. The diameter of the pores  $D$  is calculated thanks to the equation of Washburn:

$$D = -4\gamma \frac{\cos \theta}{P} \quad (3)$$

$P$  is the applied pressure;  $\theta$ , the contact angle of mercury on rutile (110°), with  $\gamma$  the surface tension of mercury ( $485 \times 10^{-3} \text{ N m}^{-1}$ ).

The apparent density is equal to the mass of the sample divided by its apparent volume. Measurements are taken with samples whose mass lies between 0.4 and 1 g. The accuracy of measurement is of  $\pm 1.5\%$  for the relative density and of  $\pm 3\%$  for the diameter.

## 4. Results and discussion

### 4.1. Electrophoretic deposition

#### 4.1.1. Determination of a minimum value of solid concentration

To evaluate the influence of several parameters, such as concentration of solid and of alcohol, we have chosen to use suspensions prepared with 0.1 wt% of Tiron because this concentration leads to the minimum of suspension viscosity while minimizing the ionic conductivity of the solution and thus supporting the migration of the particles under electric field while keeping a stable suspension.

The first experiments aim to determine the minimal solid concentration in the suspension which makes it possible to obtain a linear variation of the deposit kinetics. The solid fraction of the suspensions should lead to a minimal viscosity in order to optimize the particle mobility while ensuring a sufficient flow to have the deposit grown. Fig. 1 reports the mass variation of the deposit measured in situ versus time during the experiment of electrophoresis ( $I_{\text{app}} = 10 \text{ mA}$ ) for an aqueous suspension stabilized with 0.1 wt% of Tiron containing an increasing concentration of powder (5–20 vol%). With 5 vol% of solid, the mass deposited does not increase linearly versus time and the layer is not cohesive. It was measured that after 400 s of electric field application, the suspension contains only 1.8 vol% of powder. The particles flow arriving at the electrode becomes insufficient to allow a significant increase of the deposit mass and to generate a sufficient compressive force to maintain the layer cohesion. From 10 vol% of TiO<sub>2</sub>, the mass of the deposit grows regularly up to 600 s. And for the three higher solid loading (10, 15, 20 vol%), the

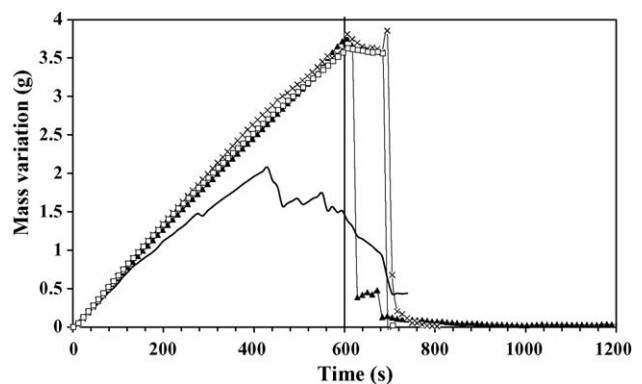


Fig. 1. Mass variation of the collecting electrode versus time.  $I_{\text{app}} = 10 \text{ mA}$ . Suspensions formulation: 100 vol% H<sub>2</sub>O, 0.1 wt% of Tiron and (—) 5, (▲) 10, (□) 15, (×) 20 vol% of TiO<sub>2</sub>.

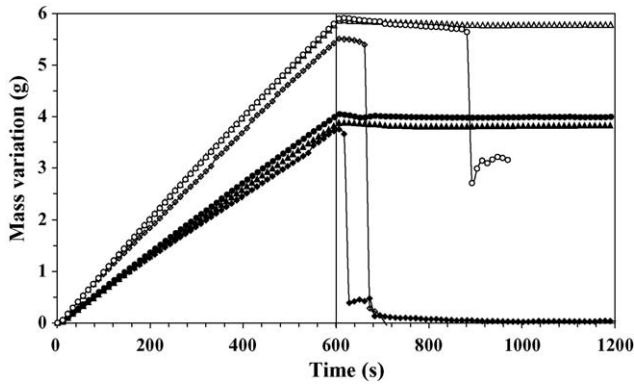


Fig. 2. Mass variation of the collecting electrode versus time. Dark symbols are for  $I_{\text{appl}} = 10$  mA and white symbols are for  $I_{\text{appl}} = 15$  mA. Suspensions formulation: 0.1 wt% of Tiron, 15 vol% of  $\text{TiO}_2$  and ( $\blacklozenge$ ,  $\diamond$ ) 0, ( $\blacktriangle$ ,  $\Delta$ ) 10, ( $\bullet$ ,  $\circ$ ) 20 vol% of ethanol.

linear coefficient of regression is  $>0.99$ . With a concentration of 15 vol%, the fraction of solid remaining in suspension is then still equal to 6.3 vol% ( $>5$  vol%) at the end of 10 min of current application. The growth of the deposit is then not impeded. The following experiments were conducted with suspensions which contain at least 15 vol% of  $\text{TiO}_2$ .

#### 4.1.2. Influence of ethanol

Fig. 2 shows the effect of ethanol on the reaction of water electrolysis through the adherence and the cohesion of the layers obtained. Several experiments ( $I_{\text{app}} = 10$  and 15 mA) were carried out starting from a suspension stabilized with 0.1 wt% of Tiron and prepared with an ethanol concentration as cosolvent included in the 0–20 vol% range. When no ethanol is added, it is not possible to obtain an adhesive layer. For a current intensity of 10 mA, 10 vol% of ethanol are enough to maintain a strong linearity of the deposit kinetic ( $R^2 > 0.99$ ) and to strongly increase the layer adherence. For an intensity of 15 mA, 20 vol% of ethanol are necessary to obtain the same properties. These experiments demonstrate that ethanol prevents the water electrolysis and the gaseous emission at the collecting electrode. A higher intensity of current increases the deposit kinetics but supports also the water electrolysis and thus requires a more important ethanol concentration in the suspension. However, ethanol decreases the particle mobility by decreasing the zeta potential and by increasing the suspension viscosity. It will thus be necessary to find a compromise between these parameters to obtain dense layers without cracks and with homogeneous microstructure and sufficient thickness.

This set of experiments shows that the mass deposited is directly proportional to the intensity of the current applied. It is also interesting to notice that for the same value of current intensity, the alcohol concentration does not influence the deposit kinetics. According to the Hamaker law, the linearity coefficient of the deposit kinetic is equal to  $N_p \mu_p I / \sigma$ . In the case of our experimental conditions, the content of solid  $N_p$  is the same at  $t = 0$  s whatever the suspension,  $I$  does not

Table 1

Calculations of the  $|\mu_p|/\sigma$  ratio according to the ethanol concentration ( $T = 25^\circ\text{C}$ )

Ethanol (vol%)	0	10	20
Conductivity ( $\text{S m}^{-1}$ )	$250 \times 10^{-4}$	$182 \times 10^{-4}$	$138 \times 10^{-4}$
ESA ( $\text{Pa m V}^{-1}$ )	$-4.25 \times 10^{-3}$	$-3.18 \times 10^{-3}$	$-1.88 \times 10^{-3}$
$\Delta\rho$ ( $\text{kg m}^{-3}$ )	3200	3214	3227
$c$ ( $\text{m s}^{-1}$ )	1490	1462	1433
$ \mu_p $ ( $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ )/ $\sigma$ ( $\text{S m}^{-1}$ )	$1.19 \times 10^{-6}$	$1.24 \times 10^{-6}$	$0.98 \times 10^{-6}$

Dispersant concentration: 0.1 wt% of Tiron, solid concentration: 15 vol% of  $\text{TiO}_2$ .

vary with time and one can consider that the particle mobility  $\mu_p$  and ionic conductivity  $\sigma$  of the suspension do not vary for the 600 s of deposition. But  $\mu_p$  and  $\sigma$  vary according to the solvent composition. We have calculated the  $|\mu_p|/\sigma$  ratio with the experimental data. The data allowing this calculation are gathered in Table 1. The velocity of sound is calculated according to a linear relationship related to the solvent composition ( $c = 1490 \text{ m s}^{-1}$  in water and  $c = 1220 \text{ m s}^{-1}$  in ethanol at  $25^\circ\text{C}$ ). The temperature of measurement for the ESA signal and the ionic conductivity was fixed at  $25^\circ\text{C}$ . For these three ethanol concentrations,  $|\mu_p|/\sigma$  ratio shows similar values justifying the same deposit kinetics observed. It would seem that the decrease of the particle mobility due to the ethanol addition is compensated by the decrease of the suspension ionic conductivity. It was shown that alcohol supports the Tiron adsorption on the rutile surface that decreases the ions concentration in the solution.<sup>11</sup>

#### 4.1.3. Influence of Tiron concentration

Fig. 3 reports the mass variation of the deposit measured versus time during the experiment of electrophoresis ( $I_{\text{app}} = 10$  mA) for suspensions containing 15 vol% of  $\text{TiO}_2$  stabilized with 0.05, 0.1, 0.3 wt% of Tiron, respectively and prepared with a solvent composition of 100 vol% of water or a mixture of 90 vol% of water and 10 vol% of ethanol. For each experiments, the value of the linear

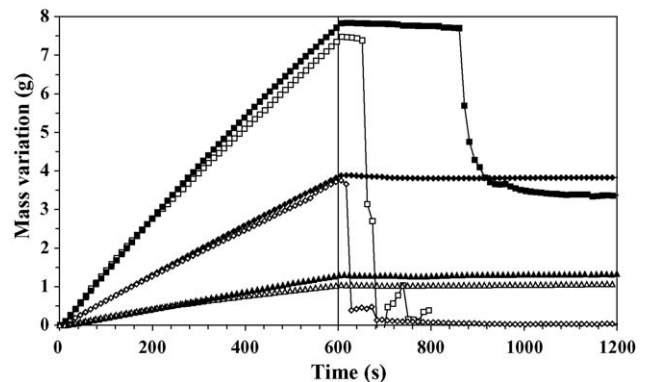


Fig. 3. Mass variation of the collecting electrode versus time.  $I_{\text{app}} = 10$  mA. Dark symbol is for 100 vol%  $\text{H}_2\text{O}$  and white symbols are for a mixture of 90 vol%  $\text{H}_2\text{O}$  and 10 vol% ethanol. Suspensions formulation: 15 vol% of  $\text{TiO}_2$  and 0.05 ( $\blacksquare$ ,  $\square$ ) 0.1 ( $\blacklozenge$ ,  $\diamond$ ), 0.3 ( $\blacktriangle$ ,  $\Delta$ ) wt% of Tiron.

coefficients of regression of the deposit kinetics is higher than 0.99.

A minimum concentration of Tiron must be added to avoid the sedimentation of the suspension during the electrophoresis. A concentration of 0.05 wt% of Tiron is sufficient to obtain a regular growth of the deposit. This value is lower than the value (0.1 wt%) given by viscosity measurements<sup>11</sup> carried out with concentrated suspensions (49 vol%). This result is mainly due to the relatively short duration of the experiment (10 min) during which the suspension keeps a suitable stability. With 0.05 wt% of Tiron, the high deposited mass leads to a strong decrease of the solid concentration in the suspension. In addition, the deposit growth is the slower as the Tiron concentration increases and in the same time, the deposits adhesion is enhanced. Two phenomena can explain this observation. Firstly, the mass deposited is higher when the Tiron concentration decreases, a more important force of gravity is thus opposed to the deposit adhesion on its support. Secondly, the oxidation of Tiron excess in the electrolyte thus prevents water oxidation and decreases the gaseous emission at the collecting electrode that permits a better adhesion. The Tiron concentration necessary to completely prevent O<sub>2</sub> emission is higher than 1 wt%; with such an amount, agglomeration and sedimentation of particles occur. Tiron can not replace ethanol.

The ethanol addition does not modify anymore the deposit kinetics but improves the layers adhesion on the electrode. The values of  $|\mu_p|/\sigma$  were calculated and the data allowing these calculations are gathered in Table 2. The variation of  $\sigma$  versus the Tiron concentration is linear that is not the same for the electrophoretic mobility. Conductivity is mainly due to the free molecules of Tiron and to sodium ions not trapped by the electrical diffuse layer.  $|\mu_p|/\sigma$  decreases as the Tiron concentration increases and these values confirm the influence of the Tiron concentration on the deposit kinetics. Because  $\sigma$  undergoes strong increases with the quantity of Tiron added compared with that undergone by electrophoretic mobility, the deposit kinetics are strongly slowed down. Calculation for 0.3 wt% of Tiron confirms that the solvent composition does not influence the deposit kinetic. The Tiron concentration leading to a sufficient flow of particles and a linear variation of the deposit kinetics is equal to 0.1 wt%; this same value leads to the minimum viscosity of the concentrated suspensions.

#### 4.1.4. Influence of the dispersant

Three different ways were used to disperse the TiO<sub>2</sub> powder by creating a strong negative repulsive potential between the particles. The addition of a strong base makes it possible to ionize the hydroxyls surface groups. Tiron is an electrolyte adsorbed on the surface by formation of a inner sphere complex via the alcohol functions and ionized sulfonate groups create the surface charge. The polyelectrolyte (PMANa) is also adsorbed on the surface and acts according to an electrosteric mechanism. Several experiments of deposit were carried out by fixing the content of TiO<sub>2</sub> at 15 vol%. The concentration of dispersant chosen corresponds to the value which leads to the minimum value of viscosity of the concentrated suspensions and to the minimum value of the ionic conductivity of the solution. The following figures represent the mass variations of the collecting electrode versus time during the application of the current and after its cessation for several intensities. The comparison between a purely aqueous system and another prepared with 10 vol% of ethanol as cosolvent was done.

**4.1.4.1. Suspensions stabilized with (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH.** Fig. 4(a) and (b) report the results obtained with 0.3 wt% of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH as dispersant. Whatever the solvent composition, this formulation does not lead to layers having a sufficient cohesion. The deposits immediately fall from the electrode immediately after the stoppage of the current in pure water and with a more progressive way with ethanol. Although leading to a strong mobility of the particles, this strong base does not make it possible to obtain a deposit usable with such a solid concentration in the suspension.

**4.1.4.2. Suspensions stabilized with Tiron.** Fig. 5(a) and (b) report the results obtained with 0.1 wt% of Tiron as dispersant. In pure water, the slope of the curve representing the evolution of the deposit mass grows with the current intensity but the adhesion is difficult to control. After ethanol addition, the mass deposited varies linearly versus time and the layer adhesion becomes perfect from a current intensity of 5 mA. The cosolvent does not affect the deposit kinetic.

**4.1.4.3. Suspensions stabilized with PMANa.** Fig. 6(a) and (b) report the results obtained with 0.3 wt% of PMANa as

Table 2  
Calculations of the  $|\mu_p|/\sigma$  ratio according to the Tiron concentration

%Tiron	0.05	0.1	0.3
(a) The solvent composition is of 100 vol% of H <sub>2</sub> O, $\Delta\rho = 3200 \text{ kg m}^{-3}$ , $c = 1490 \text{ m s}^{-1}$ ; solid concentration: 15 vol%			
$\sigma \text{ (S m}^{-1}\text{)}$	$125 \times 10^{-4}$	$250 \times 10^{-4}$	$750 \times 10^{-4}$
ESA (Pa m V <sup>-1</sup> )	$-3.82 \times 10^{-3}$	$-4.25 \times 10^{-3}$	$-4.64 \times 10^{-4}$
$ \mu_p  \text{ (m}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}/\sigma \text{ (S m}^{-1}\text{)}$	$2.14 \times 10^{-6}$	$1.19 \times 10^{-6}$	$0.43 \times 10^{-6}$
(b) The solvent composition is of 90 vol% of H <sub>2</sub> O + 10 vol% of ethanol, $\Delta\rho = 3214 \text{ kg m}^{-3}$ , $c = 1462 \text{ m s}^{-1}$ ; solid concentration: 15 vol%			
$\sigma \text{ (S m}^{-1}\text{)}$	$100 \times 10^{-4}$	$182 \times 10^{-4}$	$600 \times 10^{-4}$
ESA (Pa m V <sup>-1</sup> )	$-2.27 \times 10^{-3}$	$-3.18 \times 10^{-3}$	$-3.82 \times 10^{-3}$
$ \mu_p  \text{ (m}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}/\sigma \text{ (S m}^{-1}\text{)}$	$1.58 \times 10^{-6}$	$1.22 \times 10^{-6}$	$0.44 \times 10^{-6}$

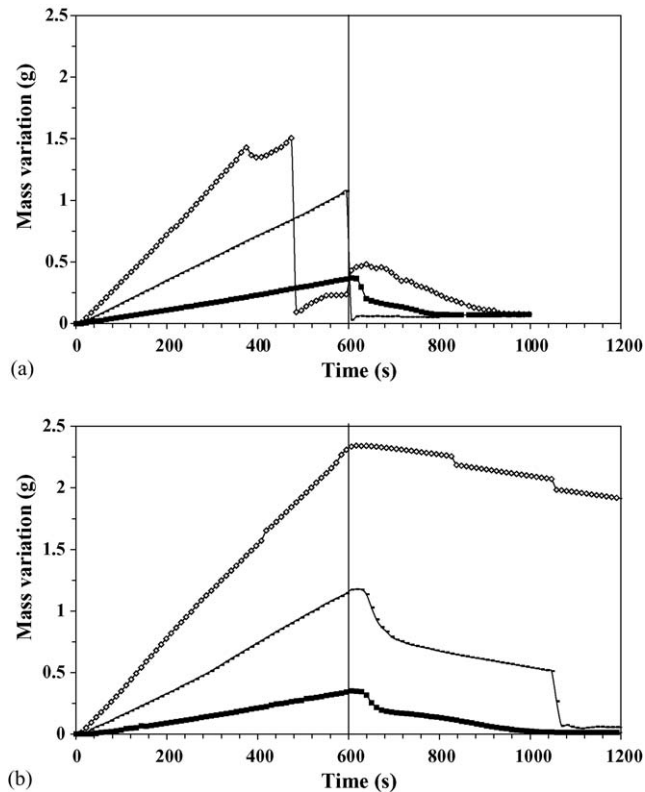


Fig. 4. (a) Mass variation of the collecting electrode versus time. Suspensions formulation: 100 vol% H<sub>2</sub>O, 0.3 wt% of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH, 15 vol% of TiO<sub>2</sub>.  $I_{\text{appl}}$  = (■) 1, (-) 2.5, (◇) 5 mA. (b) Mass variation of the collecting electrode versus time. Suspensions formulation: 90 vol% H<sub>2</sub>O + 10 vol% ethanol, 0.3 wt% of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH, 15 vol% of TiO<sub>2</sub>.  $I_{\text{appl}}$  = (■) 1, (-) 2.5, (◇) 5 mA.

dispersant. The same observations already done with Tiron on the deposit kinetic can be made but the layers obtained are dense and cohesive with a pure aqueous suspension. Moreover, the growth of the deposit is linear with pure water as solvent. Compared to the previous formulations, the benefit of the ethanol use is less sensitive with this one. For the same current intensity and the same solvent composition, a small difference is observed between the deposit kinetics according to the chemical nature of the dispersant.

According to the previous experiments, by adapting the ethanol concentration, the current intensity and the dispersant concentration, a compromise can be found to obtain an adhesive and cohesive deposit with a sufficient thickness. It is obvious that the ethanol use strongly reduces, even removes the water electrolysis and the bubbles production at the collecting electrode, then the adhesion and the cohesion of the particles are enhanced. According to the Hamaker equation:  $m = N_p \mu_p It / \sigma$ , the last parameter which can influence the mass deposited is the solid content  $N_p$ . It was checked that for all the formulations, with a TiO<sub>2</sub> concentration higher than 15 vol%, dense layers in particular when the powder is dispersed with the strong base, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH can be obtained. Nevertheless, these experiments, carried out

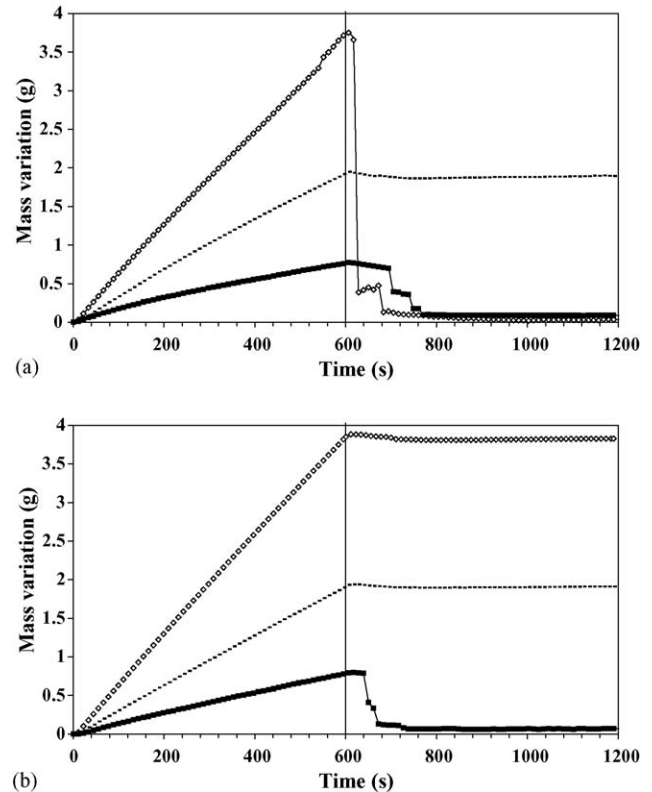


Fig. 5. (a) Mass variation of the collecting electrode versus time. Suspensions formulation: 100 vol% H<sub>2</sub>O, 0.1 wt% of Tiron, 15 vol% of TiO<sub>2</sub>.  $I_{\text{appl}}$  = (■) 2.5, (-) 5, (◇) 10 mA. (b) Mass variation of the collecting electrode versus time. Suspensions formulation: 90 vol% H<sub>2</sub>O + 10 vol% ethanol, 0.1 wt% of Tiron, 15 vol% of TiO<sub>2</sub>. (c) (■) 2.5, (-) 5, (◇) 10 mA.

with (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH show that a dispersion of particles with a high electrophoretic mobility does not constitute the only requirement to obtain a usable deposit. In this case, the surface modification is obtained by desorbing the protons whereas for the two other systems (Tiron and PMANa), it is by molecular adsorption that dispersion is obtained. At this study level and by taking into account the available techniques of characterization, it is difficult to advance assumptions concerning the influence of the chemical surface properties of the particles on its agglomeration at the electrode. At the cathode where consumption of protons occurs (production of H<sub>2</sub>), we observe with suspensions prepared with Tiron that the electrolyte becomes yellow, the color of the basic form of Tiron. At the anode where ethanol and acetic acid are produced, the pH, locally, should decrease. pH influences the surface properties of particles. For the system dispersed with Tiron, the isoelectric point of such a suspension has been measured at pH 2.<sup>11</sup> It was shown that an acidic pH contributes to adsorb additional Tiron molecules but by forming an outer sphere complex via the SO<sub>3</sub><sup>-</sup> groups.<sup>10</sup> For the system dispersed with PMANa, by neutralizing the carboxylate functions of PMANa in acidic media, the configuration of polymer changes from a stretched ionized chain to a neutral coil,<sup>15</sup> which contributes to adsorb

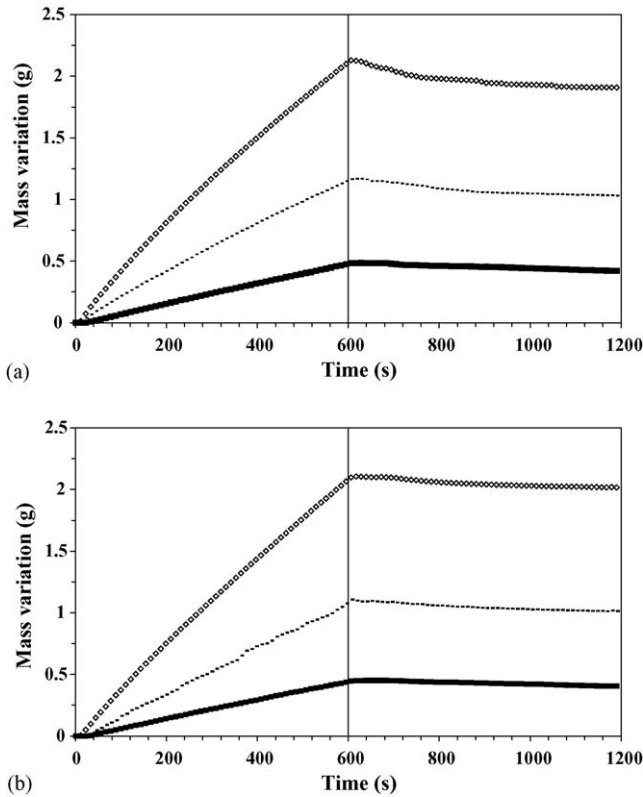


Fig. 6. (a) Mass variation of the collecting electrode versus time. Suspensions formulation: 100 vol% H<sub>2</sub>O, 0.3 wt% of PMANa, 15 vol% of TiO<sub>2</sub>.  $I_{\text{appl}}$  = (■) 2.5, (–) 5, (◇) 10 mA. (b) Mass variation of the collecting electrode versus time. Suspensions formulation: 90 vol% H<sub>2</sub>O + 10 vol% ethanol, 0.3 wt% of PMANa, 15 vol% of TiO<sub>2</sub>.  $I_{\text{appl}}$  = (■) 2.5, (–) 5, (◇) 10 mA.

some more polymer although the electrostatic attraction is not beneficial and this is different from the previous case. Concerning the dispersion at basic pH, the production of protons in the vicinity of the electrode tends to neutralize the surface charge  $\sigma_0$  due to the ionization of the hydroxyls groups. All these modifications of adsorption properties of the rutile surface, contribute for the three systems, to decrease the repulsive potential between the particles. One can then imagine the following process of agglomeration at the electrode which is built from the out proposed by Sarkar and Nicholson.<sup>6</sup> Under the effect of the electric field, the negatively charged particles concentrate in the vicinity of the anode and are forced to come in contact with others. Counter ions Na<sup>+</sup> or (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup> of the diffuse layer are pushed back, that deforms it and involves its shrinkage supporting the particles agglomeration. The species adsorbed, such as Tiron and PMANa, which are mobile on the surface, can be partly expelled, and the particles compaction is then possible. Moreover, the effect of the pH decrease which if it is important, would appreciably affect the repulsive potential between the particles and would then support its agglomeration. Finally it is possible that hydrogen bonds between hydroxyls surface groups supports the layer cohesion.



Fig. 7. Green layer fabricated with the following formulation: 90 vol% H<sub>2</sub>O + 10 vol% ethanol, 0.1 wt% of Tiron, 35 vol% of TiO<sub>2</sub>.  $I_{\text{appl}}$  = 10 mA.

#### 4.2. Characterization of green layers

Several layers were fabricated by EPD ( $I_{\text{appl}}$  = 10 mA) by using the three formulations of dispersion (10 vol% ethanol) with a solid concentration ranging between 15 and 40 vol%. A sample is shown in Fig. 7. According to the powder concentration in the suspension, the thickness varies from 0.5 to 5 mm, the length and the width are equal to 50.8–30 mm, respectively. The green layers were consolidated at a temperature of 800 °C just before the sintering step. The distribution of the pores size for each sample was measured and the density calculated. Fig. 8 reports the average value of the pores diameter and Fig. 9, the relative density versus the solid content in the suspension. With the PMANa and the base (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH as dispersants, the average diameter of the pores has the same value of 0.15 μm and does not vary according to the solid concentration. With the Tiron as dispersant, the average diameter of the pores decreases from 0.25 to 0.2 μm for 15 and 20 vol% of solid, respectively and is equal to 0.15 μm for contents of solid higher than 20 vol%. It should be noted that for each sample the distribution of the pores size is very narrow and is perfectly centered on the

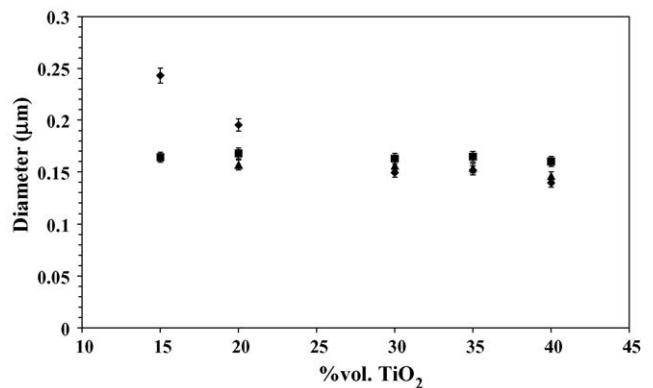


Fig. 8. Average diameter of pores (μm) of the green layers versus solid concentration in the suspension. The dispersant used is: (■) PMANa, (◇) Tiron, (▲) (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH.

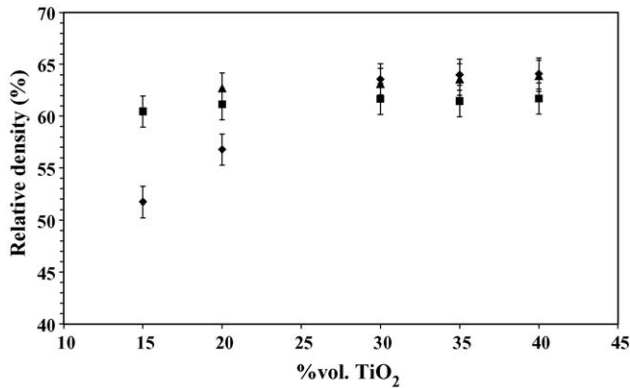


Fig. 9. Relative density of green layers versus solid concentration in the suspension. The dispersant used is: (■) PMANa, (◆) Tiron, (▲) (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH.

average value reported in Fig. 9. The average maximum value of density is 60%; for these thick layers, the roughness and the edge effect are significant, then the density values are slightly overestimated. Nevertheless, this process is efficient to obtain dense layers. For solid concentrations higher than 20 vol%, the influence of the nature of the dispersant is not sensitive any more. The differences of the density value observed according to the dispersant used can be explained by variations of the kinetics of discharge of the particles arriving at the collecting electrode. This phenomenon seems easier when the surface charge was obtained by adding PMANa or (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH. With high solid concentrations, the influence of the dispersant is attenuated. The pressure applied, to the deposit, by the high particles flow tends to optimize the particles arrangement. These results show that it could be found several formulations of suspensions which lead to the fabrication of dense layers with a thickness of several mm, with a density at least equal to 60% of the theoretical density and with a small size of pores distributed homogeneously in the layer. These objects are sintered easily at a temperature of 1400 °C.

## 5. Summary

Titania dense layers can be obtained by electrophoretic deposition by using aqueous suspensions. Ethanol addition, as cosolvent, prevents water electrolysis and gaseous emission at the collecting electrode. With the help of an experiment which permits to measure the mass variation of the collecting electrode during the deposition, the formulation of the suspension has been adapted to obtain cohesive layers. Only a perfectly dispersed system makes it possible to obtain a dense green body and to avoid particle sedimentation during experiments. Either (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH or Tiron or a salt of poly-methacrylic acid permits to achieve a high state of dispersion.

Powder and ethanol concentrations should be at least equal to 15 and 10 vol%, respectively. The dispersant concentration chosen leads to the minimum of the concentrated suspensions viscosity and of the solution ionic conductivity. The relative density of the layer obtained is of 60% and the pores size is very narrow and centered on an average size of 0.15 μm.

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