Determination of Hydrogen Thermally Evolved from Barrel-Zinc-Plated Steel: a Gas Chromatographic Method

M. Wery, F.X. Perrin & J. Pagetti

Hydrogen can be introduced into metals as a result of plating and/or cleaning processes. For coated steel parts, bake-out treatments for removal of hydrogen are often helpful. To determine the amount of hydrogen thermally evolved during baking, a sensitive apparatus, using a gas chromatograph, was developed. An investigation was made of the hydrogen desorption rate of zinc electrodeposited under barrel conditions from a cyanide electrolyte. The effects of metallurgical microstructures of steel parts and operating plating conditions upon hydrogen desorption were determined by using an experimental design. An analysis of pertinent parameters for the desorption process is given. Hydrogen removal is a specific function of the microstructure of the substrate (*i.e.*, the heat treatments performed on the steel samples). These criteria can be of help in selecting baking operating conditions for zinc-coated steel parts.

Hydrogen can be introduced into steel during the steel-making process, fabrication or service.[1] Surface treatments in aqueous solutions can generate hydrogen at the surface of the parts. Hydrogen does not only enter into the plated metal during the electroplating cycle, but throughout the cleaning cycle. When a steel is acid-pickled, hydrogen is liberated in the corrosion reaction and may enter the steel.[2] Cathodic charging in alkaline solutions (electrocleaning) may also introduce hydrogen into the metal;[3] however, this phenomenon is prevalent during metal electrodeposition and especially in zinc plating as a result of less than theoretical cathodic efficiency.[4]

Hydrogen is known to have a dramatic effect on the physical and mechanical properties of metals[5,6] and to contribute significantly to hardness and embrittlement of steels, for instance. To reduce hydrogen embrittlement, electroplaters who constantly zinc-plate high-strength nuts and bolts use alternative techniques, such as baking after plating.[5] This additional heat treatment (*e.g.*, 1-8 hr at 130-230 °C), may release hydrogen that has been occluded in the part or merely diffuse it evenly through the surface.

Prior investigations have indicated that the damaging effects of hydrogen on physical and mechanical properties of metals depend on both the process by which it is introduced, and upon the metallurgical characteristics of the material itself.[5,6] It was considered important to verify whether the influence of these parameters remains valid on hydrogen thermally evolved from zinc-coated steel parts. Moreover, it was decided that an investigation performed on steel parts plated under barrel conditions would be worthwhile because most of the previous work on hydrogen evolution and metal electrodeposition processes has consisted of stationary plating of individual test specimens. A need arose, therefore, to evaluate the hydrogen content in electrodeposited zinc.

The determination of hydrogen in metals has undergone extensive development in the last 20 years, and several review articles of this subject have published,[7,8] with particular emphasis on steels.[9] Numerous techniques have been used: vacuum,[10,11] carrier-gas method,[12,13] electrochemical methods,[14] nuclear reaction methods,[15] spectral methods[16]

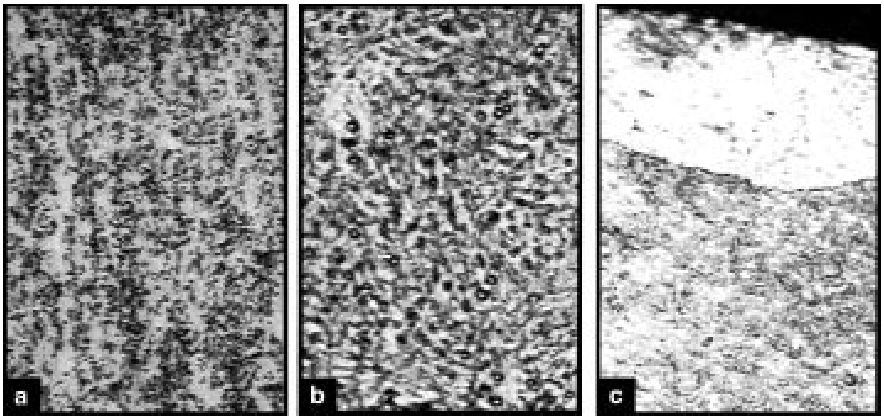

Fig. 1—Photomicrographs of cross sections of three rivets: (a) after cold-working (600X); (b) after hardening (quenched and tempered) (1400X); (c) after surface-hardening (carbonitrided and tempered) (600X), etched with 5-percent nital.

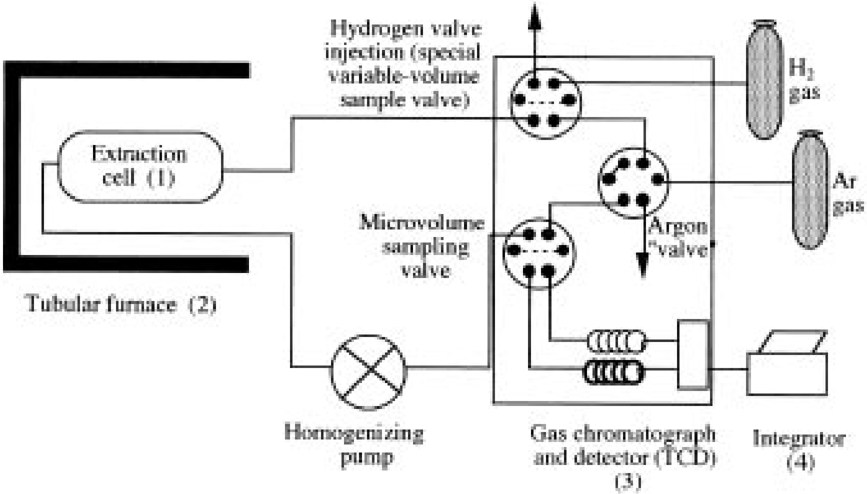

Fig. 2—Diagram of the apparatus.

Table 1
Taguchi L9 Array Configuration

	Column number			
Trial Number	**1**	**2**	**3**	**4**
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

and surface analytical methods.[17] The authors have chosen to develop a gas-carrier method that may be used in routine analyses.

The main subjects of the work in this study can be summarized as follows: (1) presentation of the outline of the apparatus for determination of the amount of hydrogen thermally evolved from zinc-coated steel parts, (2) examination of the influence of baking temperature upon the hydrogen thermally evolved, (3) evaluation of the effects of metallurgical microstructures of the steel parts and operating plating conditions on hydrogen desorption, using an experimental design.

Experimental Procedure

Specimens

Steel rivets, 6 mm in dia. and 15 mm long, were selected for use as the test pieces. All rivets used in this investigation were manufactured from the same production lot of low-alloyed steel wire (type 38Cr4 : 0.37% C, 0.18% Si, 0.81% Mn, 0.018% P, 0.007% S and 1.00% Cr). Because, in this study, our interest was in the effects of the metallurgical characteristics, the experimental plating work was carried out on three lots corresponding to three different heat treatments. Spheroidizing was usually carried out prior to mechanical cold-working to reduce the hardness of steel. Two other heat treatments were evaluated and are as follows: hardening (austenizing at 880 °C for one hr, quenching in oil at 60 °C, then tempering at 550 °C for 40 min) and surface-hardening (carbonitriding at 850 °C in a gaseous atmosphere, quenching in oil, then tempering). Figure 1a-c shows the different microstructures of heat-treated parts. Before undergoing heat treatment, specimens were dephosphated, degreased thoroughly, rinsed and dried.

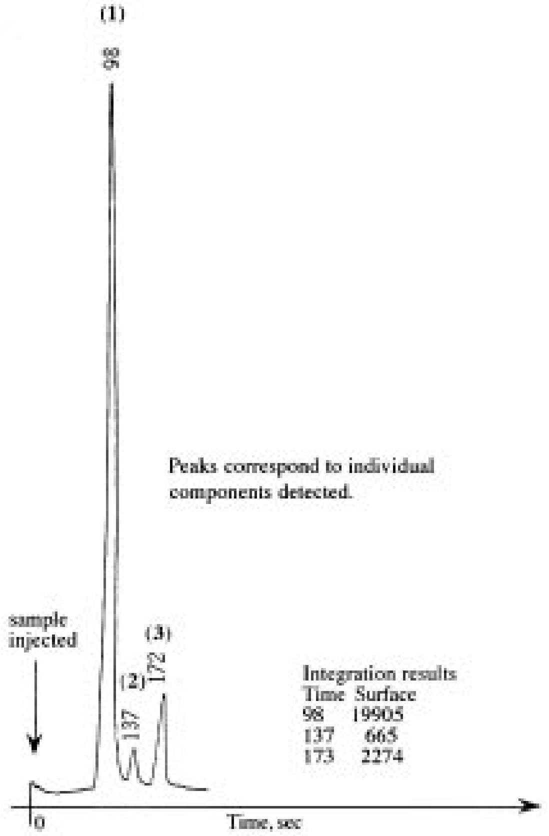

Fig. 3—Typical chart record: Column, 6.6 ft x 1/8" (2 m x 2.2 mm); Packing: Molecular sieve 13X 80/100, Temp: 65 °C; Flow rate: Argon, 25 mL/min (TCD). ***1*** *Hydrogen,* ***2*** *Oxygen,* ***3*** *Nitrogen.*

Cathode Surface Preparation & Plating of Parts

A load of 200 rivets was used because experience showed that this was the best load size in barrel plating for obtaining thickness uniformity. The samples were cleaned by three processes usually in combination (*i.e.*, alkaline soak cleaning, followed by electrolytic cleaning, then acid dipping). Because a considerable amount of hydrogen might be introduced during surface preparation, these processes were followed by baking to remove it. Prior to electroplating, acid dip to re-activate the surface was necessary, but immersion time was minimized (30 sec). In this investigation, a low- cyanide electrolyte of the following composition was used at room temperature for all experiments: NaCN, 25 g/L; NaOH, 80 g/L; Zn, 12.5 g/L. The plating lab barrel was a 110 x 60 mm horizontal cylinder, with 1-mm^2 holes. It was equipped with a flexible dangler contact to carry the current. Its rotational speed was kept constant at 8 rpm. High-grade zinc anodes in steel containers were used. A preliminary study was made to determine the appropriate anode area (steel-to-zinc-anode

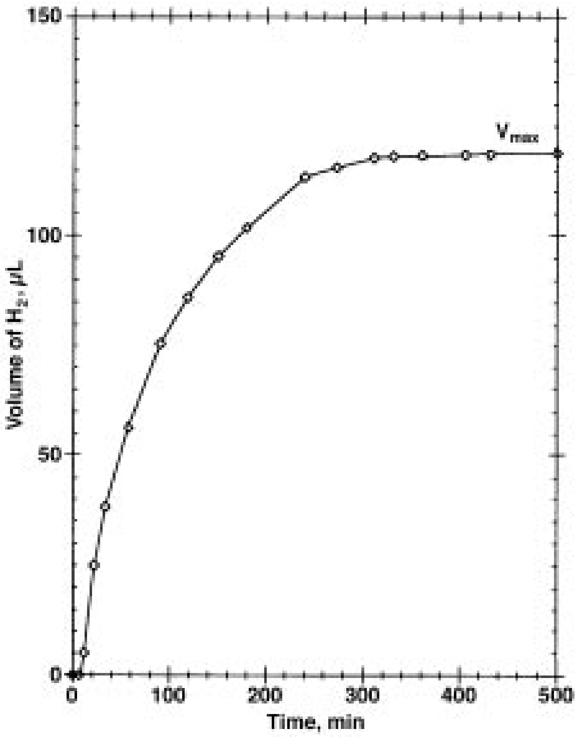

Fig. 4—Typical hydrogen evolution curve.

ratio) to maintain a stable zinc concentration in the system. The solutions were analyzed before and after electrolysis. In all cases, the change in composition of the electrolyte was found to be insignificant.

Table 2
Taguchi L9 Factors & Levels

Factors	Column	Level 1	Level 2	Level 3
Metallurgical states **(M)**	1	cold-formed	quenched-tempered	carbonitrided-tempered
Current density **(I)**	2	0.2 A/dm²	0.6 A/dm²	1 A/dm²
Current quantity **(Q)**	4	1 A-min/dm²	10 A-min/dm²	40 A-min/dm²

Development of Apparatus

The method advanced here was inspired by that of Brulé *et al.*[12] for the determination of hydrogen content in steels (Fig. 2). After zinc plating, the samples are put into a cell (1), in which the air is displaced by argon gas. After a predetermined time, the cell is transferred into the furnace (2) and the samples are heated at an elevated constant temperature. The released diffusible hydrogen is pumped, together with the carrier gas (and residual air), from the cell in the analytical section and assayed. The hydrogen is detected by a gas chromatograph of the thermal conductivity detection type (4) and the amount of hydrogen in the carrier gas (argon) is determined by an integrator (5). Measurements are repeated at arbitrarily set intervals and the total of the measured values is regarded as the amount of diffusible hydrogen. Definite amounts of standard hydrogen gas are used for calibration.

The Extraction System (cell and furnace)

Pyrex glass was used as the material for the cell in consideration of the permeability of hydrogen and for its corrosion resistance, despite brittleness. The size of the cell (30 mm in dia. and 140 mm long) is such that several small parts can be contained. After insertion of the specimens, the cap was set and the inside of the cell shut off from the outside air, using an O-ring. The tubular furnace has an opening in one end to make transfer of the cell, where the extraction takes place, as simple as possible. The furnace temperature is measured accurately and kept constant.

Carrier Gas Path to Cell

This device comprises two channels. The first channel facilitates the following: air purge of the cell after insertion of the specimens, check of gas leaks in the cell, preparation of calibration curves, etc. The second channel, connected directly to the cell, allows determination of the whole quantity of hydrogen evolved within a definite time and permits following of changes in the hydrogen evolution rate with the passage of time. Rotary multiway valves (6 ports, 2 ways) are used to change flow paths.

The hydrogen content in ppm can be calculated from a calibration curve (*i.e.*, the relationship between the hydrogen content and the surface area of the chromatographic peak). Calibration curves are prepared using H_2 gas (99.995% purity) with the aid of five calibration tubes of 232, 296, 503, 962 and 1,360 µL (measured with mercury) incorporated in the two-channel selector. The sampling loop volume is 710 µL.

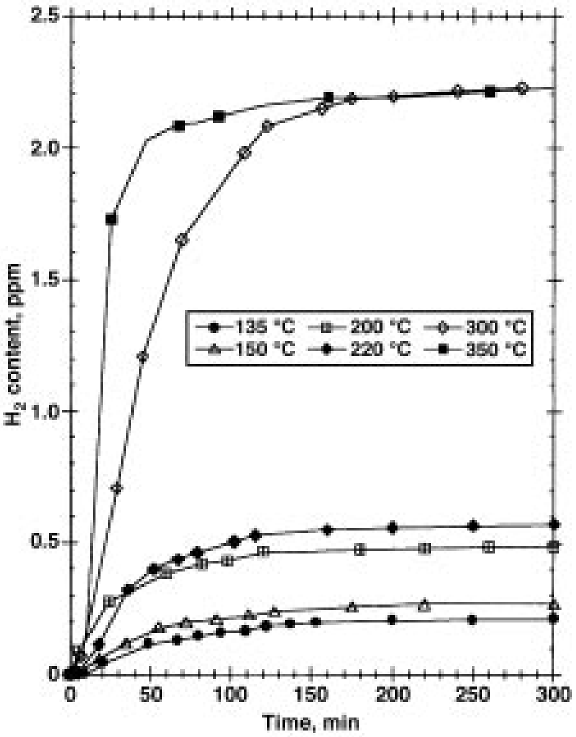

Fig. 5—Hydrogen evolution from zinc-coated steel specimens during hot extraction at various constant temperatures. Plating conditions: 1 A/dm², 15 A-min/dm², 25 °C.

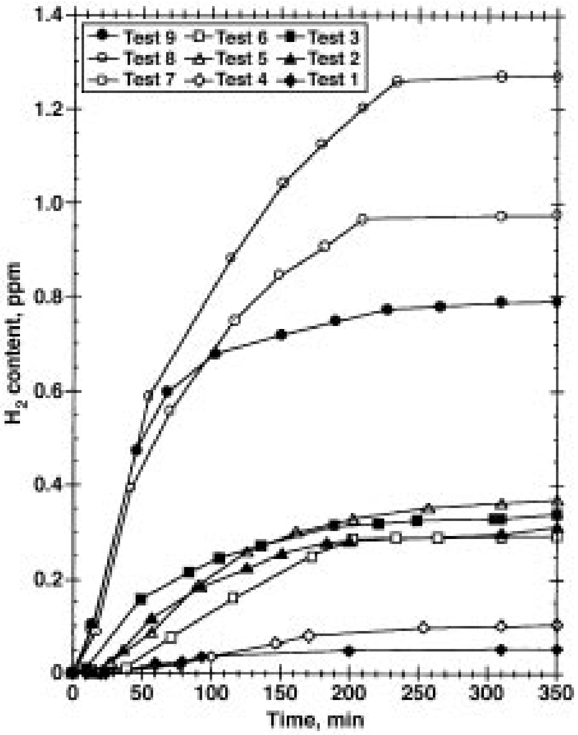

Fig. 6—Hydrogen evolution curves from zinc-coated steel samples performed under Taguchi L9 Array (220 °C).

Gas Chromatograph

The analytical system is composed of a gas chromatography of the thermal conductivity type and an integrator. The gas chromatographic column (length 2 m, inner dia. 2.2 mm) is packed with molecular sieve (80/100 mesh - SAE 30 phase). The pressure is equal to 1.4 bar, and the furnace temperature is 65 °C. Argon (99.995% purity) is used as the carrier gas instead of helium because the values of the limit of detection can be lowered. The difference in thermal conductivity between the carrier gas (Ar) and the analyzed gases (H_2, O_2, N_2) is measured in a thermal conductivity detector (TCD). The TCD employs a heated tungsten filament: four elements energized by a constant current of 70 mA. The temperature of the detector block is 105 °C.

Preliminary experiments were performed to optimize the operating conditions for the gas chromatograph.[18,19] The retention times for the gases are: hydrogen 98 sec, oxygen 137 sec, nitrogen 172 sec (Fig. 3).

Several advantages are connected with this technique, such as the ease with which the kinetics of hydrogen evolution as a function of temperature can be followed, the simplicity of the apparatus, etc. Its principal disadvantage is the range of extraction temperature available, fixed by the locking mechanism of the extraction cell, ranging from 100 to 400 °C (far below the fusion temperature of the samples).

Results & Discussion

Influence of the Extraction Temperature

Figure 4 shows a typical analysis for a zinc coated steel. Starting from zero time, the curve shows a time lag at the start, mostly because of the time required for the specimens to attain the temperature of the furnace. The volume of H_2 increases gradually after this time lag and finally becomes stationary. V_{max} represents the maximum volume of hydrogen thermally extracted from the specimens at the desired temperature. Figure 5 shows the rate of hydrogen evolution at various constant temperatures for zinc coated steels from a cyanide bath under identical conditions. Until 200 °C is reached, the hydrogen content increases only slowly. By raising the extraction temperature, the hydrogen evolved changes more rapidly, so that at 350 °C, hydrogen evolution has ended after 80-100 min, while at 300 °C, it takes 150-170 min for all the hydrogen to be released from the sample. At an extraction temperature of 220 °C, hydrogen evolution is still not complete after 150 min. Despite the great difference in the quantity of the evolved hydrogen caused by elevated temperature, the general trend of gas evolution is much the same. There is not much evolution of hydrogen below 135-150 °C. Hydrogen evolution first becomes evident above this temperature. With rising temperature, the rate of hydrogen evolution increases.

Effects of the Metallurgical Microstructures & Operating Conditions

The questions to be posed in an analysis of hydrogen evolved from a coated metal during baking, after plating processes, may be summarized as follows :

- What is the influence of the metallurgical variables (composition, microstructures, strength level, processing history, etc.)?
- How do plating conditions affect the hydrogen content?

Table 3
Taguchi L9 Treatments Results & Factors Effects

Test	Treatment results C_H (ppm)	Source	Effect
		Mean	0.50
1	0.05	**M_1**	-0.26
2	0.31	**M_2**	-0.25
3	0.34	**M_3**	0.51
4	0.10	**I_1**	-0.12
5	0.37	**I_2**	0.15
6	0.29	**I_3**	-0.03
7	0.97	**Q_1**	-0.09
8	1.27	**Q_2**	0.02
9	0.79	**Q_3**	0.07

Because of the many variables involved and the impossible task of studying one at a time, it was decided to confine the study to the structure factors and to some of the plating conditions factors.

To investigate each variable one at a time while holding all others constant would require an enormous amount of engineering time. To reduce experimentation time, a technique known as the Taguchi Method can be used. The basis for Taguchi's technique of simultaneous testing of multiple variables is the orthogonal or balanced array, which was originally developed by American and British statisticians.[20] The experimental design is a L9 array, so named because it comprises 9 treatments or combinations of factors. The array configuration is depicted in Table 1. The L9 is a three-level array. This means, that for each factor, three different values are tested. Table 2 shows the three factors studied and their levels that are independently and simultaneously evaluated in this investigation.

- *Factor 1*: Metallurgical states *(M)*.
  Microstructures may be one cause of hydrogen embrittlement. The published literature reveals that the overall ranking for steels extends from quenched and tempered martensite's being more resistant to hydrogen, through spheroidized structures having intermediate resistance, to pearlitic structure, usually with somewhat less resistance.[5] Level 1, therefore, represents typical cold-worked steel with spheroidized pearlitic structure, while Levels 2 and 3 metallurgical states represent, respectively, quenched and tempered martensite-bainite and carbonitrided and tempered microstructures.

- *Factor 2*: Apparent current density *(I)*.
  Barrel plating conditions are very different from those of still plating. This is essentially because of current fluctuations corresponding to the intermittent contact of the tumbling parts with the electrical lead. Current density affects the cathodic efficiency and, therefore, the quantity of hydrogen released during electrolysis. Level 2 represents the standard current density while Levels 1 and 3 represent the industrial limits of the current density range.

- *Factor 3*: Current quantity *(Q)*.
  The amp-hr of charge can be correlated with deposit thickness. Level 1 represents the first stages of the zinc deposition. Levels 2 and 3 represent two values of current quantity simulating industrial plating conditions.

Figure 6 shows the nine hydrogen evolution curves obtained in the experiments. The resulting data of the L9 are depicted in Table 3. These values represent the hydrogen content (ppm) thermally evolved after five hr bake (220 °C). The effects of the individual factors are given by the polynomial expression:

$$C_H = 0.50 + [-0.26 - 0.25 + 0.51]M + [-0.12 + 0.15 - 0.03]I + [-0.09 + 0.02 + 0.07]Q$$

$$C_H \approx 0.50 + [-0.26 - 0.25 + 0.51]M$$

The factor *M*, microstructure, is the most significant (85 percent of contribution). The results indicate the important effect the carbonitriding heat-treatment may have when it is employed. Even if several hypotheses are expressed, this observation may be the result of the case presence (*i.e.*, the surface region which both limits the diffusion of hydrogen through the metal lattice and renders steels "difficult to plate"). The ease of deposition (or platability) depends on the surface composition of the parts.[21] During the time required by the zinc nucleation step, called t_{Zn}, hydrogen is released only on the cathode surface, resulting in a large concentration of hydrogen in the outer surface of the sample. For example, a quenched sample is readily plated ($t_{Zn} \approx 8$ sec), while a carbonitrided specimen accepts zinc deposition 150 sec after the plating operation begins.

Factors 2 and 3, apparent current density and electric charge, are less significant in the limits of the study field. It should be noted, however, that in this array, the interactions, negligible by hypothesis, are correlated or aliased with the main effects. As a result, the effects of the factors can be exaggerated or diminished.

Summary

The apparatus developed for determining the hydrogen in coated steels comprises an extraction system in which the gas is separated from the sample by heating, and an analyzing gas chromatographic system to determine quantitatively the hydrogen content. Significant advantages are the ease of use and the non-destructiveness of the method. This apparatus allows optimization of the baking conditions generally recommended after plating processes. The results of the test program clearly suggest that the metallurgical states affect strongly the hydrogen evolved. Future study will include investigation of the amount of non-occludable hydrogen (*i.e.*, hydrogen that is trapped in the steel and cannot be easily removed by bake-out) as a function of the metallurgical microstructures of the parts and of operating plating conditions.

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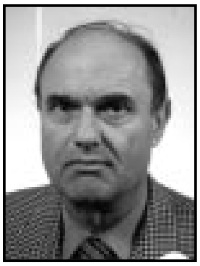
About the Authors

Dr. Martine Wery is an electrochemical engineer at the Laboratoire de Corrosion et de Traitements de Surface of the Université de Franche-Comté, 32 Rue Mégevand, 25030 Besançon Cedex, France. Since 1990, she has been a researcher of plating processes.*

F.X. Perrin is a doctoral candidate at the University of Franche-Comté. His areas of research include deposition of both organic and mineral coatings. As a chemical engineer, he is particularly involved in the perfecting of analytical methods for characterization of chemical composition.



Dr. Jacques Pagetti is professor and chief of the Laboratoire de Corrosion et de Traitements de Surface of the Université de Franche-Comté, Besançon. Prof. Pagetti teaches electrochemistry, materials and metallurgical engineering.

* *To whom correspondence should be addressed.*