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## RAMAN MICROPROBE SPECTROSCOPY OF CORROSION PRODUCTS FORMED ON ELECTRODES SUBJECTED TO CORONA DISCHARGES

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**Résumé** — Les produits de corrosion formés lors de l'interaction d'une décharge couronne avec les électrodes ont été déterminés grâce à la microsonde Raman associée aux techniques classiques d'analyse chimique.

**Abstract** — Corrosion products appearing under the interaction of a corona discharge with the electrodes have been identified by Raman microanalysis associated to classical methods of chemical analysis.

## I — INTRODUCTION

The application of an increasing d.c. voltage to a point-to-plane gap in room air leads to a loss of current above the onset voltage and to breakdown for higher voltages. Between onset and breakdown voltages, a quiet steady state exists and it exhibits some peculiar features according to the polarity. For a positive voltage applied to the point, a thin blue glow envelops the hemispherical tip of the anode whereas three regimes successively appear for a negative voltage : the Trichel regime at low currents, the transition regime at about 150  $\mu$ A and the pulseless regime for larger currents /1/. When the electrodes are subjected to corona discharges for a few hours, a corrosion clearly appears on the point and develops slowly on the plane /2/. This corrosion exhibits various aspects in terms of electrode material /3/. To elucidate the mechanism of corrosion, it is necessary to know the active species created by the discharge and the corrosion products present on the electrodes.

In the positive corona discharge (in room air and with a cylindrical geometry), the nature of positive ions has been determined near the cathode by mass spectrometry /4/. The same technique has been recently applied at lower pressures (between 5 and 300 torrs) to the point-to-plane gap for the both two polarities /5/. For positive coronas, the main species are  $H_3O^+(H_2O)_n$  ( $1 \leq n \leq 9$ ),  $NO^+(H_2O)_n$  ( $0 \leq n \leq 3$ ),  $NO_2^+(H_2O)_n$  ( $0 \leq n \leq 5$ ) and  $NO^+NO(H_2O)_n$  /5/. For negative polarity,  $CO_3^-(H_2O)_n$  ( $0 \leq n < 7$ ),  $O_2^-(H_2O)_n$  ( $1 \leq n < 7$ ),  $O_3^-(H_2O)_n$  ( $1 \leq n < 7$ ) and  $NO_2^-(H_2O)_n$  ( $1 \leq n < 7$ ) /5/ have been found. Relative humidity and ventilation of the vessel influence greatly the coefficient n.

Owing to ion reactions along the stem of the point electrode, significant particle extraction from the highly stressed electrodes seems almost impossible /6/. The nature of some species in the vicinity of the point may be deduced from known ionization processes. However, the electrical field is large (60 kV/cm) near the positive point and detachment will occur. Unfortunately, the lack of knowledge about detachment coefficients for the most abundant negative ions and clusters involved does not permit identification of the negative ions moving towards the anode together with electrons. Before a negative point,  $N_2^+$  ions and perhaps other species will be present. For both polarities, a large amount of neutral ( $O_3, NO_x$ ) and excited species will be found near the ionization region. They are progressively dragged towards the plane by the electrical wind /7/.

Whereas all electrical parameters can be easily measured on the plane for both polarities, determination of the local current density and of the electrical field at the point is difficult /8/. Infrared thermographic data reveal a small increase of the mean temperature at a positive point /9/ and at a point subjected to the Trichel regime /10/. In the pulseless regime of the negative corona, the temperature at the spot is large and can reach 1000°K /10/. For positive and negative coronas, spectral analysis of the glow shows a large amount of U.V. bands /7/.

II - EXPERIMENTAL CONDITIONS

Usually we used point made up of a 6 mm rod with an hemispherical cap. Gap length ranged between 25 and 35 mm. The plane electrode has a large diameter (about 120 mm) with a special profile and contained a 25 mm diameter disk in its centre. This disk could be analysed easily by SEM and other techniques. Experiments were performed in room air in an open set-up. Relative humidity varied between 35 and 95 % at 20-25°C. Electrodes were mechanically polished by alumina and washed with alcohol and distilled water. Before exposure to the discharge, they might stay in the room air of the laboratory from a few minutes to a few days.

III - RAMAN MICROPROBE ANALYSIS

Microanalysis of corrosion products is not easy because the active electrodes are hemispherical and the reaction products are more or less hygroscopic. When placed in a vacuum, they become very good insulating specimens and new analytical tools such as Auger, ESCA,... are difficult to apply. Thus, we have performed some analysis on the U 1000 (Jobin-Yvon) Raman microprobe. Raman spectra of corrosion products formed on points subjected to positive or negative corona discharges are shown in figures 1 to 6. Slit width of 700  $\mu\text{m}$  and laser power of about 100 mW gave spectra with suitable signal to noise (514.5 nm laser line).

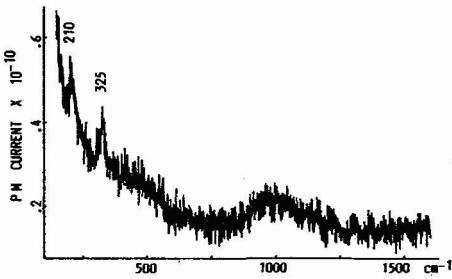


Fig. 1. - Positive stainless-steel point.

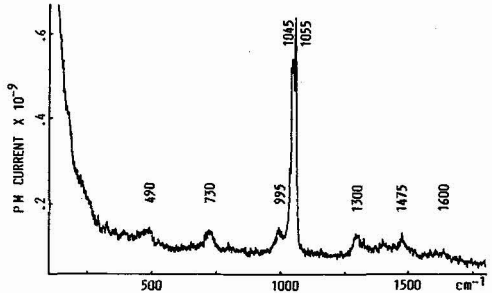


Fig. 2. - Positive nickel point.

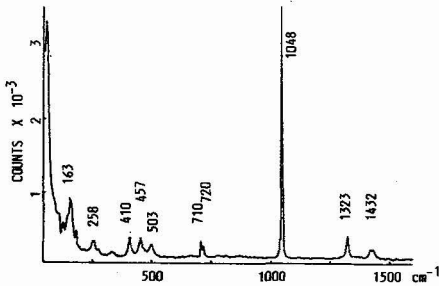


Fig. 3. - Negative copper point.

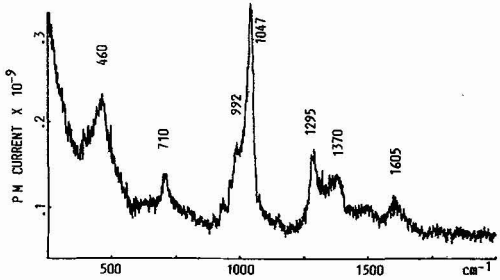


Fig. 4. - Nickel cathodic disk. Analysis of corrosion products above a pit.

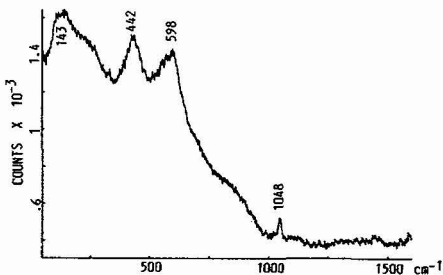


Fig. 5. - Positive titanium point.

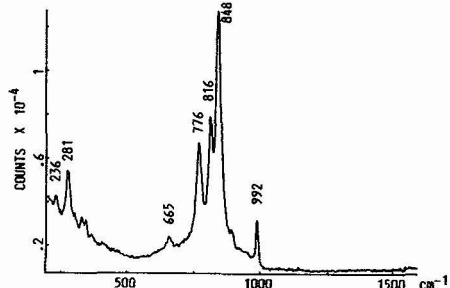


Fig. 6. - Positive molybdenum point.

#### IV – RAMAN SPECTRA OF SOME NITRATES

As all the spectra of nitrates are not found in the literature, we have directly determined some of them. The nitrates have been supplied by Prolabo (Paris). Slit width of 400  $\mu\text{m}$  and laser power of 100 mW (fig. 7–8–9) and 50 mW (fig. 10) have been used.

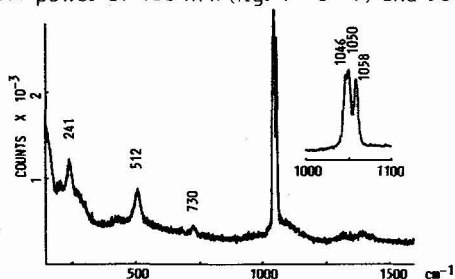


Fig. 7.— Iron nitrate :  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

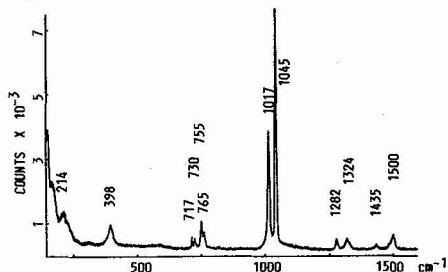


Fig. 8.— Copper nitrate :  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ .

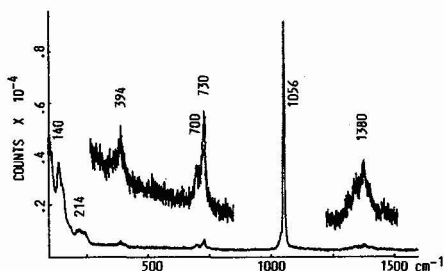


Fig. 9.— Nickel nitrate :  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

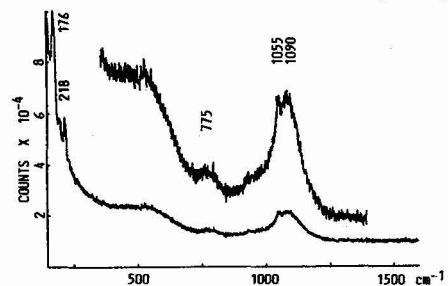


Fig. 10.— Chromium nitrate :  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

#### V – DISCUSSION

Raman spectra of corrosion products laying on electrodes (point and plane) subjected to the corona discharge exhibit some similar features for stainless-steel, copper, aluminium and nickel, namely :

- presence of the 1050  $\text{cm}^{-1}$  band ( $\text{NO}_3^-$  band)
- spectra are similar for the two polarities
- presence of the 3400 - 3600  $\text{cm}^{-1}$  band ( $\text{OH}^-$  band).

For a positive titanium point, frequencies characteristic of  $\text{TiO}_2$  oxide are easily observed in Raman spectra and the  $\text{NO}_3^-$  band appears in some spectra. For negative molybdenum points, spectra characteristic of  $\text{MoO}_3$  oxide /11/ are obtained whereas for positive molybdenum points another bands are present with spectra (fig. 6).

Spectra of corrosion products exhibit a large similarity with those of nitrates (litterature data and our own data), but they are not identical. Therefore, we have carried out some X, Auger and ESCA micro-analysis. Qualitative X analysis with a Si-Li detector attached to a field effect SEM (HPS 30B, Coates and Welter) and qualitative X analysis (Camebax) show mainly the presence of polishing products and of component parts of metals /2/. Auger analysis of stainless-steel and nickel points reveals the presence of oxygen and metals. ESCA analysis gives also oxygen and Cu for copper points.

It is possible that the nature of reaction products is not the same in the first atomic layers (Auger, ESCA results) as in the first 500  $\text{\AA}$  (Raman microprobe), but it is more likely that in a vacuum with an intense electron bombardment, a modification of corrosion products appears /12/. In order to remove this difficulty, we have scraped off the electrodes with a stainless steel knife and the resulting powder was used for the X-ray diffraction analysis and for Infra-red spectroscopy.

Table 1 : Results given by analysis of powders

Positive Points	X-ray Diffraction	Infrared Spectroscopy	Fig.
Copper	$\text{Cu}_2(\text{OH})_3\text{NO}_3$ 15.14, $\text{Cu}_2\text{O}$	Copper Hydroxinitrate	3
Nickel	amorphous	Nickel Hydroxinitrate	2-4
Stainless steel	amorphous	<u>Fe</u> , Ni, Cr Hydroxinitrate	1

As we observe in SEM, the corrosion products of positive copper points are crystalline and X-ray analysis allows their determination: copper hydroxinitrate and oxide are found in the bulk of the products. In the case of stainless steel and nickel, no X-ray pattern could be obtained due to the amorphous nature of the corrosion products but the similarity between the I.R. spectra and the one about copper shows that the same type of compounds may be expected. For the stainless steel points the color of products allows to suppose the presence of an iron hydroxinitrate. So, X-ray and Infra-red analysis of powders confirm the results obtained directly by the Raman microprobe and precise them.

#### VI – CONCLUSIONS

**Raman microprobe** spectroscopy makes easy identification of surface species without changing the environment and it gives the nature of unperturbed corrosion products. Complementary Raman spectra of some nitrates combined with X-ray and Infra-red spectroscopies on powders allow to recognize unknown Raman spectra and thus corrosion products. For the positive corona, hydroxinitrates and oxides have been found on the electrodes. For the negative corona, hydroxinitrates are present in the surrounding area of spots (pulseless regime) but at the location of spots  $\text{NO}_3^-$  and  $\text{OH}^-$  bands are absent.

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