

## Physico-chemical Characterization of Chromate Conversion Coatings Formed on Al Substrates.

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A large research effort has been devoted in the last years to the understanding of the exact nature of Chromate Conversion Coating (CCC) and its mechanism of protection against corrosion of aluminium metal and alloys. Surface analysis techniques have revealed that the composition of the coatings depends on the nature of the chemical conversion bath (1-3).

In this work we will report on the results of Photocurrent Spectroscopy (PCS) study of ageing process of CCC initially characterised by using both non-electrochemical ex situ (XANES, GDOES and TEM) and electrochemical in situ (Photocurrent Spectroscopy, PCS) analytical techniques.

In order to minimise any influence of the initial surface preparation electropolished Al (99.99%, Aluminium Werke-Berlin) samples (EP-Al) were converted in chromate baths with and without accelerator (ferricyanide) for variable immersion times (from 30" to 90'). After immersion the samples were carefully rinsed (twice) in distilled water.

In fig. 1 we report the TEM images of ultramicrotomed samples converted in chromate baths for 30". The films, about 70 and 50 nm thick with and without accelerator respectively, exhibit a two layers structure with a very thin oxide second layer of 0.6 nm at the interface between the metal and CCC.

At longer immersion times a sublinear growth law (CCC thickness roughly proportional to  $t^{0.5}$ ) was observed in presence and in absence of accelerator. The thickness of CCC was greatly affected by the initial surface treatment. Thicker CCC layers were grown on chemically etched Al surfaces with respect to electropolished ones.

XANES measurements show the presence of Cr(VI) in agreement with previous findings. The measured Cr(VI)/(total Cr) ratios are in the higher range of values reported in the literature: 39% of Cr(VI) was obtained for films formed in absence of accelerator whilst a lower percentage (around 32%) of Cr(VI) was measured in presence of accelerator.

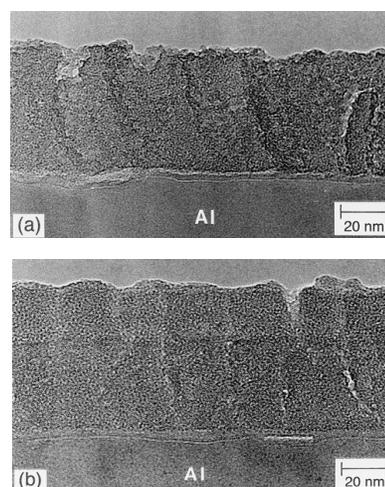
By GDOES and chemical analysis a very low (less than 1-2% in mole) of Al was usually present on carefully rinsed CCC. For films formed in presence of accelerator about 6% of iron was measured by chemical analysis. The iron mapping of ultramicrotomed sections showed that iron was incorporated in the outer part of the coating.

In fig.2 we report the cathodic photocurrent spectra of EP-Al samples before and after conversion for 5' in chromate baths with and without accelerator. The spectra were normalised for comparison. As for "fresh electrodes", a nearly constant non-direct optical band gap of about 2.50 eV was measured at constant electrode potential ( $U_e = -1.30$  V/SCE) in 0.5M  $K_2SO_4$  solutions. The measured optical band gap modified with the ageing process at room temperature. An appreciable increase in the  $E_g$  values was observed by keeping the specimens in the laboratory atmosphere for times longer than 24 hours. Larger increases in the  $E_g$  values were recorded by ageing at 60°C for various times up to 2 hours. The

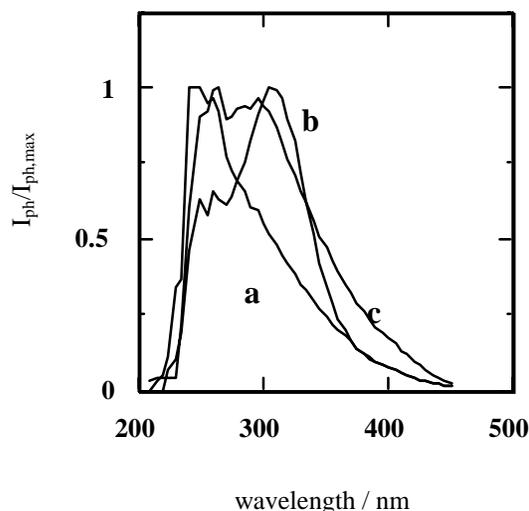
temperature of the ageing process affects both the  $E_g$  values as well as the evolution of optical band gap values measured after immersion in electrolytic solutions. The analysis of the experimental results suggests that subtle changes occur in the CCC and that such modifications could be revealed by PCS analysis. An interpretation of the ageing process based on the PCS data analysis will be given by taking into account the hypothesis of formation of mixed Cr(VI)+Cr(III) oxy-hydroxides recently suggested in the literature (4).

### References

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**Figure 1**- Transmission electron micrographs relative to electropolished aluminium samples converted in chromate bath (a) without and (b) with accelerator.



**Figure 2** - Normalised photocurrent action spectra corrected for the lamp efficiency, recorded by polarising the electrodes in 0.5M  $K_2SO_4$  at  $U_e=-1.3$  V(SCE): a) non converted EP-Al; b) EP-Al after 5' of conversion in presence of accelerator; c) EP-Al after 5' of conversion without accelerator.