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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF TRIVALENT CHROMIUM PRE-TREATED ALUMINUM ALLOYS

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DTIC QUALITY INSPECTED 2

14 DECEMBER 1993

PROGRESS REPORT

Approved for Public Release; Distribution is Unlimited

218 94-17521

Prepared for
Chief of Naval Research
Materials Block Program
800 North Quincy Street
Arlington, VA 22217

94 6 8 136

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 14 DECEMBER 1993		3. REPORT TYPE AND DATES COVERED PROGRESS
4. TITLE AND SUBTITLE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF TRIVALENT CHROMIUM PRE-TREATED ALUMINUM ALLOY			5. FUNDING NUMBERS	
6. AUTHOR(S) Dr. Vinod S. Agarwala,* Dr. Dieter W. Beckert **				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Vehicle and Crew Systems Technology Dept. * Code 6062 Naval Air Warfare Center, Aircraft Division P.O. Box 5152 Warminster, PA 18074-0591			8. PERFORMING ORGANIZATION REPORT NUMBER NAWCADWAR-94014-60	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Chief of Naval Research Materials Block Program 800 North Quincy Street Arlington, VA 22217			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Wehrwissenschaftliches Institut für Materialuntersuchungen ** (W.I.M.), German Armed Forces Landshuter Strasse 70 8058 Erding, Germany				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release; Distribution is Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A chemical conversion coating on aluminum alloys was developed using a trivalent chromium bath. Electrochemical impedance spectroscopy (EIS) was made to characterize the corrosion resistant properties of the surface films formed. The results showed a 10 to 100 fold increase in the polarization resistance of the surface films compared to the untreated aluminum alloy. These electrochemical results compared well with the corrosion behavior in salt spray tests. The trivalent chromium-treated surfaces showed no corrosion for up to 200 hours in 5% salt spray. A post-treatment with an oxidizer even further raised the coating's resistance due to an improved corrosion protection.				
14. SUBJECT TERMS Corrosion Protection, Conversion Coatings, ac-Impedance, Chromate, Aluminum Alloys			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR	

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INTRODUCTION

High strength aluminum alloys like Al 7075-T6 and 2024-T3 are widely used structural materials in the aircraft industry. These alloys, however, have poor resistance to corrosion. In order to protect them they have to be pre-treated with a corrosion inhibitor or a passivating agent which can form a corrosion resistant chemical conversion coating prior to painting. Conventionally, the process used involves hexavalent chromium that provides a high degree of corrosion inhibition. However, hexavalent chromium is a known carcinogen and has to be replaced wherever possible. The human health risk concentration for chromium(III) is at least 200 times higher than that for chromium(VI).¹

Recently an alternative method has been developed to provide high corrosion protection for aluminum alloys without using hexavalent chromium solutions². This method is based on the idea of using trivalent chromium bath to impart corrosion resistance. It has been shown that trivalent bath alone can provide corrosion protection for up to 196 hours in a 3.5% salt spray test². However, a subsequent post-treatment with an oxidizer such as hydrogen peroxide results in an added protection for more than 336 hours.

In this study electrochemical techniques have been applied to get more detailed information about the protective properties of the conversion coatings. Electrochemical impedance spectroscopy (EIS) has been proven to be a useful technique for evaluating corrosion protective layers and the mechanism of protection within a short time.³⁻⁸ Generally, the low frequency region of the EIS spectra shows the influence of the protective layers on the polarization resistance as well as their capacitance. EIS can also distinguish between electrochemical processes with different time constants, i.e., if a coating is porous or some other time dependent phenomenon is occurring.

The information about the electrochemical processes occurring at a metal surface are obtained by interpretation of the impedance spectra in terms of electrical analogs (model circuits). Earlier publications on this subject have proposed several models for the EIS behavior of aluminum alloys with protective surface layers (coatings)^{3,7,9}. Mansfeld and Shih⁹ fit the impedance spectra of a porous coating or surface layers with holes with an electrical analog that consists of both the impedances of the passive film and the holes in parallel. This suggests that as a consequence of direct contact between the metal and electrolyte at the bottom of the pores, there must be a second time constant at low frequencies. An ideal passive surface film is equivalent to a simple parallel circuit of the capacitance and ohmic resistance of the surface layer.

The dc-potentiodynamic polarization scans (E vs., log i plots) also provide valuable information about the electrochemical nature of the surface layers (cathodic or anodic), their kinetics of dissolution and passivation. A decrease in the exchange current density, i.e., increase in charge transfer resistance, indicates passivation and also a possibility that the range of the passive potential may be larger. However, the polarization scan changes the surface irreversibly, thus, can only be done once. Ac-impedance measurements require only a small amplitude signal (potential) for polarization, thus, do not affect the surface and can be repeated frequently with time.

EXPERIMENTAL PROCEDURE

Sample Preparation

The trivalent chromium conversion coatings (tccc) were applied as described in detail elsewhere². After cleaning and deoxidizing the aluminum samples (Al 7075-T6 and Al 2024-T3) were treated in a bath containing 4g/l $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ [Fluka Co. reagent], 0.4g/l Na_2SiF_6 and 20 ml/l 0.5N NaOH at room temperature for 10 minutes. The panels were rinsed with water after each step. Some of the specimens were post-treated for 30 seconds either in 10 ml/l H_2O_2 (30%) at room temperature and drain dried without rinsing or in 5g/l KMnO_4 at room temperature, and rinsed and drain dried..

For comparison, aluminum panels without any conversion coating were cleaned and deoxidized as described above, and a commercial chromate conversion coating (ccc) Alodine 1200 was applied to aluminum panels according to standard practice (MIL- C-5541).

Electrochemical Measurements

The test equipment for EIS measurements consisted of a Schlumberger SI-1255 frequency response analyzer and a PAR 273A potentiostat. Data were collected using the PAR M388 software on a 386 PC. For frequencies below 5 Hz this software creates a pseudo-random white noise signal with 20 different frequencies and calculates the impedance by Fourier transformation to make the measurement time shorter.

The test cell consisted of a glass cylinder clamped with an O-ring seal at one end to the specimen surface for the EIS measurements. The exposed surface area of the specimen was approximately 9 cm^2 and the cell contained about 45 ml of electrolyte. The counter electrode was a Pt disk with a hole in the middle to allow the capillary of the saturated calomel reference electrode tip to reach about one mm above the specimen. The impedance measurements were made as a function of exposure time to a 3.5% NaCl solution that was open to air. A sine wave of 10 mV amplitude was applied to the cell at the open-circuit potential. The frequency was changed stepwise in the range from 10 kHz to 5 mHz in most cases.

The dc-polarization measurements of conversion coated specimens in 3.5% NaCl solution were made using a PAR 273 potentiostat. The working electrode was a disk of the test material that was mounted in a Teflon specimen holder with an approximate exposed surface area of 1 cm^2 and sealed with an O-ring. A potential scan rate of 10 mV/min was used for polarization in either direction from the open-circuit potential. A new surface area was used for each scan. A seven-point averaging method was used to generate the polarization curves.

Salt Spray Tests

The results of the electrochemical measurements were compared with the direct salt-exposure tests of 3 inch x 5 inch Q-panels in a 5% NaCl salt fog chamber. Both scribed and unscribed panels were used. A standard ASTM test method B-117 was used for various exposure periods.

RESULTS AND DISCUSSION

The EIS measurements have been used to compare different kinds of conversion coating on Al 7075-T6 panels with each other. The spectra typically show the plots of impedance $|Z|$ and the phase angle versus frequency in Bode-plots. Generally, in the low-frequency domain the data, both the impedances and the phase angles, are rather scattered; it is probably because the open-circuit potentials are not steady. The spectra in figure 1 show the effect of exposure time on bare aluminum 7075-T6 alloy. The polarization resistance of bare aluminum was low, about 20 kohms according to the plateau in low frequency domain of the impedance plot, and did not change much from 1 hour to 1 day exposure, however, the shift of phase angle was quite significant between 1 hour and 1 day. At low frequencies, below 0.1 Hz, a second time constant and phase shift is indicative of pitting mechanism and its growth with time; after 1 day exposure there is no appreciable change in the phase angle plots (between 1 and 6 days). The circuit model of Mansfeld and Shih was used in this study and the results reported were in good agreement⁴. In fact, severe pitting corrosion was observed on the bare aluminum after one day of immersion.

By comparison, the spectra for trivalent chromium conversion coating with permanganate post-treatment (tccc/ KMnO_4) and chromate (hexavalent) conversion coating (ccc) were fairly smooth showing very little excursion at low frequencies and only one time constant (see Figures 2 and 3). The polarization resistance of the trivalent chromium conversion coating (tccc), which equals the low frequency plateau of $|Z|$ is either equal or higher than that of the chromium(VI) conversion coating (ccc). Actually, both the tccc and ccc curves show no plateau within the low frequency limits of the measurement, thus, the polarization resistance has to be at least 1 Mohm (see Figure 2). This high resistance is an indication of excellent corrosion protection by tccc, at least 2 to 3 orders of magnitude better than the bare surface. The spectra show very little change with exposure periods, e.g. from 1 hour to 6 days. The shift of phase angle is almost insignificant for ccc and only very slight after 1 hour exposure for tccc (cf. Figures 2 and 3). The conversion coated specimens show a broad maximum of the phase angle. This appears in cases of compact highly resistive coatings on a metal surface. Even though most of the samples had few pits after several days (4 to 15 d) of immersion, the impedance spectra hardly showed any decrease in polarization resistance and no second time constant appeared other than expected from measurements of pitted aluminum^{4,9}. The reason becomes obvious when calculating the resistance of the pitted tccc sample. Based on the polarization resistance of the bare aluminum and the estimated pit area of $0.7 \times 10^{-3} \text{ cm}^2$, the pit resistance in parallel with the coating resistance would be 30 Mohms, which is about 30 times higher than that of the coating. This means a second time constant is only possible at lower frequencies than the coating resistance plateau beyond the measurement range. Only in cases where severe pitting occurred, a plateau or increase in the phase angle could be observed at the low frequency limits.

With both conversion coatings, the resistance increases initially and remains at its very high level for days. This initial increase of the low frequency resistance limit is assumed to be due to filling of pores in the conversion coating with corrosion products which retarded corrosion reactions at the anodic sites. It has been found that rinsing the surface and changing the electrolyte has no effect on the resistance and capacitance. This means there is no layer that can be removed easily. On the other hand, after rinsing bare aluminum the resistance goes down towards the initial value again.

To demonstrate the effect of passivation on the polarization resistance of aluminum, a comparative measurement of the impedance spectra was done in a test

solution containing 5% $\text{Na}_2\text{Cr}_2\text{O}_7$. It was found that the resistance of bare aluminum and tccc without the post-treatment went up by a factor of 10. The polarization resistance of post-treated tccc doubled. Thus the higher resistance observed with oxidized tccc or ccc was most likely due to anodic passivation at defect sites of coating. It is because, the hexavalent chromium formed during the process or present in the ccc type coating has been known to form a passive film.

In order to study the pitting effects the conversion coated surface were scribed and then studied with EIS measurements. It was shown that like in the case of pitted surface there did not appear a second time constant within the measurement range of the EIS, and the capacitance did not increase markedly. However, with a scribe surface area of 0.02 cm^2 the total polarization resistance was lowered to the range of 400 to 1000 kohm.cm^2 . Although this method does not directly relate to pitting behavior, the values of resistance of such scratched surfaces would reflect upon their susceptibility to pitting or healing.

Figures 4 and 5 show the plots of polarization resistance, R_p and the capacitance, C versus time for various post-treatments of tccc coatings, respectively. The points on the curves represent average values of the data obtained from at least four separate measurements. Whenever there was no low frequency plateau of the $\log |Z|$ vs. $\log f$ plot the curve has been extrapolated to 0.001 Hz to obtain a value of R_p . The higher resistance of the post treated samples compared to non post-treated samples means that corrosion is retarded. The coating resistance of the post treated samples stayed at a level which was about 50 to 100-fold higher than for bare aluminum even after a long exposure (more than 20 days). After about two weeks of immersion the resistance of the tccc went down no matter what the post-treatment was and pitting was observed. The EIS behavior, i.e. resistance and capacitance has been similar to that observed with an artificial pit (scratch).

The improved corrosion protection of tccc with oxidative post-treatments was also evident from salt spray test results². After 336 hours of salt spray exposure there was no corrosion on the permanganate post-treated panels; the peroxide post-treated panels were only slightly corroded and the non post-treated panels were slightly more, > 5% corroded. This is well corroborated by the polarization resistance data as shown in Figure 4. A chemical analysis of the post-treated conversion coating indicated that the coating contained some hexavalent Cr; only less than 2% of trivalent Cr was converted into hexavalent form after the oxidizing post treatment.

The ccc coating unexpectedly showed a lower resistance than the oxidized tccc in the first three weeks of immersion, however, it remained at that level for a longer period of time indicating a better long term protection (see Figure 4).

The capacitance as reported in Figure 5 has been calculated using the equation:

$$C = 1 / 2 \pi f^* \cdot Z'' \cdot A \quad (1)$$

The frequency f^* at the maximum of the phase angle proved to give the best values for capacitance C with an equivalent test circuit, Z'' is the imaginary component of the impedance and A is the surface area of the panel exposed to electrolyte.

According to Figure 5, initially there is some increase in the capacitance, suggesting that the conversion coating is becoming thinner, porous or there is some soaking with water. The latter seems to be more likely because after about one day there is a saturation and the capacitance stays at a rather constant level. Compared to tccc, the

lower capacitance of the ccc indicates a higher coating thickness which was verified by SEM. The initial capacitance of bare aluminum is only slightly higher than that found with conversion coatings suggesting that there is a thin layer on its surface, obviously an oxide film whose thickness is almost like that of the conversion coating provided its dielectric constant remains the same. Here, a large increase in C shows severe degradation of the oxide film because there is no passivation.

The corrosion resistance of aluminum alloys, with or without a conversion coating, can be further improved by a post-treatment with an inhibiting mixture of quaternary ammonium salts of dichromate, nitrite, borate and molybdate called DNBM. This DNBM system was studied earlier as a post-treatment for Alodine 1200 conversion coating and was found highly effective in enhancing corrosion resistance⁸. Hence, the use of DNBM treatment on trivalent chromium conversion coating of aluminum Al 7075-T6 alloy was of interest, thus studied via EIS measurements. Figures 6, 7 and 8 show the results of these measurements as Bode $|Z|$ and phase angle plots. In general, the EIS data show a much broader phase angle maximum and higher impedance plateau (polarization resistance) for the bare aluminum treated with DNBM (see Figure 6) than for the non-oxidized (without post-treatment) conversion coating (see Figure 7) and compared to those in Figure 1. Also the impedance data in the low frequency domain are much more stable during immersion time. The post-treated conversion coatings, however, could not be improved further by the DNBM treatment (see Figure 8) most probably because post-treatment provided sufficient passivating property to the coating to start with. The effect of DNBM on the polarization resistance within the first few days of exposure in 3.5% NaCl solution has been summarized in Figure 9. After a longer exposure time, however, the protection by the DNBM diminished as its R_p value went down and pitting initiated. The value of capacitance did not change by DNBM treatment indicating that the coating thickness did not change. A 216h salt spray exposure test proved that the tccc treated panels had good ratings, with and without DNBM. Bare aluminum panels with DNBM showed more corrosion than the tccc treated panels without DNBM.

Electrochemical dc polarization measurements of conversion coatings were also made and are reported in Figure 10, (a) through (d). It was interesting to note that immersion (pre-treatment) time in trivalent chromium bath was directly related with the shift of polarization curves at point of inflexion or E at $I=0$ to more negative potentials. This was true with the tccc panels post-treated with $KMnO_4$ or H_2O_2 . However, the non post-treated tccc panels showed a more nobling effect of this potential as the immersion time increased. From 5 to 40 min. immersion time in trivalent chromium bath, the potential shift was >50 mV [cf. Figure 10(a) to Figure 10(d)]. The shift in potential, E at $I=0$, for permanganate post-treated tccc surface was most significant, almost 200 mV, after 40 min. treatment time. When this is compared with the ccc coating, the hexavalent chromium treatment, the effect of treatment time was insignificant. Thus, alluding to the fact that the trivalent coating is very much different from the hexavalent coating in its electrochemical nature, cathodic versus anodic controls, respectively, and it does change after the post-treatment. Compared to the ccc, the tccc coatings after the post-treatment are highly cathodic in nature and do not provide the same passivating effects as offered by hexavalent chromium ions, even after a post-treatment with an oxidizer.

SUMMARY AND CONCLUSIONS

Electrochemical impedance measurements have shown that trivalent chromium conversion coatings on Al 7075-T6 alloy can provide high corrosion resistance by itself

and even much greater protection when post treated by an oxidizer. This was evident from their polarization resistance values as being about 100 times higher than that of the bare aluminum for up to two weeks of exposure in a 3.5% NaCl solution. After two weeks the resistance dropped as some pitting occurred. The polarization resistance of a conventional chromate (Cr^{+6}) conversion coating was also in the same range, but stayed fairly constant for a long period of time indicating a better long-term protection. The EIS plots also showed a broad maximum of the phase angle as long as the coatings were protective. The DNBM post-treatment showed enhanced corrosion protection of the trivalent chromium conversion coating and also some what better than with the peroxide or permanganate oxidizers.

Initially, the capacitance value of the ccc was somewhat lower than for the tccc, thus suggesting its higher coating thickness. However, after a day of immersion it became constant and almost the same for both, irrespective of their nature of protection. This implied that the capacitive region of the impedance spectrum does not relate to the beginning of pitting corrosion unlike the polarization resistance. The capacitive behavior of bare aluminum and its magnitude implies that it is covered with an oxide film which is almost as thick as for the tccc. However, this oxide film does break-down within few hours as was evident from the increase in its capacitance and observation of pitting.

The dc-polarization measurements, E vs. $\log i$ plots, indicate that the trivalent chromium coatings are predominantly cathodic in nature in contrast to hexavalent Cr which provides a more noble (passive) potential to the aluminum surface when treated. As the tccc coating gets thicker with longer pre-treatment in trivalent bath, the anodic polarization curve shifts to more noble values but after post-treatment with an oxidizer it shifts to more cathodic domain. Thus, suggesting a very different mechanism of corrosion protection and predominantly by controlling cathodic processes.

In order to determine the relevance of EIS measurements for predicting the corrosion protection properties offered by the coatings, its results were compared with that of salt spray exposure testing of panels. There was an accordance in that the oxidizer post-treatments of the tccc improved corrosion protection considerably. However, in the salt spray tests the post-treatment with permanganate was rated higher than for peroxide whereas from the impedance measurements it could not be shown different. The impedance spectra for ccc predicted a somewhat better long-term protection and was in accordance with long-term salt spray corrosion tests.

ACKNOWLEDGMENT

The authors acknowledge technical contributions of Fred Pearlstein in the development of trivalent chromium pre-treatment for aluminum alloys and Alan Fabiszewski for carrying out dc electrochemical measurements. Thanks also go to ONR Materials Block Program, and the International Program Office for the scientific exchange with Defense Scientific Institute for Materials Testing (W.I.M.), German Armed Forces, for allowing travel and financial support for one of the authors (Beckert).

REFERENCES

1. "Water Quality Criteria Summary," U.S. Environmental Protecting Agency, Washington, D.C., May 1, 1991

2. F. Pearlstein, V.S. Agarwala, "Chemical Conversion Coatings for Aluminum Alloys using Trivalent Chromium Solutions," Symposium on the Search for Environmentally Safer Deposition Processes for Electronics, Proceedings of AESF Conference, January 1993, pp. 112-123; Updated version submitted for publication in Journal of Plating and Surface Finishing.
3. F. Mansfeld, M.W. Kendig, J. Electrochemical Society, 135 (1988): p. 828.
4. F. Mansfeld, et al., J. Electrochemical Society, 137 (1990): p. 78.
5. T.D. Burleigh, A.T. Smith, J. Electrochemical Society, 138 (1991): p. 134.
6. C.T. Liu, O.F. Devereux, J. Electrochemical Society, 138 (1991): p. 3349.
7. A.J. Griffin, F.R. Brotzen, C.F. Dunn, J. Electrochemical Society, 139 (1992): p. 699.
8. V.S. Agarwala, M.W. Kendig, "DNBM Modified Conversion Coating for Aluminum Alloys," CORROSION/90 Conference, paper No. 456, (Houston, TX: NACE, 1990).
9. H. Shih, F. Mansfeld, Corrosion 45 (1989): p. 610.

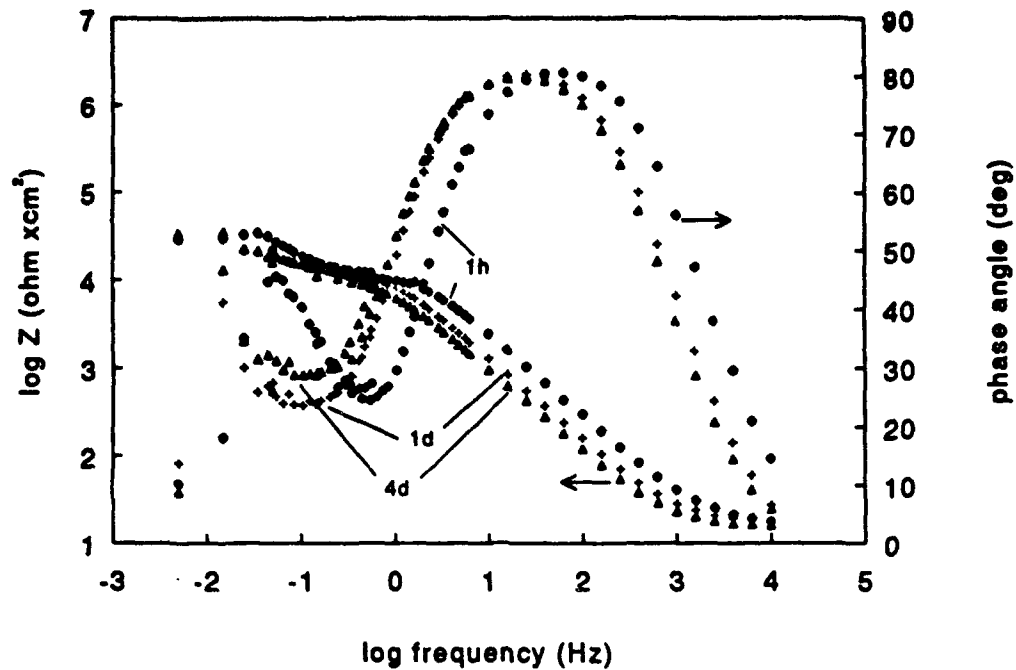


Figure 1 - Bode-plots for bare Al 7075-T6 during exposure to 3.5% NaCl solution.

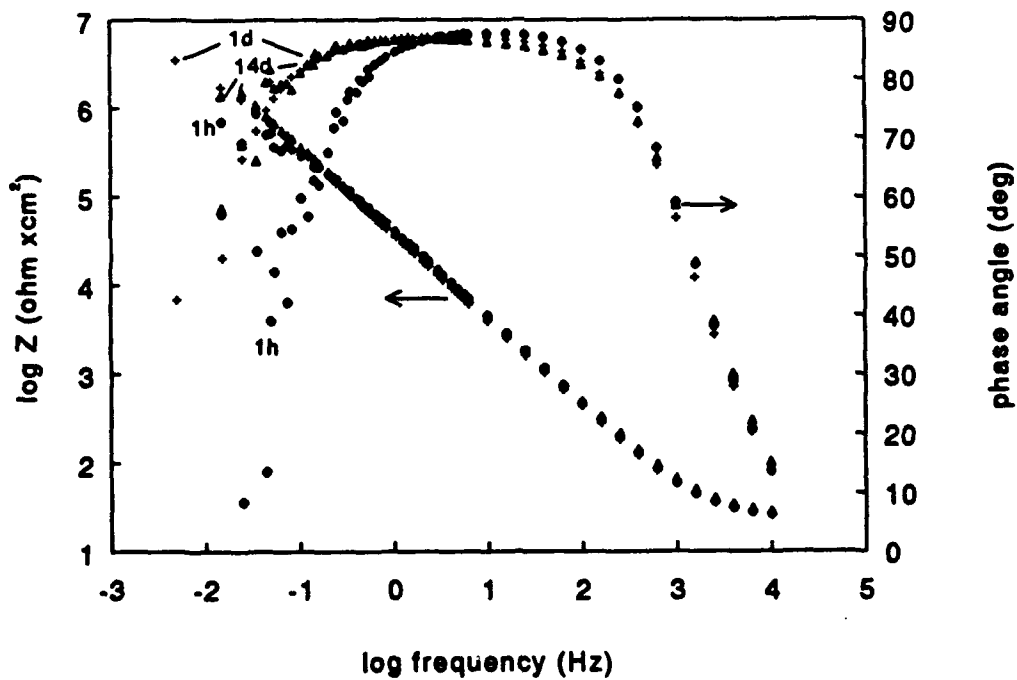


Figure 2 - Bode-plots for Al 7075-T6 with trivalent chromium conversion coating (tccc) post treated with KMnO_4 during exposure to 3.5% NaCl solution.

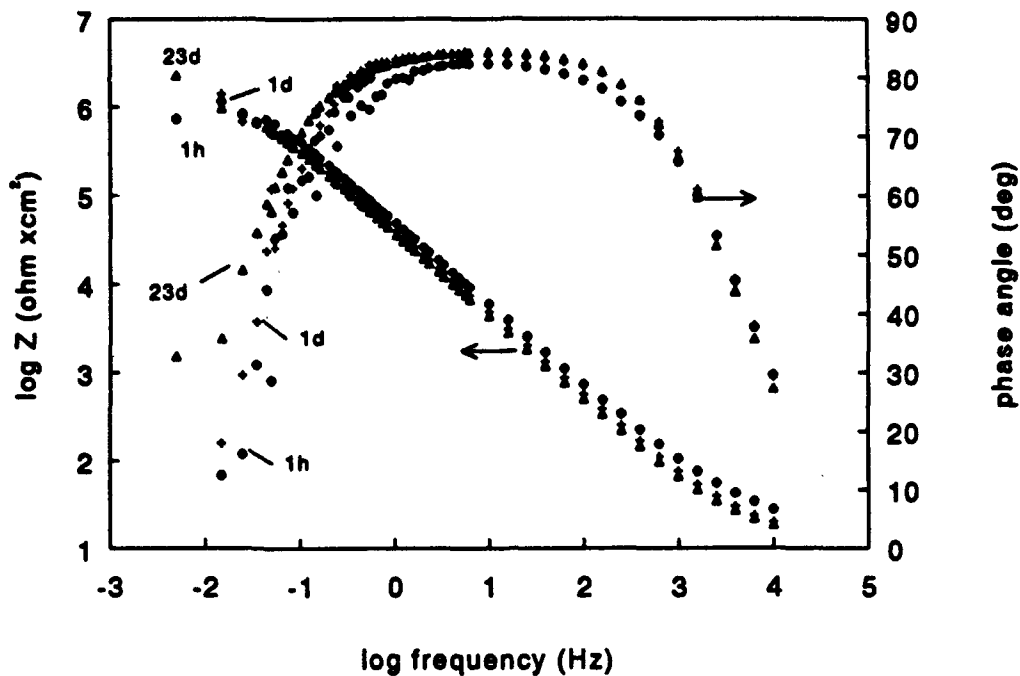


Figure 3 - Bode-plots for Al 7075-T6 with chromate conversion coating Alodine 1200 (ccc) during exposure to 3.5% NaCl solution.

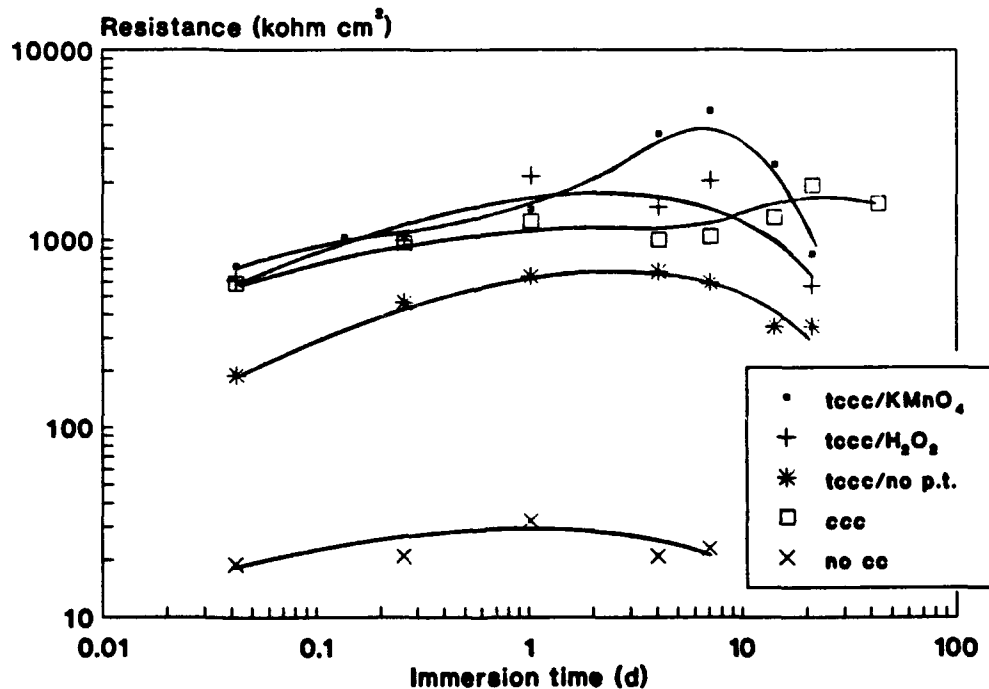


Figure 4 - Time dependence of the polarization resistance R (average of 4 measurements) for Al 7075-T6 bare, with ccc and with different post treatments of tccc.

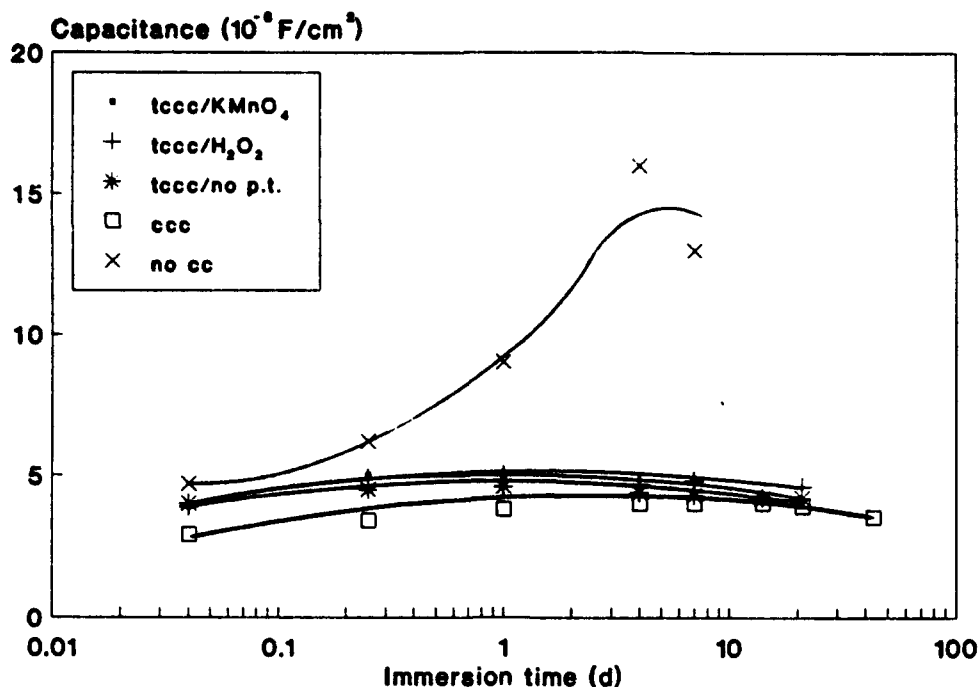


Figure 5 - Time dependence of the coating capacitance C (average of 4 measurements) for Al 7075-T6 bare, with ccc and with different post treatments of tccc.

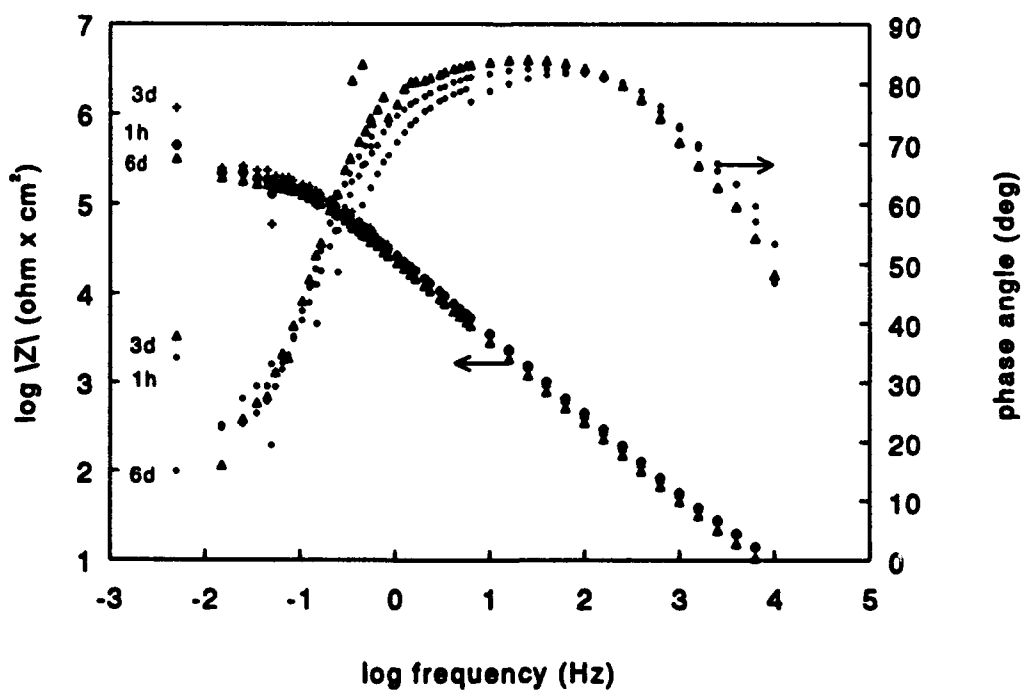


Figure 6 - Bode-plots of bare Al 7075-T6 after DNBM- treatment during exposure to 3.5% NaCl solution.

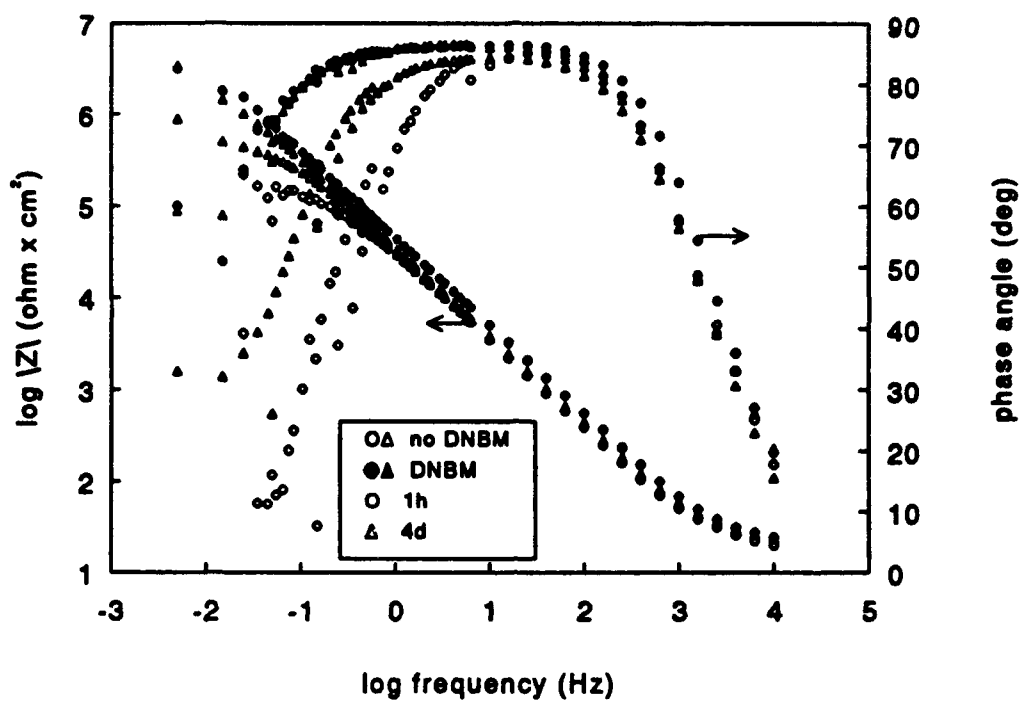


Figure 7 - Effect of DNB-treatment on Bode-plots for Al 7075-T6 with tccc without post treatment (no p.t.) during exposure to 3.5% NaCl solution.

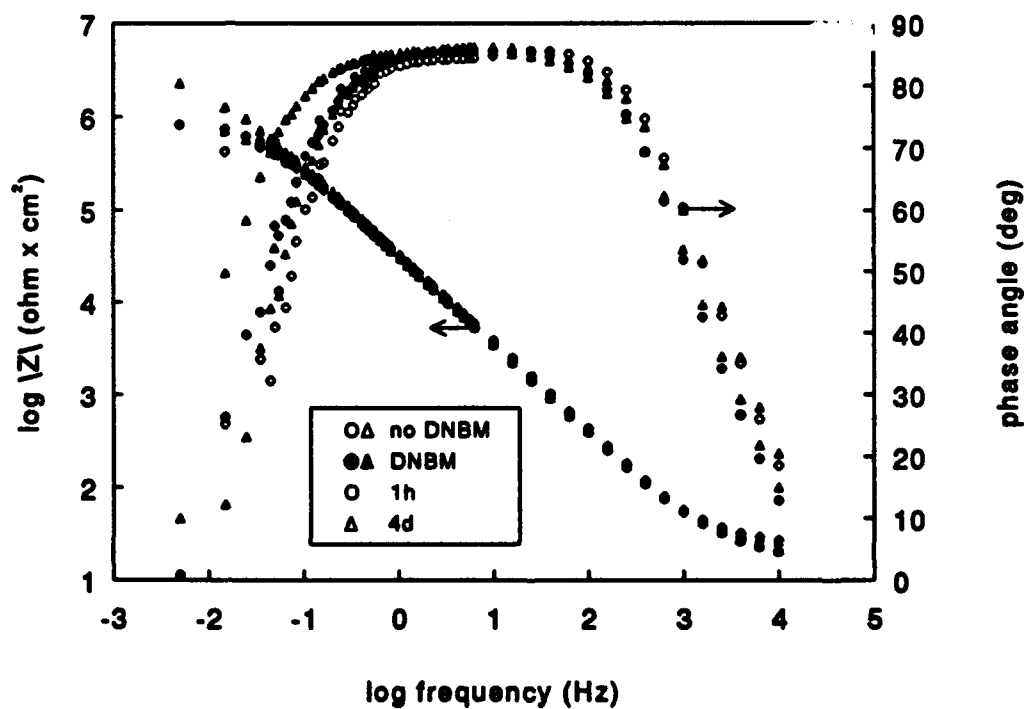


Figure 8 - Effect of DNB-treatment on Bode-plots for Al 7075-T6 with tccc with post treatment (p.t.) KMnO_4 during exposure to 3.5% NaCl solution.

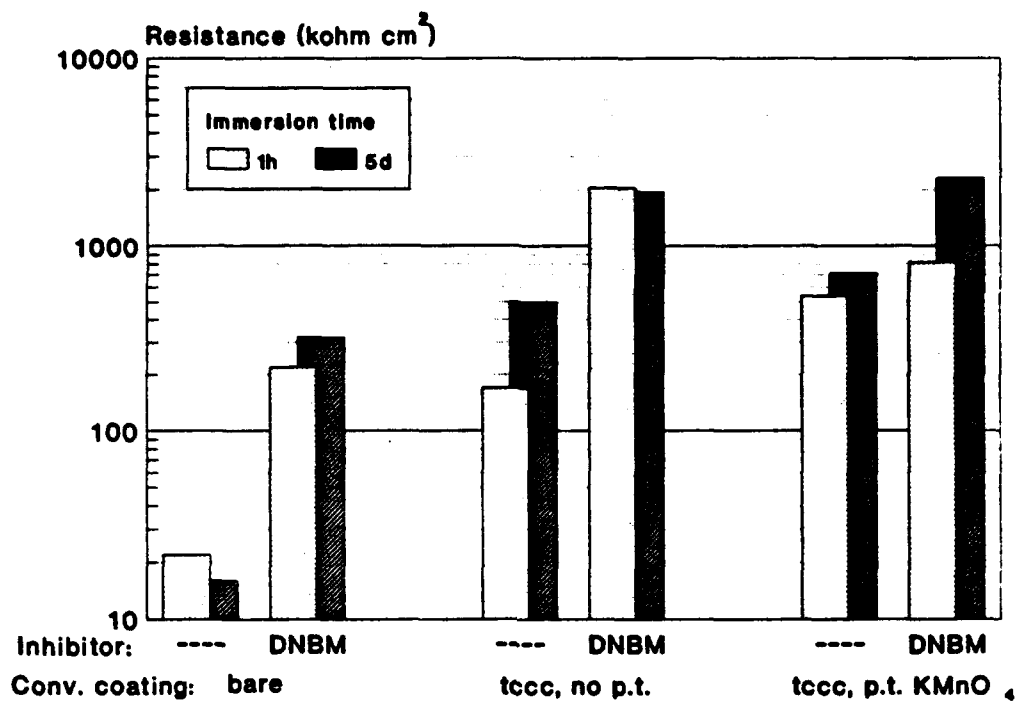


Figure 9 - Polarization resistance of panels like shown in Figures 6, 7 and 8 with and without DNBM treatment.

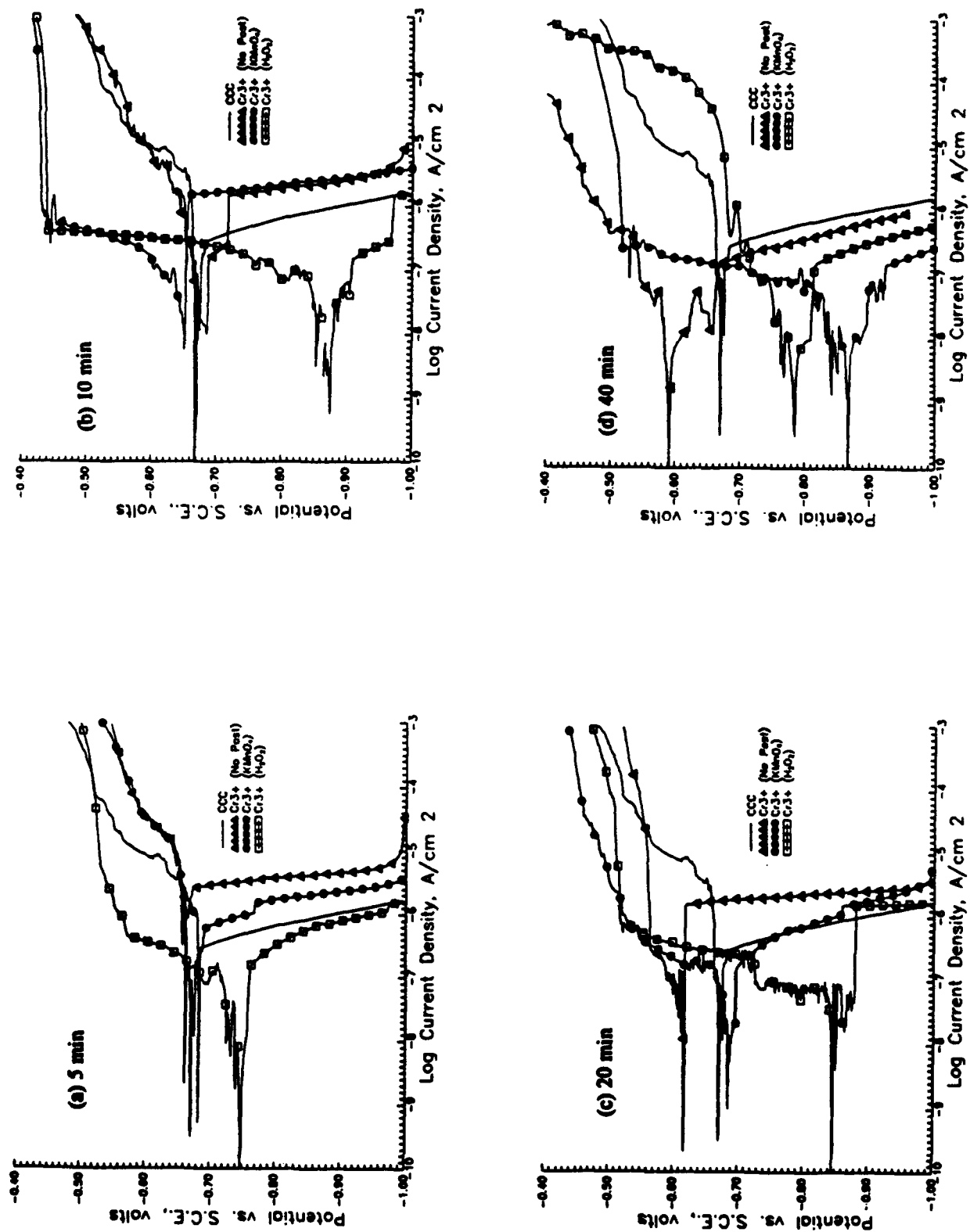


Figure 10 - Effect of pre-treatment (immersion) time in trivalent and hexavalent chromium conversion coating baths on the electrochemical polarization behavior of Al 7075-T6 in 1% NaCl solution; also shown are the response of oxidizer post-treatments on trivalent coatings.

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