

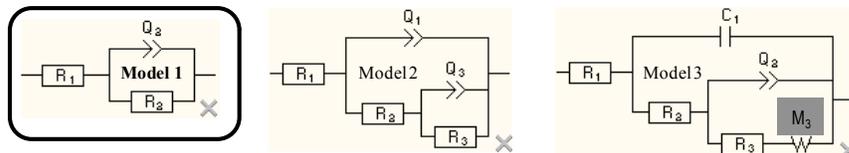


## Falex Litigation Technical Investigations Corrosion Mechanism Case Study

Falex Litigation Technical Investigations conducts failure analysis investigations for insurers and litigators, which sometimes involve testing of materials, lubricants, and fuels to determine the cause of corrosion. This case study demonstrates our comprehensive approach to obtaining reliable corrosion mechanism data for difficult-to-measure systems. In this case, we examine coatings on 8620 steel. Our results show what insight can be obtained from our approach, which can go well beyond just the corrosion rate and provide extremely valuable information on the structure of coatings, such as the porosity and rate of water uptake, so that reliable, long-term estimates of performance can be obtained.

The results in this study fit one of three models (next Figure), each of which has specific, significance relative to the performances of the coatings.

The first (left) Bare Metal Model in the next Figure is the simplest one and it fits the data from bare metals in salt solution. The model consists of a resistor,  $R_1$ , that is in series with a parallel combination of another resistor,  $R_2$ , and a constant phase element,  $Q_2$ .  $R_1$  represents the uncompensated resistance between the reference electrode and the working electrode (i.e. the metal specimen).  $R_2$  is the charge transfer resistance, which is inversely proportional to the flow of charge (i.e. current) at the solution - metal interface and thus  $R_2$  is inversely proportional to the corrosion rate. The final component is a capacitor,  $C_2$ , or a non-linear element,  $Q_2$ , that represents the double layer capacitance at the solution - metal interface.



Equivalent Circuit Model 1: Bare Metal

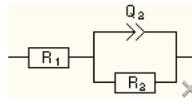
The double layer capacitance can be represented by a conventional capacitance,  $C_2$ , when the surface of the metal is uniform. The constant phase element,  $Q_2$ , has to be used when the metal surface is non-uniform. Non-uniform corrosion causes a distribution of time constants over the corroding surface and modeling. This requires the constant phase element. The impedance of the constant phase element,  $Q_2$ , has the general form  $A(j\omega)^{-a}$ , and is characterized by two parameters. If the value of  $a$  is -1, then this non-linear impedance becomes linear and is equivalent to a capacitor whose value is  $A^{-1}$ . If the value of  $a$  is 0, then this non-linear impedance again becomes linear and  $A$  is a pure resistance. Values for  $a$  between 0 and 1 represent a mixed, non-linear, element that is a transmission line.

The following table shows the results of equivalent circuit modeling for bare 8620. The first (left) Bare Metal Model, described in the above in Figure, is observed as expected. The results for bare 8620 show that there is substantial non-uniformity of the corrosion of the surface ( $a_2 = 0.71$ ) by 2 hours of exposure, and that the non-uniformity increases as the exposure time increases ( $a_2 = 0.59$  at 47 hours).

Equivalent Circuit Model for Bare 8620

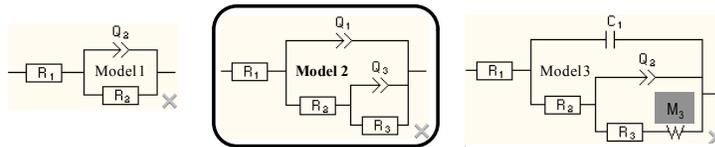


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Exp Time, Hr	E <sub>ocv</sub> , V	CASP			EIS				
		I <sub>corr</sub> , uA	B <sub>3</sub> , mV	B <sub>o</sub> , mV	R <sub>pl</sub> , Ohm	I <sub>corr</sub> , uA	R1, ohm	Q2, F.s <sup>-(a-1)</sup>	a2
2	-0.535	16.28	100.1	141.5	1036	24.572	31.08	2.38E-04	0.7052
17	-0.575	14	61.18	95.98	1326	12.235	30.33	4.60E-04	0.6386
23.5	-0.582	16.86	72.11	149.6	1467	14.402	29.56	5.52E-04	0.6216
42.25	-0.578	19.26	73.99	131.2	1367	15.028	30.75	6.85E-04	0.6034
47	-0.58	32.01	108	352.2	1463	24.532	29.76	7.48E-04	0.5941

The second (middle) Insulating Barrier Coating Model, in the Figure below, is a very typical model for a good quality, electrically insulating coating on a metal surface. This is a far more complex model because the coating is a good electric insulator.  $R_1$  is the uncompensated solution resistance as defined above.  $C_1$  is the bulk capacitance of the coating,  $R_2$  is the resistance due to solution penetration into pores in the coating,  $Q_2$  is the double layer capacitance at the coating - 8620 interface (which is equivalent to  $Q_2$  in the Bare Metal Model above), and non-uniformity (as described above) requires a constant phase element instead of a conventional capacitor.  $R_3$  is the charge transfer resistance that is inversely proportional to the corrosion rate, and is thus equivalent to  $R_2$  in the Bare Metal Model.  $M_3$  is a very complex circuit element that models finite length diffusion of species through the coating.



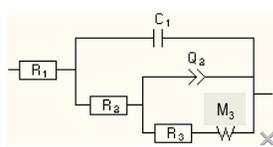
Equivalent Circuit Model 2: Insulating Barrier Coating

The next table shows the results of equivalent circuit modeling for the Advanced Coating on 8620. The Insulating Barrier Coating model fits the data, indicating that the Advanced Coating is an electrically insulating barrier coating. The fact that a diffusion element,  $M_3$ , is needed and that it is a finite length diffusion element as opposed to a semi-infinite diffusion element, as would be needed to account for poor convection and/or very fast electron exchange, establishes that the Advanced Coating acts as an effective barrier coating.  $M_3$  consists of the parameters  $RD_3$  and  $td_3$ .  $RD_3$  represents the resistance to diffusion and  $td_3$  indicates the timescale of the diffusion process. The variation of these parameters indicates that initial hydration of the Advanced Coating is required for it to become an effective diffusion barrier, and that the effectiveness is relatively constant (after initial hydration) for about 72 hours, after which the effectiveness decreases, but still remains substantial. The initial hydration is further confirmed by the variation of the coating resistance,  $R_2$ , which drops substantially from the first measurement at 0.75 hours to the next measurement at 18 hours, and then is relatively steady. One might also expect a substantial change in the coating capacitance,  $C_1$ , because of the high dielectric constant of water, and this is observed in paint films as they hydrate, but this is not observed for the Advanced Coating because it is much thinner than paint films. The thinness of the Advanced Coating and its low dielectric constant are also indicated by the small capacitance of the film, which is only about 230 pf.



# Falex Litigation Technical Investigations Corrosion Mechanism Case Study

Equivalent Circuit Model for the Advanced Coating on 8620



Exp Time, Hr	E <sub>corr</sub> , V	CASP			EIS								
		i <sub>corr</sub> , uA	B <sub>a</sub> , mV	B <sub>c</sub> , mV	R <sub>p</sub> = R <sub>3</sub> , Ohm	i <sub>corr</sub> , uA	R <sub>1</sub> , ohm	C <sub>1</sub> , F	R <sub>2</sub> , ohm	Q <sub>2</sub> , F.s <sup>n</sup> (a <sub>2</sub> -1)	a <sub>2</sub>	td <sub>3</sub> , s	Rd <sub>3</sub> , ohm
0.75	-0.455	0.244	284	1881	524440	0.204	204.8	1.96E-10	15752	6.23E-07	0.573	8.96E-03	1140
18	-0.53	0.356	134.6	180.5	22728	1.473	217.2	2.19E-10	6152	1.31E-05	0.2504	1.10E+00	52635
23	-0.4	0.555	132.7	134.8	14371	2.020	239.3	2.29E-10	7774	1.07E-05	0.305	4.45E+00	49418
41	-0.515	0.416	108.6	124.1	23187	1.085	132.8	2.24E-10	4306	1.51E-05	0.1769	2.17E+00	52635
47	-0.424	0.912	166.6	177.8	21495	1.737	323.7	2.44E-10	8802	2.28E-05	0.2645	2.98E+00	36705
68	-0.492	0.818	138.3	143.6	14406	2.123	226.4	2.47E-10	9304	2.04E-05	0.3243	4.71E+00	35490
71.5	-0.528	1.106	171.3	179.4	18284	2.081	190.6	2.41E-10	7910	2.84E-05	0.2338	3.97E+00	41984
90.5	-0.439	1.568	186.5	190.9	14600	2.806	164.7	2.39E-10	7349	2.27E-05	0.2338	4.39E+00	18488
95	-0.506	1.333	165.8	166.9	14427	2.503	173.4	2.41E-10	7983	2.52E-05	0.2697	3.43E+00	16837
162	-0.462	2.419	208.7	217.1	8409	5.495	133.9	2.45E-10	6864	4.05E-05	0.2333	9.20E+00	23933
164	-0.499	2.415	200.7	207.2	10586	4.182	144.6	2.46E-10	6476	5.99E-05	0.2717	8.29E+00	28543

The charge transfer resistance, R<sub>3</sub>, which is inversely proportional to the corrosion rate, changes slowly and modestly, which is consistent with the independent measurement of the corrosion current by harmonic analysis (CASP). The need for a constant phase element for the double layer capacitance at the 8620 surface is similar to that for bare 8620 and indicates that corrosion is non-uniform, as it was for the bare 8620 surface. Q<sub>2</sub> and a<sub>2</sub> are the parameters for the constant phase element, and comparing these to bare 8620 indicate that the presence of the Advanced Coating reduces the double layer capacitance and causes even greater non-uniformity of the corrosion, probably due to the Advanced Coatings effectiveness as a barrier coating. The double layer capacitance increases as the exposure time increases due to the buildup of ions at the 8620 - Advanced Coating interface.

The porosity of paint films has been determined by:

$$F \% = \frac{R_p(8620)}{R_p(\text{coated } 8620)} * 10^{-\frac{|E_{corr(8620)} - E_{corr(\text{coated } 8620)}|}{\beta_a(8620)}}$$

Where F % is the percentage porosity, R<sub>p</sub> is the polarization resistance, E<sub>corr</sub> is the free (equilibrium) corrosion potential, and β<sub>a</sub> is the anodic Tafel coefficient. This can also be applied to the Advanced Coating, in which case F starts out around 1% and slowly increases to about 5% at 164 hours exposure, which is the end of the test.

More detail on the technical methods and tests we use can be found in:

- *Electrochemical Corrosion Testing Methodology*
- *Electrochemical Corrosion Test Methods*
- *Corrosion Rate Case Study*