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A Novel Under-film Corrosion Tester Using Current Interrupter Technique

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Recently a variety of electrochemical techniques have been used for the measurement of under-film corrosion of coated steel. Each method has its own characteristic and is suitable to determine some kinds of anti-corrosive mechanisms of coating film. We developed a new under-film corrosion tester (UFCT) which adoped current interrupter technique in principle.

Electrochemical parameters can be measured by UFCT. It is possible for the novel under-film corrosion tester to evaluate under-film corrosion of steel covered with high electric resistance coating film which has no defect and is not easy to evaluate it by other methods.

Finally some experimental results of protective coating performance obtained by UFCT were discussed.

Keywords *: coating, under-film tester, electrochemical method, polarization resistance, coated steel*

1. Introduction

Corrosion protection by organic coatings is popular and important technology. High performance organic coatings have been developed for the protection of steel structures so far. So the evaluation method of anti corrosive paints have been required because of short term development of high performance coatings.

We have been studying an electrochemical technique which makes possible to measure the protection performance quantitatively in short measuring period.

Corrosion tester for coated steel using current interrupter technique was developed as the result.

The advantages of the corrosion tester for coated steel are ;

(1) It is possible to measure a high performance coated steel bearing the film resistance of more than 10GΩ.

(2) Five parameters, that is, film resistance, film capacitance, polarization resistance, polarization capacitance and natural potential are available.

(3) The current interrupter technique adopted to the corrosion tester for coating steel is easier to operate and take shorter period to measure electrochemical parameters compared to A.C impedance technique. It has been difficult to measure high resistance film without scratch so far. The results obtained by UFCT was reliable compared to that of AC impedance technique. The UFCT and its application examples are reported in this paper.

2. Experiment

2.1 Circuit for measurement by UFCT

The circuit for the measurement of electrochemical parameters, that is, polarization resistance, double layer capacitance, film resistance, film capacitance and natural potential of coated steel by UFCT is shown in Fig. 1.

The accuracy of the current pulse by UFCT was 10^{-12}A. A potential response to a small current applied to the coated steel was detected by UFCT.

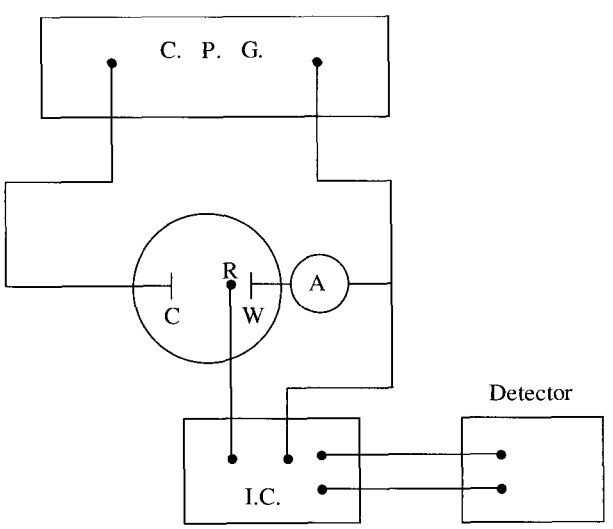

Fig. 1. Circuit of measuring underfilm corrosion.

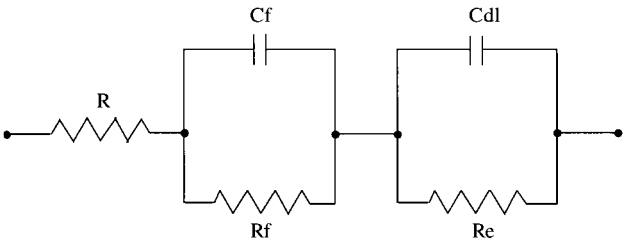

Fig. 2. Equivalent circuit of coated mild steel.

2.2 Measurement by UFCT using dummy cell.

The performance of UFCT was examined by use of dummy circuit, which consists of the equivalent circuit shown in Fig. 2. Each dummy component and measurement value by UFCT was investigated.

2.3 Test samples and cell for measurement

2.3.1 Test samples of alkyd paint

Mild steel (JIS-G-3141) was prepared for coating, which was polished by #240 emery paper, degreased by xylene and finally dried. The mild steel panel was coated with alkyd paint for the purpose of studying the performance of alkyd paint using zinc phosphate pigment.

2.3.2 Test samples of moisture cured polyurethane

Blasted steel was prepared for coating moisture cure polyurethane (MCU).

It was coated in different film thickness of 50 μm and 100 μm, and dried in different temperature of 5°C and 20°C.

The coating application was carried out by general-use air spray as alkyd paint application.

The measurement cell was filled with 3 wt% sodium chloride solution. The area exposed to test solution was 9.06 cm^2.

3. Result and discussion

3.1 The principle of measurement on electrochemical parameters by UFCT using current interrupter technique.

The current interrupter method used is the way that the transitional polarization behavior of coated steel is measured in order to obtain polarization resistance, double layer capacitance as well as the paint film resistance and capacitance when a small constant current is applied.

Generally coated steel is composed of two elements that the paint film bearing the time constance of msec or so and that of metal coated bearing the time constance of sec or so.

The remarkable difference of the two figs. makes possible to separate each other.

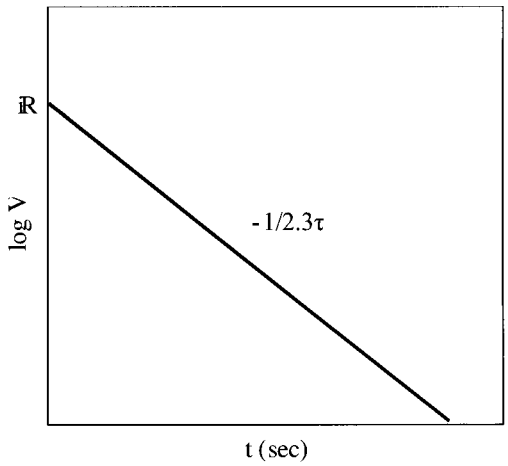

Fig. 3. Relation between potential and time.

Accordingly, the evaluation of protective performance of coated steel bearing high film resistance can be achieved without any destruction.

The principle of measurement is as follows.[1)]

Equivalent circuit of coated steel is shown in Fig. 2

Potential decay of coated steel after charging and switching off is shown in Eq.(1).

$$V = iRe^{-t/\tau} \quad (1)$$

Equation (3) is derived from Eq.(1)

$$\log V = \log iR - t/2.3\tau \quad (2)$$

Fig. 3 is shown by Eq.(2)

Time constance τ, film resistance R and Film capacitance C are obtained.

The corrosion reaction occurs at the surface of the mild steel beneath the paint film in the test solution even when a small current is applied.

In an oxidation-reduction system, an equation is shown in Eq.(3) is derived.

$$i = C_{dl}(d\eta/dt) + i_o[\exp(\alpha nF\eta/RT) - \exp(1-\alpha)nF\eta/RT]] \quad (3)$$

Where, i_o : exchange current density
η : overvoltage
α : n, F, R and T have their usual meaning

In case that $nF\eta/RT$ is smaller than one, that is, $\eta \leq 10$mV, Equation (4) is derived.

$$i = C_{dl}(d\eta/dt) + i_o nF\eta/RT \quad (4)$$

The differential equation is solved.

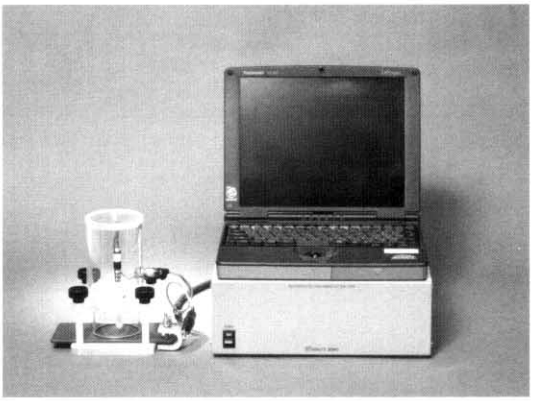

Fig. 4. Photograph of underfilm corrossion tester (HL201)

$$\eta = (i / i_o)\,(RT / nF)\ \{1-\exp(-t/\tau)\} \quad (5)$$

Where, τ is $C_{dl}RT / nFi_o = C_{dl}R_e$

$R_e = RT/nFi_o$

From Equation (5), τ, R_e, C_{dl}, can be obtained as the same way of Equation (2).

The underfilm corrosion tester (UFCT) developed is shown in Fig. 4.

4. Results and discuassion

4.1 Measurement of dummy circuit using UFCT

The result obtained using UFCT is shown in Table 1.[2)]

Two different dummies was examined. Each value obtained accorded with nominal value even when it had high resistance.

Table 1. Comparison of nominal values and measured values of fixed elements

Model circuits	Nominal Values				Measured Values			
	Rf	Cf	Re	Cdl	Rf	Cf	Re	Cdl
No.1	95MΩ	330pF	105MΩ	0.01μF	95.9MΩ	320pF	105.9MΩ	0.01μF
No.2	100MΩ	1000pF	100MΩ	0.01μF	102MΩ	980pF	98.4MΩ	0.012μF

4.2 The example of measurement using UFCT

4.2.1 The effect of anti corrosive pigment used in paint.

Two alkyd paints which were with and without zinc phosphate pigment (same PVC) were measured using UFCT.[3)]

The change of film resistance with time was shown in Fig. 4. The alkyd paint with zinc phosphate pigment had higher film resistance still after 10^3 hours.

Similar trend were obtained in case of measuring polarization resistance shown in Fig. 5.

However the difference between the two kinds of paints was larger in polarization resistance than in film resistance. These results showed that alkyd paint formulated with zinc phosphate pigment had better protective performance and it may suggest that the protective surface layer is formed by the anticorrosive pigment.

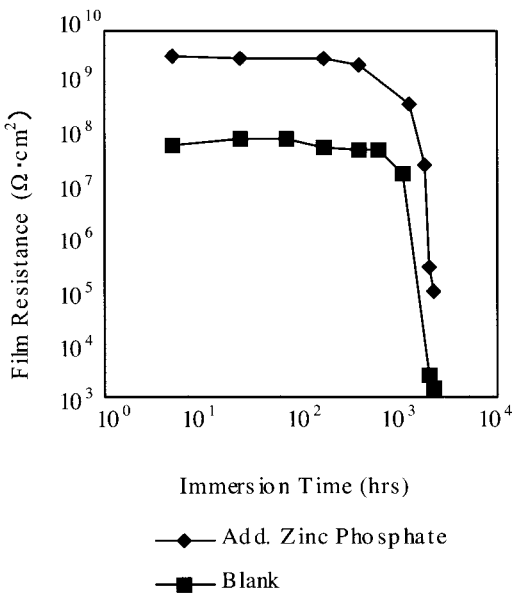

Fig. 5. Change in film resistance after immersion in 3wt% NaCl soln.

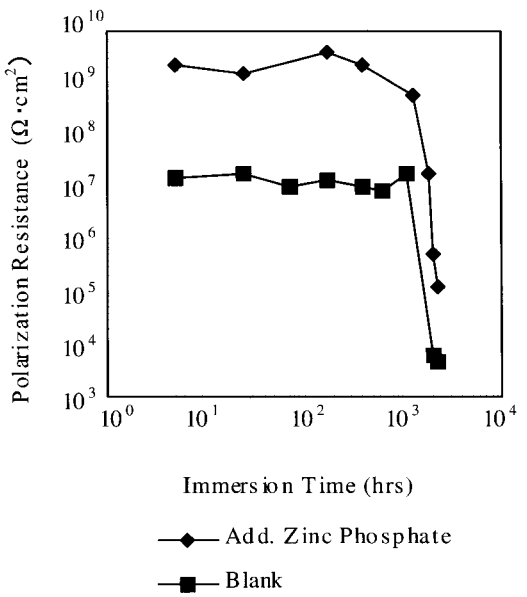

Fig. 6. Change in Polarization resistance after immersion in 3wt% NaCl soln.

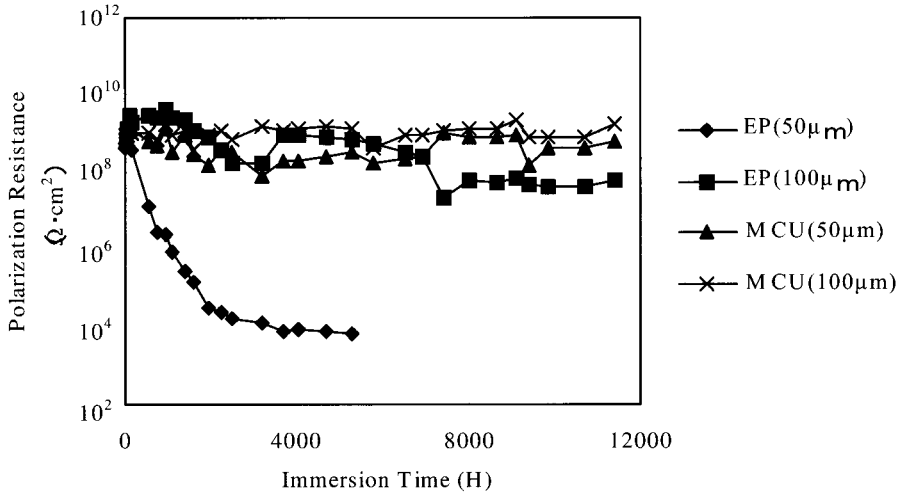

Fig. 6(a). Change in polarization resistance after low temperature drying (5℃ × 3days)

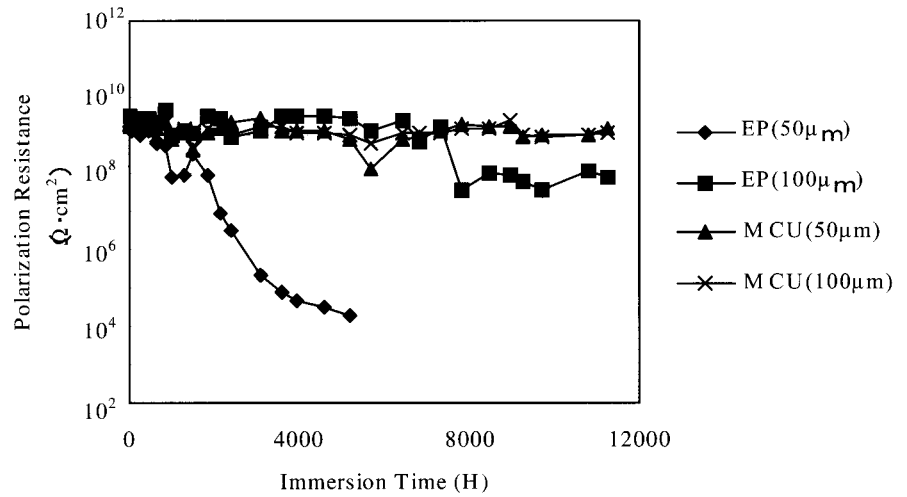

Fig. 6(b). Change in polarization resistance after low temperature drying (5℃ × 7days)

4.2.2 The protective performance of moisture cured polyurethane paint (MCU paint)

Electrochemical parameters of MCU painted steel was measured using UFCT.[4)]

Heavy duty coatings including epoxy paints have been used for the protection of steel structures so far.

Generally, two pack type paints such as epoxy paints does not cure enough at the temperature lower than 5℃ and so protective performance is not achieved enough.

MCU paint has been used often as good performance paint even if cured at low temperature.

In this report, MCU paint was coated in film thickness of 50 μm and 100 μm, and cured at 5℃ for 3 days and 7 days.

Then the coated panels were measured in 3 wt % NaCl solution at 23℃. Electrochemical parameters were measured. The change of polarization resistance with time is shown in Fig. 6(a) and Fig. 6(b).

MCU paints showed excellent polarization resistance in both film thickness of 50 μm and 100 μm.

In other hand, epoxy paint showed excellent polarization resistance only in film thickness of 100 μm. The high value of polarization resistance was kept for 11000hours.

The very similar trend was obtained for MCU paint panel which cured at 5℃ for and 7 days.

5. Conclusion

Under-film corrosion tester using current interrupter technique was developed. The advantages were found as follows.

(a) Coated steel having high resistance of 10Gohm was measured successfully.

(b) Electrochemical parameters, that is, film resistance, film capacitance, polarization resistance double layer capacitance and natural potential were obtained in measurement. They are useful for evaluating coated panel.

(c) The measurement operation was easy and took short period to measure by adopting current interrupter technique. It is good for test samples and save time for measurement.

(d) The tester has a potential of on-site measurement.

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