Original Paper

J. Jpn. Soc. Colour Mater. (SHIKIZAI), 72(3), 141-149(1999)

Comparison of Deterioration of Protective Coatings in Various Aqueous Solution Systems by Scanning Vibrating Electrode Technique (SVET)

Araceli M. MONSADA*, Yukihiro SEKIYAMA*, Shin-ichi HAYASHI*,
Makoto YUASA*,** and Isao SEKINE*,**

Abstract

The deterioration behavior of protective coatings in various aqueous solution systems was investigated by scanning vibrating electrode technique (SVET). In aqueous salt solutions of potassium carbonate (K_2CO_3) and sodium sulfate (Na_2SO_4), the ability of corrosion protection was in the order epoxy (EP) > polyester (ES) > polyvinyl chloride (VC) resins; this order corresponded to that in aqueous sodium chloride (NaCl) solution as previously reported. In aqueous HCOOH solution, the current density (i) by SVET of each paint film was in the order ES < VC; this order corresponded to those in aqueous CH_3COOH and H_3PO_4 solutions as previously reported, and also to that in aqueous K_2CO_3 and Na_2SO_4 solutions. From the previous and present data, in various aqueous solution systems, i increased in the order 100 ppm ($2.0\text{mmol} \cdot \text{dm}^{-3}$) NaCl < $0.5\text{mmol} \cdot \text{dm}^{-3}$ Na_2SO_4 < $0.5\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 < $0.3\text{mmol} \cdot \text{dm}^{-3}$ H_3PO_4 < 1% ($0.26\text{mol} \cdot \text{dm}^{-3}$) HCOOH. A linear correlation between current density determined by SVET and lifetime (or film resistance) determined by electrochemical impedance spectroscopy (EIS) exists in various aqueous solution systems. This linear correlation was shifted to higher current density (i) in more corrosive aqueous solutions.

Key-words: Coating deterioration, Protective coatings, Aqueous solution systems, Scanning vibrating electrode technique (SVET), Electrochemical impedance spectroscopy (EIS)

1. Introduction

Evaluation methods for the deterioration of corrosion protective coatings have been report-

ed by many researchers¹⁻²⁾. The authors have systematically performed the evaluation for deterioration of protective coatings by electrochemical measurements such as electrochemical impedance spectroscopy (EIS), current interrupter (CI) method and scanning vibrating electrode technique (SVET), which are able to measure quickly and quantitatively³⁻¹⁶⁾. In particular, the deterioration of various coatings has been evaluated by SVET in aqueous solutions containing

Received September 1, 1998

* Faculty of Science and Technology, Science University of Tokyo, 2641 Yamazaki, Noda 278-8510, Japan

** Institute of Colloid and Interface Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

sodium chloride (NaCl)^{4,8,10)}, hydrochloric acid (HCl)⁴⁾, sulfuric acid (H_2SO_4)^{4,12)}, nitric acid (HNO_3)⁴⁾, phosphoric acid (H_3PO_4)¹⁵⁾ and acetic acid (CH_3COOH)^{4,5)}. In this paper, the deterioration behavior of protective coatings consisting of polyester (ES), polyvinyl chloride (VC) and epoxy (EP) resins was investigated by SVET in various aqueous solutions containing potassium carbonate (K_2CO_3) and sodium sulfate (Na_2SO_4) as salts, or formic acid (HCOOH) as an organic acid. Comparison of deterioration behavior of organic coatings in various types of aqueous solutions, specifically NaCl , K_2CO_3 and Na_2SO_4 as salts, H_3PO_4 as inorganic acid and HCOOH as organic acid, was discussed in this study.

2. Experimental

2.1 Materials

2.1.1 Paints

Clear paints based on polyester resin (ES), polyvinyl chloride resin (VC) and epoxy resin (EP) (Dai Nippon Toryo Co.) were used in the study. The composition (mass%) of these paints are as follows: 1) ES, phthalic acid resin varnish 87.0, dryer & additive 3.0 and solvent 10.0; 2) VC, vinyl chloride resin varnish 83.0, plasticizer & additive 2.0 and solvent 15.0; 3) EP, epoxy resin varnish 60.0, phenol resin varnish 24.0, additive 1.0, aromatic solvent 7.0 and glycolic solvent 8.0.

2.1.2 Metal substrate

Cold rolled steel plates (JIS G3141 SPCC/SB, Nippon Test Panel), 70 x 150 x 0.80 mm were used as metal substrates for coating. Chemical analysis of the steel (mass %) was C 0.08, Si trace, Mn 0.35, P 0.04, S 0.018 and Fe balance.

2.1.3 Immersing solutions

The aqueous solutions used as immersing solutions or corrosive environments were salt solutions of $0.5\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 and $0.5\text{mmol} \cdot \text{dm}^{-3}$ Na_2SO_4 , with $0.26\text{mol} \cdot \text{dm}^{-3}$ HCOOH as organic acid solution. These solu-

tions were prepared using chemicals of analytical reagent quality dissolved in pure water ($1.19\mu\text{S}/\text{cm}$). The same solutions were used for electrochemical measurements.

2.2 Preparation of coated steel samples

The surface treatment of steel plates involved degreasing with xylene, polishing with #280 SiC-type of emery paper to silvery metal, washing with xylene and complete drying by hot air blower. Paints were coated on these plates by means of a doctor blade to a desired dry paint film thickness of about $20\mu\text{m}$. The coated samples were allowed to cure at room temperature for a period of one week, then cut to a smaller size (70 x 50 x 0.8 mm) for electrochemical measurements.

2.3 Electrochemical Measurements

2.3.1 Scanning vibrating electrode technique (SVET)

The coated steel plates were cut to a smaller size (5 x 7 cm) and then fixed face up in a hard VC plastic container. The edges and surfaces of the coated samples were covered with a rosin-paraffin wax melt except for an area (4.52cm^2) enclosed in a plastic O-ring which served as the effective measuring area. Paint film of each coated sample was artificially cut to a length of about 0.50 cm at the center of the measurement area by a cutter in conformance with the method of the cross cut test according to the Japanese Industrial Standards (JIS K5400). The immersing solutions used were aqueous $0.5\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 , $0.5\text{mmol} \cdot \text{dm}^{-3}$ Na_2SO_4 and $0.26\text{mol} \cdot \text{dm}^{-3}$ HCOOH .

The apparatus used for SVET measurements was NF Electronic Instruments SVET-1000. Measurements were carried out on specimens immersed in different aqueous solutions at room temperature for various periods. The potential gradients in the solution as a result of current flowing between the local anode and local cathode were mapped and measured at 400 points within an area of 1 x 1 cm. Samples were scanned repeatedly in the

x-direction and with steps in the y-direction between each scan where both x and y coordinates were divided into 20 parts. The scanning and data analysis were facilitated by computer control.

The potential gradients produced from a lock-in amplifier were displayed in a three-dimensional plot. The vibrating electrode was made of a platinum (Pt) needle and was vibrating perpendicular to the surface of the coated sample. Other important operating parameters, as referred to in the previous report of Yuasa, et al.⁴⁾, were as follows: vibrating frequency, 221 Hz; electrode amplitude, 150 μm ; distance between center of amplitude and coated steel surface, ca. 150 μm ; scanning step, 500 μm .

2.3.2 Electrochemical Impedance Spectroscopy (EIS)

The measurements of EIS were carried out as reported in other papers^{4,11)}. The measurement cell was composed of working, counter and reference electrodes. The coated steel plate as a working electrode was covered (both sides) with rosin-paraffin wax melt except for a circular area of 4.52 cm^2 which was enclosed by a plastic O-ring. This area was put in contact with the corrosive medium, specifically the aqueous solution, and used as the measurement area of the working electrode. A platinum (Pt) plate (12 cm^2) was used as the counter electrode, and a Ag/AgCl electrode as reference electrode.

Coated samples were immersed in different aqueous solutions such as 0.5 $\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 , 0.5 $\text{mmol} \cdot \text{dm}^{-3}$ Na_2SO_4 , and 1% (0.26 $\text{mol} \cdot \text{dm}^{-3}$) HCOOH . Film resistance (R_f) of the coated steel samples was determined as a function of immersion time. The evaluation of the corrosion protective properties of the coating films in terms of R_f was based on the electric equivalent circuit as previously reported^{4,11)}.

The measurements of EIS were carried out

at the open circuit potential using a potentiostat (Toho Technical Research, PG-Model 2000) and a frequency response analyzer (FRA) (NF Electronic Instruments, FRA-5020) over a range of 20 kHz to 10 mHz. The reference signal voltage of the sinusoidal wave was 9 mV (rms).

3. Results and Discussion

3.1 SVET in aqueous K_2CO_3 and Na_2SO_4 solutions

Figure 1 shows three-dimensional maps of ES coating film on steel immersed in 0.5 $\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 for 6 and 48 hours, respectively. The figure displays the electrical potential distribution and locates the cut part of the coating film. The central peak becomes the control part of the local anode (cut area) and the flat part becomes the control part (coating film) of the local cathode.

Fig. 1 Three-dimensional maps of potential (E) distribution of polyester (ES) coated steel in aqueous 0.5 $\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 solution after immersion for (a) 6 and (b) 48 hours.

Corrosion of metals in an aqueous solution is an electrochemical process involving oxidation of metal (anodic) and reduction of species from the solution (cathodic)¹⁷⁾. The local corrosion proceeds on a metal when both anodic and cathodic processes take place at separated areas. As a principle, the current flows in the electrolyte solution from a local anode to the cathodic area and equipotentials are produced around the local anodic area^{17,18)}. The flow of electrons within the metallic phase does not involve significant ohmic potential differences because of the high conductivity of metal. The potential gradients (E) are being developed around the corroded metal surface immersed in the solution due to the ionic current flowing through the solution between the local anodic and cathodic areas. By scanning the vibrating electrode tip (Pt) at close distance over the surface of the metal, potential distribution in the solution is measured corresponding to the current flow. The potential changes are markedly observed over the local anodic area. The measurement of the distribution of potential gradients leads to an evaluation of the corrosion behavior of the metal in terms of current density (i). The degree of potential gradient is proportional to the current density of corrosion. Isaacs et al.^{17,18)}, have emphasized however, that the voltage variations observed during the SVET are a direct measure of the current density flowing parallel to the vibration direction of the vibrating electrode tip, not potential variations of the metal substrate. They are a measure of the potential (IR) gradients in the solution rather than any potential at the metal/electrolyte interface^{17,18)}. The SVET is a method used to locate the anodic and cathodic sites and to study the electrochemical processes during the localized corrosion *in situ*.

This behavior can likewise be observed from a bird's eye view of the distribution of potential gradient (E) at the local anode as shown in

Fig. 2. By means of the E distribution graph as shown in **Fig. 3**, the E values at the local anode (E_a) and at the local cathode (E_c) were obtained. To evaluate the deterioration of coating film, the degree of growth of the corrosion is given by the difference of potential gradient (ΔE): $\Delta E = E_a - E_c$, where E_a is a mean value of the three highest E values at the local anode part (central peak) and E_c is a mean value of potential gradient values at the local cathode part (flat part). The ΔE is then determined and converted to current density by using the conductivity of the immersing solution.

Results are shown in **Fig. 4** where the current density (i) values and the immersion time (t) in $0.5\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 aqueous solution of the metal samples coated with paint films of ES, VC and EP resins are plotted. It shows

Fig. 2 Bird's eye view of potential gradient (E) distribution of ES coated steel in aqueous $0.5\text{mmol} \cdot \text{dm}^{-3}$ K_2CO_3 solution after immersion for (a) 6 and (b) 48 hours.

that the current density gradually increases with the increase of immersion time but reaches a constant value after 3 days of

immersion for all the coating films. Such increase in the current density value can be explained by the growth of the anodic area (cut part) during immersion in the solution. It is thought that the solution penetrates the cut part, inducing swelling and disbonding of the coating from the steel, thus increasing the anodic area^{13,19}. **Figure 5** also shows a similar trend for the i values as a function of immersion time for the same coating films immersed in $0.5\text{mmol} \cdot \text{dm}^{-3} \text{Na}_2\text{SO}_4$ aqueous solution. Both aqueous salt solutions were found to be corrosive to some degree. With respect to the coatings, the ability of corrosion protection was in the order $\text{EP} > \text{ES} > \text{VC}$. This order corresponded to the order in aqueous NaCl solution⁴.

3.2 SVET in aqueous HCOOH solution

Figure 6 shows typical three-dimensional plots of an ES coated steel plate immersed in $0.26\text{mol} \cdot \text{dm}^{-3} \text{HCOOH}$ solution after 1, 24 and 48 hours, respectively. No distinct peak was yet observed at the cut part of the coating film after the first hour of immersion but central peaks became evident after 24 hours. More intense random peaks were observed at the cut part of the coating film after 48 hours. These results indicate that corrosion progresses with increasing immersion time in the given solution.

Fig. 3 Potential gradient (E) distribution of ES coated steel in aqueous $0.5\text{mmol} \cdot \text{dm}^{-3} \text{K}_2\text{CO}_3$ solution after immersion for (a) 6 and (b) 48 hours.

Fig. 4 Current density (i) vs. immersion time (t) curves of various coated steels in aqueous $0.5\text{mmol} \cdot \text{dm}^{-3} \text{K}_2\text{CO}_3$ solution.

Fig. 5 Current density (i) vs. immersion time (t) curves of various coated steels in aqueous $0.5\text{mmol} \cdot \text{dm}^{-3} \text{Na}_2\text{SO}_4$ solution.

The current density (i) vs. immersion time (t) curves of steel samples coated with paint films of ES and VC immersed in $0.26\text{mol} \cdot \text{dm}^{-3}$ HCOOH are shown in **Fig. 7**. The current density value increases with increasing immersion time for all coating films. The current density value of each paint film was in the order $\text{ES} < \text{VC}$. This order in aqueous HCOOH solution corresponded to the orders in aqueous CH_3COOH ⁵⁾, H_2SO_4 ¹²⁾ and H_3PO_4 ¹⁵⁾ solutions as previously reported, and also in aqueous K_2CO_3 and Na_2SO_4 solutions as above.

3.3 Comparison of deterioration behaviour of protective coatings in various aqueous solutions

The current density (i) vs. immersion time (t) curves of ES coated steel in various aqueous

solutions are shown in **Fig. 8**. Generally, the current density value increases with increasing immersion time. These results reflect that all aqueous solutions are practically corrosive with respect to steel but vary in the extent of corrosion taking place on the metal. As shown in the figure and from the results above, the current density value increased in the order $100\text{ ppm } (2.0\text{mmol} \cdot \text{dm}^{-3}) \text{ NaCl}^{14)} < 0.5\text{mmol} \cdot$

Fig. 6 Three-dimensional maps of potential (E) distribution of polyester (ES) coated steel in aqueous $0.26\text{mol} \cdot \text{dm}^{-3}$ HCOOH solution after immersion for (a) 1, (b) 24 and (c) 48 hours.

Fig. 7 Current density (i) vs. immersion time (t) curves of ES and VC coated steels in aqueous $0.26\text{mol} \cdot \text{dm}^{-3}$ HCOOH solution.

Fig. 8 Current density (i) vs. immersion time (t) curves of ES coated steel in various aqueous solution systems. The data for $100\text{ ppm } (2.0\text{mmol} \cdot \text{dm}^{-3}) \text{ NaCl}$ and $0.3\text{mmol} \cdot \text{dm}^{-3} \text{ H}_3\text{PO}_4$ are from ref. 4) and 15), respectively.

$\text{dm}^{-3} \text{Na}_2\text{SO}_4 < 0.5\text{mmol} \cdot \text{dm}^{-3} \text{K}_2\text{CO}_3 < 0.3 \text{ mmol} \cdot \text{dm}^{-3} \text{H}_3\text{PO}_4^{15)} < 0.26\text{mol} \cdot \text{dm}^{-3} \text{HCOOH}$. Comparison with other aqueous solution systems like $\text{HCl}^{4)}$, $\text{HNO}_3^{4)}$ and $\text{CH}_3\text{COOH}^{5)}$ was not possible in this particular study because the concentrations of HCl , HNO_3 and CH_3COOH in the earlier studies were higher. It is however noted that concentration of an immersing solution significantly affects the rate and extent of corrosion on the metal. On the other hand, Isaacs and Vyas¹⁸⁾ reported that peak heights (refer to **Fig. 1**) at the anodic area give a direct measure of the intensity of the corrosion currents from the anodic region, indicating that the effect of the conductivity of the electrolyte immersing solution was very minimal. With respect to the coating films, EP was found to possess a superior corrosion protective property.

Coating film deterioration behavior of various coated metals immersed in different aqueous solutions was also investigated using EIS. The film resistance (R_f) was determined by Cole-Cole plot of EIS data. **Figure 9** shows the variation of the R_f with immersion time (t) of ES, VC and EP coated steel in aqueous $0.5 \text{ mmol} \cdot \text{dm}^{-3} \text{K}_2\text{CO}_3$ solution. For each coating film, R_f gradually decreases with increas-

Fig. 9 Variation of coating film resistance (R_f) with immersion time (t) of various coated steels in aqueous $0.5\text{mmol} \cdot \text{dm}^{-3} \text{K}_2\text{CO}_3$ solution.

ing immersion time. The decrease in the R_f is attributed to the deterioration of the ability of the coating to protect the metal from the penetration of water and other corrosion-promoting contaminants. Until R_f value reaches the resistance of the metal substrate ($10^4 \Omega \cdot \text{cm}^2$)¹³⁾, the coating film continues to inhibit corrosion reactions on the metal. The EP coating film was found to have a superior corrosion protective property compared with other paints as indicated from the results of SVET measurements.

The results of SVET can be correlated with those from other common electrochemical techniques used in the study of corrosion like EIS. The correlation between SVET and EIS was determined by a graph of i and lifetime(t_s). The t_s is a parameter used to evaluate the coating film deterioration and is the time when coating film resistance (R_f) obtained by the EIS measurement reaches the resistance of the substrate steel plate ($10^4 \Omega \cdot \text{cm}^2$)^{13,20)}. The t_s incidentally determines the lifetime of a protective coating film under any corrosive environment. Specifically, **Fig. 10** shows a relationship between lifetime(t_s) by EIS and the current density (i) by SVET for various coated steels immersed in aqueous $0.5\text{mmol} \cdot \text{dm}^{-3} \text{K}_2\text{CO}_3$ (salt) and $0.3\text{mmol} \cdot \text{dm}^{-3} \text{H}_3\text{PO}_4^{15)}$ (acid) solutions. The figure clearly shows that as

Fig. 10 Relationship between the current density (i) and the lifetime (t_s) for various coated steels in aqueous $0.5\text{mmol} \cdot \text{dm}^{-3} \text{K}_2\text{CO}_3$ and $0.3 \text{ mmol} \cdot \text{dm}^{-3} \text{H}_3\text{PO}_4$ solution systems.

the i value is higher, the lifetime (t_s) of coating film is shorter. While as the i value is lower, the t_s of coating film is longer. A good correlation between the lifetime and the current density, that is, a good correlation between SVET and EIS, thus exists. In various aqueous solution systems, this linear correlation was shifted to higher current density in the order 100 ppm ($2\text{mmol} \cdot \text{dm}^{-3}$) $\text{NaCl}^{(4)} < 0.5\text{mmol} \cdot \text{dm}^{-3}$ $\text{Na}_2\text{SO}_4 < 0.5\text{mmol} \cdot \text{dm}^{-3}$ $\text{K}_2\text{CO}_3 < 0.3\text{mmol} \cdot \text{dm}^{-3}$ $\text{H}_3\text{PO}_4^{(15)}$. That is, the linear correlation is shifted to higher current density in more corrosive aqueous solutions. Anyhow, a linear correlation between SVET (i) and EIS (R_f or t_s) was obtained in various aqueous solution systems.

4. Conclusion

The deterioration behavior of protective coatings during immersion in various types of aqueous solution systems was investigated by SVET. Several conclusions were drawn based on the results as follows:

- (1) In aqueous salt solutions such as K_2CO_3 and Na_2SO_4 , the ability of corrosion protection was in the order $\text{EP} > \text{ES} > \text{VC}$. This order corresponded to the order in aqueous NaCl solution as previously reported.
- (2) In aqueous acid solutions such as HCOOH , the current density by SVET of each paint film was in the order $\text{ES} < \text{VC}$. This order corresponded to the orders in aqueous CH_3COOH , H_2SO_4 and H_3PO_4 solutions as previously reported and also that in aqueous K_2CO_3 and Na_2SO_4 solutions as above.
- (3) From the previous and present data, in various aqueous solution systems, the current density by SVET increased in the order 100 ppm ($2\text{mmol} \cdot \text{dm}^{-3}$) $\text{NaCl} < 0.5\text{mmol} \cdot \text{dm}^{-3}$ $\text{Na}_2\text{SO}_4 < 0.5\text{mmol} \cdot \text{dm}^{-3}$ $\text{K}_2\text{CO}_3 < 0.3\text{mmol} \cdot \text{dm}^{-3}$ $\text{H}_3\text{PO}_4 < 0.26\text{mol} \cdot \text{dm}^{-3}$ HCOOH .
- (4) A linear correlation between SVET (current density, i) and EIS (film resistance, R_f or lifetime, t_s) exists in various aqueous solution

systems. This linear correlation was shifted to higher current density in more corrosive aqueous solutions.

References

- 1) Y. Sato: "Bosei-Boshoku Toso Gijutsu", p. 82, Kogaku-Tosho, Tokyo, (1981).
- 2) I. Sekine: "Boshoku Tomaku no Saishin Hyoka-ho", p.5, Maki-Shoten, Tokyo, (1991).
- 3) I. Sekine, K. Moriya, and M. Yuasa: *Boshoku Gijutsu*, **38**, 365 (1989).
- 4) M. Yuasa, M. Ichikawa, K. Moriya, I. Sekine, H. Fukumoto, H. Mizuki, and T. Murakami: *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, **57**, 1061 (1989).
- 5) I. Sekine, K. Moriya, and M. Yuasa: "Advances in Corrosion Protection by Organic Coatings", Proc. Vol. **89-13**, p.218, Electrochem. Soc., Inc., (1989).
- 6) I. Sekine, K. Sakaguchi, and M. Yuasa: *Bull. Chem. Soc. Jpn.*, **63**, 1237 (1990).
- 7) I. Sekine, K. Sakaguchi, and M. Yuasa: *J. Coat. Tech.*, **64**, 45 (1992).
- 8) I. Sekine, M. Yuasa, K. Tanaka, M. Fuke, and L. Silao: *J. Jpn. Soc. Colour Material (Shikizai Kyokaishi)*, **65**, 684 (1992).
- 9) I. Sekine, J. Ito, M. Yazawa, H. Tada, H. Jimi, T. Chiaki, M. Yuasa: *J. Jpn. Soc. Colour Material (Shikizai Kyokaishi)*, **66**, 709 (1993).
- 10) I. Sekine, N. Toshima, and M. Yuasa: *J. Jpn. Soc. Colour Material (Shikizai Kyokaishi)*, **66**, 724 (1993).
- 11) I. Sekine, M. Yuasa, K. Tanaka, T. Tsutsumi, F. Koizumi, N. Oda, H. Tanabe, and M. Nagai: *J. Jpn. Soc. Colour Material (Shikizai Kyokaishi)*, **67**, 424 (1994).
- 12) I. Sekine, A. Takaoka, M. Moriya, and M. Yuasa: "Advances in Corrosion Protection by Organic Coatings II", Proc. Vol. **95-13**, p.151, Electrochem. Soc., Inc., (1995).
- 13) I. Sekine, T. Suzuki, M. Yuasa, K. Handa, K. Takaoka, and L. Silao: *Prog. Org. Coat.*, **31**, 185 (1997).
- 14) I. Sekine, H. Haruyama, and M. Yuasa: "Advances in Corrosion Protection by Organic Coatings III", Proc. Vol. **97-41**, p.150, Electrochem. Soc., Inc., (1998).
- 15) L. Silao, I. Sekine, M. Yuasa, and H. Nishida: "Advances in Corrosion Protection by Organic Coatings III", Proc. Vol. **97-41**, p. 206, Electrochem. Soc., Inc., (1998).

- 16) A. M. Monsada, H. Haruyama, M. Yuasa, and I. Sekine: "Advances in Corrosion Protection by Organic Coatings III", Proc.Vol. **97-41**, p. 263, Electrochem. Soc., Inc., (1998).
- 17) H.S. Isaacs and B.Vyas: "Electrochemical Corrosion Testing", p.3, American Society for Testing and Materials, USA, (1981).
- 18) H.S. Isaacs and Y. Ishikawa: "Electro-chemical Techniques for Corrosion Engineering", p.17, NACE, Texas, USA, (1986).
- 19) A.M.Monsada, Y.Sekiyama, S. Hayashi, M. Yuasa, I.Sekine, N.Hirose, and T.Tanaki: *J. Jpn. Soc. Colour Material (Shikizai Kyokaishi)* (1998) under submission.
- 20) I. Sekine: *Prog. Org. Coat.*, **31**, 73 (1997).

走査振動電極法 (SVET) による各種水溶液系での防食塗膜の劣化比較

アラセリ モンサダ*・関山之郭*・林 慎一*・湯浅 真**・関根 功**

*東京理科大学理工学部 千葉県野田市山崎 2641 (〒278-8510)

**東京理科大学界面科学研究所 東京都新宿区神楽坂1-3 (〒162-8601)

要 旨

各種水溶液系での防食塗膜の劣化挙動を走査振動電極法 (SVET) により検討した。 K_2CO_3 および Na_2SO_4 の塩水溶液において、防食能はエポキシ樹脂 (EP) > ポリエステル樹脂 (ES) > ポリ塩化ビニル樹脂 (VC) の順となり、この順は以前に報告した塩化ナトリウム水溶液の順に対応した。ギ酸水溶液において、各塗膜の SVET による電流密度は $ES < VC$ の順となり、この順は以前に報告した酢酸、硫酸およびリン酸の水溶液の順および K_2CO_3 および Na_2SO_4 の水溶液の順に対応した。以前および本実験のデータより、各種水溶液系において、SVET による電流密度は 100ppm ($2.0\text{mmol} \cdot \text{dm}^{-3}$) $NaCl < 0.5\text{mmol} \cdot \text{dm}^{-3} Na_2SO_4 < 0.5\text{mmol} \cdot \text{dm}^{-3} K_2CO_3 < 0.3\text{mmol} \cdot \text{dm}^{-3} H_3PO_4 < 1\%$ ($0.26\text{mol} \cdot \text{dm}^{-3}$) $HCOOH$ の順に増加した。SVET による電流密度と電気化学的インピーダンススペクトロスコピー (EIS) による塗膜寿命 (または塗膜抵抗) の直線的な相関が得られた。より腐食性の高い溶液の直線的な相関ほど高電流密度側に移行した。