COMPUTER–AIDED SCANNING ELECTRODE TECHNIQUE FOR THE INVESTIGATION OF CORROSION FAILURES IN ORGANIC–COATED TINNED PLATES

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IN ORDER TO DETERMINE THE EXISTENCE AND LOCATION OF DEFECTS OF A COATING ON A METAL, A SCANNING ELECTRODE TECHNIQUE HAS BEEN DEVELOPED BY COMBINING THE RADIAL MOTION OF THE MICROELECTRODE WITH THE ROTATION OF THE SAMPLE. MEASUREMENT SYSTEM CONTROL, DATA COLLECTION AND EVALUATION WERE CARRIED OUT WITH A PROGRAM USING A MICROCOMPUTER.

THE DEFORMATION OF THE POTENTIAL FIELD CAUSED BY EXTENSIVE DAMAGE AND ACCUMULATED CORROSION PRODUCTS NECESSITATED AN EXACT MATHEMATICAL EVALUATION OF THE POTENTIAL MAPS. THROUGH THE METHOD OF GENERALISED SECOND DIFFERENCES, THE HEIGHT AND BASELINE WIDTH OF THE PEAKS CAN BE EXPRESSED NUMERICALLY. THE POINTS WHERE THE SECOND DIFFERENCES EXCEED A PRELIMINARILY CHOSEN LIMIT CAN BE DISPLAYED IN A DIAGRAM WHICH REPRESENTS THE SAMPLE. IN THIS WAY THE DEFECT SITES PROMOTING CORROSION CAN BE VISUALISED.

Introduction

Tinned cans protected with organic coatings may undergo certain corrosion failures when in contact with food products. Besides the corrosivity of the product and the quality of the tin and the organic coating (porosity, thickness and brittleness), the handling of the plates and the cannery technique can account for the increased corrosion of the inner side of the cans, *e.g.* the reinforcement embossing and identification numbers can cause fractures of the coating on the container ends. These techniques may cause not only mechanical damage, but also permanent stress.

When in contact with an electrolyte, the mechanically damaged areas are preferred sites for corrosion, due to the formation of local action cells. With a view to selecting

damaged series before use, it is reasonable to determine the possibility and distribution of the formation of local action cells by means of a non–destructive method.

The application of polarization methods may promote processes which do not occur during ordinary use. Optical methods, *e.g.* simple visual observations, are very useful, but need a long pretreatment or exposure time, may be affected by subjective factors and can hardly be automated. The scanning reference electrode technique provides an *in situ* method for studying the differences in electrochemical properties of a metal surface [1–9].

The existence and location of defects on a coating can be detected by a scanning micro–reference electrode with a fine capillary tip, situated close to the surface so as to intersect the potential field lines in the electrolyte due to the current of electrons in the metal and the ion migration in the solution [4,9].

The distance of the microelectrode from the surface affects the values on the potential contour map to a great extent. Changes in distance may result in noisy or hardly evaluable signals in the region of defects and may lead to the complete overlooking of certain defects near the reinforcement embossing. The microelectrode should be able to follow the embossed unevenness of the can ends.

The aim of this work was to develop a computer–aided scanning reference electrode technique and examine its performance on tinned can ends protected with organic coatings.

Apparatus and experimental technique

A schematic diagram of the applied measuring apparatus is shown in Fig. 1.

The embossed ends of containers served as test specimens (Fig. 1,1). The corroding medium was 0.05% NaCl. Signal generation was achieved with two Ag/AgCl reference electrodes. The potential distribution in the electrolyte close to the surface was measured by a scanning microelectrode (Fig.1,3) referred to the other Ag/AgCl electrode (Fig. 1,4). The sensing tip of the scanning electrode was set at a distance of some 20–30 μm from the surface, while the other one, in the bulk of the electrolyte, sensed the average potential of

the sample. The application of reference electrodes of the same type in this configuration increases the precision of the measurements.

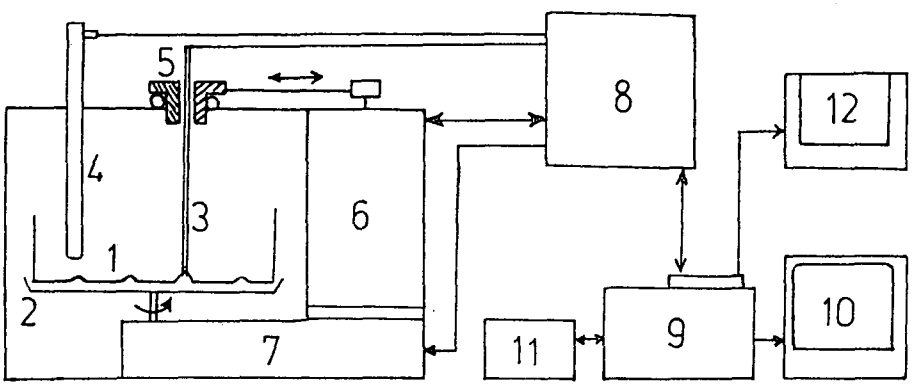

Figure 1: Block diagram of measuring system
1– sample, 2– sample holder, 3– micro–reference electrode, 4– stationary reference electrode, 5– carriage, 6– push–pull motor, 7– rotating motor, 8– AD–DA converter, 9– microcomputer, 10– monitor, 11– data storage, 12– printer

The scanning microelectrode was made in two different ways. A silver wire 0.25 mm in diameter was fixed in a glass capillary with "TORR SEAL" resin in the first case, and it was placed in a Teflon tube in the other case. The suitable profile of the resin or Teflon sliding foot of the electrode, which ensured the necessary 20–30 μm distance between the sample and the silver wire, was achieved by means of polishing. After formation of the electrode, an AgCl layer was electrodeposited onto it.

The microelectrode, fixed in a glass capillary, can move freely up and down in

accordance with the unevenness of the plate when placed in the Teflon sheath of the carriage (Fig. 1,5), which is equipped with bearings and pulled horizontally by an electric motor (Fig. 1,6). The sample holder with the can on it can be rotated around a vertical axis by another electric motor (Fig. 1,7). The electric motors (6) and (7) can operate either synchronised or individually.

As the container ends are symmetric with respect to rotation, a simple combination of the rotation of the container with the radial motion of the carriage carrying the electrode can result in a full coverage of the surface of the plate. Radial movements must be performed in such a way that the electrode is passed over the centre of the plate. Regular distribution of the scanning pathways can be ensured by synchronisation of the rotation and radial motion, and therefore electric motors with variable *rpm* values were applied. The method provides the possibility of variation of the scanning pathway distances (*i.e.* variation of the angle between the pathways). Of course, an increase of the scanning density results in an increase in the time required for testing, which cannot be compensated by increasing the sweep rate to any extent. Therefore, the optimal sweep rate and testing time should be determined experimentally.

Measurement system control, data collection and evaluation were carried out with a program for a personal microcomputer (Fig. 1,9). The computer is connected to an AD–DA converter (Fig. 1,8) through an interface which receives measurement data (positions and potentials) in two channels and is able to control relays for switching rotation and radial motion with reverse. The program controlling the AD–DA converter is written in ASSEMBLER code and is accessible from the main program in BASIC. The data–collecting segment (also in BASIC) stores about 6000 data pairs in a compact form. The intersections of the potential map and time data picked up are displayed on a monitor (Fig. 1,10).

The results of mathematical evaluation of intersections can be copied by a printer (Fig. 1,12) or saved (Fig. 1,11) and evaluated following the measurement process.

Results and discussion

In order to determine the optimal sweep rate and to test the reproducibility, the first experiments were conducted on plates subjected to intentional damage.

In the case of radial scanning (without rotation), the location and even the shape of the peaks referring to a given defect site depend on the sweep rate. This can be attributed to the facts that at greater speed the probe cannot be balanced sufficiently quickly and the potential distribution is perturbed by stirring of the solution.

In the experiments it was found that the reproducibility was acceptable if the sweep rate of the electrode did not exceed 30 mm/min. At higher sweep rates (*e.g.* at 60 mm/min.) the locations of the peaks depend on the scanning direction (Fig. 2).

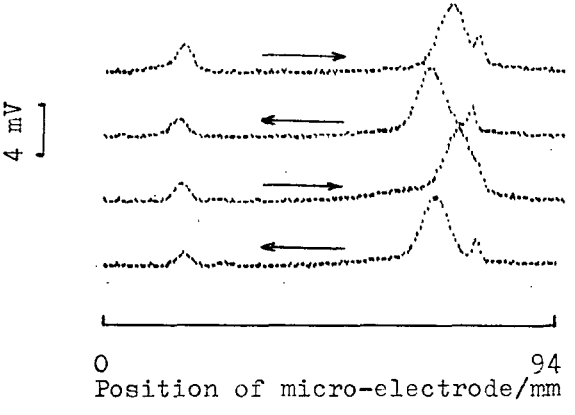

Figure 2: Influence of scanning direction on locations of potential peaks without sample rotation. Scanning rate: 60 mm/min

Optimal measurement time and scan rate could be achieved at 90 min/full rotation. As the advancing motor is stopped for only a few seconds at the endpoints, the route covered by the microelectrode is approximately symmetric and the distance between pathways do not exceed 5 mm anywhere.

Figure 3 shows a potential map of a container with a strongly corroded casing weld. Lines 3 and 4, which were recorded in the vicinity of the soldering, curve significantly. Deviation of the curves of this kind could be observed in every case when the damage was extensive and corrosion products had accumulated. Besides deformation of the potential field, data noise may also increase in such cases, and therefore an exact mathematical evaluation of the potential maps seemed to be reasonable in addition to simple observation of them.

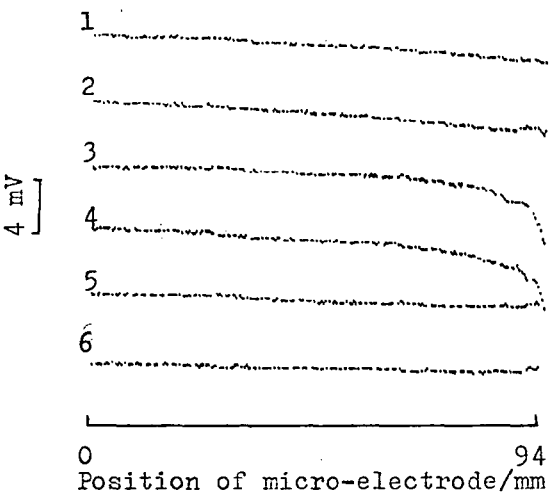

Figure 3: Influence of a strongly corroded soldering on contour lines. Scanning rate: 30 mm/min. Time of full rotation: 90 min.

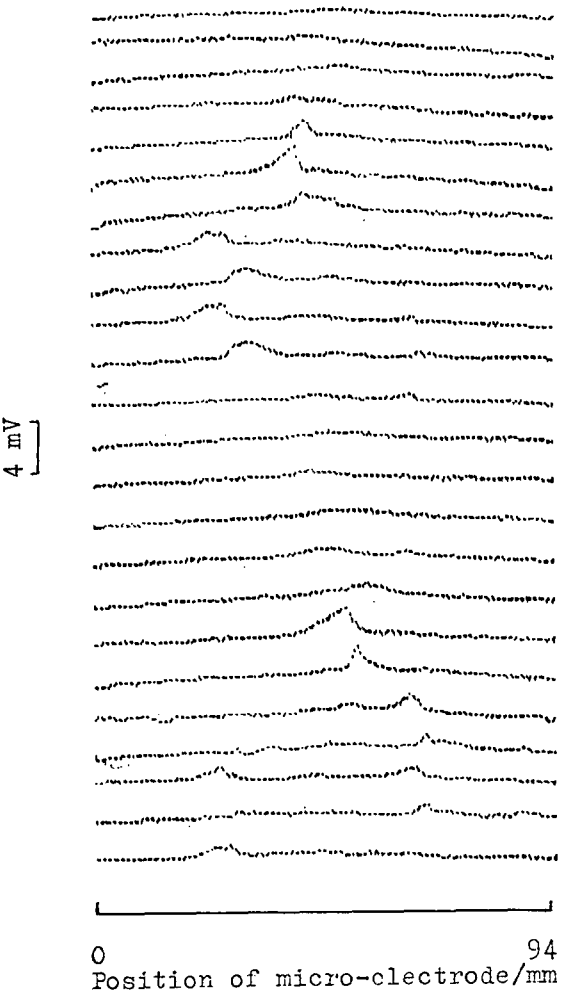

Figure 4: Potential contour map obtained on a can after 4 days exposure to electrolyte. Scanning rate: 30 mm/min. Time of full rotation: 90 min.

When the method of generalised second differences is applied, the height and baseline width of the peaks can be expressed numerically. The points where the second differences exceed a preliminarily chosen limit can be displayed on a monitor in a diagram which represents the can end. In this way the defect sites promoting corrosion can be visualised.

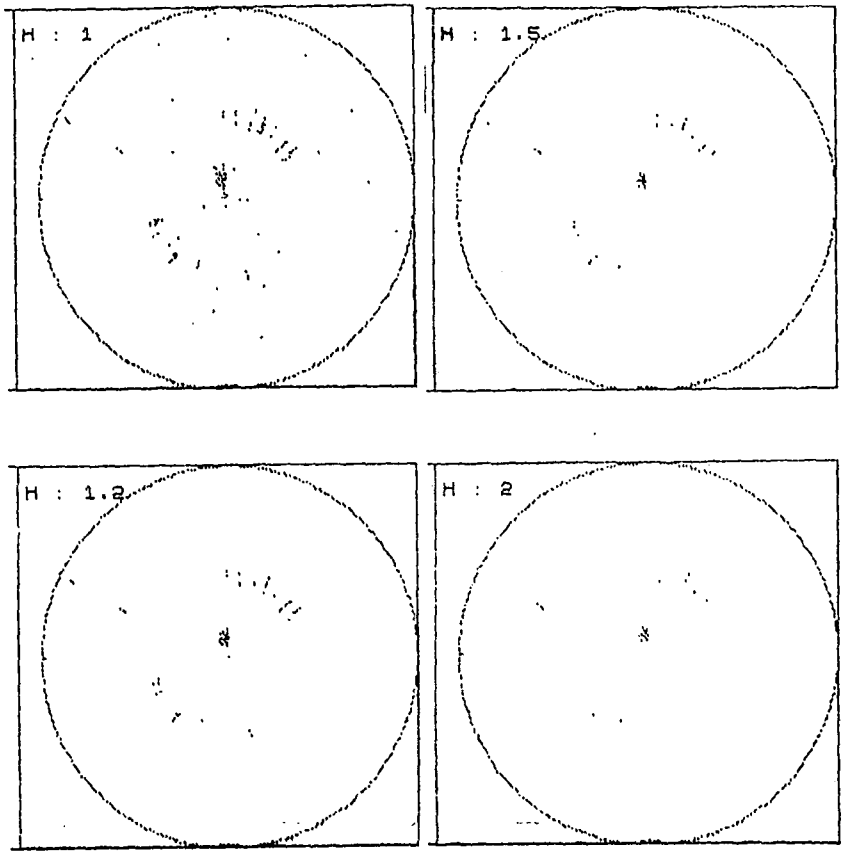

Figure 5: Distribution of defects evaluated from data of Fig. 4 according to different limiting values H.

Figures 4 and 5 depict the potential map intersections of a rotated sample exposed to 0.05% NaCl solution for four days, and the defect site distributions referring to different limiting values H of the second difference, respectively. The distributions reveal that corrosion occurs mainly at the innermost reinforcement embossing and at the identification numbers in the centre.

In a further series of experiments it was found that the height and width of the peaks increased with exposure time, showing the increase in local action cell activity, and the widening and deepening of the surface fractures and pits. As the probe passed over the defect sites, certain negative peaks also occurred in the diagrams of the intersections. This phenomenon must be connected with the formation of fractures and damage, and consequently cathodic and anodic sites of different sizes and characters. If the cut reaches the base metal, the steel functions as an anodic site and its environment as a cathodic site. In this case, the organic–coated surface, the passive tin layer and the steel corrosion products can all function, even simultaneously, as cathodic sites. If only the organic coating is damaged, the free tin surface can function as an active anode referred to the organic–coated surface. In the case of pitting corrosion of the tin, only a relatively small part of the surface functions as an anode. On the other hand, the cathodic character of the free tin surface referred to the defect sites reaching the steel is more marked than that of the organic–coated surface where the diffusion barrier of reducible components is much more expressed.

Though all these phenomena must influence the potential distribution in a very complicated way, there is no doubt that all of the sudden positive and negative shifts ("peaks" and "holes" in the map) indicate defect sites. Thus, the location and density of the points obtained by the method of generalised second differences (applying the empirically determined limiting factor H) are connected with the destruction of the surface layer.

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КОМПЮТЕР УПРАВЛЯЕМАЯ ЭЛЕКТРОДНАЯ ТЕХНИКА ДЛЯ ИССЛЕДОВАНИЯ КОРОЗИОННЫХ ПОВРЕЖДЕНИЙ СУРЬМИРОВАННЫХ ПОВЕРХНОСТЕЙ ПОКРЫТЫХ ОРГАНИЧЕСКИМ ВЕЩЕСТВОМ

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Для определения наличия и расположения изъянов в покрытиях металлов,

разработана сканирующая электродная техника при комбинации радиального движения микроэлектрода с вращением образца. Деформация потенциального поля, происходящая в результате расширения повреждений и накопления корозионных продуктов, требует точного математического расчета карты потенциалов. При применении обобществленного метода вторых разностей, высота и ширина базовой линии пиков могут быть численно выражены. Точки, в которых значения вторых разностей превосходят предварительно избранный предел, могут быть изображены на диаграмме, которая будет характеризовать образец. Таким образом положение дефектных мест, способствующих корозии, может быть визуализировано.