Original Paper

J. Jpn. Soc. Colour Mater. (SHIKIZAI), 74(2), 57-62(2001)

Degradation Evaluation of Pigmented Long Oil Alkyd Resin Paint Film by Nanoindentation and Scanning Acoustic Microscope

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Abstract

The degradation behavior of pigmented long oil alkyd resin (LAR-P) painted on steel in an aqueous 3% NaCl solution was investigated by nanoindentation and scanning acoustic microscope (SAM).

Young's modulus (E) and hardness (H), obtained by nanoindentation, of the LAR-P paint film on steel increased at short immersion time and then decreased with increasing immersion time. Furthermore, it was clarified that the SAM image shows a heterogeneous E distribution. The lower E areas in paint film were observed at short immersion time, while the blisters were observed in the lower E area in the SAM images. The spread of lower E area and blister growth with increasing immersion time, which are difficult to observe by optical method, were clarified by evaluation of the SAM images.

Key-words : Paint film, Degradation behavior, Scanning acoustic microscope, Nanoindentation

1. Introduction

Organic paint films are used to protect steel and other material surfaces from the attack of various corrosive environments. Therefore, several researches on the degradation evaluation of corrosion protective paint films by various measurements have been reported¹⁻³⁾. As a standard and simple measurement, the visual inspection by optical observation of blister and corrosion rust of the paint film is an important evaluation method. However, since the subjectivity and skill of operator affect the visual evaluation, the observations of blister interior and pigmented resin paint film/substrate interface by visual inspection are difficult.

The purpose of this study is the detection and evaluation of blister generation, growth and distribution of paint film by measurement of mechanical property and imaging. Consequently, Young's

modulus (E) and hardness (H) as the mechanical properties of paint film against immersion time were investigated by nanoindentation^{4,5)}. Furthermore, the blister growth was imaged by scanning acoustic microscope (SAM)⁶⁻⁸⁾ as a visual evaluation.

In this manner the mechanical properties were compared with the SAM images, and the meaning of SAM image was discussed. The paint film at blister was further evaluated by scanning electron microscope (SEM) and qualitative analysis.

2. Experimental procedures

2.1 Materials

2.1.1 Substrate

Cold rolled steel plates (JIS G3141 SPCC/SB, Nippon Test Panel, 70×150×0.80 mm) were used as the substrate material. Chemical composition of the steel (mass%) was C 0.08, Si trace, Mn 0.35, P 0.04, S 0.018 and Fe balance. The surface treatment by JIS K5410 was applied to the steel plates.

2.1.2 Paint

A red pigmented long oil alkyd resin paint (LAR-P) containing lead cyanide (Pb(CN)₂) and calcium carbonate as a corrosion protective pigment and filler, respectively, and a clear long oil alkyd resin paint without pigment (LAR-C) (Dai Nippon Toryo

Received July 26, 2000

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Co., Ltd.) were painted on the steel and glass plates by means of a doctor blade to desired dry paint film thickness of approximately $20\mu\text{m}$.

2.1.3 Specimen

The painted specimens were allowed to cure for one week at room temperature, and then cut to $50 \times 70 \times 0.8\text{mm}$. The cut specimens were fixed face up in a hard plastic container, and except for an area (4.52cm^2) enclosed in a plastic O-ring which served as the effective measuring area, the edges and surfaces of the specimens were sealed with a rosin-paraffin wax. The specimens were then immersed in a 3% sodium chloride (NaCl) aqueous solution at room temperature.

LAR-P on steel, LAR-P on glass, LAR-C on steel and LAR-C on glass specimens were prepared, and are abbreviated as LAR-P/Steel, LAR-P/Glass, LAR-C/Steel and LAR-C/Glass, respectively.

2.2 Measurements

2.2.1 Measurement of E and H values by nanoindentation

The E and H values were measured by nanoindentation tester (ERIONIX Co., Ltd.: ENT-1100) with Berkovich penetrator having the edge angle of 2 radian. The stability of nanoindentation was confirmed by measurement of monocrystal silicon as standard specimen before measurement of the specimen. The specimens were measured after drying at 300K for 24h. The load-displacement curves by nanoindentation are shown in **Fig. 1**. The E and H values were calculated using Eq. (1) and (2)^{4,5)}.

$$E = S\pi^{1/2}/2A^{1/2} = 0.1818 P_{\max}/(h_{\max} - h_1)h_1 \quad (1)$$

$$H = P_{\max}/A' = 37.84 P_{\max}/h_{\max}^2 \quad (2)$$

where the units of E and H are GPa and MPa, respectively, and A is the projected area of the elastic contact, A' is the projected area of contact at peak

load and S is the slope near peak load at un-loading. The $P_{\max}$ (mN), $h_{\max}$ (μm), h_1 (μm) and S (mN/ μm) are defined in Fig. 1.

2.2.2 Observation using SAM

SAM (Hitachi Kenki Co., Ltd., present name, Hitachi Kenki Fine Tech Co., Ltd.: AT-5000) was used with a 25MHz transducer for observation of paint film surface and paint film/substrate interface. Since an acoustic wave is attenuated in air at this frequency, water or oil is required as a coupler to propagate the acoustic wave into sample in actual measurement. Consequently, at the observation of SAM, the specimens were immersed in distilled water. The white and black areas in the SAM image are large and small echo intensity from specimen, respectively.

2.2.3 Cross sectional observation and qualitative analysis

The cross sectional observation and the qualitative analysis of paint film and substrate were conducted by SEM (ERIONIX Co., Ltd.: ERA-8000) with an energy dispersive X-ray spectroscopy (EDX). The element exists at each scanning position, and then the correlative position in the element mapping image becomes white.

2.2.4 Paint film thickness measurement

The paint film thickness on substrate was determined by the micrometer of $0.1\mu\text{m}$ accuracy (Nikon Co., Ltd.: DIGIMICRO MH-15M). The thickness was measured after removing of water drops on paint film, the film thickness change (TC) was calculated using Eq. (3).

$$TC = [(t_a - t_b)/t_b] \times 100 \quad (3)$$

where t_a and t_b are paint film thickness after immersion test and before the test, respectively.

3. Results and Discussion

3.1 Evaluation of mechanical property by nanoindentation

The effect of pigment existence in paint film on E and H values was investigated in further detail. The E and H values are affected by the combination of paint film and substrate. The maximum displacement, which is one tenth of paint film thickness, was $2\mu\text{m}$ in this study. **Figure 2** shows the values against immersion time. In the case of LAR-P/Steel, the values decrease before 3h, increase with increasing immersion time till 50 h, and decrease again after 50 h. In the case of LAR-C/Steel, the values increase rapidly at 30h, and the blister growth was too large to

Fig. 1 Load-displacement curves of LAR-P film on steel (un-immersed).

Fig. 2 Nanoindentation hardness and Young's modulus against immersion time.

measure by nanoindentation at approximately 2000 h.

The change of the E and H values of LAR-P/Steel and LAR-C/Steel may be explained on the basis of the process of wet-swelling and desolvation in paint film^{9,10}. The current density (i) vs. immersion time of steel coated with tar epoxy resin paint in a 100 ppm NaCl solution at room temperature has been studied¹⁰. According to this result, the i value increased with increasing immersion time because of the wet-swelling of paint film, and reached to the highest value after 24 h. After that, the i value slowly decreased with immersion time, because of the desolvation of paint film based on the strong water-tight property of the film.

Further, the E and H values of LAR-P/Steel against immersion time over about 30 h show some scatter. This scatter would be ascribed to the heterogeneous E distribution of paint film.

Since the wet-swelling and desolvation may affect paint film thickness, the TC against immersion time was also measured. The results are shown in Fig. 3. When the substrate is steel, the TC of LAR-P film against immersion time differs from that of LAR-C film. The downtrend of TC for LAR-C/Steel, and up and downtrend of TC for LAR-P/Steel are shown in this figure.

Fig. 3 Thickness change of LAR film against immersion time.

The changes of TC on steel are larger than that on glass, and the TC of LAR-P is larger than that of LAR-C. The TC of LAR-C/Glass is very small, thus, the wet-swelling and desolvation of paint film against immersion time is also small. The TC of LAR-C/Steel decreases and the TC of LAR-P/Steel increases and then decreases with increasing immersion time.

These results show that wet-swelling and desolvation are affected by pigment and substrate. Glass substrate weakly affects wet-swelling and desolvation of paint film. Steel substrate strongly affects wet-swelling and desolvation of paint film and the effects depend on pigment in paint film. Therefore, mechanical property of paint film depends on substrate and pigment, and the property changes with increasing immersion time.

Blisters were observed on all specimens after immersion test. Although, the size and distribution of blister area are affected by the mechanical property of paint film, which depends on combination of paint film and substrate, as shown in Figs. 2 and 3.

3.2 SAM observation of paint film

To observe the blister, the echo from steel where paint film is disbonded was detected, and the echo intensity was used to make SAM imaging^{7,8}.

The acoustic wave reflected from paint film is affected by surface shape, and the SAM surface image shows surface shape.

Figure 4 shows the surface images and the paint

Immersion time	SAM image		H:MPa E:GPa
	Surface image	Interface image 2mm	H:83 E:7.26
72h			(0.2%) H:73 E:6.29
144h			(1.6%) H:32 E:3.22 H:47 E:4.70
240h			(3.1%) H:34 E:3.50 H:44 E:4.39
316h			(52.6%) H:15 E:2.24

Fig. 4 Surface images and interface images of LAR-P/steel against immersion time. Percentage of blister area is described in parentheses. E means Young's modulus and H means hardness obtained by nanoindentation.

film/substrate interface image against immersion time. The value in parentheses shows blister area against observation area. The white area of the interface image shows blister. The difference of SAM image in the vicinity of the blister appears with increasing immersion time. The SAM image is affected by focal plane. The focal plane is fixed at the surface for surface image. Since the reflection time of acoustic wave from the paint film surface away from blister is equal to that in the vicinity of blister, it is considered that the undulation of paint film in the vicinity of blister is about the same as that away from blister.

The other reason is the heterogeneous E distribution. The E value relates to sound velocity¹¹⁾, and affects the acoustic impedance which is density multiplied by the sound velocity. Consequently, the E value relates to the reflection ratio of acoustic wave¹²⁾.

In addition Fig. 4 shows the E and H values by nanoindentation (maximum load: 19.6 mN) that correspond to the indicated point in the SAM image. The

Fig. 5 SAM (interface) images and optical image of LAR-P/steel against immersion time.

E and H values decrease with increasing immersion time. These values in the vicinity of blister are smaller than those from the far blister in the same sample. Therefore, the SAM image illustrates not only the blister but also the lower E area.

Figure 5 shows the blister growth and lower E area at the same area against immersion time. The blister and lower E area are not seen before immersion test, but they are seen after 48h. With increasing immersion time, new blisters appear, while old blisters grow further and connect. The lower E area also spreads and connects together with other near by lower E areas.

The blister is observed in the lower E area, but the blister is not seen in the early stage of decreasing E value. Therefore, at first lower E area appears and then the blister appears in the area. The blister can be observed optically by visual inspection, though lower E area cannot be recognized (Fig. 5). Because the amplitude of reflected acoustic wave is sensitively affected by the elastic difference, the lower E area can be observed as the difference of contrast in SAM image.

Figure 6 shows the SAM images of same immersion time. In these figures, the differences of lower E areas and blisters can be seen. In Figs. 2 and 3 stated above, mechanical properties scatter after 30h, the scatter is affected by the appearance of heterogene-

Fig. 6 SAM (interface) images of three specimens of LAR-P/Steel (immersion time : 600 h).

Fig. 7 SEM image (secondary electron image) and element mapping images by EDX of LAR-P/steel (cross section) before immersion in 3% NaCl solution.

ous E distribution. From above results, the speed of blister growth differs locally.

3.3 Dispersion of elements in cross section

SEM image and the element distributions in LAR-P film before immersion test are shown in **Fig. 7**, and the condition in the vicinity of blister after immersion test is shown in **Fig. 8**. In **Fig. 8**, iron oxide appears at the paint film/steel interface. The exfoliated space is also seen at the oxide/steel interface. The components of lead (corrosion protective pigment) and calcium (filler) in paint film disappear from the paint film in the vicinity of blister after immersion test. Furthermore, a part of the steel disappears and iron oxide is observed in and out along the paint film. It is thought that this is due to iron ion from the steel plate passing through the paint film.

Not only wet-swelling and desolvation but also the disappearance of pigment and filler affect the mechanical property of paint film, and then decrease E value and promote the blister growth.

In general, the blister of paint film is macroscopically explained by electrochemical

Fig. 8 SEM image (secondary electron image) and element mapping images by EDX of LAR-P/steel (cross section) after immersion for 1400 h in 3% NaCl solution.

technique^{7-10,13,14}). In this study, the mechanical property in the vicinity of blister, the growth of blister and the spread of lower E area against immersion time were clarified by microscopic evaluation by nanoindentation and macroscopic observation by SAM. From the above result, the paint film becomes breakable with long immersion time because of decreasing mechanical property, and the holding force of paint film/steel interface decreases because of increasing lower E area and blister. Consequently, the paint film can be peeled off by smaller force with increasing immersion time.

4. Conclusions

The degradation behavior of pigmented long oil alkyd resin painted steel in an aqueous 3% NaCl solution was investigated by nanoindentation and scanning acoustic microscope (SAM). The results are as follows.

1) The values of Young's modulus (E) and hardness (H) of the paint film by nanoindentation varied

according to the presence of pigment and the kind of substrate with increasing immersion time. The up and downtrends of E and H values against immersion time were dependent on the combinations of paint film and substrate.

2) By comparison of the E value and the SAM image in the vicinity of blisters, it was clarified that the difference of SAM image was caused by the heterogeneous E distribution. Therefore, the growth of blister and the spread of lower E area were recognized in SAM image.

3) The components of lead (corrosion protective pigment) and calcium (filler) disappeared from the paint film in the vicinity of blister after immersion test. And a part of the steel disappeared and iron oxide was observed in and out along the paint film.

4) It was observed in the SAM images that at first the lower E area appears, and then the lower E area spreads and the blister appears in the area. The degradation of paint film/substrate interface around the blister was observed to be wider than the blister area observed by visual inspection.

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ナノインデンテーション法および超音波顕微鏡による顔料入り長油性アルキド樹脂塗膜の劣化評価

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要 旨

3% NaCl 水溶液中における鋼板上の長油性アルキド樹脂 (LAR-P) の劣化挙動をナノインデンテーションおよび走査型超音波顕微鏡 (SAM) を用いて検討した。

ナノインデンテーションにより得られる LAR-P 塗膜のヤング率 (E) および硬さ (H) は短時間の浸漬で増加し、浸漬時間の増加とともに減少した。さらに、SAM 像は E 値との比較により、不均一な E 分布を示していることが明らかになった。短時間の浸漬で SAM 像に塗膜中の低 E 領域が観察され、膨れはその低 E 領域内に観察された。浸漬時間の増加にともなう低 E 領域および膨れの広がり方は、光学的な観察ではむずかしいが、SAM 像の評価により明らかになった。