On the Mechanism of the Permeation of Ions Through Paint Films

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Temperature characteristics of direct current conductivity of polyvinyl acetate and epoxy resin paint films in 3% sodium chloride solution were found to be altered markedly at the border of the glass transition temperature of paint films. As direct current conductivity of paint films in electrolytic solutions had been proved to be entirely ionic, it was concluded that ions activatedly diffuse through paint films themselves rather than through pin-holes.

Alternative current conductivity of paint films in sodium chloride solution was established to be the sum of alternative conductivity of dry films and direct current conductivity owing to the diffusion of ions. Therefore, if the difference of permeability constant of ions among many paint films is much larger than the difference of dielectric constant and loss, ionic permeability which is the measure of the anti-corrosive property of paints must be able to be estimated by the measurements of $\tan \delta$ of painted steel panels in electrolytic solution as already suggested by Okamoto, Morozumi, and Yamashina. In order to demonstrate the significance of the $\tan \delta$ method, the values of $\tan \delta$ and direct current conductivity of about thirty kinds of painted steel panels in electrolytic solutions were compared each other. It was recognized that $\tan \delta$ kept pace with direct current conductivity as far as the values of $\tan \delta$ exceeded 0.1.

Introduction

The author previously measured the self-diffusion coefficient of ions in paint films with radio-isotopes and deduced from the results that ions activatedly diffuse through paint films themselves rather than through pin-poles¹⁾.

Temperature characteristics of various physical properties of amorphous polymers are altered markedly at the border of the glass transition temperature of polymers. If the above deduction is correct, temperature characteristics of ionic permeability of films should also be affected with the glass transition of paint films. On this aspect, in the present paper, temperature characteristics of ionic permeability of paint films were measured at a range of temperature including glass transition temperature in order to verify the above deduction.

Experimental Method

As it had been already verified that direct current conductivity of paint films in electrolytic solutions is entirely ionic¹⁾, temperature characteristics of direct current conductivity of painted tin-plate panels in 3% sodium chloride solution was measured instead of the direct measurement of ionic permeability.

Unpigmented polyvinyl acetate and epoxy resin paints were examined. In the case of polyvinyl acetate, panels were coated three times at the intervals of 24 hours and then dried for 3 hours at 80°C. In the case of epoxy resin, panels were also coated three times and were dried for 10 minutes at 70°C in each time, and when the last coating was finished panels were baked for 30 minutes at 100°C.

Impedance of painted panels acquired steady values about ten days after immersion (Fig. 1-2). As the corrosion rate of tin-plate panel in sodium chloride solution is very small, deteriorations of paint films, for example blistering and peeling, did not appear, and so the values of impedance of coated panels are considered to be mainly affected with the swelling of paint films in sodium chloride solution.

Fig. 1 Frequency characteristics of impedance of the test panel painted with polyvinyl acetate in sodium chloride solution

Fig. 2 Frequency characteristics of impedance of the test panel painted with epoxy resin in sodium chloride solution

apparatus being similar to the Kuroda's one³⁾.

Results and Discussions

Considering from the experimental results in Fig. 7, polyvinyl acetate is in glassy state below 17°C, in transitional state between 17°C and 29°C, and in viscous fluid state above 29°C, and epoxy resin is in glassy below 60°C, in transitional between 60 and 71°C and in viscous fluid state above 71°C.

Temperature characteristics of direct current conductance of paint films in sodium chloride solution obviously correspond to the experimental results of thermal expansion (Fig. 5 & 6). Therefore, the deduction described at the outset was verified. When the experimental results about paint films in sodium chloride solution are compared with the ones by dilatometers about dry films, the influence of water must generally be taken into consideration, but from the results of above experiments the plasticizing

After the steady values of impedance had been acquired, temperature characteristics of conductance of panels were measured. Direct current conductance was measured by Bacon's method²⁾. Alternative current conductance was measured with the apparatus previously reported³⁾.

The experimental temperature was limited to the ranges in which the conductance of panels returned to the original value gradually when the temperature fell to room temperature from the highest one for the experiments.

Impedance of dry paint films had been measured in mercury before panels were immersed in sodium chloride solution (Fig. 3~4).

Thermal expansion of dry films was measured with dilatometers in order to determine the glass transition temperature of paint films. The capacity of dilatometers was about 20 cc and the volume of the tested films was about 11 cc. Inside diameter of the capillary tubes of dilatometers was about 2 mm. Accuracy of the measurements of temperature was 0.1°C and of the height of mercury column was 0.01 mm.

In these experiments, the velocity of raising temperature was maintained at 0.42-0.50°C/min. in the use of the

Fig. 3 Temperature characteristics of impedance of the dry test panel painted with polyvinyl acetate

Fig. 4 Temperature characteristics of impedance of the dry test panel painted with epoxy resin

Fig. 5-(1) Temperature characteristics of conductance of the test panel painted with polyvinyl acetate in sodium chloride solution (D.C.)

Fig. 5-(2) Temperature characteristics of conductance of the test panel painted with polyvinyl acetate in sodium chloride solution (A.C.)

Fig. 6 Temperature characteristics of conductance of the test panel painted with epoxy resin in sodium chloride solution

Fig. 7 Thermal expansion of polyvinyl acetate and epoxy resin paint films

action of water seemed to be slight. Herwig⁴⁾ had described the similar view.

Activation energy of direct current conductance (kcal/mol) is 16 (below 17°C), 21 (above 29°C) in the case of polyvinyl acetate, and is 6.6 (below 60°C), 18 (above 71°C) in the case of epoxy resin. But the value of activation energy in polyvinyl acetate above 29°C is not certain, because the measured values of conductance were scattered about. The value obtained below 17°C is coincident with the one reported by Herwig⁴⁾ about direct current conductivity of dry polyvinyl acetate.

Movement of ions and protons are said to be a main part of direct current conductivity of dry organic polymers^{4),5)}. Experimental results described above, can be explained consistently by the fact that activated diffusion of sodium ion and chloride ion through films is a main part of direct current conductivity of paint films in sodium chloride solution.

Meares⁶⁾ reported that activation energy (kcal/mol) of diffusion of gases through polyvinyl acetate films was 4.2-11.4 (below 17°C), 0-8.0 (between 17°C and 26°C), 5.4-16.5 (above 26°C). The results are quite similar to the ones about the direct current conductance of paint films in sodium

chloride solution, therefore, the mechanism of diffusion of gases and ions are guessed to be identical.

Mayne⁷⁾ reported that many fine isolated droplets of water had been observed by phase-contrast microscope in paint films dipped in sodium chloride solution for several hours. As long as the distribution of water droplets is not dense, probably ions can scarcely diffuse from one droplet to another through the intervening polymer, but after the long contact with water, the distribution becomes dense and ions will diffuse more easily.

Supposing we have the model like this, temperature and frequency characteristics of alternative current conductivity of paint films in sodium chloride solution must be at first almost the same as the ones of dry films and after films are in contact with water for a sufficient time the effect of direct current conductivity owing to the diffusion of ions must be appreciable.

Experimental results in Fig. 1-6 agree well with the above description. Temperature and frequency characteristics of alternative current conductance of paint films in sodium chloride solution were the sum of the characteristics of alternative current conductance of dry films and direct current conductance owing to the diffusion of ions.

Consequently, if the difference of ionic permeability constant among many paint films is much larger than the difference of dielectric constant and loss, ionic permeability which is the measure of the anti-corrosive property of paints must be able to be estimated by the measurement of $\tan \delta$ of painted steel panels in electrolytic solution as already suggested by Okamoto, Morozumi, and Yamashina⁸⁾.

Fig. 8 D.C. conductivity and $\tan \delta$ of painted steel panels in electrolytic solution

In Fig. 8 direct current conductivity and $\tan \delta$ of many painted steel panels in electrolytic solution are compared. The tested paints contain oil paints, long oil alkyd resin paints, oil modified phenol resin paints, alkyl phenol resin paints, polyvinyl chloride resin paints, epoxy resin paints, polyurethane resin paints, cumarone-indene resin paints, coal tar enamels and epoxy coal tar enamels. It was observed that $\tan \delta$ kept pace with direct current conductivity as far as the value of $\tan \delta$ exceeded 0.1. Accordingly $\tan \delta$ is qualified to be the measure of ionic permeability of paint films.

The anti-corrosive property estimated by $\tan \delta$ method has already been proved to be coincident with the results of outdoor exposure test⁹⁾ and in this paper the physical meaning of this method is demonstrated.

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