Photodegradation of Epoxy Paint Films

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Introduction

A basic cause of degradation of polymer coatings is the chemical breakdown of the organic matrix of coatings. This breakdown often occurs as a result of photo-oxidation of the polymer by the action of UV radiation. The polymer degradation in air are responsible for the loss of mechanical and other physical properties of a polymer material such as color, gloss, impact strength, adhesion, etc.. The polymer becomes brittle, cracks and holes are formed at the surface and gradually in bulk.

Epoxy paint is used extensively for corrosion resistance in various environments such as chemical fumes in chemical processing equipments, high humidity in air conditioners, and high temperature in motors, pipings, etc. That is because of its excellent adhesion, chemical resistance, high flexibility and abrasion resistance. However, it becomes rapid chalking on exterior exposure. That is the result of UV radiation as described above. The study of photodegradation of epoxy paint film will be an important key to improve its properties to be more durable.

Experiment

Two samples of epoxy paint, a white and a clear, were studied. The white epoxy base with hardener (polyamide varnish) was used as received from Kansai Paint Co.,Ltd. The clear sample was obtained by seperation of pigment from the white base using centrifugal technique. Before coating, white and clear epoxy base were mixed with hardener by the weight ratio of 4:1 (base:hardener). Both samples were coated on four 5 x 15 cm^2 - glass plates using a bar coater. The coated specimens were allowed to dry at room temperature overnight, and then at 50°C for 18 hours. Three specimens of both samples were exposed to UV radiation from xenon lamp for 82, 255, and 410 hours, respectively. The intensity of UV radiation was 17 W/m^2 measured by Solar Cell Actinometer. The FTIR spectra of coated films before and after exposure to UV radiation were performed using Fourier transform infrared spectrophotometer model JASCO FTIR-8000. The constituents of pigment separated from white epoxy base were investigated using JASCO FTIR-8000.

Results and Discussion

FTIR spectra of white and clear epoxy films were illustrated in figure 2 and 4. Both spectra showed strong absorption peaks of O-H streching at 3380 cm^{-1}, C-H streching at 2920 cm^{-1}, C-H bending at 1600, 1520 cm^{-1} and C-O bending at 1250 cm^{-1}. No peak of carbonyl group (C=O) around 1700-1800 cm^{-1} was found in these original films. The broad absorption band around 700-300 cm^{-1} of white epoxy film was resulted from the absorption of white pigment as FTIR spectrum of the separated pigment showed strong absorption bands of titanium dioxide (TiO_2, rutile) around 700-300 cm^{-1} (figure 1). Moreover, the spectrum of pigment showed absorption bands of calcium carbonate ($CaCO_3$, calcite) at 1450, 875 cm^{-1} and of aluminium hydroxide silicate ($Al_2Si_2O_5(OH)_4$, kaolinite) at 1040cm^{-1}.

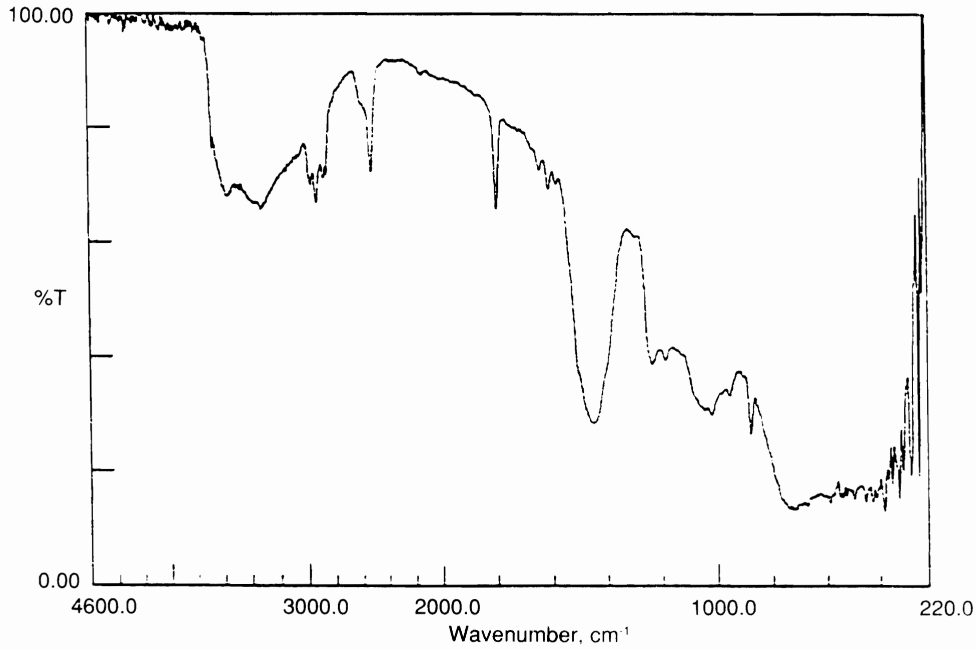


Figure 1 FTIR spectrum of white pigment in epoxy paint base

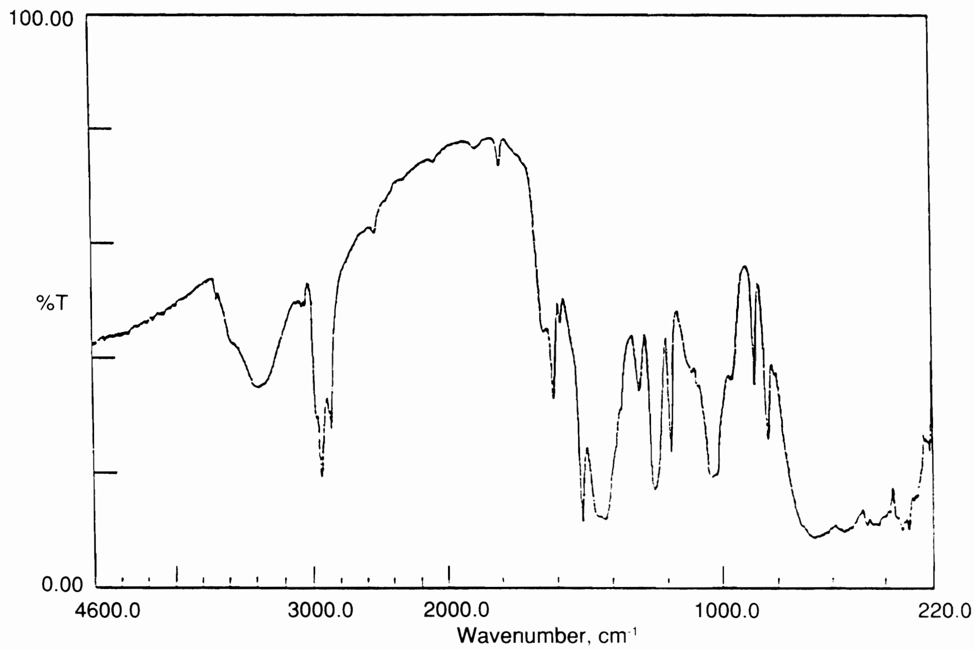


Figure 2 FTIR spectrum of white epoxy film

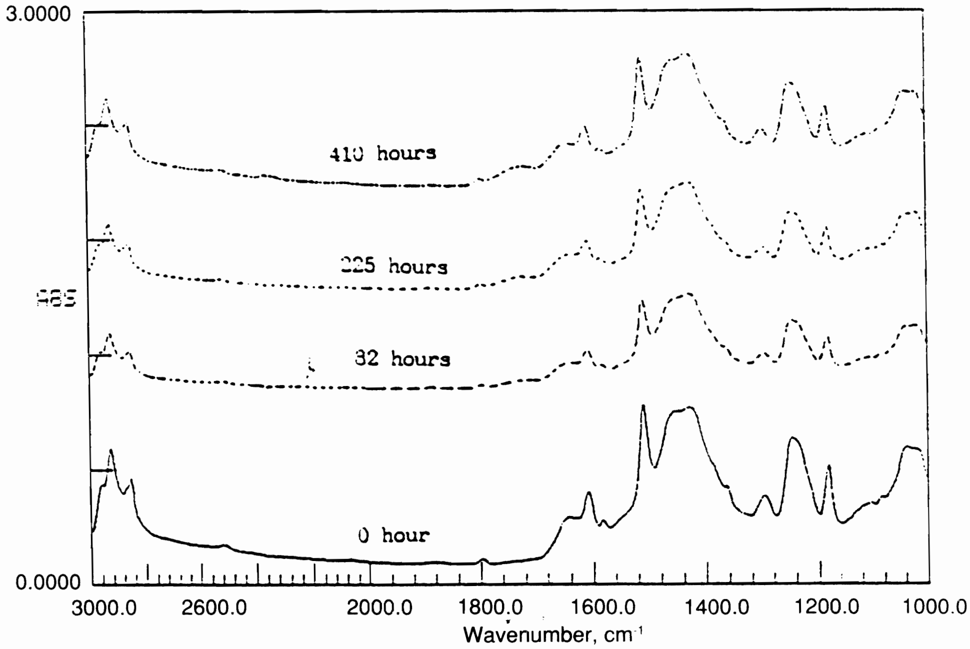


Figure 3 FTIR spectra of white epoxy films before and after exposure

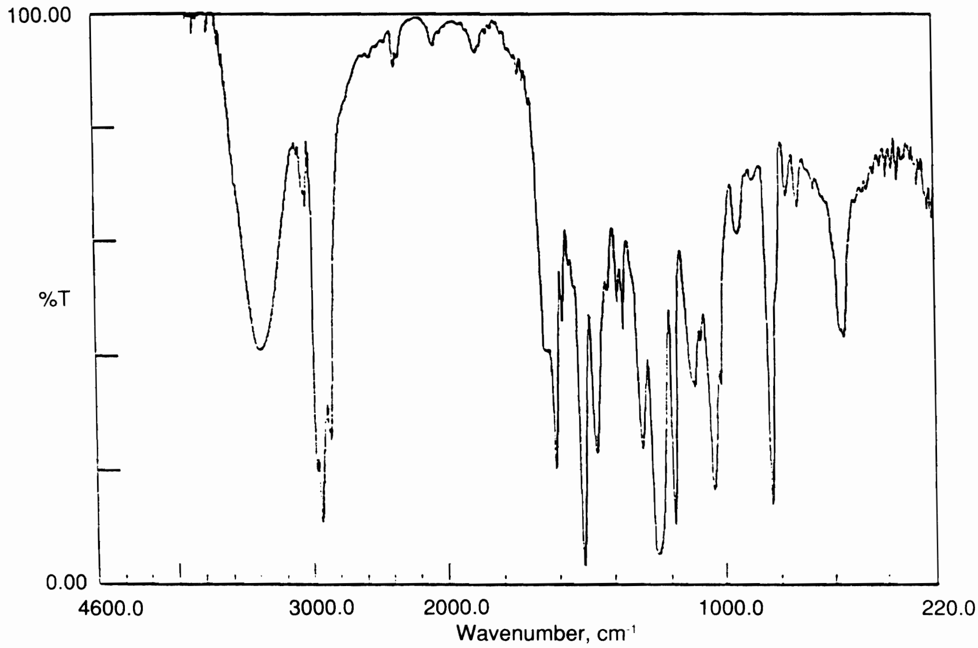


Figure 4 FTIR spectrum of clear epoxy film

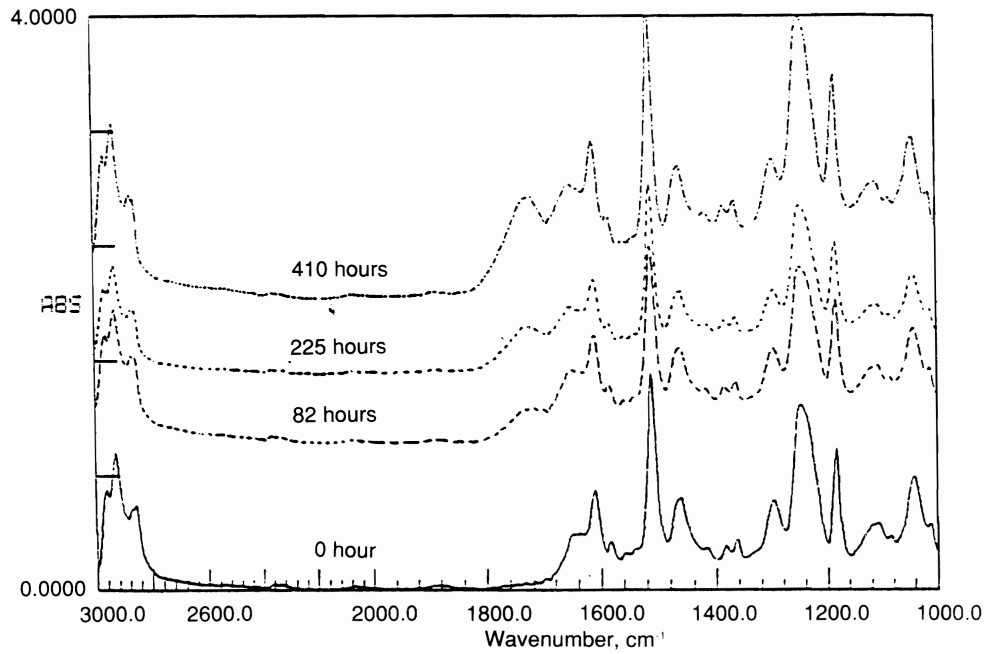


Figure 5 FTIR spectra of clear epoxy films before and after exposure

FTIR spectra of white and clear epoxy films after exposure to UV radiation for 82, 225, and 410 hours, compared with the original ones, were given in figure 3 and 5 respectively. In each spectrum, there was an absorption peak which corresponds to C=O stretching at 1724 cm^{-1}. Moreover, the increase in absorbance with the exposure time was also observed. This showed that there was a formation of carbonyl group which was generated through photochemical decomposition process during UV irradiation. The polymer photodegradation might develop by the following steps: initiation, chain propagation and termination, as shown in scheme 1.

Rates of photochemical oxidation of epoxy films were determined by monitoring the formation and the increase of absorbance of carbonyl group (I_{co}) at 1724cm^{-1} using the following expression:

$$I_{co} = \frac{\text{Absorbance at 1724 cm}^{-1}}{\text{Absorbance at 2926 cm}^{-1}}$$

The absorbance of C-H streching peak at 2926 cm^{-1} compensated for changes in film thickness. Rates of photodegradation of epoxy films were shown in figure 6. It was obvious that the rate of photodegradation of clear film was greater than that of the white one. This is largely owing to the property of UV absorbance of rutile which was found in the white pigment.

Conclusion

The irradiation of UV caused photochemical oxidation in epoxy paint films and carbonyl group was generated through the process. Rates of photodegradation could be determined by monitoring the increase of absorbance of carbonyl group at 1740 cm^{-1} in FTIR spectra. The white film was more durable to UV radiation than the clear one. This is because the property of UV absorption of rutile, white pigment in paint film.

Initiation

$$R\text{-}H \longrightarrow R^{\cdot} + H^{\cdot}$$

$$PH + O_2 \longrightarrow (PH\text{-}O_2) \xrightarrow{h\nu} (PH\text{-}O_2)^{*} \longrightarrow P^{\cdot} + HO_2^{\cdot}$$

$$2\,HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 \longrightarrow 2HO^{\cdot}$$

$$HO^{\cdot} + PH \longrightarrow P^{\cdot} + H_2O$$

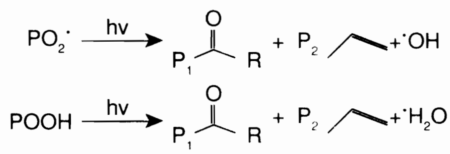
PH = polymer

RH = external low molecular weight impurities

Propagation

$$P^{\bullet} + O_2 \longrightarrow PO_2^{\bullet}$$

$$PO_2^{\bullet} + PH \longrightarrow POOH + P^{\bullet}$$



Termination

$$P^{\bullet} + P^{\bullet} \longrightarrow P\text{-}P$$

$$PO_2^{\bullet} + P^{\bullet} \longrightarrow POOP$$

$$PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow P{=}O + POH + O_2$$

Scheme 1 The photodegradation process of polymer

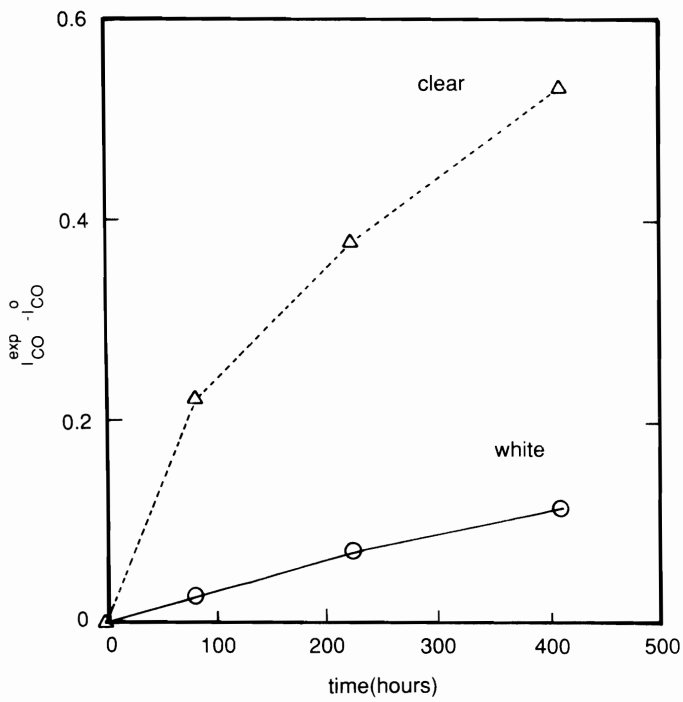


Figure 6 Rates of photodegradation of epoxy film

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