Fading Mechanism of Paint Films Composed of Insoluble Azo Pigment and Titanium Dioxide

Shingo OKAMOTO* and Hiroaki OHYA-NISHIGUCHI†
Nippon Oil & Fats Co., Ltd., Totsuka Factory, 296 Shimokurata-cho, Totsukaku, Yokohama 244
†Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606
(Received August 23, 1989)

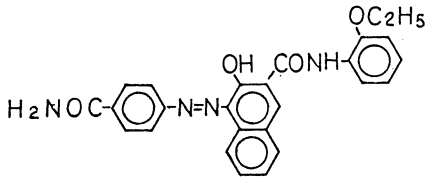
The fading mechanism of paint films comprising an insoluble azo pigment and titanium dioxide was investigated using ESR and FT-IR spectrometers and the results of outdoor exposure tests. Some paramagnetic species were found in paint films at room temperature. They showed no hyperfine structure and their g-values drastically changed according to sample preparation, the measurement temperature and treatments with a base or acid. These paramagnetic species are proposed to be O_2^- in an adsorbed state on a TiO_2 surface and O^- of the TiO_2^+. It is suggested that film fading occurs through an attack of these active oxygens on the insoluble azo pigment.

Typical paint films generally comprise various kinds of resins, hardners, and pigments. It is sometimes observed that remarkable fading in paint films occurs with special combinations of an organic pigment and an inorganic pigment of titanium dioxide under exposure to outside weather conditions. One of these combinations is an insoluble azo pigment and titanium dioxide; it is still unknown why fading occurs in this combination film, compared with that comprising only an insoluble azo pigment or titanium dioxide. Many papers concerning the photochemistry of titanium dioxide exist,[1-6] and studies[7-9] concerning the species of adsorbed oxygen on titanium dioxide by using ESR have been reported. Bickley et al.[10] studied the adsorption and exhaust process of O_2 on titanium dioxide under UV-irradiation; they showed that both holes and electrons are first formed on the titanium dioxide; then, O_2^- is generated by a reaction of the adsorbed O_2 and electrons. The chemistry of chalking on paint films containing titanium dioxide was outlined by Völz et al.[11] They detected Ti^{3+}, hydroxyl radicals and peroxides by ESR measurements and showed that UV light, water and oxygen are essential factors for the TiO_2-catalyzed degradation of the binder. On the other hand, there have been a few studies[12,13] concerning the degradation of organic pigments. Yao et al.[12] studied the degradation mechanism of an azo pigment under water.

Generally, the particles of the organic pigment aggregate with each other and behave as polymers. Their properties differ according to the degree of aggregation, even if the chemical structures are the same. It is therefore very difficult to determine the degradation process of organic pigments, and more difficult to investigate the fading mechanism of paint films comprising a combination of an organic pigment and titanium dioxide. We have studied the fading mechanism of a combination paint film by using ESR and found some paramagnetic species, the concentration of which correlates well with the fading of the paint films. In this paper we give an outline of the fading mechanism of paint films comprising an insoluble azo pigment and titanium dioxide, based on the results of ESR and FT-IR measurements. Finally, we compare these results with those from an outdoor-exposure test.

Experimental

Outdoor Exposure Test. A 60% xylene solution of an oil-free polyester resin was synthesized from isophthalic acid and other monomers. A butylated melamine resin was used as a hardner. The solid matter-ratio of the resin to the hardner (R/H) was 7/3 by weight. For the organic and inorganic pigments, an insoluble azo pigment (Pigment Red 170 Scheme 1.) and titanium dioxide JR-602 (Teikoku-kako Co., Ltd.) were used, respectively.



Scheme 1.

By using these raw materials two groups of paints for both outdoor exposure tests and ESR measurements were prepared (Table 1). In the case of paints (P-1 and P-2) the solid-matter ratio of the pigment to binder (P/B) and that of the organic pigment to titanium dioxide were 0.6/1.0 and 1.0/1.0 by wt, respectively. These pigments were dispersed as 10 μm particle into the binder using a paint conditioner. Galvanized-steel panels were coated with paints, P-1 and P-2, and were cured for 20 min at 150 °C. Painted panels (PT-1 and PT-2) with a dry-film thickness of 50 μm were exposed for 17 months at Omaezaki, Japan. Their gloss retentions and color differences were measured in order to evaluate their fading degree by using a gloss meter (Model TC-108-D, Tokyo Denshoku Co., Ltd.) and a color-difference meter (Model SM-1, Suga Weathering Technology Foundation). The gloss retention was calculated from G_1/G_0 where G_0 is

Table 1. Paint Formulations for Outdoor Exposure Test and ESR Measurement (% wt)

Constituents	Paint No.								
	P-1	P-2	EP-1	EP-2	EP-3	EP-4	EP-5	EP-6	EP-7
Resin (1)[a]	51.5	51.5	69.6	69.6	69.6	68.9	68.9	68.9	
Resin (2)[b]									76.8
Hardner (1)[c]	22.1	22.1	29.8	29.8	29.8	29.5	29.5	29.5	
Hardner (2)[d]									21.6
Organic pigment[e]	26.4	13.2		0.6	0.3	0.3	0.3	0.12	0.12
Titanium dioxide		13.2	0.6		0.3	0.3	0.3	0.48	0.48
TEA						1.0		1.0	1.0
PTS							1.0		
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

a) Oil-free polyester, 60% solution. b) Epoxy resin, 40% solution. c) Butylated melamine resin, 60% solution. d) Urea resin, 60% solution. e) Insoluble azo pigment (P.R. 170).

the specular gloss[14] of the coated panel before the outdoor exposure test, and G_1 is that after the exposure test. The color difference (ΔE) consists of three component differences: the light-index difference (ΔL) and two chromaticity differences (Δa and Δb). Here, ΔE is calculated from[15]

$$\Delta E=[(\Delta L)^2+(\Delta a)^2+(\Delta b)^2]^{1/2},$$

and

$$\Delta L=L_1-L_0,\ \Delta a=a_1-a_0,\ \Delta b=b_1-b_0.$$

where L_0, a_0, and b_0 refer to the three components of the coated panel before the outdoor exposure test; L_1, a_1, and b_1 refer to those after the exposure test.

ESR Measurements. For ESR measurements paints EP-1 to EP-7 were prepared (their combinations are also listed in Table 1). The same binder and paint R/H as those of P-1 and P-2 were used for paints EP-1 to EP-6 and epoxy resin (Epikote # 1007, Yuka Shell Co., Ltd.). For the binder, urea resin was used for paint EP-7. EP-1 contained only titanium dioxide, and EP-2 only the organic pigment; the others contained both pigments. The (P/B) of FP-1 to FP-7 was 1.0/100 by wt. The solid-matter ratios of the organic pigment to titanium dioxide of EP-3 to EP-5, and those of EP-6 and EP-7 were 1.0/1.0 and 1.0/4.0 by wt, respectively. Triethylamine (TEA) was added into EP-4, EP-6, and EP-7, and p-toluenesulfonic acid (PTS) was added into EP-5 in order to examine the effects of a base and an acid. These pigments for paints EP-1 to EP-7 were dispersed into the binders for 5 h by using a paint conditioner. The outsides of sample tubes for ESR measuments were coated with paints EP-1 to FP-7 up to 5 cm from the bottom of tubes. The coated films were cured for 20 min at 150 °C. The dry films (ES-1 to ES-7) with an averaged thickness of 30 μm were thus obtained on the tubes. The ESR spectrometer JEOL JM-FE-3X was used. Some of these films were measured under the exposure of UV light having a main wavelength of 365 nm at room temperature. Cr^{3+} doped in MgO was used as an ESR intensity standard, its g-value being 1.9800. For measurements of the FT-IR spectra JEOL JIR-100 was used. The spectra were obtained with KBr by a diffused-refraction method.

Results and Discussion

ESR Measurement. The ESR measurements of ES-1 to ES-3, made from paints EP-1 to EP-3, were carried out without UV-irradiation at room temperature. From the films of ES-1, (which comprised only titanium dioxide) and ES-2 (which comprised only organic pigment), no signal was observed, except for that due to Cr^{3+} in MgO of the standard sample. On the other hand, from some films of ES-3 comprising both pigments, either of the broad structureless signals ((A), (B), or (C) in Fig. 1) was observed with a probability of 10% of all the films of ES-3. All of the ES-3 films from which no signals were observed were analyzed by the ESR after UV-irradiation for 20 minutes at room temperature; however, signals (A) to (C) were not newly observed. To enhance the probabil-

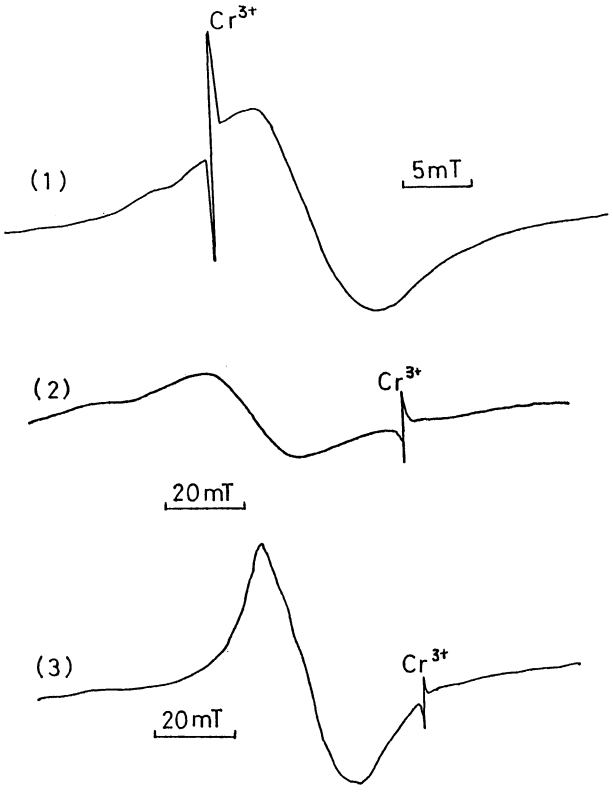


Fig. 1. ESR spectra generated from ES-3 with the organic pigment and TiO_2: (1) Signal (A), (2) Signal (B), (3) Signal (C).

ity of generating a signal among (A) to (C), the effect of TEA, PTS and an increase of the titanium dioxide content to the organic pigment were tested for films ES-4 to ES-6. Each of them independently showed some enhanced probability. Especially, in the case of the films of ES-6, the probability to generate either one of signals (A) to (C) increased from 10 to 50%.

The probability of generating signal (A) in ES-3 films was very low, and the g-value of signal (A) was 1.942 at room temperature. When a film showing signal (A) was irradiated for 30 minutes at room temperature, the g-value was drastically changed with the irradiation time, while keeping the ESR intensity constant (Fig. 2). After 30 minutes of irradiation, the g-value became 2.079 (Fig. 2-(6)); one hour after turning off the UV-light, however, it returned to 1.942, while keeping the ESR intensity constant. Signal (A) was identified as being a paramagnetic species based on Ti^{3+} with O_2 generated in titanium dioxide, its g-value ranging from 1.94 to 2.00.[16]

Signal (C) was observed in some films of ES-3 to ES-7. Its ESR intensity was extremely larger than those of signals (A) and (B). The g-value of signal (C) was 2.175 at room temperature, but the ESR shape and g-value anisotropy varied with the temperature. The change in signal (C) observed in ES-4 at temperatures from 50 °C to −140 °C is shown in Fig. 3. At 50 °C the signal was very sharp and large, without any hyperfine structure. The g-value asymmetry was

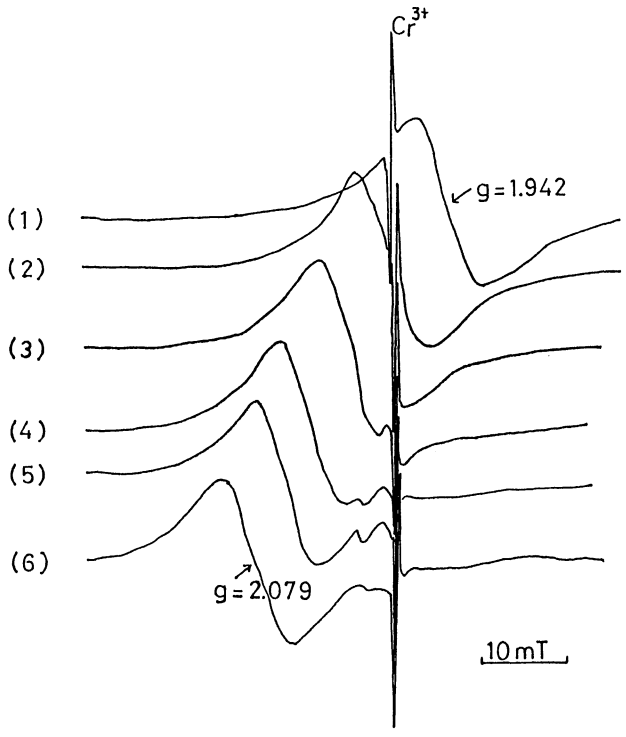


Fig. 2. Time dependences of UV-irradiation on ESR spectra of the signal (A): (1) Before irradiation, (2)—(6) After irradiation during 5 min to 30 min at room temperature.

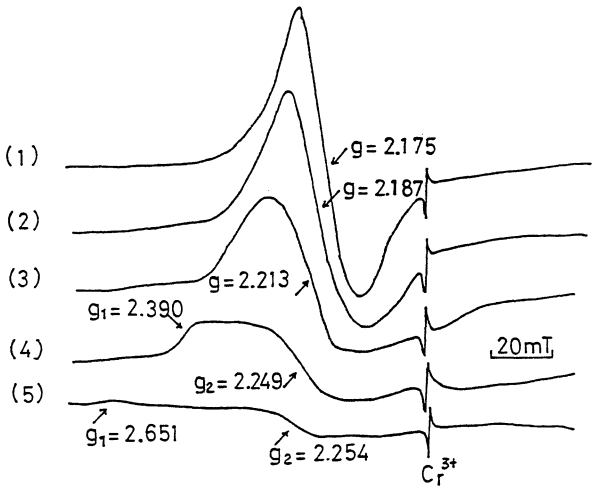


Fig. 3. Temperature dependences of the ESR spectra of the signal (C) without UV-irradiation on cooling from 50 °C to −140 °C: (1) 50 °C, (2) 0 °C, (3) −50 °C, (4) −75 °C, (5) −140 °C.

enhanced with lowering temperature: g_1=2.390 and g_2=2.249 at −75 °C, and g_1=2.651 and g_2=2.254 at −140 °C (Fig. 3). The g-value of signal (C) at room temperature did not change upon UV-irradiation. It is presumed from these results that the most probable candidate for signal (C) is the paramagnetic species of O^-,[17] or TiO_2^+ generated in titanium dioxide.

Though the ESR intensity of signal (B) was the smallest, the probability of observing it for ES-3 to ES-6 was highest among the three signals. Signals (A) and (C) generated from ES-3 to ES-6, respectively, had the same g-values and shapes at room temperature, respectively. On the contrary, the g-value and shape of signal (B) were quite variable. Moreover, signal (B) also appeared from ES-7, the binder of which was different from that of the other films. The g-value and shape of signal (B) often changed upon ESR sample preparation as well as the measurement temperature and treatments with a base or acid. As an example, these variations are shown for ES-7 in Fig. 4. Fig. 4-(1) is the result of the first measurement of ES-7 and Fig. 4-(2) is that of a second measurement one hour later. Although the measurement temperature of (2) was only 2 degrees higher than that of (1), the g-value as well as the shape of (2) were remarkably changed. After the measurement of (2), the film was dipped into ethyl alcohol for 60 seconds; it was then dried with cool air by a drier. As can be seen in Fig.4-(3), the ESR intensity after an EtOH treatment decreased with a delicately different g-value from those of (1) and (2). Fig. 4-(4) and (5) were obtained as follows:

After the measurement of (3), the sample film was dipped into a 10% solution of NaOH for 60 seconds in the case of Fig. 4-(4) and then a 10% solution of HCl for the same time in the case of Fig. 4-(5). It was then washed with pure water and dried with cool air. In

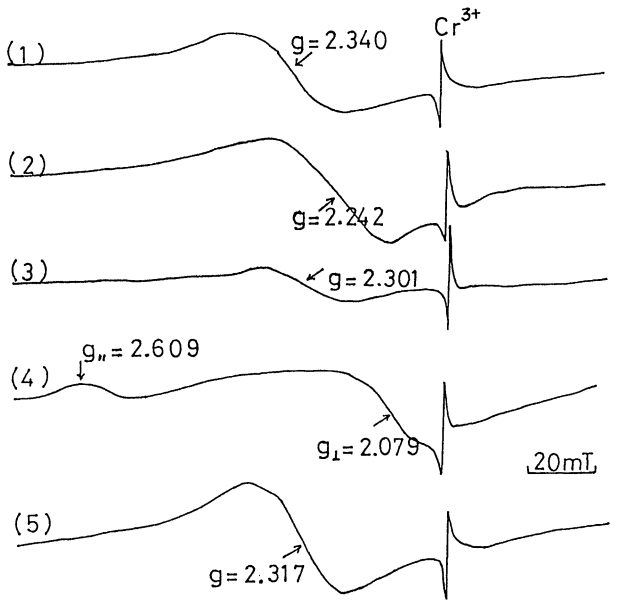


Fig. 4. ESR spectra of the signal (B) for various treatments at room temperature: (1) No treatment, (2) Measurement one hour later after measurement of (1), (3) Treatment with EtOH, (4) Treatment with NaOH, (5) Treatment with HCl.

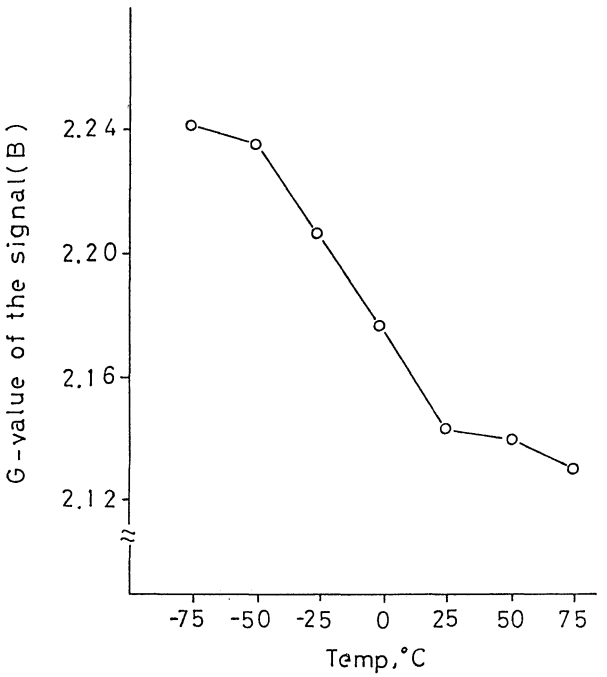


Fig. 5. Temperature dependences of the g-values of ES-7.

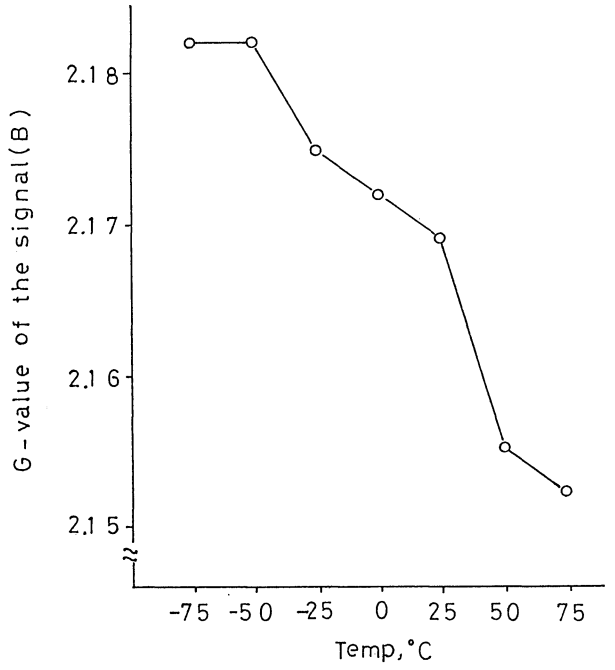


Fig. 6. Temperature dependences of the g-values of ES-6.

the case of (4), the g-values of the signals shown in Figs. 4-(1) to (3) diminished and a new signal with a $g_{\parallel}$ of 2.609 and a $g_{\perp}$ of 2.079 appeared. When the film was treated with HCl, as in the case of (5), signals similar to those shown in (1) to (3) appeared again and the g-value recovered to 2.317, almost the initial value. It is very rare to observe such a labile signal depending on the atmosphere of the sample. Therefore, it is very difficult to identify the species which produces signal (B). However, it is most probable to consider that the species comes from molecular oxygen in the air, based on the experiments described above. If the active site of Ti^{3+} on the surface couples with O_2 in air, the superoxide ion O_2^- is easily produced.[16] Treatment with NaOH increases Ti^{3+}, and O_2^- increases as the result.[18] Thus, O_2^- appeares more clearly in Fig. 4-(4) than in Figs. 4-(1) to 4-(3). On the contrary, the HCl treatment decreases O_2^- according to[18]

$$H^+ + O_2^- \longrightarrow HOO\cdot$$

and

$$2\,HOO\cdot \longrightarrow H_2O_2 + O_2. \quad (1)$$

Thus, by taking the experimental procedures described above as well as the obtained g-value into account, it is supposed that signal (B) is produced by O_2^- in the adsorbed state on the TiO_2 surface. Moreover, any hydrogen peroxide generated from the reaction described in Eq. 1 changes to the hydroxyl radical and the hydroxyl ion under Ti^{3+}, as shown in Eq. 2.[11] The hydroxyl radical appears as O^- on ESR signal in accordance with pH condition of the sample.

$$Ti^{3+} + H_2O_2 \longrightarrow Ti^{4+} + OH^- + \cdot OH. \quad (2)$$

After these treatments, the film was tested again at various temperature from −75 °C to 75 °C; the g-value shifted drastically to a small value with increasing temperature (Fig. 5). The g-value against the measurement temperature, showed the same tendency obtained from the film of ES-6 having a different binder system (polyester/butylated melamine, as

shown in Fig. 6). In Figs. 5 and 6 the g-values were reversible, showing that the g-values of signal (B) depend on measurement temperature. These results support the possibility that signal(B) is O_2^- in the adsorbed state on the TiO_2 surface. The reasons for this are as follows: There have been many papers proving the existence of O_2^- on titanium dioxide.[19-23] The asymmetric g-values of O_2^- described in these papers were smaller than those of signal(B) found in the present work; those of O_2^- found by M. Meistrich[24] were larger than those of signal (B). Thus, the g-values of signal (B) is most likely somewhere between those reported in these papers. Moreover, it has been explained by P. Kasai[25] that the g-value of O_2^- drastically changes depending on environment. It is considered from these papers that the labile O_2^- is generated in paint films.

Outdoor Exposure Test and FT-IR Measurements. —Fading Mechanism of Paint Films. Panel PT-1 comprising only insoluble azo pigment after 17 months weathering at Omaezaki had a gloss retention value of 40% with a color difference value (ΔE) of 13; panel PT-2 of the insoluble azo pigment mixed with titanium dioxide exhibited only an 18% gloss retention and a color difference value of 18. These results clearly show that the degree of degradation of PT-2 of mixed pigments is larger than that of a single pigment, PT-1. It is reasonable to consider that there exists a close correlation between the remarkable fading of panel PT-2 and the concentration of the paramagnetic species found in ES-3 to ES-7. It is assumed that these paramagnetic species are mainly produced by reactions between the organic pigment and titanium dioxide. The reasons for this are as follows:

1) These species were not generated from films containing only the organic pigment or titanium dioxide, but from those containing mixed pigments.

2) Because these species are generated in both films comprising different binders, there may be no relationships between these species and the binders added to paint films.

3) Moreover, the possibility of producing these species was increased by increasing either the titanium dioxide content in the films, or by adding TEA or PTS to the paints.

Though the UV effect is not certain at the beginning of the reaction between titanium dioxide and the organic pigment in this experiment, it is conceivable to consider that UV light takes part in the reaction, and that the addition of TEA or PTS increases the possibility of an electron-transfer between titanium dioxide and the organic pigment:

$$TiO_2 + \text{Organic pigment} \xrightarrow[(\text{TEA or PTS})]{h\nu} \begin{cases} Ti^{3+} + \text{Organic pigment}^+ \\ TiO_2^+ + \text{Organic pigments}^- \end{cases} \quad (3)$$

The Ti^{3+} or TiO_2^+ generated from equation (3), followed by reactions with O_2 in films, yields an intermediate, $Ti^{3+}\cdots O_2$, finally yielding O_2^- in the adsorbed state on the TiO_2 surface (Eq. 4).

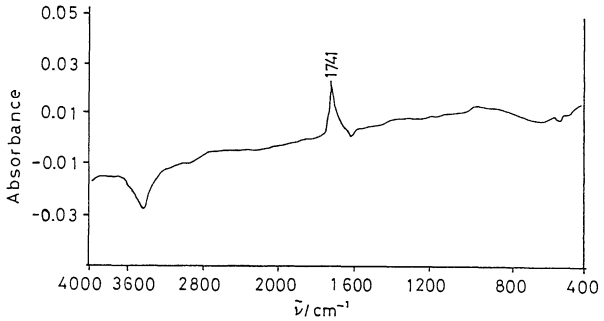


Fig. 7. Difference spectrum of FT-IR between the spectrum of the film of ES-7 with ESR signal (B) and that without ESR signal (B).

$$Ti^{3+} + O_2 \rightarrow Ti^{3+}\cdots O_2 \rightarrow [Ti^{4+}\cdots O_2^-] \quad (4)$$

The generated TiO_2^+ probably establishes equilibrium with one form of localized hole, $O^{2-}—Ti^{4+}\cdots O^-$ (Eq. 5).

$$TiO_2^+ \longleftrightarrow O^{2-} — Ti^{4+}\cdots O^- . \quad (5)$$

Thus, ESR signals (A), (B), and (C) described above probably correspond to $Ti^{3+}\cdots O_2$, $Ti^{4+}\cdots O_2^-$, and $O^{2-}—Ti^{4+}\cdots O^-$, respectively.

The difference spectrum of FT-IR was obtainted by subtracting the spectrum of the film of ES-7 without an ESR signal from that showing signal (B) (Fig. 7). In the case of the film indicating signal (B), the IR peak which corresponds to an aggregated or polymerized *o*-quinone appeared at 1741 cm^{-1} [26,27] and the peak corresponding to a polymeric hydroxyl group diminished between 3400—3600 cm^{-1}. Such behavior was also recognized in the film of ES-6 comprising a different binder. It is thus conceivable that the behavior of the difference spectrum of FT-IR was caused from a reaction between the organic pigment and titanium dioxide. J. Griffiths et at.[28-30] studied the photochemical fading of 4-arylazo-1-naphthol dye in methyl alcohol and reported that the dye was attacked by $^1O_2$ and changed to 2, 4-bis(*p*-tolylazo)-1-naphtol. In the case of O_2^- or O^-, it is reasonable to consider that first a hydrogen atom is abstracted from the hydroxyl group of the organic pigment, and then O_2 joins the phenoxyl radical generated from the pigment; at last, *o*-quinone is generated.

In the case of paint panels under outdoor exposure, the O_2^- in the adsorbed state on the TiO_2 surface and O^- originated in TiO_2^+ will attack not only the organic pigment, but also the binder; it is presumed that the remarkable fading and decreasing gloss retention occured on PT-2.

In conclusion, the reaction of an insoluble azo pigment with titanium dioxide occurs through the electron-transfer reaction; the most important factor concerning fading is thought to be the active oxygens

of O_2^- in the adsorbed state on a TiO_2 surface and O^- originating in TiO_2^+, and produced by the mechanism described above.

The authors wish to thank Prof. Noboru Hirota of the Faculty of Science, Kyoto University, for his kind advice and helpful discussions. This work was partially supported by the Grant-in-Aid for Scientific Research No. 01612005 on Priority area of "Macromolecular Complexes" from the Ministry of Education, Science and Culture.

References

1) C. W. Parmelee and A. E. Badger, *J. Am. Ceram. Soc.*, **17**, 1 (1934).
2) A. G. Vonjids and W. W. Clark, *Nature (London)*, **198**, 278 (1963).
3) A. E. Jaeobson, *Ind. Eng. Chem.*, **41**, 523 (1949).
4) D. C. Cormemeyer, *Phys. Rev.*, **113**, 1222 (1959).
5) H. F. Clay, *J. Oil Colour Chem. Assoc.*, **40**, 935 (1957).
6) R. L. Saur, *ASTM Bull.*, **207**, 61 (1955).
7) C. Naccache, P. Meriaudeau, M. Che, and A. J. Tench, *Trans. Faraday Soc.*, **67**, 506 (1971).
8) P. C. Gravelle, F. Tullet, P. Meriaudeau, and S. Tichner, *J. Piscuss. Faraday Soc.*, **52**, 140 (1971).
9) R. D. Iyenger and M. Codell, *Adv. Colloid Interface Sci.*, **3**, 365 (1972).
10) R. I. Bickley and F. S. Stone, *J. Catalysis*, **31**, 389 (1973).
11) H. G. Völz, G. Kampf, and H. G. Fitzky, *Prog. Org. Coat.*, **2**, 223 (1973/74).
12) H. C. Yao and P. Resnick, *Plastics Chem. Preprints*, **23**, (2) 486.
13) N. Kuramoto and T. Kitao, *J. Soc. Dyers Colour*, **95**, 257 (1979).
14) Annu. Book ASTM Stand, **06. 01**, 80 (1984).
15) Anna. Book ASTM Stand, **06. 01**, 394 (1984).
16) C. Dyrek and R. N. Schindler, *Z. Naturforsch.*, **32a**, 501 (1977).
17) J. R. Brailsford, J. R. Morton, and L. E. Vannotti, *J. Chem. Phys.*, **49**, 2237 (1968).
18) H. G. Völz, G. Kampf, and A. Klaeren, *Farbe+Lack*, **86**, 1047 (1980).
19) P. Meriaudeau and J. C. Vedrine, *J. Chem. Soc., Faraday, Trans. 2*, **72**, 476 (1976).
20) M. Che and A. J. Tench, *Chem. Phys. Lett.*, **18**, 199 (1973).
21) M. Che, A. J. Tench, and C. Naccache, *J. Chem. Soc., Faraday, Trans. 1*, **70**, 263 (1974).
22) R. D. Iyengar, M. Codell, H. Gisser, and J. Weisberg, *Z. Phy. Chem. Frankfurt/Main*, **89**, 325 (1974).
23) C. Naccache, *Chem. Phys. Lett.*, **11**, 323 (1971).
24) M. L. Meistrich, *J. Phys. Chem. Solids*, **29**, 1111 (1968).
25) P. H. Kasai, *J. Chem. Phys.*, **43**, 3322 (1965).
26) Marie-Louise Josien, N. Fuson, Jeanne-Marie Lebas, and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).
27) Marie-Louise Josien and N. Fuson, *Bull. Soc. Chem. Fr.*, **19**, 389 (1952).
28) J. Griffiths and C. Hawkins, *J. Chem. Soc., Chem. Commun.*, **1972**, 463.
29) J. Griffiths and C. Hawkins, *J. Chem. Soc., Parkin Trans. 2*, **1977**, 747.
30) J. Griffiths and C. Hawkins, *J. Appl. Chem. Biotechnol.*, **27**, 558 (1977).