

Physical Properties and Photocatalytic Performance of TiO_2 Coated Stainless Steel Plate

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Abstract—This research was conducted for the development of TiO_2 thin film coated stainless steel useful in environmental and sanitary fields such as removal of indoor air pollutants and prevention of harmful microorganisms in the kitchen and bathroom. For this purpose, the research was focused on the examination of physical properties of coated surfaces as well as the photocatalytic performance of the steel plates. The coated steel's cohesiveness and anti-corrosion effect were good enough to be used even in the hard environments. To test the photocatalytic performance of the TiO_2 thin film coated stainless steel plate, photodegradations of *m*-xylene, a typical air pollutant produced by automobiles, and *E. coli*, under 365 nm UV irradiation, were conducted. The TiO_2 coated stainless steel plate considerably enhanced the degradation efficiencies of *m*-xylene and *E. coli*.

Key words: Photocatalysis, Dip Coating, Stainless Steel, Cohesiveness, Corrosion, *E. coli*

INTRODUCTION

Inorganic coatings, which have been used for stainless steel and other metals, improve the chemical and physical properties of the metal surfaces relative to corrosion, friction and wear without altering the original properties of strength and toughness of the substrates [Shreir, 1976; Uhlig et al., 1985; Jones et al., 1992]. Recently, stainless steel has been recognized as a marvelous coating support due to its good wear resistance [Dai et al., 1996] and superior corrosion resistance [Atik et al., 1995; Pan et al., 1997]. Also, stainless steel has been the most widely used material in cookware, kitchen sinks, etc. Therefore, stainless steel manufacturers have tried to develop a coated product for application as an in-house construction material.

The preparation and characteristics of sol-gel films with specific chemical functions have not been sufficiently studied. TiO_2 - SiO_2 composite coating is known to prevent alkali diffusion, and chemical corrosion and oxidation of mild steel, carbon steel and stainless steel [Atik et al., 1994].

Previously, numerous studies have examined photocatalysis as a possible process for water and air treatment [Reutergardh et al., 1997]. This study evaluates not only the photocatalytic and bactericidal properties of TiO_2 - SiO_2 composite film on stainless steel, but also its proven physical characteristics, e.g., cohesiveness, flexibility and chemical resistance.

In this work, the preparation TiO_2 - SiO_2 composite film coated on stainless steel and its physical properties along with its photocatalytic behavior over *m*-xylene and *E. coli* are reported.

EXPERIMENTAL

1. Plates

Stainless steel was used for coating substrate on which TiO_2 can

be coated to form thin films. The composition (wt%) of stainless steel was 67.25 Fe, 18.55 Cr, 11.16 Ni, 2.01 Mo, 0.026 Cu, 0.15 Si and 0.028 C. Plates (100 mm 100 mm 1 mm) were mechanically cut from large foils and then degreased ultrasonically in acetone. This material was chosen because of the heat treatment necessary for the densification of the coatings. Therefore, low carbon content steel was judged more convenient since it is less susceptible to sensitization, which in turn might promote corrosion [Uhlig et al., 1985]. In addition, stainless steel is a material widely used in chemical and structural industry environments [Sedriks et al., 1979].

2. Film Preparation

TiO_2 films were coated on stainless steel (100 100 mm) using a standard dip coating process. A solution of (TiO_2 30 mole%, SiO_2 70 mole%) was prepared from a mixture of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$, absolute ethanol and glacial nitric acid as precursors, solvent and catalyst. The mixture was submitted to intense ultrasonic radiation (20 kHz) until the liquid became homogeneous and clear. The substrates were withdrawn from the solution at a constant rate of 7 cm/min and the gel films were dried at 100 °C for 3 minutes. This was followed by heat treatment in a furnace at 200, 400 and 650 °C for 30 min.

3. Characterization of the Films

The elemental composition of the film layer such as Ti, Si, O, and C was obtained by electron spectroscopy for chemical analysis (ESCA, NSAM 800 pci, Kratos Analytical). The binding energy of outer electrons was 459.2, 102.9, 531.3, and 285.2 eV for Ti, Si, O, and C, respectively. The film thickness was measured with a high-resolution digital analytical scanning electron microscope (SEM, JEOL, Japan) at a magnification of 10000.

The cohesiveness of TiO_2 coated on stainless steel plates was evaluated by a scratch tester (REVETEST/AMI, France), whose tiny diamond tip scratched a line on the surface. The amount of stress ranged from 0 to 100 Newton and the point of break-up was monitored by acoustic sensor. The flexibility of coated plates was determined by subjecting them to a bending machine (Universal Test Machine, Germany) at a specific range of angles at 90° and 180°.

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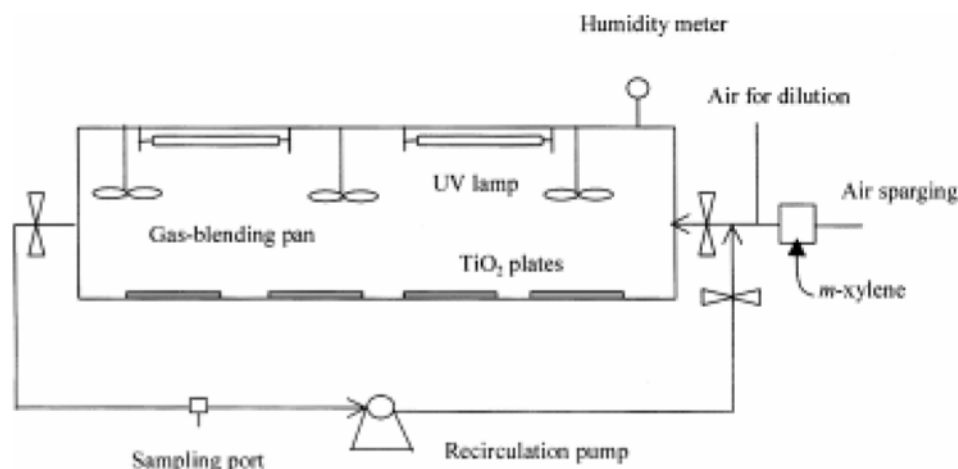


Fig. 1. Schematic diagram of photocatalytic reactor.

The coated plate was also examined following acid and alkaline exposure for corrosion resistance. The test was performed by exposing the coated plates to a 2% sulfuric acid solution and a saturated calcium hydroxide solution, maintained at a temperature of 20 °C, for 15 days.

4. Photoreactor

The batch-type photoreactor used in this study is shown in Fig. 1. The stainless steel reaction vessel (350 mm · 200 mm · 150 mm) was equipped with a UV light, temperature controller, inside fan for circulation, and mass flow controller (MFC). The UV light passed through a quartz window placed on the top cover. A heating band wrapped around the recirculation tube maintained the reaction temperature. The gaseous *m*-xylene was diluted to a nominal concentration by employing a mass flow controller (Brooks) and continuously mixed by a built-in fan. Two UV lamps (20 W, SANYO DENKI) with a wavelength 354 nm were used as a light source. Light intensity, which was measured with a Blak-Ray (UVP), was kept at 1 mW/cm² throughout the experiment.

5. Analysis of *m*-Xylene

m-Xylene was analyzed by HP 6890 Gas Chromatography as given in Table 1. Decomposed compounds of *m*-xylene were characterized by using a GC-MS (Perkin Elmer, Q-Mass 910 Mass Spectrometer).

6. Bactericidal Test

Bactericidal effect of TiO₂ coated stainless steel was performed with *E. coli* under UV illumination with various conditions. The cells were cultivated at 37 °C for 12 hrs in 10 ml of Luria-Bertani

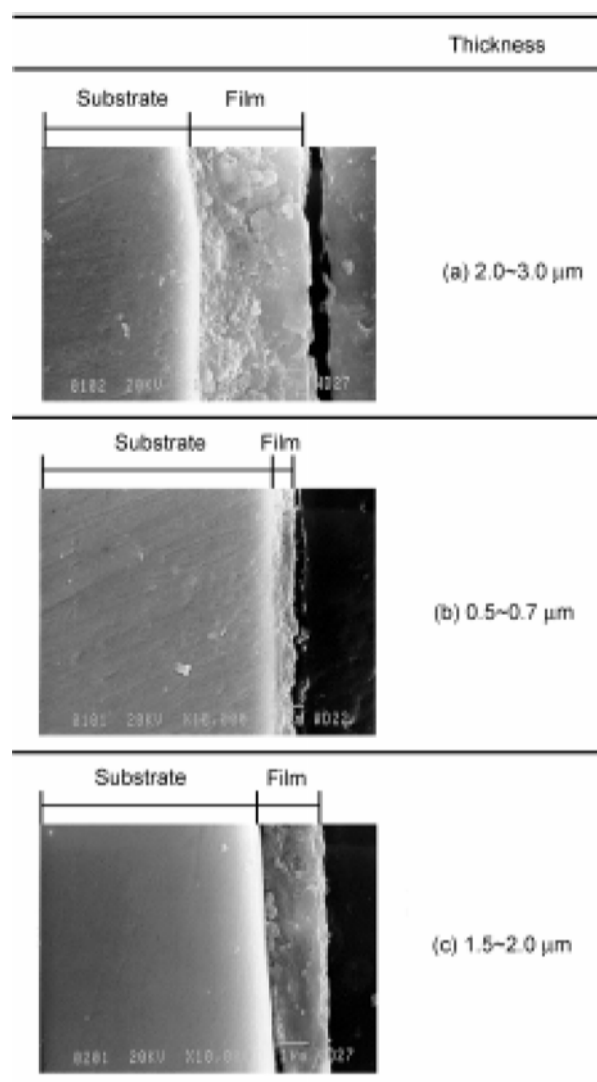


Fig. 2. Cross-sectional SEM micrograph of TiO₂ thin films deposited onto stainless steel plates and treated under the following conditions. (a) 200 °C in atmosphere, (b) 400 °C in nitrogen gas, (c) 650 °C in hydrogen gas

Table 1. The operating condition of gas analyzer (GC)

GC detector	Flame ionization detector
GC column	HP-5 5% phenyl methyl siloxane
Oven temperature	60 °C (3.5 min)
Carrier gas	N ₂ , 100 ml/min
Detector temperature	280 °C
Injection temperature	250 °C
Injection volume	250 μl
Injection mode	Splitless

(LB) medium (pH 7.0). Then, cell suspension was diluted to 10^3 or 10^6 folds with 0.8% NaCl (normal saline) solution to produce 200 viable cells per ml. The diluted suspension was applied to TiO_2 coated plates and was illuminated by 365 nm UV light. The number of viable cells in the sample was determined by membrane filter method (Standard Methods, USA). Samples were taken at specified time intervals and were filtered with cellulose-acetate filter paper (diameter, 47 mm, pore size; $0.45 \mu\text{m}$). The filter was mounted on Bacto m Endo agar Les (Difuco Company) media, incubated for 16 hours at 37°C . *E. coli* was identified by its characteristic metallic color.

RESULT AND DISCUSSION

1. Characterization of the Films

The film thickness, ranging from 0.5 to $3 \mu\text{m}$, was observed by scanning electron microscope. Variations were noted (Fig. 2) depending on the heat treatment temperature. The film heat treated at 200°C in an air environment showed the greatest thickness, which indicates that some inorganic molecules from the starting materials were sustained due to the lower heating temperature. Fig. 2(b) shows the TiO_2 film, treated in a ni-trogen environment, in thin, uniform layers on the substrate. The film treated in a hydrogen environment [Fig. 2(c)], a reductive condition, was weakly coated on the substrate. This result may be due to the different expansion and compression rates between ceramic and steel in the high-temperature heat treatment. The coverage of each molecule through TiO_2 film depth was analyzed by ESCA to determine the distribution pattern of Ti and Si, which were used as photocatalyst and binder molecules, respectively. For this experiment, TiO_2 film heat-treated at 400°C was used. The result is shown in Fig. 3.

This Figure reveals that Ti and Si molecules were uniformly distributed throughout the film depth without any molecular diffusion during heat treatment. This result implies the surface of TiO_2

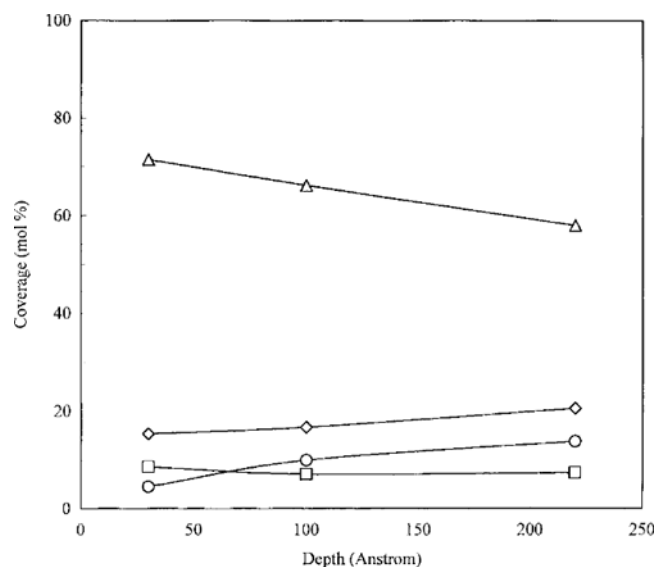


Fig. 3. Depth variable compositions of several compounds coated on the substrate.

△ titanium; □ Silicone; ▲ Oxygen; ○ Carbon (heat-treated at 450°C)

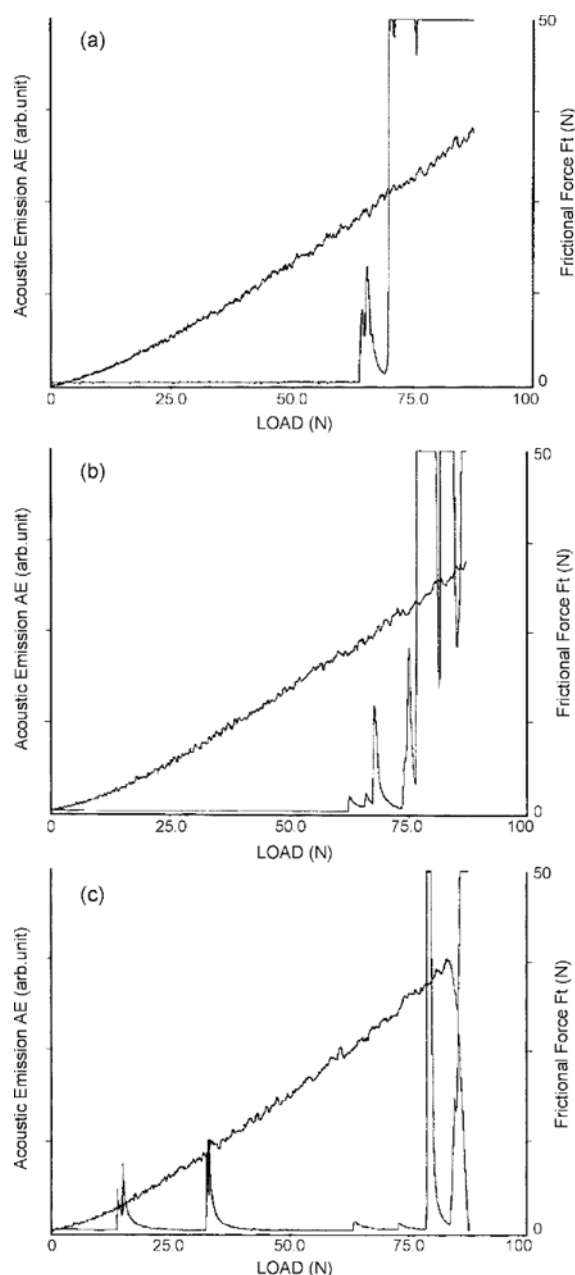


Fig. 4. Scratch tests of TiO_2 thin films deposited onto stainless steel plates treated at: (a) 200°C , (b) 400°C , (c) 650°C .

(a) breakthrough load: 62-65 N, (b) breakthrough load: 60-62 N, (c) breakthrough load: 13-30 N

coated plates can have uniform photocatalytic activity. The forced scratch test was conducted for the substrates to verify their durability against applied external stresses. Fig. 4 shows the film durability against a range of given external stresses.

The breakthrough load detected by the scratch test of the films shown in Fig. 2a and 2b was 62-65 N and 60-62 N, respectively. These results reflect that the cohesiveness of TiO_2 film coated on stainless steel under given experimental condition is extremely strong. While, as demonstrated in Fig. 2(c), the film treated at 650°C was breakable at 13-30 N. However, even this result exceeds the 9.8 N, which is the requirement of the Korean Industrial Standard (K S M

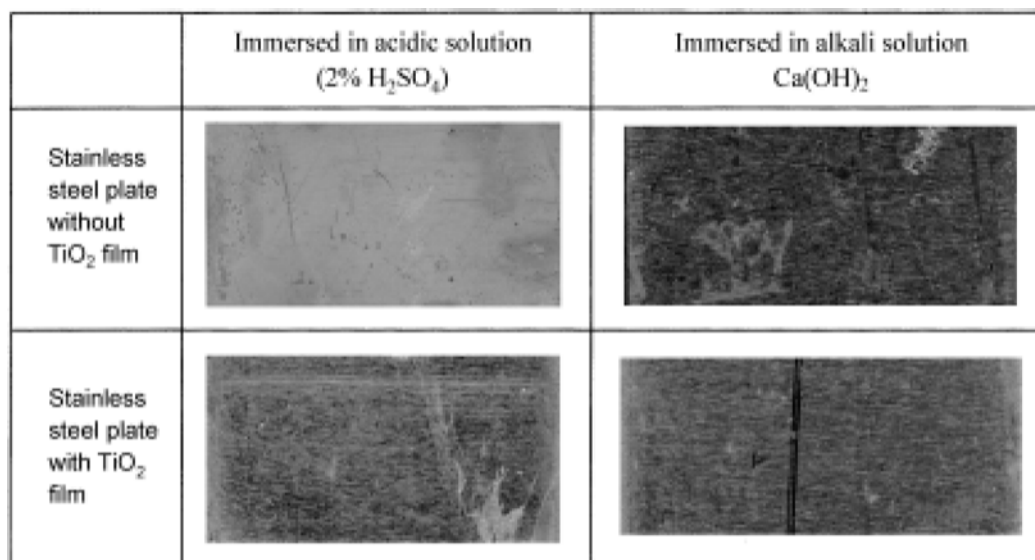


Fig. 5. Chemical resistance against pH of TiO₂ films on stainless steel plate (heat treated at 200 °C).

5981) for coating materials. These results suggest that the film coated on the stainless steel substrate would be scarcely affected by exposure to manufacturing processes, e.g., bending and twisting.

To assess the influence of TiO₂ film's protective property against chemical corrosion, the substrate was exposed to acidic and alkaline chemicals at 25 °C for 15 days. Fig. 5 shows the corresponding observations obtained in a 2% H₂SO₄ and Ca(OH)₂, while the controls were concurrently tested.

The results of Fig. 5 suggest that the coatings offer stainless steel similar protection against chemical corrosion while the control is significantly eroded. This property means steel substrate coated TiO₂ film can be useful for photocatalytic application and in strong corrosive environments.

As described earlier, *m*-xylene is one of the primary automobile emission compounds. The photocatalytic degradation of *m*-xylene by TiO₂ coated stainless steel plates (90 cm² · 4 ea) was compared with no plates by using a photoreactor assessment. The TiO₂ coating process on stainless steel was sol-gel method with SiO₂ binder. The initial concentration of *m*-xylene was 130±5 mg/l and the reaction temperature was maintained at 34±1 °C. As shown in Fig. 6(a), the control test used only UV light at 254 nm and 354 nm without stainless steel plates. The control's degradation rate of *m*-xylene was greater exposed to UV 254 nm than 354 nm. UV 254 nm has a higher energy due to the short wavelength, and therefore, it has been used for degradation of organic matter in wastewater and antimicrobial action. Both the degradation kinetics showed first-order and after 65 hr, the reaction had reached an endpoint. At this time, removal efficiency is 42% for UV 354 nm and 90% for 254 nm, respectively. Also, a degradation rate constant was shown as 0.071 day⁻¹ for UV 354 nm and 0.281 day⁻¹ for UV 254 nm. Fig. 6(b) showed the effect on *m*-xylene degradation by UV 254 nm and 354 nm illumination with TiO₂ coated stainless steel plates. When compared with the results with Fig. 6(a), *m*-xylene degradation was enhanced by UV 365 nm when the TiO₂ coated stainless steel plates were applied, while under UV 254 nm illumination, the photocatalytic effect was negligible. After 65 hours of illumination by 354 nm

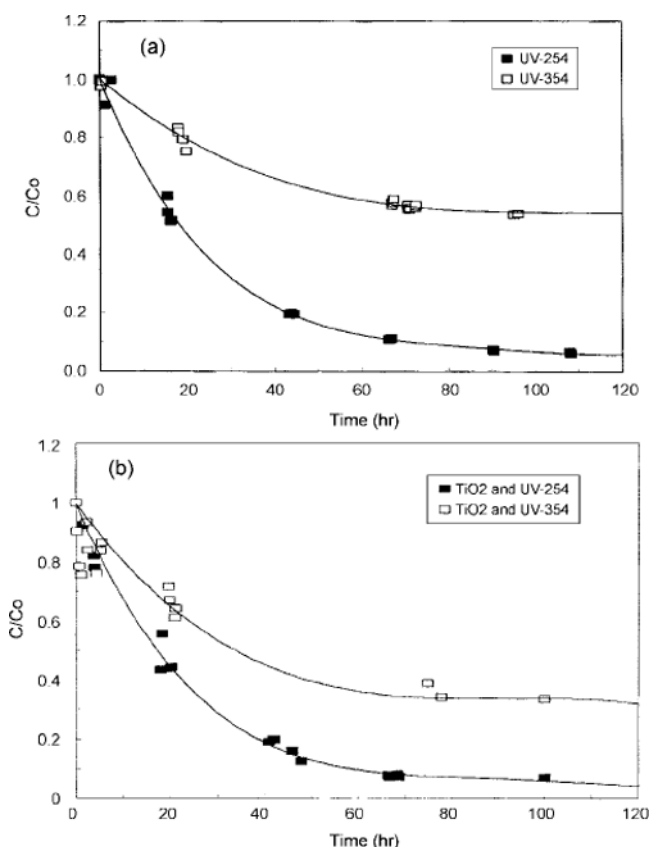


Fig. 6. Comparative decomposition of *m*-xylene: (a) UV-254 and U-354 nm illumination without plates (b) UV-254 and UV-354 nm illumination with TiO₂ coated stainless steel plates (90 cm² · 4).

(Plate: TiO₂-SiO₂ film on stainless steel treated at 200 °C, Initial *m*-xylene: 130±5 mg/l, Temperature: 34±1 °C)

with coated plates, removal efficiency of *m*-xylene was 61%; a 19% increase when compared with only UV illumination. Also, the reac-

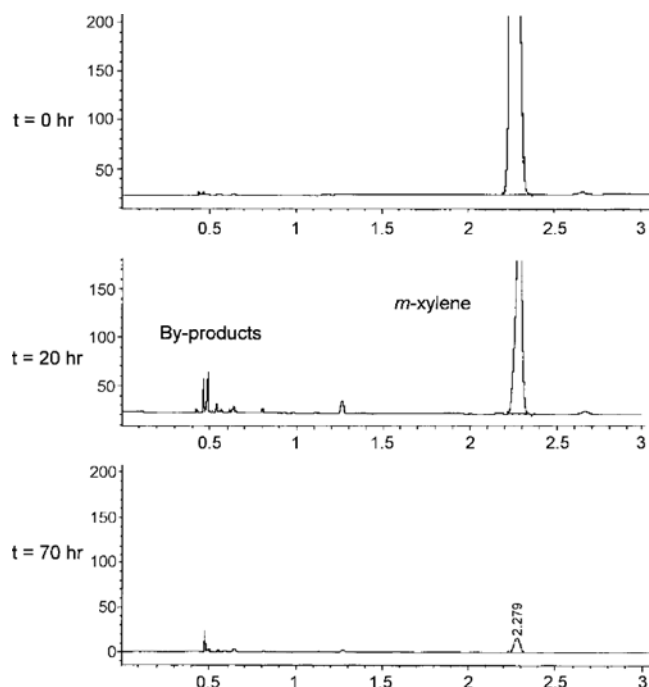


Fig. 7. Occurrence and disappearance of intermediates during the degradation of *m*-xylene.

tion rate was 0.103 day^{-1} , a 1.5 factor increase compared with that obtained from UV 365 nm illumination only.

An investigation of intermediate products from *m*-xylene degradation was performed by GC-MS analysis. The sample was exposed for 20 hours under UV 354 nm illumination with TiO_2 plates. As a result, two daughter products were identified as benzene and toluene. They might have been formed from the removal of one or two methyl groups of *m*-xylene. These compounds completely disappeared after 70 hours of further reaction, as shown in Fig. 7. Therefore, it is presumed from the above results that the first step of degradation pathway begins a methyl group removal, followed by the degradation of the aromatic ring structure into CO_2 and H_2O .

Finally, the hygienic properties of the TiO_2 film were investigated by using *E. coli* as a representative microorganism related with sanitation. Shown in Fig. 8, the bactericidal effect of *E. coli* on the TiO_2

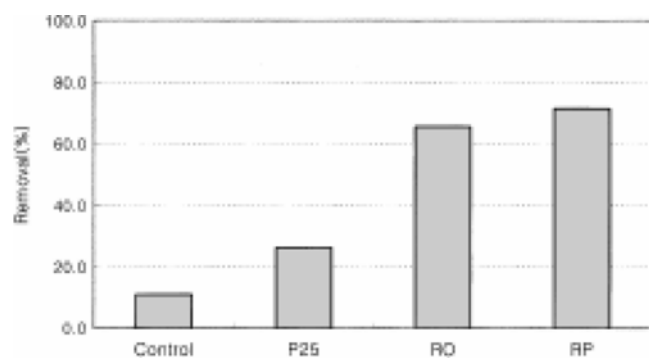


Fig. 8. Comparison of bactericidal effects of *E. coli* by TiO_2 films. Control: only UV-354 nm without any plate, P25: Coated with Degussa P25, RO: Coated with Lab-prepared TiO_2 , RP: Coated with 3% Pt doped TiO_2 .

plate under UV 354 nm illumination was remarkably increased by a factor of 6 compared to that obtained from the blank test without any plates. When platinum, known as an anti-microbial metal, was amended to TiO_2 film, similar removal efficiency was seen. However, the commercial P25 revealed a relatively lower degree of anti-microbial effect compared to the lab-prepared coatings.

The photocatalytic degradation of *E. coli* by the TiO_2 powder was investigated with variations in light intensity, applied TiO_2 concentrations, and agitation [Wel et al., 1994]. According to the results, removal of *E. coli* was enhanced when the amount of TiO_2 increased, when light intensity increased, and sufficient oxygen supply by pure oxygen or agitation. Although it is not clear, the mechanism of *E. coli* cell degradation by hydroxyl radical was discussed in several reports [Matsunaga et al., 1995; Huang et al., 2000]. Matsunaga suggested that the hydroxyl radical is a factor in the degradation of intracellular material, Coenzyme-A. Huang investigated the photocatalytic degradation of ONPG, a cell wall and membrane component of *E. coli*, and concluded that *E. coli* cell death was due to the disruption of the cell wall or cell membrane by the hydroxyl radical.

From the results of photocatalytic degradation of *m*-xylene and *E. coli* by the TiO_2 coating film on stainless steel plates, it is concluded that the film can be used for sanitary purposes in concerned markets, i.e., drinking water, food storage and kitchenware.

CONCLUSION

The property of TiO_2 film coated on stainless steel was studied with respect to physical properties, degradability of organic compounds, and bactericidal effects. The physical properties of TiO_2 film, especially for film thickness and cohesiveness were dependent on heat treatment temperature. Among studied conditions, heat treatment at 450°C showed the best performance in the two properties. Also, the film showed a resistance to corrosion in experiments where films were exposed to strong acids and alkaline chemicals for 15 days. The degradation test of *m*-xylene, an organic pollutant from automobiles, using TiO_2 stainless steel plate under UV illumination (354 nm) demonstrated an approximate 50% increase of degradation rate compared to only UV illumination. Benzene and toluene were detected by GC-Mass analysis as intermediate degradation compounds. This means that the demethylation is the initial step in the degradation of *m*-xylene. Bactericidal effects of TiO_2 film coated on stainless steel were 65% greater in removal efficiency of *E. coli* than the control. These experiments demonstrate the feasibility of using TiO_2 coated stainless steel to enhance the sanitizing effects on household surfaces, appliances, water-storage tanks, etc.

REFERENCES

- Atik, A. and Zarzycki, J., "Protective TiO_2 - SiO_2 Coatings on Stainless-Steel Sheets Prepared by Dip-Coating," *J. Mat. Sci. Lett.*, **13**, 1301 (1994).
- Atik, M. et al., "Sol-gel TiO_2 - SiO_2 Films as Protective Coatings Against Corrosion of 316 L Stainless-Steel in H_2SO_4 Solutions," *J. Appl. Electrochem.*, **25**, 142 (1995).
- Dai, W. W. et al., "Wear Mechanism of Plasma-Sprayed TiO_2 Coating Against Stainless Steel," *Wear*, **196**, 238 (1996).

- Huang, Z. et al., "Bactericidal Mode of Titanium Dioxide Photocatalysis," *J. Photochem. Photobiol.*, **130**, 163 (2000).
- Jones, D. A., "Principles and Prevention of Corrosion," Maxwell-MacMillan, USA (1992).
- Matsunaga, T. et al., "Photoelectrochemical Sterilization of Microbial Cells by Semiconductor Powders," *FEMS Microbiol. Lett.*, **29**, 211 (1985).
- Pan, J. et al., "Corrosion Resistance for Biomaterial Applications of TiO₂ Films Deposited on Titanium and Stainless Steel by Ion-Beam-Assisted Sputtering," *J. Biomed. Mat. Res.*, **35**, 309 (1997).
- Reutergardh, L. B. and Iangphasuk, M., "Photocatalytic Decolourization of Reactive Azo Dye: A Comparison Between TiO₂ and CdS Photocatalysis," *Chemosphere*, **35**, 585 (1997).
- Sedriks, A. J., "Corrosion of Stainless Steels," J. Wiley & Sons, New York (1979).
- Shreir, L. L., "Corrosion, Vol. 2," Newnes-Butterworths, USA (1976).
- Uhlig, H. H. and Revie, R. W., "Corrosion and Corrosion Control," J. Wiley & Sons, New York (1985).
- Wel, C. et al., "Bactericidal Activity of TiO₂ Photocatalyst in Aqueous-Media-Toward a Solar-Assisted Water Disinfection System," *Environ. Sci. Technol.*, **28**, 934 (1994).