

# Application of TiO<sub>2</sub> for Self Cleaning in Water Based Paint with Polyethylene Glycol (PEG) as Dispersant

Nining Kusmahetingsih<sup>a</sup>, Dyah Sawitri<sup>b</sup>

Departement of Engineering Physics, Faculty of Industrial Engineering, Sepuluh Nopember Institute of Technology,  
Kampus ITS Keputih-Sukolilo Surabaya 60111INDONESIA  
E-mail : niningf43@gmail.com<sup>a</sup> , joe@ep.its.ac.id<sup>b</sup>

## Abstract :

TiO<sub>2</sub> anatase and rutile having composition of 1%, 1.5%, and 2 % have been applied as a self-cleaning in water based paint containing dispersant polyethylene glycol (PEG) with molecular weight of 6000. Anatase TiO<sub>2</sub> is used for self-cleaning and rutile TiO<sub>2</sub> for ultraviolet protection. Mud and dye were used as pollutant for self cleaning test. Atomic Force Microscopy (AFM) was employed for evaluating TiO<sub>2</sub> distribution. Image J was used to calculate area of pollutant and distribution of TiO<sub>2</sub>. The results show that 2% TiO<sub>2</sub> with ratio of anatase : rutile 90:10 has the minimum pollutant area indicating the best self cleaning properties. FTIR characterizations show absorbance peak at 1080 cm<sup>-1</sup> wave numbers indicating characteristic peaks of PEG. The increase of peaks at around that wave number indicates maximum TiO<sub>2</sub> aggregation. It was found that 2% TiO<sub>2</sub> with ratio of anatase : rutile 90:10 has the minimum peak at that particular wave number. The AFM image for this composition shows that aggregate distribution of TiO<sub>2</sub> in the film paints are more homogenous compare with other samples leading to an improved self cleaning properties.

**Keywords:** anatase, PEG, rutile, self cleaning, TiO<sub>2</sub>

## 1. Introduction

Paint is mostly used to cover a surface of building as decorative. Environmental pollution like dust, mud, and bacteria could make the surface become dirty. Therefore, paint with self cleaning properties is required to solve those problems.

TiO<sub>2</sub> has been known for its photocatalyst and also hydrophilic properties, which provide self cleaning coating. A self-cleaning coating of photocatalytic TiO<sub>2</sub> is used for photodegradation of organic compounds into CO<sub>2</sub> and H<sub>2</sub>O with UV irradiation. Hydrophilic surface allows dirt or stain to be easily washed away with water. But, photocatalytic activity in paint comprising organic binder is considered undesirable [1]. Photocatalytic activity can oxidize the organic binder which may result in flaking of the paint film [2]. TiO<sub>2</sub> anatase and rutile were used in this research to give self cleaning properties in paint without causing the film to flake too fast. Anatase crystal was used as photocatalytic effect for self cleaning application and rutile crystal was used as an UV stabilizing to protect the organic binder [1].

TiO<sub>2</sub> catalyst is generally in the powder form, so it tends to aggregate in suspension and decrease its photocatalytic activity. Recently, previous studies investigated polyethylene glycol (PEG) was used to stabilize nano-TiO<sub>2</sub> in aqueous suspension [3]. In this research, PEG will be added to reduce the aggregation of TiO<sub>2</sub> in paint, in such a way it can improve photocatalytic activity and hydrophilic properties of catalyst that could work in self cleaning application.

## 2. Material and Methods

Nano-TiO<sub>2</sub> used in this research was Degussa P25 consisting of anatase and rutile crystal. The PEG with average relative molecular mass of 6000, distilled water, and white water based paint were used in the experiments. Table 1 shows the composition of TiO<sub>2</sub> and the ratio of anatase : rutile.

The first step of preparation was making a suspension of TiO<sub>2</sub> and distilled water with composition anatase : rutile based on table 1. Then, the suspension was mixed using magnetic stirrer for 2 hours at 50°C. After that PEG 6000 with mass four times of TiO<sub>2</sub> catalyst weight was added. Finally the suspension was mixed again using magnetic stirrer for 15 minutes at 60°C. The water based paint modified with nano-TiO<sub>2</sub> was mixed for 2 hours using mixer. The variations of TiO<sub>2</sub> suspension are 1%, 1.5%, and 2% from the paint weight.

Characterizations of this research are XRD, FTIR, AFM, and SEM. X-ray Diffraction (XRD) Phillips X'Pert MPD using Cu-K $\alpha$  radiation (wavelength of 1.5418 Å) was used to determine the crystalline phase of TiO<sub>2</sub>. The chemical interaction between PEG and TiO<sub>2</sub> was determined using Fourier Transform Infrared (FTIR) thermo scientific nicolet iS10 type. NEOS N8 Atomic Force Microscope (AFM) was used to observe the TiO<sub>2</sub> distribution in the dried paint films. Aggregate size of TiO<sub>2</sub> was evaluated using Scanning Electron Microscope (SEM) ZEISS EVO<sup>®</sup> MA 10 equipped with Brücker Quantax Energy Dispersive X-ray (EDX).

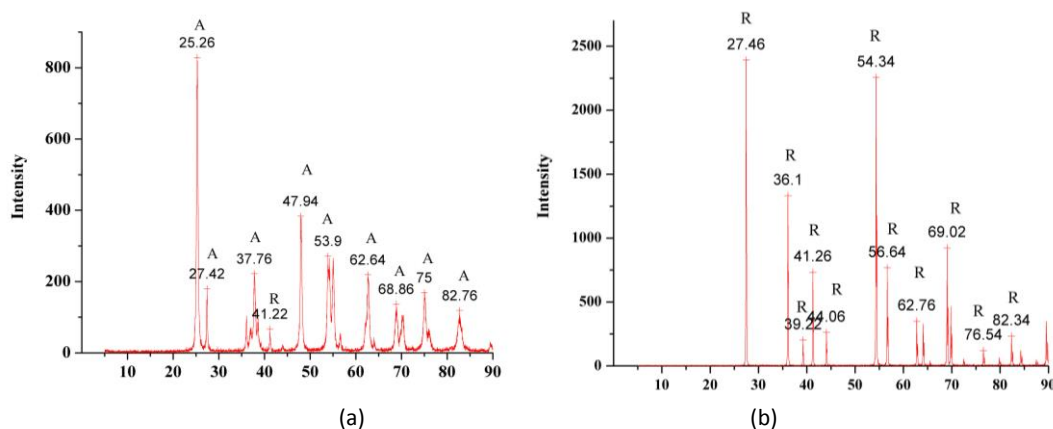
For self cleaning test, water based paint modified with nano-TiO<sub>2</sub> is coated in asbestos board with dimensions 10 x 10 cm<sup>2</sup>. In this test, mud and dye were used as pollutant. The samples were exposed to UV irradiation from sunlight for 40 hours. The images of the samples were captured every 10 hours. Image processing by using software ImageJ (from National Institute of Health (NIH), USA) was used to characterize self cleaning properties of each sample.

**Table 1.** Concentration of TiO<sub>2</sub>

No.	TiO <sub>2</sub> (%)	Anatase : Rutile
1	1	10 : 90
2	1	50 : 50
3	1	90 : 10
4	1.5	10 : 90
5	1.5	50 : 50
6	1.5	90 : 10
7	2	10 : 90
8	2	50 : 50
9	2	90 : 10
10	Water based paint	-

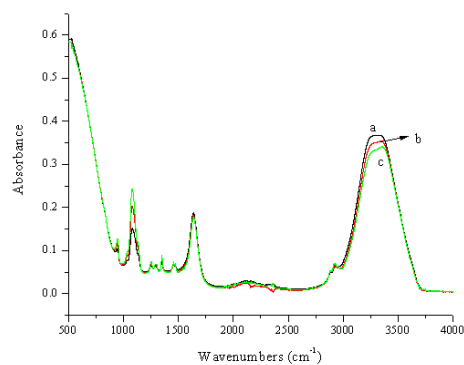
### 3. Result and Discussion.

The results of XRD characterization are shown in Figure 1. From Figure 1 (a), it could be known that almost all of the crystal type is anatase (marked with A). Peaks of TiO<sub>2</sub> anatase are shown at 2 $\theta$  = 25.26 ; 37.76 ; 47.94 ; 53.9 ; and 62.64. Figure 1 (b) shows peaks at 2 $\theta$  = 27.46; 36.10; 44.06; 54.34; and 56.64 that indicate the rutile crystalline phase of TiO<sub>2</sub> (marked with R).



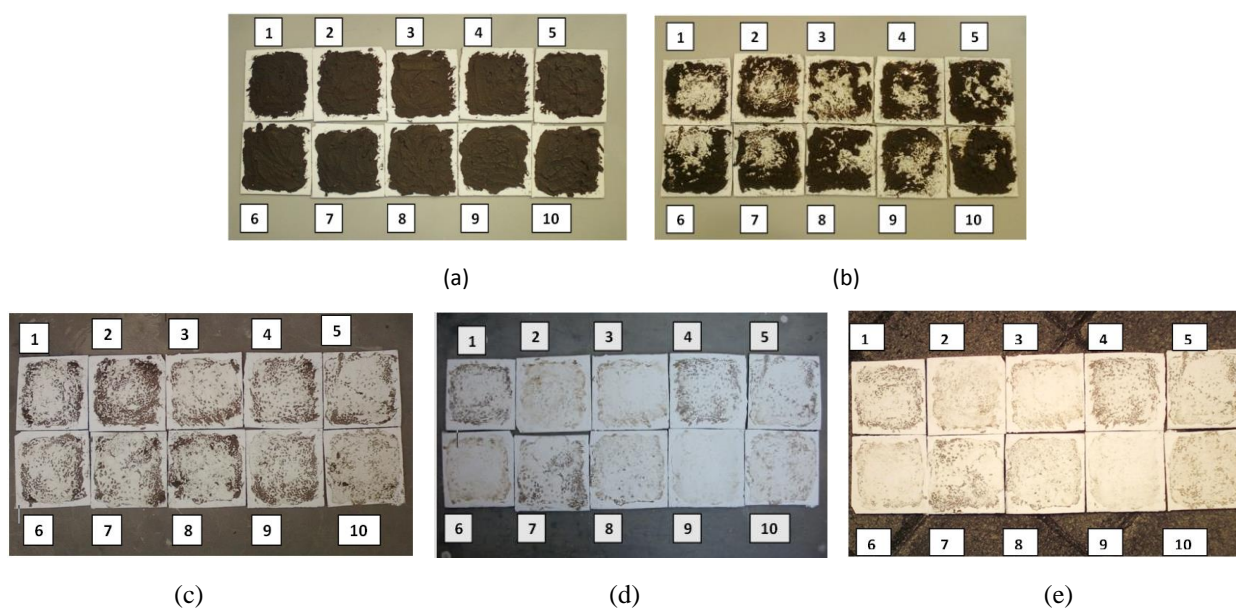
**Figure 1.** XRD result of nano-TiO<sub>2</sub> Degussa P25 a) anatase, b) rutile

Figure 2 illustrates the FTIR characterization of suspension nano-TiO<sub>2</sub>/ PEG 6000. Figure 3, there are peaks at 3000-3500 cm<sup>-1</sup> wave numbers indicates hydroxyl (OH) and 1600 cm<sup>-1</sup> wave numbers indicating H-O-H bond. On the other hand, peaks at around 1080 cm<sup>-1</sup> wave numbers indicates the characteristic peaks of PEG were found in all samples [3].

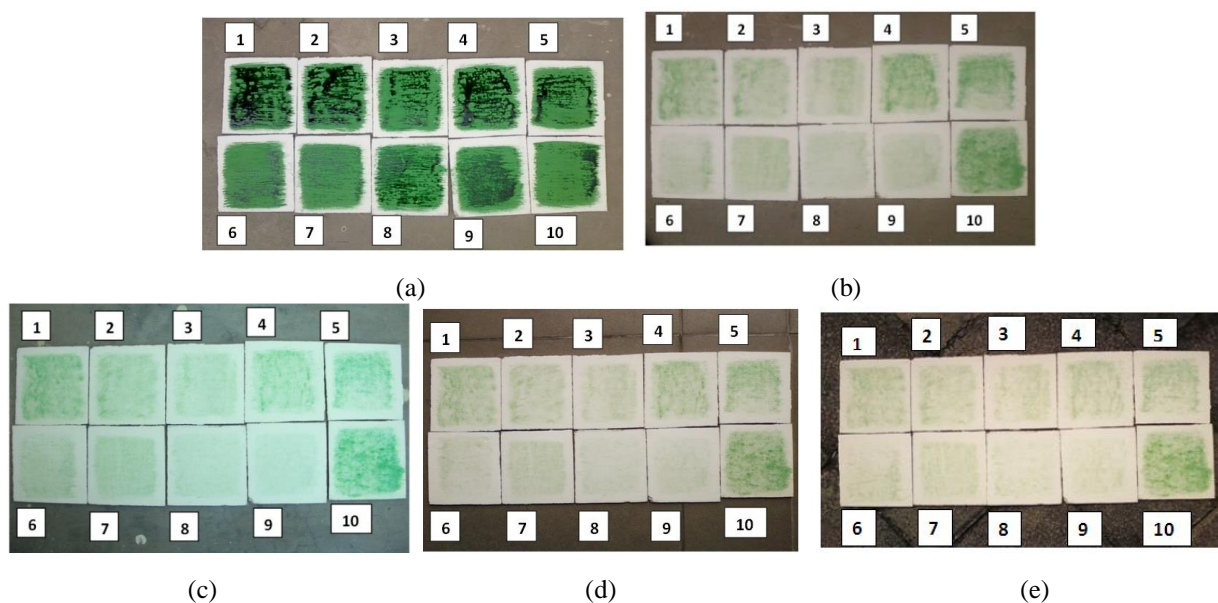


**Figure 2.** FTIR spectra of suspension nano-TiO<sub>2</sub>/PEG 6000 with ratio anatase : rutile 10:90, a) TiO<sub>2</sub> 1%, b) TiO<sub>2</sub> 1.5%, c) TiO<sub>2</sub> 2%

The results of self cleaning test with mud pollutant are shown in Figure 3.



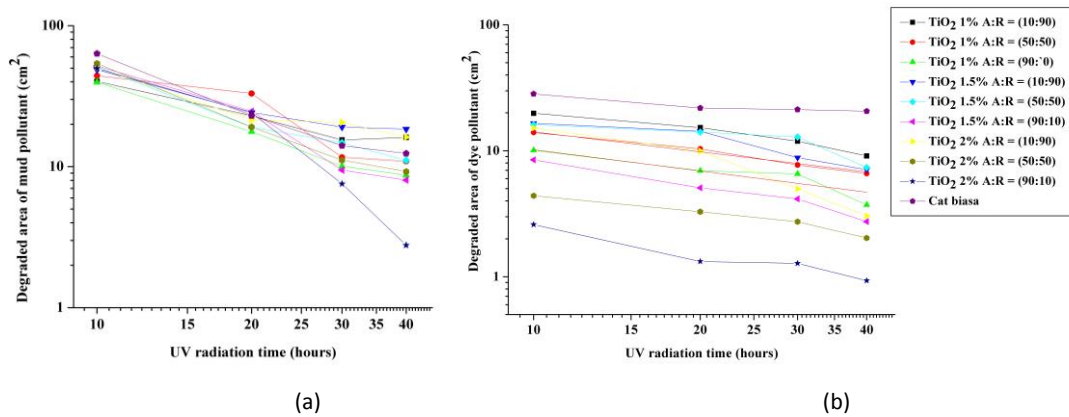
**Figure 3.** Self cleaning test with mud pollutant, a) 0 hour, b) 10 hours, c) 20 hours, d) 30 hours, e) 40 hours; number 1 to 10 indicate sample condition as listed in Table 1



**Figure 4.** Self cleaning test with dye pollutant, a) 0 hour, b) 10 hours, c) 20 hours, d) 30 hours, e) 40 hours, number 1 to 10 indicate sample condition as listed in Table 1

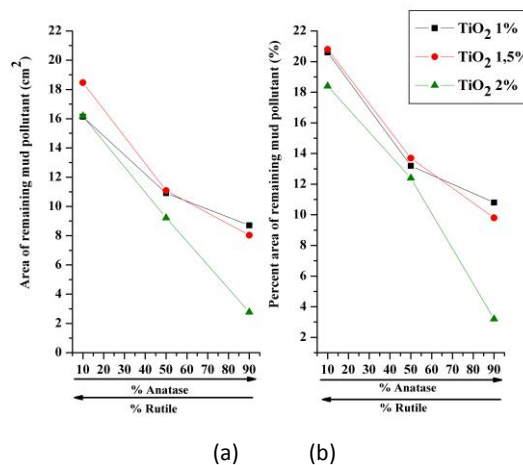
From Figure 3 it is seen that the mud pollutants are gradually decreased as the UV radiation time is prolonged. The results of self cleaning test with dye pollutant are shown in Figure 4. Similar to the previous test, it is seen that the dye pollutants are gradually decreased with increasing UV radiation time.

Figure 3 (e) and Figure 4 (e) were image processed using ImageJ. The results of image processing give information about area of remaining pollutant and percent of remaining pollutant. The results were summarized and displayed in Figure 5 for mud and dye pollutant, respectively.



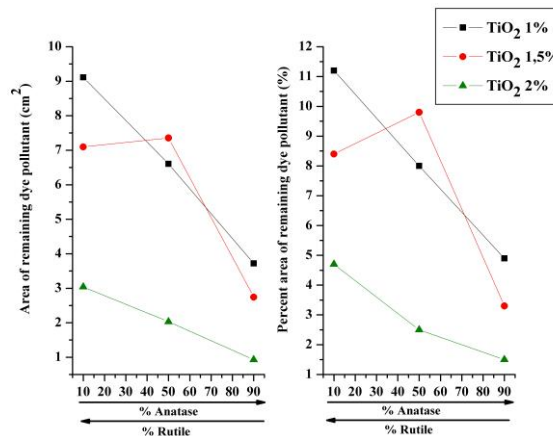
**Figure 5.** The influence of UV radiation time to pollutant degradation, a) mud pollutant, b) dye pollutant

From Figure 5 it can be seen that area of pollutant decreases by adding UV radiation time. This results show that the longer radiation process in the surface of TiO<sub>2</sub>, the more photon energy was absorbed [4]. It means that the more radical hydroxyl and hole interacted with pollutant at the surface [4]. Photocatalyst activity to pollutant degradation reaches optimum condition when UV radiation for 40 hours. It could degrade 96.8% and 98.5% for mud and dye pollutants, respectively.



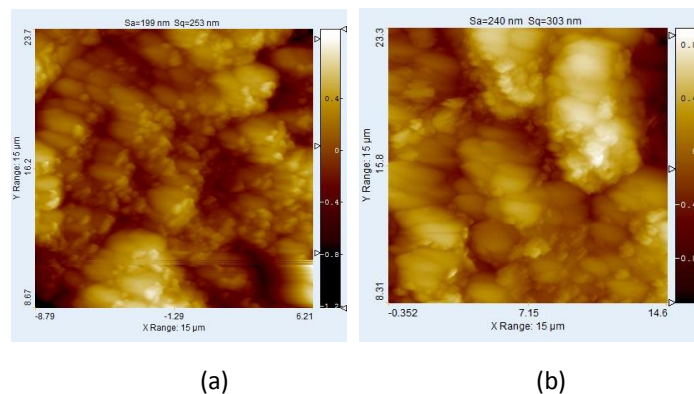
**Figure 6.** Results of image processing for self cleaning test with mud pollutant for 40 hours UV radiation, a) Area of remaining mud pollutant, b) Percent area of remaining mud pollutant

Figure 6 and Figure 7 shows that TiO<sub>2</sub> 2 % with ratio of anatase : rutile 90 :10 has the minimum area and percent area of remaining pollutant. It means that this composition, TiO<sub>2</sub> catalyst can perform self cleaning properties better than other samples.



**Figure 7.** Results of image processing for self cleaning test with mud pollutant for 40 hours UV radiation, a) Area of remaining mud pollutant, b) Percent area of remaining mud pollutant

The surface morphology of TiO<sub>2</sub> 1% with ratio anatase : rutile 50 : 50 and TiO<sub>2</sub> 2% with ratio anatase: rutile 90 :10 are taken using AFM in phase imaging mode and shown in Figure 8.



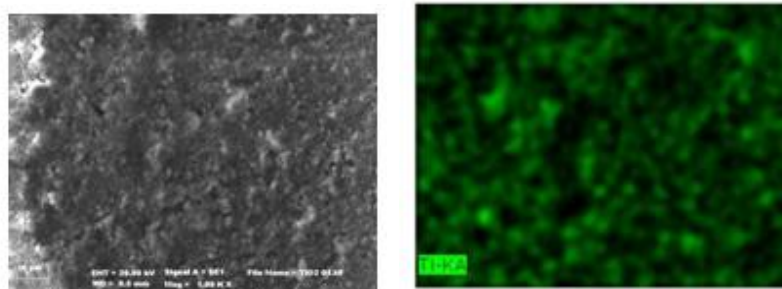
**Figure 8.** AFM image a) TiO<sub>2</sub> 1% with ratio anatase : rutile 50:50, b) TiO<sub>2</sub> 2% with ratio anatase : rutile 90:10

As shown in Figure 8, the surface morphology reveals the nano-crystalline TiO<sub>2</sub> grains [5]. Area, average size, and percent area of TiO<sub>2</sub> is summarized in Table 2. From the data, it is found that the TiO<sub>2</sub> grains at composition TiO<sub>2</sub> 2% with ratio anatase: rutile 90 :10 has smaller size compare to other samples.

**Table 2.** The results of image processing for AFM test

No.	TiO <sub>2</sub> (%)	Anatase : Rutile	Area of TiO <sub>2</sub> (cm <sup>2</sup> )	Average Size (cm <sup>2</sup> )	Percent Area of TiO <sub>2</sub> (cm <sup>2</sup> )
1	1	50:50	117.19	0.215	52.2
2	2	90:10	120.68	0.112	53.8

In order to corroborate the AFM results, the samples have been investigated by SEM. The dispersion of TiO<sub>2</sub> in sample containing TiO<sub>2</sub> 2% with ratio anatase: rutile 90 : 10 was studied using SEM-EDX. The secondary electron images as well as the respective EDX results are shown in Figure 9. It is clear that TiO<sub>2</sub> particles are dispersed homogenously throughout the sample. Such distribution is advantageous in enhancing the self cleaning properties. These results are in agreement with earlier findings that the decreasing of TiO<sub>2</sub> aggregates in samples containing adequate PEG is caused by PEG ability to form surface barrier thereby the Ti particles agglomeration are reduced [6].



(a)

(b)

Figure 9. SEM Image of TiO<sub>2</sub> 2% with ratio anatase : rutile 90:10, a) SEM image, b) EDX image

#### 4. Conclusion

The application of TiO<sub>2</sub> in water based paint with PEG dispersant has been done studied and some conclusions can be drawn as follows:

1. Nano- TiO<sub>2</sub> applied to water based paint, results in paint self cleaning properties.
2. Best self cleaning properties were obtained for 40 hours radiation time sample containing TiO<sub>2</sub> 2% with ratio anatase: rutile 90:10 with 96.8% mud pollutant and 98.5% dye pollutant being degraded.

#### Acknowledgement

The author would like to thank to Directorate General of Higher Education for funding this research through student creativity program 2012

#### References

- [1] Burgess K.D. Self Cleaning Titania-Polyurethane Composites. 2007. Faculty of Graduates Studies, The University of Western Ontario, London.
- [2] Hillebrandt Poulsen, et al. 2010. Self Cleaning Coating Composition. *International Application Published under The Patent Cooperation Treaty*. PCT WO 2010/269997 A1.
- [3] PENG Bing, et al. 2007. Influence of polymer dispersants on dispersion stability of nano-TiO<sub>2</sub> aqueous suspension and its application in inner wall latex paint. *J. Cent. South Univ. Technol.* 04-0490-06 DOI : 10.1007/s11771-007-0095-z pages : 491-495.
- [4] Aprilita N.H. 2007. Preparation of Self-Cleaning Glass Based on TiO<sub>2</sub> Films for Photodegradation of Palmitic Acid. *International Conference on Chemical Sciences (ICCS)* pages : 1-5.
- [5] Hasan M.M, et al. 2008. Effects of Annealing Treatment on Optical Properties of Anatase TiO<sub>2</sub> Thin Films. *International Journal of Chemical and Biological Engineering* 1:2 pages : 92-95.
- [6] Tristantini et al. 2011. Modification of TiO<sub>2</sub> Nanoparticle with PEG and SiO<sub>2</sub> for Anti-fogging and Self-cleaning Application. *IJET-IJENS* Vol: 11 No: 02 pages : 80-85.