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Characterization and Application of TiO_2/ZnO Nanoparticles as Pigments in Matt-Type Water-Based Paint

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Abstract. This study investigates the characteristics of TiO_2/ZnO nanoparticles and the application of TiO_2/ZnO in matt-type water-based paint as a pigment. This study aims to determine the quality of TiO_2-ZnO pigments in water-based paints in terms of whiteness, hiding power, dispersibility, and gloss. Matt-type water-based paint has been made by mixing water and additives substances in a high-speed mixer to result in a mill base paste, which is mixed with the pigment of TiO_2/ZnO (25:75), $CaCO_3$ filler, water, and additives, then filtered and mixed again with the C-817 binder. The characterization results showed that TiO_2/ZnO nanoparticles contained TiO_2 of 18.62% and ZnO of 77.49%, with an average particle diameter of 151.54 nm. TiO_2/ZnO has a crystal size of 28.4 nm and a crystallinity degree of 72.3%. The application of TiO_2/ZnO nanoparticles as a pigment in matt-type water-based paint resulted in good dispersion and hiding power and achieved whiteness of 82.2 and gloss at 60° of 2.00 better than TiO_2 of 81.8 and gloss at 60° of 1.77.

Keywords: Matt-type water-based paint; Pigment; TiO_2; TiO_2/ZnO; ZnO

1. Introduction

Paint is a complex mixture consisting of resins, pigments, solvents, fillers, and other additives used to coat the surface of a material to beautify, strengthen, or protect the material. There are two types of paint, namely water-based paint and solvent-based paint. Water-based paint commonly used is the matt type which gives an even and non-reflective finish. This matt water-based paint is the most popular choice because it is easy to apply on smooth interior surfaces. The matt-type application is generally used on ceilings and walls with an even finish and a sheen level of less than 10%, giving it a non-reflective appearance (Chen *et al.*, 2022; Peruchi *et al.*, 2021).

In the paint industry, the main white pigment popularly used is titanium dioxide (TiO_2) because of its whiteness, high coverage, refractive index, covering power, achromatic force, good dispersion, and resistance to ultraviolet (UV) rays (Islam *et al.*, 2020; Karakaş and Çelik, 2018). These advantages have caused TiO_2 to be widely developed and researched and become the main choice in its application as a pigment compared to zinc oxide (ZnO), lithopone, and others (Gao *et al.*, 2022; Costa *et al.*, 2017).

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The TiO_2 cannot be obtained naturally but is extracted from ilmenite ore. TiO_2 can also be synthesized using the sol-gel method (Solanki *et al.*, 2021; Yuwono *et al.*, 2014), sonochemical (Rosales *et al.*, 2021), hydrothermal, solvothermal (Mamaghani, Haghighat, Lee, 2019; Sofyan *et al.*, 2019, 2018), microwave (Li *et al.*, 2021), co-precipitation (Bhogaita and Devaprakasam, 2021), and direct oxidation (Daraee *et al.*, 2018). However, the synthesis of TiO_2 is limited by the environmental pollution generated by industrial processes, the shortage of titanium resources, and the high selling price. Therefore, it is necessary to develop TiO_2 by mixing it with other white pigments with better or almost similar quality to reduce the high demand for TiO_2 nanoparticles (Isfa *et al.*, 2022; Razali *et al.*, 2022; Dell'Edera *et al.*, 2021; George *et al.*, 2021).

Zinc oxide (ZnO) is the main white pigment that has long been used in the organic paint industry because of its environmentally friendly nature. ZnO is naturally found in the form of the mineral zincite. The advantages of ZnO as a pigment are that it is stable against UV rays (does not change color), long lasts on both water-based and oil-based paints, and increases color retention. Compared with the other white pigments, ZnO has the least tendency to turn yellow (Papp *et al.*, 2022; Ma *et al.*, 2019; Adiwibowo, Ibadurrohman, Slamet, 2018). Based on the advantages of ZnO as a pigment, it is necessary to develop research related to ZnO combined with TiO_2 to result in TiO_2/ZnO nanoparticles and implement the use of matt-type water-based paints. The novelty in this work is related to the application of TiO_2/ZnO mixtures as a pigment in matt-type water-based paints.

A few previous studies related to the development of TiO_2/ZnO nanoparticles have been reported, including Miklečić *et al.* (2015), which studied the effect of TiO_2/ZnO nanoparticles on the properties of waterborne polyacrylate coatings in outdoor conditions, where the existence of ZnO nanoparticles reduced coating flow time, increased pH, and decreased elongation. In contrast, the TiO_2 increased the glass transition so that the combination of TiO_2/ZnO increased color stability. El-Kader *et al.* (2021) observed morphological, structural, and antibacterial on TiO_2/ZnO (50:50) nanocomposites from *Hibiscus rosa-senensis* extract, which produced an increase in the crystal size growth of ZnO with uneven distribution and irregular particle shape. It is different with the crystal size growth of TiO_2 was inhibited the distribution particles and shape were evenly and uniform. Baudys *et al.* (2015) conducted a weathering test and photocatalytic activity on self-cleaning acrylic paint based on ZnO and TiO_2, where the results showed that the paint sample TiO_2-based pigment increased photoactivity during exposition on the QUV panel, while the paint sample ZnO-based ones showed a high initial photocatalytic activity but decreased during exposition in the QUV panel. Lv *et al.* (2019) studied radiation stability in solar reflective coatings using TiO_2 and ZnO pigments, where the particle size affects the stability of the paint coating from radiation. Using TiO_2/ZnO mixture as pigments in acrylic paints has achieved better photocatalytic activity than pure TiO2 and ZnO (Song *et al.*, 2021; Jašková, Hochmannová, Vytřasová, 2013). The objective of this study is to characterize TiO_2/ZnO nanoparticles and observe the quality improvement of TiO_2/ZnO nanoparticles applied as pigments in matt-type water-based paints.

2. Methods

2.1. Materials

Titanium dioxide rutile (SR-2377) was obtained from Shandong Dongjia Group Co., Ltd. Shandong, China. Zinc oxide (ZnO) was supplied by Evergreen Chemical Factory Co., Ltd. Shaanxi, China. Calcium carbonate (Omyacarb-6 GD) as a filler was obtained from PT. Camco Omya Indonesia, Jakarta, Indonesia.

The styrene-acrylic binder (C-817) and super-plasticizer (SPC) were received from PT. Inawan Chemtex Sukses Abadi, Jakarta, Indonesia. The optical brightener agent (OBA) was supplied by PT. Graha Jaya Chemical, Jakarta, Indonesia. Dispersing agents, anti-foaming agents, wetting agents, coalescent agents, antimicrobial agents (biocide), thickening agents, and ethylene glycol are used for commercial water-based paint recipes.

2.2. Nanoparticles Characterization

The chemical composition of the pigments (TiO_2, ZnO, and TiO_2-ZnO) was analyzed by X-Ray Fluorescence (XRF) - PANalytical Epsilon 3. The pigments' crystal structure, size, and crystallinity degree were determined by X-Ray Diffraction (XRD) - PANalitycal X'Pert PRO MPD. Morphological of the pigments were characterized by Field Emission - Scanning Electron Microscope (FE-SEM) - FEI Inspect F50. The TiO_2-ZnO (25:75) nanoparticle pigments characterized were made from a mixing process using a planetary mixer (KNS-60 LB).

2.3. Manufacturing Process of Matt-Type Water-Based Paint

Water, thickening agent, wetting agent, dispersing agent, antimicrobial agent, anti-foaming agent, and ethylene glycol were added to a high-speed mixer according to Table 1, stirred using a zirconium ball mill at 2000 rpm for 1 hour, filtered with a sieve (mesh 200) and allowed to cool at room temperature. The results obtained are in the form of mill-base paste. The mill base paste, pigment (TiO_2, ZnO, or TiO_2-ZnO), optical brightener agent, super-plasticizer, $CaCO_3$ filler, water, and coalescing agent were added into a high-speed mixer according to Table 1, stirred at 800 rpm for 30 min, filtered with a sieve (mesh 200), and dispersibility of the pigment was observed. Next, the C-817 binder was added and stirred at 100 rpm for 15 min. The results obtained are matt-type water-based paint with various pigments, referred to as a P sample (Karakaş and Çelik, 2018; Somtürk *et al.*, 2016).

Table 1 Matt-type water-based paint recipes with various pigments

Ingredient	P1 (g)	P2 (g)	P3 (g)	P4 (g)
Water	326.06	326.06	326.06	326.06
Thickening agent	6.66	6.66	6.66	6.66
Wetting agent	0.69	0.69	0.69	0.69
Dispersing agent	1.77	1.77	1.77	1.77
Antimicrobial agent	5.43	5.43	5.43	5.43
Anti-foaming agent	2.83	2.83	2.83	2.83
Ethylene glycol	16.28	16.28	16.28	16.28
TiO_2	73.27	18.32	18.32	-
ZnO	-	54.95	54.95	109.90
Optical brightener agent (OBA)	-	-	1.00	1.00
Super-plasticizer (SPC)	-	-	1.77	-
$CaCO_3$ filler	439.68	439.68	439.68	439.68
Water	44.62	44.62	44.62	44.62
Coalescing agent	2.72	2.72	2.72	2.72
C-817 binder	80.00	80.00	80.00	80.00
Total	1000.00	1000.00	1000.00	1000.00

Note: P1 = Paint with TiO_2; P2 = TiO_2/ZnO (25/75), P3 = TiO_2/ZnO/OBA/SP (25/75/1/1.75), and P4 = ZnO

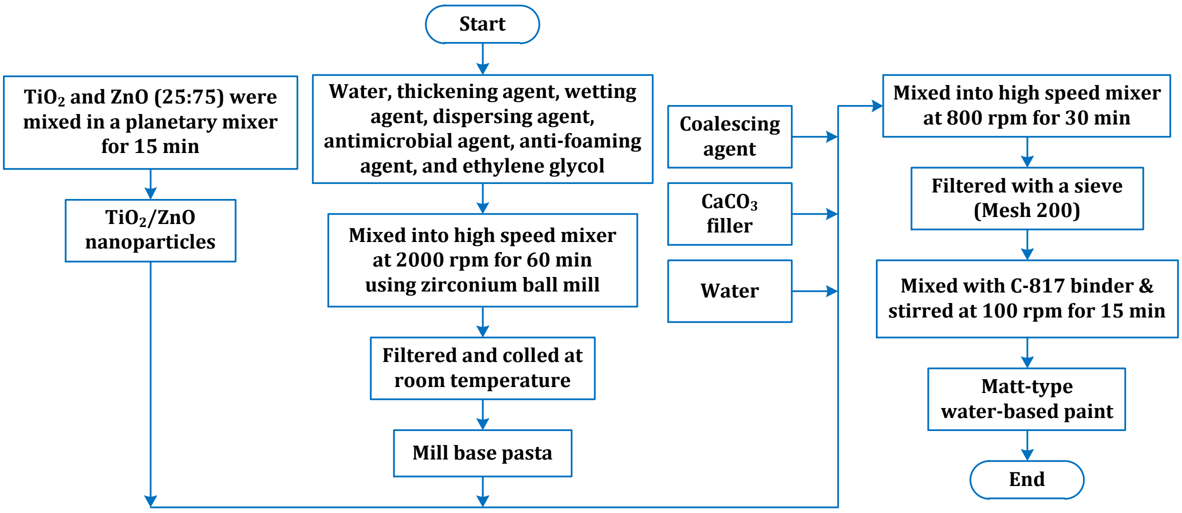

Figure 1 Preparation and application of TiO_2/ZnO in matt-type water-based paint

2.4. Application of Nanoparticles in Matt-Type Water-Based Paint

Matt-type water-based paint is applied to the surface of the panel paper using a rod coating (100µ), allowed for 24 h, and the obtained result was visually observed the hiding power in panel paper. Next, whiteness and gloss were measured using a whiteness meter (BGD 585) and a gloss meter (BGD 516).

3. Results and Discussion

3.1. XRF Analysis of Pigments

The results of XRF analysis on TiO_2, ZnO, and TiO_2/ZnO nanoparticles (Table 2) displayed that rutile had a TiO_2 concentration of 94.57%. Zinc oxide nanoparticles had a ZnO concentration of 96.11%. In the TiO_2-ZnO mixture, the concentration of TiO_2 is 18.62%, and ZnO is 77.49%. These results indicate that the mixing of TiO_2/ZnO with a composition of 25:75 showed no significant difference with the concentration of TiO_2/ZnO in the mixture, which means that there is no chemical interaction. The concentration of TiO_2 rutile was not significantly different from previous research (Sisca *et al.*, 2021; Mikleĉić *et al.*, 2015).

Table 2 Chemical Composition of TiO_2, TiO_2/ZnO, and ZnO

TiO_2		TiO_2/ZnO		ZnO	
Compound	(wt/%)	Compound	(wt/%)	Compound	(wt/%)
TiO_2	94.57	TiO_2	18.62	ZnO	96.11
Al_2O_3	1.65	ZnO	77.49	SO_3	2.28
P_2O_5	1.51	SO_3	2.06	P_2O_5	0.66
ZrO_2	0.95	P_2O_5	0.71	CaO	0.33
Ag_2O	0.56	CaO	0.35	Na_2O	0.30
CaO	0.30	Na_2O	0.33	SiO_2	0.15
SiO_2	0.20	Al_2O_3	0.19	Al_2O_3	0.11
Nb_2O_5	0.13	SiO_2	0.16	Fe_2O_3	0.03
CdO	0.06	V_2O_5	0.07	NiO	0.01
Fe_2O_3	0.05	Fe_2O_3	0.03	CuO	0.01
ZnO	0.03	K_2O	0.02	K_2O	0.01

3.2. XRD Analysis of Pigments

The crystallinity degree, size, and shape crystal of TiO_2, TiO_2/ZnO, and ZnO were analyzed by XRD. The XRD pattern is displayed in Figure 2. The characteristic peaks of TiO_2 at 2θ are 27.43°, 36.08°, 39.21°, 41.26°, 44.09°, 54.36°, 56.67°, 62.81°, 64.11°, 69.06°, 69.86°, 82.40°, and 89.63°. The peaks are suitable to the characteristic peak of rutile (01-087-0290), which has a crystallinity degree of 24.0 % and a crystal size of 29.8 nm with a tetragonal shape. This result also corresponds to previous reports (Razali *et al.*, 2022; Daniyal, Akhtar, Azam, 2019).

The characteristic peaks of TiO_2/ZnO at 2θ are 27.41°, 31.74°, 34.40°, 36.23°, 44.00°, 47.54°, 54.33°, 56.61°, 62.87°, 66.40°, 67.99°, 69.10°, 72.47°, 76.99°, 89.62°, 92.71°, 95.34°, and 98.57°. The peaks are suitable to the characteristic peak of TiO_2 rutile (01-072-4814) and zincite (03-065-3411), which has a crystallinity degree of 72.3 %, a crystal size of 28.4 nm with tetragonal and hexagonal shapes. This result corresponds to crystals of TiO_2/ZnO (El-Kader *et al.*, 2021; Mazabuel-Collazos, Gómez, Rodríguez-Páez, 2019).

The characteristic peaks of ZnO at 2θ are 31.70°, 34.36°, 36.19°, 47.49°, 56.56°, 62.83°, 66.37°, 67.92°, 69.05°, 72.58°, 76.90°, 81.43°, 89.61°, 92.65°, 95.24°, and 98.55°. The peaks are suitable to the characteristic peak of zincite (01-075-7917), which has a crystallinity degree of 64.1 % and a crystal size of 25.4 nm with a hexagonal shape. This result corresponds to previous reports (El-Kader *et al.*, 2021).

In TiO_2/ZnO pigment, there was a decrease in crystal size, which is not significantly different from TiO_2 rutile, so TiO_2/ZnO can achieve a good whiteness and is not significantly different when applied to water-based paint. The high crystallinity degree of TiO_2/ZnO can increase the gloss of water-based paints compared to TiO_2 pigments.

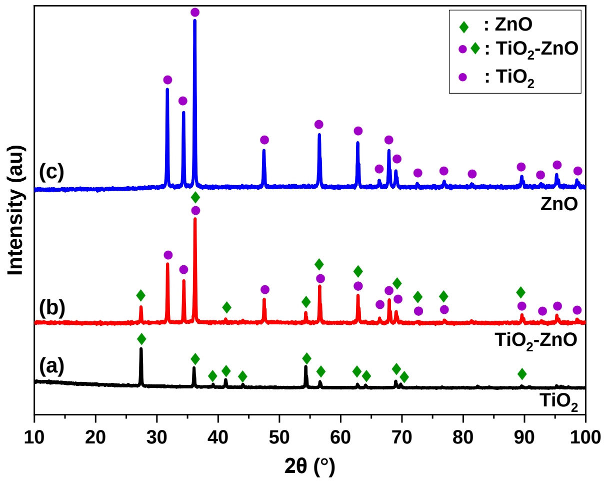

Figure 2 XRD of (a) TiO_2; (b) TiO_2/ZnO; and (c) ZnO

3.3. SEM Analysis of Pigments

The morphological analysis results of nanoparticles using FE-SEM with a magnification of 10,000x (10 μm) and 100,000x (1 μm) (Figure 3) has displayed that all pigments have very small sizes (<200 nm), smooth, and uniform shapes (Mazabuel-Collazos, Gómez, Rodríguez-Páez, 2019; Karakaş and Çelik, 2018; Miklečić *et al.*, 2015).

The nanoparticle diameter distribution was measured using the ImageJ and originLab application based on the SEM image result (Figure 4). The nanoparticles diameter of TiO_2 is 80.98 – 469.04 nm with an average of 182.07 nm, TiO_2/ZnO is 67.61 – 446.20 nm with an average of 151.54 nm, and ZnO is 57.93 – 300.62 nm with an average of 127.96 nm. These results indicate that the diameter of the three pigments is smaller than that of a sieve (mesh 200) and suitable for use in the preparation of matt-type water-based paints because the pigments can be ensured that evenly distributed, which is indicated by the absence of pigments left on the sieve (El-Kader *et al.*, 2021; Miklečić *et al.*, 2015).

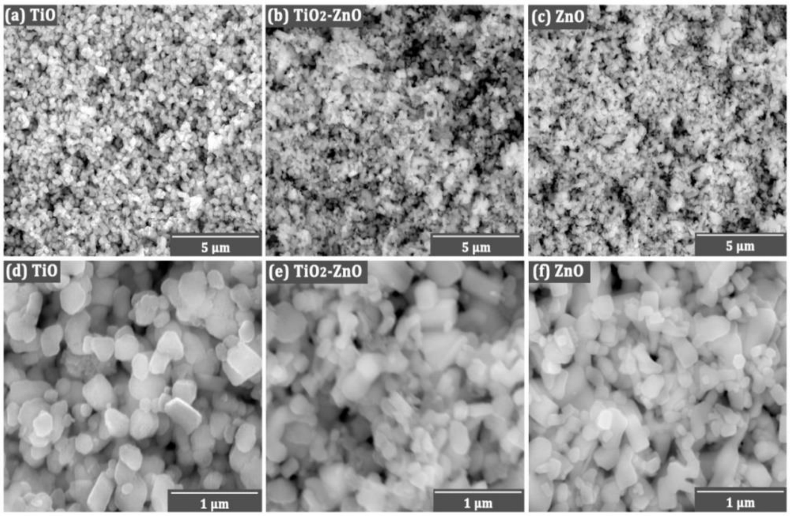

Figure 3 SEM Images of (a,d) TiO_2; (b,e) TiO_2/ZnO; and (c,f) ZnO

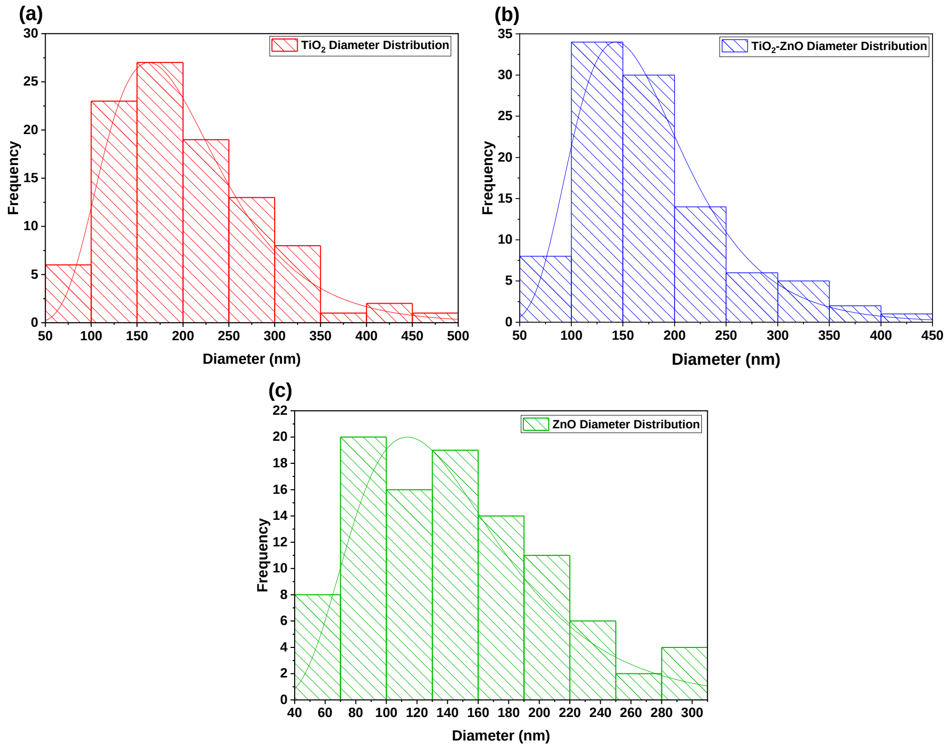

Figure 4 Diameter distribution of (a) TiO_2; (b) TiO_2/ZnO, and (c) ZnO

3.4. Application of Nanoparticles as Pigments in Matt-Type Water-Based Paint Against Dispersibility, Hiding Power, Whiteness, and Gloss

Nanoparticles such as TiO_2, TiO_2/ZnO, and ZnO, used as pigments, have good dispersibility in water-based paints (Table 3). It refers to the result of the second filtering process, where no pigment particles are left in the sieve (Mesh 200), which indicates that the pigment particles have been evenly dispersed (no agglomeration occurs) (Karakaş and Çelik, 2018).

Table 3 The Whiteness, Gloss, Hiding Power, and Dispersibility of Matt-Type Water-Based Paints with Various Pigments

Recipe Name	Whiteness	Gloss			Hiding Power	Dispersibility
		20° (95.1)	60° (96.3)	85° (99.7)		
P1	81.80 ± 0.10	1.13 ± 0.06	1.77 ± 0.06	4.60 ± 0.10	Good*	Good**
P2	82.20 ± 0.10	1.17 ± 0.06	2.00 ± 0.10	4.83 ± 0.05	Good*	Good**
P3	79.63 ± 0.15	1.13 ± 0.07	1.93 ± 0.06	6.57 ± 0.15	Good*	Good**
P4	80.77 ± 0.15	1.13 ± 0.06	1.87 ± 0.06	4.70 ± 0.06	Medium*	Good**

Note:

* Evaluation of hiding power results is carried out based on visual observations of the paint coating on panel paper, which refers to the standard color of white and black.

** Evaluation of pigment dispersibility was carried out based on the number of nanoparticles left on the sieve (mesh 200), which were observed visually.

Samples P2 and P3 have resulted in the same good hiding power quality as sample P1, which was evaluated by visual observation (Figure 5). While sample P4 resulted in a medium hiding power quality. These results indicate that TiO_2/ZnO and TiO_2/ZnO with the OBA and SPC are good for use as pigments.

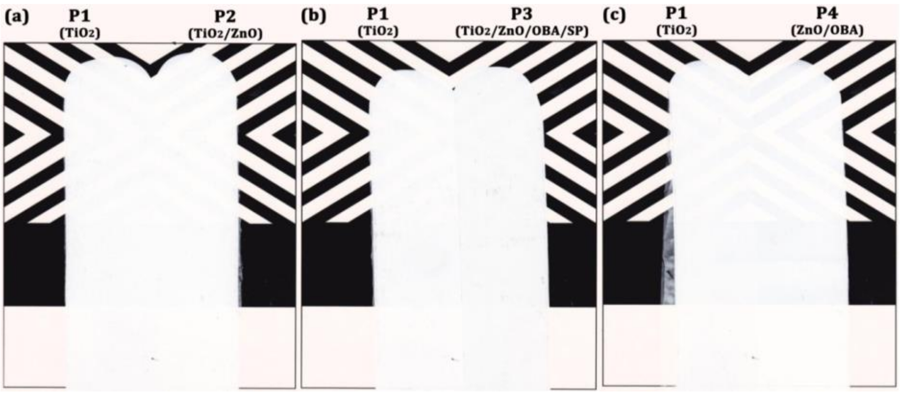

Figure 5 A Hiding Power of (a) P1 (TiO_2) & P2 (TiO_2/ZnO); (b) P1 (TiO_2) & P3 (TiO_2/ZnO/OBA/SPC); and (c) P1 (TiO_2) & P4 (ZnO/OBA)

Based on the whiteness (Figure 6a), it is known that sample P2 has more good whiteness qualities than others. The whiteness percentage of sample P2 is 0.48% is higher than sample P1. While sample P3 has resulted in a whiteness percentage of 2.65%, which is lower than sample P1. These results indicate that TiO_2/ZnO pigment has good whiteness. But, when the TiO_2/ZnO is combined with OBA and SPC, it causes a decrease in whiteness (Karakaş and Çelik, 2018).

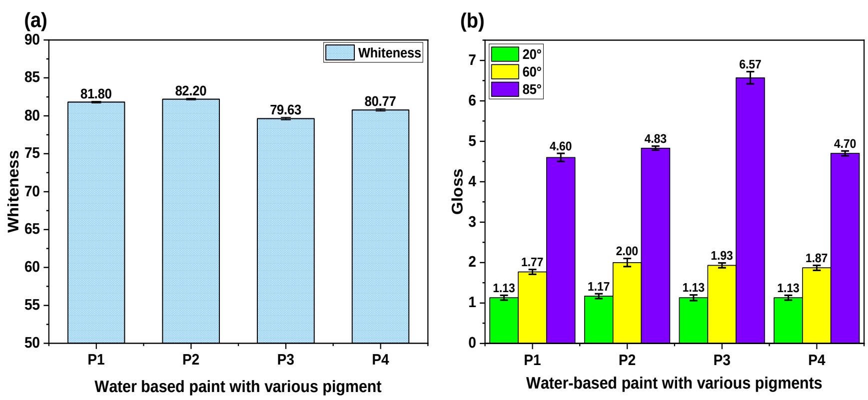

Figure 6 (a) Whiteness and (b) Gloss of Water-Based Paint with Various Pigments

Reflection angles of 20° and 60° in sample P2 have resulted in better gloss values than other samples (Figure 6b), which is influenced by the high crystallinity degree of TiO_2/ZnO nanoparticles. Meanwhile, at a reflection angle of 85°, sample P3 has resulted in a significant increase in the gloss value of 6.57, which was influenced by the presence of OBA and SPC in sample P3.

In terms of dispersibility, hiding power, whiteness, and gloss, it is known that sample P1 using TiO_2/ZnO nanoparticles as a pigment has better quality than sample P1 when applied to matt-type water-based paint. The amount of pigment in water-based paint formulas commonly for the matt-type is 7-10%, semi-gloss is 20-25%, and gloss is above 35%. With a gloss value below 10%, the water-based paint was categorized as a matt-type.

4. Conclusions

The TiO_2/ZnO nanoparticles have been successfully combined with the composition (25:75), which resulted in a crystallinity degree of 72.3%, a crystal size of 28.4 nm with tetragonal and hexagonal shapes. These nanoparticles contain 18.62% TiO_2 and 77.49% ZnO compounds, with an average particle diameter of 151.54 nm. TiO_2/ZnO nanoparticles also have been successfully applied as pigment to a matt-type water-based paint which achieved good dispersibility and hiding power and resulted in a whiteness of 0.48% and a gloss at 60° of 12.99% were better than TiO_2. In the future, a TiO_2/ZnO mixture will be made using a chemical method applied to a matt-type water-based paint with a composition according to the current works.

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