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Influence of TiO_2 Nanocrystals on Alkyd Resin Paint Films to Protect Metals

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Authors' contributions:

This work was carried out in collaboration among all authors. Author LHH designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author LMXT managed the analyses of the study. Author NQT managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aim and Objectives: Nowadays, nanomaterials technology is developing very quickly and bringing high economic efficiency for many industries including paint. The purpose of this study is to assess the effect of paint properties when replacing TiO_2 powder coating with nano TiO_2 at different ratios.
Materials and Methods: The research method is selecting the traditional alkyd paint formula, then replacing this coating powder TiO_2 with nano TiO_2 to monitor the properties of the paint film over time. Methods of analyzing the properties of the paint film are based on Vietnam standards.
Results: The study results showed that TiO_2 coating powder replaced by TiO_2 nanomaterials has increased the properties of the paint film, improving the thickness, gloss, and durability of the paint film. Nano TiO_2 increases from 0.5% to 24% by weight, the impact increased by about 11% (73 to 82 kg.cm), Glossy 60° increased by about 12%, Glossy 85° increased by about 12%, especially the durability of paint film over time increased nearly double. Nano TiO_2 is a more expensive material than TiO_2, so it should replace less than 4% by weight to increase the quality of the paint film, this ratio is changed according to the actual equipment requirements.

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Conclusions: The higher the rate of replacing TiO_2 materials with TiO_2 nano, the better the properties of the paint film. Therefore, nano-material TiO_2 is a good coating in alkyd resin for metal paint, it improves the properties of paint film better than TiO_2 material.

Keywords: Coating materials; durable life; gloss; impact level; standards.

1. INTRODUCTION

Nanomaterials are increasingly used in many fields of science, technology, medicine, and life, so it is being paid attention to research and development by scientists [1]. Nano is small in size (1 nm = 10^{-9}m), it has many outstanding properties compared to conventional materials especially in the field of covering and sterilizing. Nanoscale materials have been used in industrial paper [2,3], antibacterial paper products [4,5]. In medicine, nanomaterials are used in sterilization and antiseptic which bring high efficiency [6,7,8].

In the field of paints, there are many types of nanomaterials that have been researched with lots of applications such as nano TiO_2, Al_2O_3, SiO_2, ZnO, $CaCO_3$. The field of creating coatings is paid much attention to many nano-sized materials such as TiO_2 for coatings in paint and coatings in cosmetics [9,10]. The production of TiO_2 nanomaterials has also been noted to create nanoscale materials by various methods for effective testing [11,12]. Iron-doped TiO_2 (Fe:TiO_2) nanoparticles were synthesized by the sol-gel method, followed by hydrothermal treatment, drying, and annealing [13]. A new synthesis method was proposed to obtain anatase titanium oxide (TiO_2) nanocrystals anchored into a molecular sieve, as a matrix assigned by the in-situ anchoring (ISA) method [14]. Synthesis of TiO_2 nanoparticles and good dispersion on SBA-15 mesoporous materials for high photocatalytic activity, the results of this study will be useful in enhancing the photocatalytic efficiency of TiO_2 nanocatalyst materials [15]. Researchers discovered that the 2,2′-bipyridine (bipy) was a good additive candidate for TiO_2 nanoparticles-based dye-sensitized solar cells using natural dyes [16].

TiO_2 is a material typically used, has three types of crystal structures - anatase, rutile, and brookite forms. Each type has a different density, refractive index, and other properties. Anatase and rutile type titanium oxide powders, the types most commonly used for industrial applications. TiO_2 nanoparticles are produced in the rutile and anatase forms. Unlike larger TiO_2 particles, TiO_2 nanoparticles are transparent rather than white. Some spectroscopy characterization data of titanium oxide and titanium dioxide nanoparticles have been studied. The band gap of titanium oxide was measured using a UV spectrophotometer. Since UV-visible absorption spectra are used to confirm the excitation wavelengths, they serve as the most fundamental of tools for evaluating TiO_2. Titanium oxide, which is a material typically used, has three types of crystal structures - anatase, rutile, and brookite forms. Each type has a different density, refractive index, and other properties. The band gap was determined for anatase and rutile type titanium oxide powders, the types most commonly used for industrial applications, by measuring the diffuse reflectance [17].

Many studies on the properties of TiO_2 nanomaterials, the properties of paints with TiO_2 nanomaterials as coatings have been evaluated [18,19,20]. Some prominent studies such as research on the application of modified TiO_2 nano in acrylic interior wall latex paint [21], surface modification of nanometer TiO_2 [22], studies on the surface coating of nano-sized titania [23], the construction coating is prepared with nano-TiO_2 composite [24], modulation and properties of nano-TiO_2 modified interior wall paint [25]. There are still many problems in using nanomaterials as coatings in paints that need further research such as durability of paint films overtime when replacing TiO_2 coatings with TiO_2 nanomaterials, the relationship between replacement rate, and economic efficiency in using this paint.

The purpose of this study is to assess the gloss, impact resistance, and time durability of metal coatings using TiO_2 nanomaterials to replace TiO_2 at different ratios. This study focuses on the durability of paint films, which contributes to the addition of the use of TiO_2 nanomaterials in metal coatings, as a basis for practical application on an industrial scale.

This study helps manufacturers to choose the TiO_2 coating replacement rate with TiO_2

nanomaterials that are suitable for each painting with different requirements for quality and price.

2. MATERIALS AND METHODS

2.1 Materials

Nano TiO_2 Coating BR05: Particle size 5-30nm, purity 99.99%, white color, inertness, fine powder, dispersed in water and oil. This type of TiO_2 nano is often used as a coating for printing ink and paint with the rate used in the formula from 2-25%. Nano TiO_2 has very good sun protection. The sun protection mechanism of nano TiO2 is reflective of sunlight, protecting the painted object under radiation, so it has the ability to stabilize the coating to extend the life. Place of origin: Anhui, China.

TiO_2 coating BLR501 has a median particle size in the 200–300 nm range (the average particle size 250nm), purity 97.5%, white color. The use of TiO_2 is very diverse. TiO_2 is a compound with high melting point (heat resistance), little chemical effect (chemical resistance), abrasion resistance, large hardness but remains stable, good plasticity, less cracking, TiO_2 has high coverage, fine particles, good oil permeability, and very durable under the effect of moist air, seawater, H_2S, SO_2 and non-toxic. TiO_2 is not denatured over time. It is widely used in the TiO_2 paint industry with high corrosion resistance, so it is used to manufacture paint for bridges, constructions, and anti-corrosion equipment of the atmosphere. TiO_2 is impervious to water, has high chemical and thermal stability, so it is used to paint ship shells, aircraft hulls, heat-resistant pipes, water-immersion devices such as fishing tools, ship, submarine, TiO_2 paint film has mechanical strength, so it is used for priming in the coating on equipment under high pressure. Chinese origin.

TiO_2 coating BLR501 is a very popular material in the Vietnamese market and is widely used in the paint industry. The technical properties of the **TiO_2 coating BLR501** are equivalent to that of P25-TiO2-Degussa.

Alkyd resin CR 1486-70 DT: Oil length 49%. Acid index (mg KOH / g solid) 5-12. Solid content 70 ± 1%. Feature fastness, fast dry, stable, used in paint. Indonesian Origin.

Anti-sedimentation agent FGEL 170: An easily dispersed organic additive is used in low to medium polar solvent-based systems of organic liquids. It is an anti-settling agent in paints, inks, and adhesives. Chinese origin.

Airex 900 foam breaking agent: As a foam breaking agent, it breaks down bubbles formed in the process of mixing, grinding, or coating to make the paint film smooth and glossy. Chinese origin.

Dispersant Disper 710s: A highly effective dispersant that disperses organic and inorganic additives in the paint to create a gloss for paint film. Chinese origin

Oct Co Surface Desiccant: Cobalt octoate 10% is a metal salt used as a drying agent for oil paint systems. Appearance is purple, clear liquid, solid content of 55-65%, the metal content of 9.8 - 10.2, specific gravity 0.93-1.03. Dura origin (India).

Oct Pb Surface Drying Agent: Product name lead octoate (32% Pb). Lead Octoate is a surface-based drying agent that hardens the entire surface by drying the entire film-forming agent, often combined with Cobalt and Calcium Octoate. Liquid, clear yellow, solid content of 62-72%, Pb content 32 ± 0.2%. Density 1.2-1.3 g / ml. Application as a desiccant for paint. Thai origin.

Xylene solvent: Xylene is a clear colorless liquid with a pleasant aroma. Density at 20^oC is 0.865-0.875 kg/L. Auto-ignition temperature 500^0C. This mixture is liquid, colorless, and often used as a solvent. Chinese origin.

2.2 Research Methods

Using the method of comparing the properties of the paint when replacing TiO_2 coating with TiO_2 nano-coating in paints use alkyd resin as a film-making agent. We made different paint formulas with the replacement rate of TiO_2 coating material with TiO_2 nanomaterials then consider the extent of the effect of nanomaterials on the properties of the paint film. Each paint formula sample is painted on 15 metal sheets with dimensions of 70x150 mm and a thickness of 0.5 mm with the same film thickness. From empirical data compared with each other to draw conclusions, evaluate the advantages of using nanomaterials.

Creating a uniform thickness paint is relatively difficult, so we create many models to choose

from. There are many tools for creating paint coatings, such as paintbrushes, rollers, spray equipment, manual and automatic film-drawing rulers, etc. The common tool for creating laboratory coatings is a manual paint film ruler. Currently, there are many types of manual paint film ruler, it creates paint film based on the method of creating the Doctor Blade technique. We use the manual pull ruler model BGD 201/5 with a 100 µm scale from the Biuged manufacturer. The manual paint film ruler Biuged is made of stainless steel with an accuracy of 2%, used easily, and created relatively uniform paint film. The metal plates used for testing are weighed before and after coating for 24 hours to determine the amount of coating on the surface. We choose metal tin sheets with the same amount of coating (error of 2%) to determine the index of the paint film.

2.3 Methods of Analysis

Gloss 60°, 85° is determined according to Vietnam Standard TCVN [26].

Drying time of the paint film is determined according to TCVN [27].

Adhesion is determined according to TCVN [28].

The impact is determined according to TCVN [29].

Coverage of dry paint film is determined according to TCVN [30].

3. RESULTS AND DISCUSSION

We create paints based on traditional formulas from formulas 1 to 8 with the same ingredients but different in TiO_2 and nano TiO_2 coating ratios. The total TiO_2 and nano TiO_2 coatings in all samples were 22% by weight (Table 1)

Formula 1:

- Step 1: Dissolve 5 gams Anti-sedimentation agent (FGEL 170), 2 gams Foam breaking agent (Airex 900), 5 gam Dispersant substance (Disper 710S) in 50 gram of xylene solvents.
- Step 2: Dissolve 0.5 gams Drying additives (Oct Co), 0.5 gams (Oct Pb), in 50 grams of xylene solvent.
- Step 3: Dissolve 440 grams of Resin membrane adhesion substance for paint (Alkyd-CR 1486-70) in 227 grams of xylene solvent in a 3-liter agitator adjusted at 25 rpm.
- Step 4: Slowly add 220 grams of powder coated with TiO_2 to the film-forming resin solution dissolved in xylene
- Step 5: Add the dissolved mixture in step 1 and step 2 to stir for another 45 minutes.
- Step 6: Crushed by ball grinding equipment for180 minutes.

Formula 2, 3, 4, 5, 6, 7. 8: Proceed in the same way as formula 1 and replace TiO_2 with nano TiO_2 in proportion to the formula in Table 1. All paint formulas are carried out and presented under the same conditions but only differ in the speed of replacing TiO_2 coating material with TiO_2 nanomaterials. The paint formulations are applied to metal tin sheets to assess the basic quality indicators of the paint film. We use BGD 201/5 manual ruler model with 100 scales to create the paint film. Each paint formula sample is painted on 15 metal sheets with the same film thickness. After the film has dried, weigh the tin plates to select the panels with the same coverage 83 g/m2 to check and evaluate the quality indicators of the paint film. From empirical data, we compared to each other to draw conclusions, evaluate the advantages of using nanomaterials.

From Table 2 shows that when increasing the concentration of nano TiO_2, the level of impact also increased. The impact level in formula 2 to formula 4 increases fast from 74 to 79 kg. cm then slows down until completely replacing TiO_2 with nano TiO_2, the impact level is 82 kg.cm.

From the data and graphs shown in Table 1 and 2, it shows that the gloss of 60° and 85° is increased when replacing TiO_2 coating with TiO_2 nanomaterials with a higher replacement rate, the faster the glossiness increases. This can be explained by the fact that the TiO_2 nano-coating is very small and smooth, so it gives the metal surface a gloss so the finer the material, the glossier it is.

3.1 The Change of Adhesion Over Time

Adhesion overtime of the paint films in the formulas evaluated (Fig. 1).

The higher ratio of using nano-coating materials, the less change in adhesion. It means that it is

more durable, the life of the paint film is higher when using TiO_2 nanocoating material. This can be explained by the fact that the metal surface structure is not smooth and ideal, but from a micro perspective, it is also rough with very small slots, holes that make the coating of different sizes permeate deep into the surface at different levels. Due to the size of nano TiO_2 is very small from 5-30 nm, it easily penetrates to the metal surface, so the adhesion force between the coating and metal surface is better than the adhesion force of TiO_2 coating, it makes the paint more durable or the life of the coating with the coating material is nano TiO_2 higher.

Unlike larger TiO2 particles, TiO2 nanoparticles are transparent rather than white. Ultraviolet (UV) absorption characteristics are dependent on the crystal size of titanium dioxide and ultrafine particles have strong absorption against both UV-A (320-400 nm) and UV-B (280-320 nm) radiation. Light absorption in the UV occurs because of the presence of strongly bound excitons [31]. Nano TiO_2 Coating BR05 particles have a small size of 5-30nm, so it resists the influence of UV rays better than TiO_2 coating BLR501 with a size of 200-300 nm. Therefore, nano-TiO_2 in alkyd paint has improved paint properties. Experiments show that when adding nano-TiO_2 to paint, properties such as Impact level, Glossy, Adhesion overtime are better, and the ability to resist the effects of the environment is better.

TiO_2 usually has an average particle size of about 250 nm, TiO_2 powder contains a variety of sizes, they can have a small fraction of nano-sized particles even if the average particle size is larger. The blend of TiO2 and nano-TiO_2 can give superior properties, so it is not entirely that the properties obtained in the paint are due to nano-TiO_2.

Experiments show that the replacement of TiO2 powder coatings with TiO2 nanomaterials in metallic protective alkyd paints has brought better results for paint film properties such as gloss, impact resistance, and especially service life of paint film over time. The impact level, glossy, adhesion over time increased rapidly at the rate of replacing TiO_2 coated material with nano TiO_2 from 0.5% to 4% then increasing slowly. Because TiO_2 nanomaterials are more expensive than TiO_2 coatings, the replacement should only be applied on a case by case basis. Metal surfaces of ordinary, inexpensive objects, tools, equipment if using alkyd paint with nano TiO_2 coating need to be considered economically because this type of paint is more expensive than that used with powder coatings TiO_2. To improve the quality of paint film for this equipment, only TiO_2 coating material with nano TiO_2 should be replaced at a rate of less than 4% weight of the paint. However, in case of requiring good quality paint film, high gloss, durability over time for metal surfaces of valuable tools and equipment, paints with TiO_2 coating material are replaced with nano TiO_2 with a high ratio that is very suitable.

Table 1. Composition of paint formulations

No	Raw materials	Uses	Formula Wt.% Ratio							
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1	Alkyd- CR 1486-70 DT	Resin adhesion for paint	44	44	44	44	44	44	44	44
2	Nano TiO_2	Cover substance		0.5	1	2	4	8	16	22
3	TiO_2	Cover substance	22	21.5	21	20	18	14	6	
5	FGEL 170	Anti-sedimentation agent	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
6	Airex 900	Foam breaking agent	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
7	Disper 710S	Dispersant substance	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
8	Oct Co	Drying substance	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
9	Oct Pb	Drying substance	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
10	Xylen	Solvent	32.7	32.7	32.7	32.7	32.7	32.7	32.7	32.7
	Total		100	100	100	100	100	100	100	100

Table 2. Properties of paint

No	Properties	Formula							
		1	2	3	4	5	6	7	8
1	Face dry time (minutes)	34	34	33	33	32	32	30	29
2	Natural drying time (hours)	18	18	17.5	17	16.5	16	15.5	15
3	Impact level (kg.cm)	73	74	77	79	80	81	82	82
4	Coverage of dry paint film g / m2	83	83	83	83	83	83	83	83
5	Glossy 60°	85	87	90	92	92	93	94	95
6	Glossy 85°	82	84	86	88	89	90	91	92

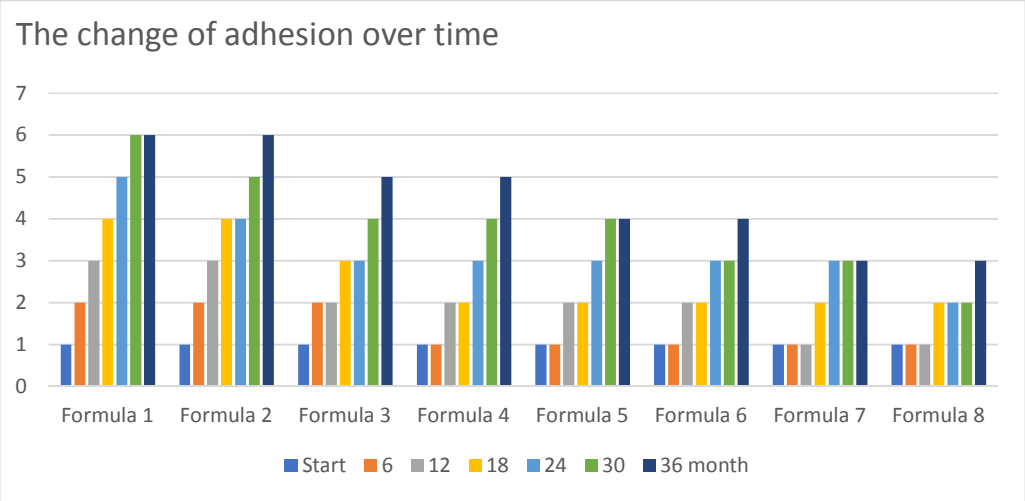

Fig. 1. The change of adhesion over time

4. CONCLUSION

Replacing TiO_2 by nano TiO_2 in alkyd resin for metal paint has increased the adhesion of TiO_2 coating to the metal surface, which makes the film glossier, the better impact resistance of paint film, and the life of the paint film is more durable under the impact of the environment.

The higher the rate of replacing TiO_2 materials with TiO_2 nano, the better the properties of the paint film. Therefore, nano-material TiO_2 is a good coating in alkyd resin for metal paint, it improves the properties of paint film better than TiO_2 material.

Because TiO_2 nanomaterial is more expensive than TiO_2, in order to improve the quality of paint film, it is recommended to replace TiO_2 coating material with nano TiO_2 with a rate of less than 4% of the weight, in case of good paint quality, high gloss and durability over time for metal surfaces of valuable tools and equipment the replacement should be at a higher rate.

ETHICAL APPROVAL

It is not applicable

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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