Preparation of Nano Titanium Dioxide Using the Sol-Gel Method to Use in Friendly Environment Coatings

1Abeer Abd Saleh*, 2Quraish Abbas, 3Seenaa Ibraheim, 4Ibrahim Muhammed, 1Mayes Sameer Hameed, 1Rukiya Abd Alsahb Lafta, 1Sarah Gameel Dawood, 3Ban Mazan

1National Center for Packing and Packaging/Corporation of Research and Industrial Development – Iraq
2Chemical and Petrochemical Research Center/Corporation of Research and Industrial Development – Iraq
3Department of Physics, College of Science, University of Baghdad – Iraq
4State Company for Mining Industries, Ministry of Industry and Minerals – Iraq

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*Corresponding Author:
Abeer Abd Saleh
zoozaphysics3@gmail.com

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Abstract

In this research, preparation of titanium dioxide nanomaterial (TiO2) using sol-gel method was achieved. 2.5 g weight of the titanium dioxide nanoparticles were added to the local paint using the casting method. Thin films were prepared by drop casting the paint onto the surface of pre-prepared samples, then several tests were carried out including adhesion test, hardness test (Shore B), brightness and whiteness, friction test, contact angle, and antibacterial activity. The nanomaterial at a percentage of 12% showed the best results when it was added to the paint. These results include adhesion strength, hardness strength, and exposing to weather conditions of temperature, and humidity. The adhesive strength increased when adding the nanomaterial from 112 to 139 before exposure to the weather and from 58 to 108 after exposure. The hardness also increased from 77.9 to 86.5 before exposure to the surrounding environment and from 94.2 to 96.8 after exposure. In addition, the paint with TiO2 nanoparticles exhibited antibacterial activity against two types of bacteria Escherichia coli (E. coli), staphylococcus aurous (S. aurous) and antifungal candida. Paint with TiO2 nanoparticles is more efficient as antibacterial agents with E. coli as compared with S. aurous and candida.

1. Introduction

In this research, preparation of titanium dioxide nanomaterial (TiO2) using sol-gel method was achieved. 2.5 g weight of the titanium dioxide nanoparticles were added to the local paint using the casting method. Thin films were prepared by drop casting the paint onto the surface of pre-prepared samples, then several tests were carried out including adhesion test, hardness test (Shore B), brightness and whiteness, friction test, contact angle, and antibacterial activity. The nanomaterial at a percentage of 12% showed the best results when it was added to the paint. These results include adhesion strength, hardness strength, and exposing to weather conditions of
temperature, and humidity. The adhesive strength increased when adding the nanomaterial from 112 to 139 before exposure to the weather and from 58 to 108 after exposure. The hardness also increased from 77.9 to 86.5 before exposure to the surrounding environment and from 94.2 to 96.8 after exposure. In addition, the paint with TiO₂ nanoparticles exhibited antibacterial activity against two types of bacteria *Escherichia coli* (*E. coli*), *staphylococcus aurous* (*S. aurous*) and *antifungal candida*. Paint with TiO₂ nanoparticles is more efficient as antibacterial agents with *E. coli* as compared with *S. aurous* and *candida*.

2. Experimental Procedure

Sol-gel technique is a wet synthetic cycle that permits a metal oxide to be delivered from naturally altered precursor materials at lower handling temperatures than a customarily made inorganic oxides [6]. The sol-gel method depends on inorganic polymerization responses. It incorporates four stages: hydrolysis, polycondensation, drying and warming disintegration. Hydrolysis of the antecedents of the metal or non-metal alkoxides takes place with water or alcohols [7].

\[
\text{Ti(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 + 4\text{ROH} \quad \text{(hydrolysis)} \quad (1)
\]

where \( R = \text{alkyl bunch} \).

In addition to water and alcohol, an acid or a base also helps in the hydrolysis of the precursor. After condensation of the solution to a gel, the solvent is removed [7].

\[
\text{Ti(OH)}_4 \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} \quad \text{(condensation)} \quad (2)
\]

Materials

The weight ratio of chemical materials to prepare the local paint is shown in Table (1).

| Material                  | Weight ratio (%) |
|---------------------------|------------------|
| Alkyd resin               | 55               |
| Titanium dioxide          | 12               |
| Calcium carbonate         | 12.5             |
| Thickener material        | 3                |
| Dilute material           | 14.6             |
| Cobalt dryer              | 0.6              |
| Lead dryer                | 0.4              |
| Calcium dryer             | 1.2              |
| Dilute grinding assistant | 0.5              |
| Anti-flake                | 0.2              |

Preparation of Nano TiO₂ Solution

A 1 ml of concentrated hydrochloric acid was added to 15 ml of titanium trichloride (TiCl₃). 250 ml of distilled water then gradually added to the previous solution followed by adding 150 ml of ethyl alcohol. The formed solution was then stirred continuously at 70°C for 5 hours. Afterward, 60 ml of ammonium hydroxide solution added while stirring is continued. The resulted solution was left for 24 hours to complete the reaction quietly.
Preparation of Local Paint
The alkyd resin is weighed, then added the dilute grinding assistant and mixed well. The pigment is added to the alkyd resin, so it will be nano- or microparticles. Calcium carbonate and thickener are added respectively, to the mixture and mixed well after each addition. The mixture was left one day to moisturize the solids well with alkyd resin. On the second day, the solvents, dryers, and anti-flakes are added to the mixture and mixed them well after each addition. The TiO$_2$ mixture with a percentage of 12% was added to the dye and mixed well until it became homogeneous by the magnetic mixer. And then the composite materials were mixed with a local paint, and poured on the plates made of iron with dimensions of 10 cm $\times$ 5 cm and left for a whole day till the dye dried up. Several assays were made including the hardness, paste, and color degree examination such as whiteness, brightness, and exposure to weather conditions (heat and moisture) to accelerate weather conditions impacts.

3. Results and Discussion
Surface Topography
Figure (1) shows the atomic force microscope (AFM) test of the nanometres titanium oxide powder obtained by the (sol-gel) process thin fime prepared from TiO$_2$ by spraying the material on a glass base, with a thickness of 56 nm, an area of (1000 $\times$ 1000) nm square, and the average roughness is about 6.76 nm. The record was previously taken from the published research [9].

Adhesion Pull-Off
The bond strength of nano TiO$_2$ paint is significantly higher than micro TiO$_2$ paint for both cases; before exposure to weather conditions and after exposure to weather conditions (ultraviolet, visible, and moisture). The quality of interface and the strength of the adhesion at the interface determine the load transfer between the matrix and the nano fillers [10]. Table (3) shows that TiO$_2$ nanoparticles content can improve adhesion. This positive result can be attributed to the reinforcement provided by the good dispersion and high compatibility between the paint and the nano TiO$_2$. The importance of adhesion is the ability of a coating to resist removal from the surface to which it is applied [11]. Such adhesion can be between substrate and coating or between a primer coating and a top coating.
Table (3). Adhesion strength of the paint before and after exposure to weather conditions.

| Paint with micro TiO₂ | Paint with nanoTiO₂ |
|------------------------|---------------------|
| Adhesion before exposure to weather conditions (MPa) | 112 | 139 |
| Adhesion after exposure to weather conditions (MPa) | 58 | 108 |

**Hardness Test (Shore B)**

Coating hardness is the ability to resist permanent indentation, scratching, cutting, and penetration by a hard object [11]. Different methods of evaluating hardness yield different results, because they measure different qualities of the material. Figure (2) shows the improvement in hardness of the paint with nano TiO₂. Hardness results show an excellent interaction between TiO₂ nanoparticles and the paint matrix. Moreover, the good dispersion of the particles, leads to an increase in the surface area of the filler. Mechanical properties of the nano composites can be altered by various factor: properties of the matrix, filler particles size and morphology, particles loading and distribution, interfacial adhesion between filler particles and matrix [12]. Figure (3) shows that hardness values increase for both paints (nano and micro) after exposure to weather conditions.

**Figure (2).** A histogram of Shore hardness for micro and nano TiO₂ paints before exposure to weather.

**Figure (3).** A histogram of Shore hardness for micro and nano TiO₂ paints after exposure to weather.
Friction Test
The samples of micro paint failed before and after exposure to weather conditions and after the 48 cycles. While the nano paint sample succeeded after exposure to weather conditions. Although, this sample was failed before exposure to weather conditions after 48 cycles.

Brightness and Whiteness
The brightness of the micro paint was faded after exposure to the weather conditions, whereas the nano paint exhibited a sharper brightness after weather conditions exposure as shown in Table (4). TiO$_2$ is the most widely used white pigment because of its brightness and very high refractive index [13]. Table (5) tabulates the brightness results, where one can see that micro pained samples exhibit a decrease in whiteness after weather exposure compared to its value before the exposure. On the other hand, nano pained samples demonstrate an increase in whiteness after weather exposure.

| Samples          | Before exposure to weather conditions | After exposure to weather conditions |
|------------------|--------------------------------------|-------------------------------------|
| Paint with micro | 175.96                               | 169.56                              |
| Paint with nano  | 165.86                               | 176.38                              |

Table (5). Whiteness of paint with micro and nano TiO$_2$

| Samples          | Before exposure to weather conditions | After exposure to weather conditions |
|------------------|--------------------------------------|-------------------------------------|
| Paint with micro | 141.32                               | 128.03                              |
| Paint with nano  | 130.76                               | 139.38                              |

Contact Angle
Contact angle measurement is shown in Figure (4). When the contact angle increases to more than 90˚, the surface is considered a hydrophobic, but when the surface contact angle is less than 90˚, the surface is hydrophilic. In the present work, with ultraviolet radiation, sun, moisture and TiO$_2$ nanoparticles, the surface contact angle converts from hydrophilic to super hydrophilic for TiO$_2$ nano and micro paints. Exposure to weather conditions results in a decrease in contact angle for both micro paint and nano paint surfaces which creates a hydrophilic surface. Hydrophiliicity depends on both the surface roughness and the chemical composition [14].
Figure (4). Contact angle: (a) paint with micro TiO$_2$ before exposure to weather condition (b), paint with micro TiO$_2$ after exposure to weather condition, (c) paint with nano TiO$_2$ before exposure to weather condition, and (d) paint with nano TiO$_2$ after exposure to weather condition.

The paint with TiO$_2$ nanoparticles was investigated as antibacterial in two different bacteria: *Escherichia coli* (*E. coli*), *Staphylococcus aureous* (*S. aureus*), and fungal *Candida*, as well. Paint with TiO$_2$ nanoparticles showed greater antibacterial activity. The exact mechanisms of the antibacterial action have not yet been clearly identified. TiO$_2$ nanoparticles have bactericidal effects on both Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria. The antibacterial activity of TiO$_2$ nanoparticles depends on the surface area and concentration, while the crystalline structure and particle shape have little effect. Zone of inhibition values determined nanocomposites is shown in Table (6) and Figure (5). TiO$_2$ nanoparticles pronounced significant growth inhibitory effect against both bacteria due to their large surface area by their nanosize. However, TiO$_2$ nanoparticles superior antibacterial activity against *E. coli* bacteria than with *S. aureus* bacteria which are clearly visualized in the antibacterial photographs [15].

Table (6). Zone of inhibition (mm) of paint with TiO$_2$ Nano particle.

| Samples | *S. aureus* | *E. coli* | *Candida* |
|---------|-------------|-----------|-----------|
| Area 1  | 17          | 18        | 14        |
| Area 2  | 17          | 18        | 14        |
| Area 3  | 17          | 18        | 14        |
Figure (5). Antibacterial and antifungal activity of Nano paint.

4. Conclusions
The TiO$_2$ nanoparticles prepared by chemical method (sol-gel) gave good results. When adding it to the local dye when conducting several dye tests, including adhesive and hardness and contact angle. Examined the dye before it was exposed to weather conditions and after exposure in a micro-form once and in a nano, in the other, the adhesion strength and hardness increased with adding the nanomaterial.

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