Characterization of TiO\textsubscript{2} nanopaint for automotive application

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Abstract. Nanopaint is a coating that can modify the properties of a surface or substance according to user-defined parameters. Like ordinary paint, nanopaint is applied as a liquid and then hardens. Nanopaint is a suspension of liquid containing metal or non-metallic nanoparticles of typical size (1-100 nm) dispersed into the basecoat paint. Single composite of Titanium oxide nanoparticle is considered an extension of research work for single nanopaint, which can be carried out through dispersed composites in basecoat paint. This paper presents characterization of single composition of TiO\textsubscript{2} nanopaint for automotive application. The nanopaint mixture was prepared at volume concentration of 1.0\% using two-step method. The nanoparticles used namely TiO\textsubscript{2} is dispersed in a base fluid of polyester white paint. The investigation on the characterization for the nanopaint in the present study is conducted through adhesion cutter, SEM, Gloss meter and surface roughness meter. The findings from the investigations on the characterization of nanopaint show that the paint each all the required value for the normal paint characterization. Comparison data between 1\% weight concentrations for nanopaint to the normal paint also confirm the increase in the surface roughness quality which is 0.10 less surface deviation compare to normal paint and gloss value up to 26\% more glossier. It can be concluded that the nanopaint were successfully prepared and achieved good characterization.

1. Introduction
Automotive paint is one of the industries that move forward with the automotive technology to improve the surface performance [1]. Several techniques have been carried out to reduce the problem address by the end-user such as corrosion, mitigation and protection, durability, UV and heat resistance, strength and durability in thinner films or light weight substrate water and dirt repellence, anti-fouling, and enhanced colour [2]. Automotive clear coats are subjected to different kinds of environmental damage for instance UV radiation, acid rain, tree sap, bird droppings, stone chipping and marring. Marring is mainly due to car wash brushes, decreases the gloss of automotive paint and alters the colour [3]. Outdoor durability of an automotive coating especially the clear coat layer is one of the main concerns of automobile manufacturers. This concern arises from the fact that for most customers, retained appearance during service life is the most important criterion. Generally, basecoat is the colour producing layer, whilst the clear coat improves physical and chemical properties of the
automotive coating system as well as enhancing its appearance [4]. Currently the clear coat formulation was add with HALS (hindered amine light stabilizer) and organic UV-absorbers. These ingredients considerably enhanced weathering performance, in addition to have high price, they can migrate to other layers and prone to undergo decomposition during service life.

The technology of nanoparticle dispersion was used in various engineering applications [5-9]. Currently, nanopaint is considered in the stage of research-and-development phase. Nowadays industries are targeting to explore more on the nanotechnology even in the painting and coating area. Such industries include the construction, automotive, aerospace and electrical component [10]. One of the most common materials to be used in the general coating application is Titanium Dioxide (TiO$_2$). In 1995, the concept of nanofluids was first introduced by Choi [11]. The attention receive by the researcher for TiO$_2$ nanoparticles because of its potential application in a wide range of fields such as photo catalytic and electro chromic devices, gas sensors, dye-sensitized solar cells, and energy-storage devices [12]. TiO$_2$ micro particle used in paints, mainly used as a white pigment. Only micrometres sized TiO$_2$ causes such white colouring. Nano scale TiO$_2$ functions as ultraviolet (UV) filter protecting the paints' binder material. Equally, it degrades organic materials via generation of radicals (photo catalytic activity), which is used for self-cleaning surfaces. The physicochemical properties of TiO$_2$ nanoparticles can be improve by controlling the particle size and morphology of the material. Some research groups have reported the formation of hierarchical urchin-like TiO$_2$ (U-TiO$_2$), composed of numerous Nano rods, by a facial hydrothermal process or precipitation at low temperatures, and its enhanced dielectric and photo catalytic properties [13].

2. Methodology

2.1. Material

The preparation of nanopaint involved a single nanoparticles namely TiO$_2$ mixed and dispersed in the polyester basecoat white paint as the base fluid. The TiO$_2$ nanoparticles were procured from US Research Nanomaterials, Inc. The respective nanoparticles size for TiO$_2$ is 30 nm with purity of 99.99%. The properties of TiO$_2$ nanoparticles are tabulated in table 1.

| Properties                      | TiO$_2$ |
|--------------------------------|---------|
| Molecular mass, g mol$^{-1}$   | 79.86   |
| Average particle diameter, nm  | 50      |
| Density, kg m$^{-3}$           | 4230    |
| Thermal conductivity, W m$^{-1}$ K$^{-1}$ | 8.4    |
| Specific heat, J kg$^{-1}$ K$^{-1}$ | 692    |

2.2. Preparation of single nanopaint

The two-step method is used for the preparation of single nanopaint. The nanopaint was prepared by mixing single nanoparticle (TiO$_2$) together; undergo a mixing and sonication process. Figure 1 shows the brief process in the nanopaint preparation. The preparation of the nanopaint was initially started with the calculation of the required weight according to the concentration. In the present study, the nanopaint was prepared at weight concentration of 1%. The normal paint was first prepared as per comparison to the nanopaint.

Sample preparation of single coating is done by dispersing nanoparticles into raw basecoat paint. nanoparticles exist in pigments, instead of measuring in volume, we need to consider the equation to calculate the concentration weight. Different concentration weight 1.0% of nanoparticles are dispersed into 100 ml raw basecoat paint. The equation (1) is used to calculate the concentration weight.

$$\omega = \frac{\omega_{np}}{\omega_{np} + \omega_{paint}} \times 100\%$$ (1)
The perfect spray viscosity of the paint are measured using viscosity cup (DIN 4@28c) about 13 ± 1 s. The mixing ratio of basecoat to solvent (slow thinner) is usually 1:0.8 according to the original viscosity of the paint (without nanoparticle). The perfect spray viscosity of the paint are measured using viscosity cup (DIN 4@28c) about 13 ± 1 s. To ensure the paint is not separated, it was stirred again by using magnetic stirrer for about 20 minutes (single nanopaint) then subjected to sonication process for another 30 minutes (single) to make sure the nanoparticle is dispersed uniformly inside the paint.

![Diagram of sample preparation of composite nanopaint.](image)

**Figure 1.** Sample preparation of composite nanopaint.

2.3. **SEM**
A scanning electron microscope (SEM) was used to observe the surface morphology of nanopaint at an accelerating voltage of 5 kV. A SEM image was taken to view the differences between the surface structures of single nanoparticles basecoat mixture with original basecoat without nanoparticles addition. The best concentration of single nanoparticles basecoat mixture was selected, to compare between the original basecoat. Scanning electron microscopy gave the information of much more value in the study of antifouling paint films than was obtained from the conventional release test.

2.4. **Gloss**
Gloss is a measurement proportional to the amount of light reflected from a surface. In order to achieve best results the correct measurement geometry should be chosen based on the reflectance of the material. Firstly, measure the gloss unit value at 60°. If the GU is between 50-70, use 60°, if more than >=70 GU, use 20° and if GU<=20, use 85°. These angle 20°, 60° and 85° which where light transmitted to the surface are intended for several measurement purpose. Standardly, for surface matt finish 85° was used as its measurement geometry, while mid gloss surface at 60° and high gloss and metallics at 20°. However, for this study, all three measurements geometry are taken into consideration to simplify the properties characterization.

2.5. **Surface roughness**
Surface roughness is one of the criteria that need attention when it comes to coating. Surface texture component of a coating often in cooperate with the surface roughness. It was noted that if the deviation is stated bigger, mean the surface not smooth. Smooth surface meaning small deviation. In this present study the comparison of the surface roughness between the concentrations of the nanoparticles for single nanopaint were being measure using the simple surface roughness meter. The unit is in µm. Lt: 5.600 mm, Lc: 0.800*n; n:5. The comparison between normal paint and 1 wt% nanopaint are taken into account.

2.6. **Adhesion**
The coating adhesion experiment was conducted using test method B that is ASTM standard D3002/D3359 and ISO 2409. For Test Method A, an X-cut was made through the film and the substrate,
pressure-sensitive tape is applied over the cut and then removed. The adhesion was then assessed qualitatively on the 0 to 5 scale. Test Method B, a lattice pattern with either six or eleven cuts in each direction is made in the film and to the substrate, pressure-sensitive tape is applied over the lattice and removed, and then evaluate the adhesion by comparing with the descriptions and illustrations. The apparatus and material needed are: i. Cutting Tool- BYK crosscut hatch, ii. Ruler-tempered steel ruler graduated in 0.5 mm for measuring individual cuts, iii. Tape (Tesa, 4124), iv. Rubber eraser, v. Illumination (aplanatisch) and vi. Magnifying glass. The magnifying glass is an illuminated magnifier to be used while making individual cuts and examining the test area.

![Tape, Scissor, Cutter, Brush, Magnifying Glass, Illumination](image)

**Figure 2.** Crosscut hatch apparatus.

### 3. Results and discussion

#### 3.1. Gloss characterization for TiO$_2$

The observation of gloss from 1% is shown in figure 3. The gloss of nanopaint is linearly increasing with the increasing of weight concentration. Based on the experiment conducted for gloss measurement for single TiO$_2$ nanoparticles, the trend in figure 4 shows that with the addition of nanoparticle, there are significant changes happened to the surface appearance, which is the gloss unit value, GU. Roughly, it can be concluded that with the increase of N-TiO$_2$ weight concentration, the surface is getting glossier. There are many possible reasons for those findings. The nanoparticle concentration is a crucial factor because they can impact rather negatively if there is a surplus of nanoparticles.

Based on figure 4, the comparison between percentage change of gloss between TiO$_2$ and normal paint were made. TiO$_2$ nanopaint had an increase of gloss value by approximately 26.45% with 1.0 wt. percentage of nanoparticles measured at an angle of incident 85°, 6.8% at 60°, and 2.3% at 20°. Based on the obtained results, it was evident that the nanopaint with 1.0 wt.% concentration of TiO$_2$ nanoparticles was the best sample of the nanopaint considered for gloss properties.
Figure 3. Graph of light incident angle against gloss value for single nanoparticle TiO$_2$.

Figure 4. Graph of light incident angle against percentage change of gloss for single nanoparticles TiO$_2$.

3.2. Surface roughness

Based on figure 5 for single nanoparticles, the surface roughness of the coating can be investigated. The trend in figure 5 shows a decrease in surface roughness with addition of N-TiO$_2$. This also means that there is less porosity and the gap between the particles are very small resulted in smoother surface. The reason for this is because of TiO$_2$ does provide glass coating surfaces. Thus, the surface friction is also higher in normal paint surfaces compared with TiO$_2$ nanopaint.
3.3. Adhesion
Adhesion is the most important criteria properties for coating film. Based on the experiment conducted for adhesion testing using crosscut hatch, the result shows a positive outcome for 1.0 wt.% of single TiO$_2$ nanopaint. The adhesion has then been complied with the classification of ISO2049 based on the adhesion test as shown in figure 6. The result shows none of flakes is detached at the intersection. The edges of the cuts are smooth, no square lattice is detached. This gave the 1.0% weight concentration of TiO$_2$ adhesion the rating of 5B. Hence, the adhesion evaluation has confirmed the nanopaint is same level with the current basecoat.

![Figure 6. Result of adhesion test for added N-TiO$_2$ with different weight concentration.](image)

3.4. SEM
Scanning electron microscopy technique (SEM) is used to illustrate the morphology of the nanostructures for the single N-TiO$_2$ and normal paint. Figure 7 shows that the single nanoparticles; TiO$_2$ and SiO$_2$ helps decreases porosity when compared with 0 wt.% nanoparticles. It is observed also in figure 7 that microstructure and pattern of normal paint and single N-TiO$_2$ are different and can be easily distinguished.
4. Conclusion
This paper gave a comprehensive and up-to-date result of these new coating formulation to be of value to researchers. In conclusion the result of nanopaint characterization from the experimental investigation were thoroughly summarised. TiO$_2$ nanoparticles when mixed with basecoat paint lead to better surface appearance and structure such are increased in gloss unit value, reduce the surface roughness and improve adhesion to the substrate-primer surfacer. In view to the fact that the nanoparticles has their significant advantages to the properties mentioned. The final judgement of preliminary testing result based on characteristic selection criteria, 1wt% composition are the best mixing in terms of glossiness, surface roughness, adhesion, and SEM.

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