

PRELIMINARY STUDY OF SELF-CLEANING COATING BY APPLYING NANO TITANIUM DIOXIDE ADDITIVE

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1.0 INTRODUCTION

With the populations exceeding 30 million people in the country like Malaysia, there are high tendency of acid rain with elevated NO_x and SO_x in our surrounding environment, which the condition worsened at manufacturing areas. Pollutants such as air-borne and water-borne particulates adversely affect the health of human especially in the urban region. These harmful particulates in the atmosphere can trigger cardiovascular issues, cause respiratory problems, reduce visibility, and destruct buildings. (Masters et.al., 2008) By incorporating photocatalysts such as Titanium Dioxide (TiO₂) in existing paint formulation to reduce ambient pollutants is an effective method to save cost as several studies have been conducted (Vallee et.al., 2004; Cassar et.al., 2003; Amrhein and Stephan, 2010) and scientifically proven the building surfaces exhibit self-cleaning properties due to photocatalytic capabilities of such materials. This initiative was designed to serve to provide a cleaner environment while maintaining esthetic building appearance after exposure under the harsh weather.

With the continuing growth of nanotechnology and nanomaterials being applied more and more in consumer products, nanometric Titanium Dioxide has been noticed as a promising raw material to be studied and developed. It is believed to possess higher photocatalysis efficiency for self-cleaning purposes due to its enormous surface area when it is in nanometric form. The property of photocatalysis contributes to the decomposition of organic substances such as hydrocarbons which exist on the surface of anatase-form nanoparticles. (Dastjerdi et.al., 2010; Cassaignon et.al., 2007; Jung et.al., 1999; Watson et.al., 2003) With the irradiation of UV of appropriate wavelength (>300nm), redox reactions and molecular transformations are able to be initiated when light excited states are achieved. Free radicals (electrons and protons) are very useful and strong oxidants, which are destructive to most organic compounds. NO_x and SO_x can then be turned into nitrates and sulphates, which

these chemicals are less harmful to the environment i.e. nitrates can be used as a fertilizer for soil. (Benedix et.al., 2000)

Maury-Ramirez et al. (Maury-Ramirez et.al., 2012) observed that direct contact of TiO_2 to pollutants and photons are effective in promoting self-cleaning ability on masonry wall and it turned out to be an interesting alternative, Zhang et.al (Zhang et.al., 2013) further reported that the issue of organic compounds which cause damage to organic paints can be solved by manipulating oxidants induced from photocatalysts. Thus, inorganic coatings such as silicate coatings with combination of photocatalysts were found most effective. However, no test has been carried out by incorporating Nano TiO_2 as a form of additive in coatings. Hence, a different approach is being studied by incorporating Nano TiO_2 as an additive in the existing acrylic paint formulation to see the efficiency of self-cleaning property. This preliminary study presents an experimental trial to evaluate the ability of nanoparticles in the form of additive to deteriorate organic pollutants in particles form and enable the surface of the coated specimens to self-clean. An optimal proportions of Nano TiO_2 in the acrylic coating was determined from the experiments.

1.1 Objectives

Self-Cleaning Coatings have attracted increasing attention in today's construction sector due to the harmful environmental effects towards painted masonry wall. Thus, the objectives of this project are:

- 1.1 To formulate and develop a coating system which contains self-cleaning ability with excellent dirt pick-up and weather resistance characteristics by incorporating Nano TiO₂.
- 1.2 To study on the aesthetic performance, physical, and mechanical properties of self-cleaning coating in terms of wet paint as well as fully-cured paint film.

2.0 LITERATURE REVIEW

2.1.0 Fundamentals of Paint

2.1.1 History

As general, paint can be described as a fluid material which will form a solid, adherent and cohesive film when spread over a substrate surface in the formation of a thin layer. The wet paint contains four major ingredients—pigment, binder or film former, solvent (can be water or thinner) and additives. Relative proportions of these ingredients are modified to produce films with specialized and desirable physical and application properties. The characteristics of the main ingredients can be concluded as follows.

Pigment—pigment is needed in order to provide colour and opacity (or hiding power). Besides, it can also improve film long-lastingness and hardness while provides corrosion resistance property in metal primers. Pigments in lamellar form are used to lower down the moisture absorption of films.

Binder or film former—the binder acts like a “cement” that bind the pigment molecules into lucid film and to adhere to the surface. Binder plays an important role in terms of mechanical and resistance properties of paint film in modern paint technology.

Thinner or solvent—the pigment/binder mixture fluid can be distributed precisely by using adequate amount of solvent or thinner for a uniform film formation. The thinner should have the ability to evaporate completely in order to form a film consisting of pigment and binder only. Organic solvents (ketones, hydrocarbons, alcohols, esters, etc) and water (in latex emulsion and water-soluble paints) are commonly used in the industry.

Additives—paint may possess small amount of driers, anti-foam and anti-skinning agents, surface-active agents to enhance dispersion of pigment and fungicides or bactericides in addition to the major components.

2.1.2 Film Formation

This can take place simply by evaporation of the thinner or solvent (“non-convertible type paint) or by evaporation of thinner followed by chemical reaction in the film (“convertible” type). In the latter the chemical reaction can take one of several forms, namely (a) oxidation by atmospheric oxygen, (b) reaction between two film components (two-pack types), (c) polymerization by heat (stoving types), and (d) polymerization by irradiation (electron beam and ultraviolet). In emulsion paints, film formation involves loss of water followed by coalescence of the polymer particles.

The protection afforded by a paint film is proportional to thickness, and these paints provide a means of achieving the desired film build or thickness with the minimum number of coats. Airless spray is the common method of application. Labour costs are appreciably lower than with the traditional types of paints. These thick films are usually formulated to cure by chemical reaction (i.e. they are two-pack materials such as epoxies or polyurethanes) or are non-convertible types (e.g. chlorinated rubber or vinyls) which dry solely by solvent evaporation.

Very thick film should contain a minimum of solvent. Films of normal thickness can retain small amounts of solvent for a considerable time (Chapman and Hall, 1979) and this is more pronounced with thick films since migration of solvent molecules is retarded by increasing rigidity of the film. This must be borne in mind when multicoat systems are applied—recoating intervals must be adequate. With oxidizable media, there is a limit to film thickness since oxygen is required for cure and must be available throughout the film until it is dry and hard. With thick films, oxidation of surface layers produces a “skin” which reduces the rate of oxygen penetration to the lower layers. These can remain soft for the considerable time.

During the last two or three decades many new resins have been introduced as well as modifications to existing types. The consequence has been the development of paints suited to practically every type of usage and exposure condition, including long-term (15-20 years) weather resistance. Whilst decorative paints continue to be applied by brush or roller, newer methods have been introduced in the maintenance and industrial fields. Among these are (a) electro-deposition, both anodic and cathodic, used mainly for primers for metals and made possible by the introduction of water-soluble resins, and (b) airless and air-assisted spray which permits the rapid coating of large areas and is capable of applying “high build” or thixotropic paints to give greater film build than is possible with conventional paints.

The demand from a number of industries for shorter drying or curing times has been met by the use of new and modified resins; industrial air-drying primers and undercoats with drying times of 10-20 minutes and over-coating times of 1-2 hours are now common. Films which cured by a free radical mechanism are cured very rapidly by irradiation with either electron beams or ultraviolet. The electron beam method has been applied to metal strip (coil coating) whilst ultraviolet irradiation is suited to wood finishes. (Morgans, 1969)

2.1.3 Classification of Paints

Paints can be categorized into two distinguished types—non-convertible and convertible. It can also further subdivide according to curing mechanism (air-dry, baking, etc) and characteristics of performance (corrosion resistance, flame retardance, etc), especially with convertible coatings. A further, very general classification is based on the order of application, a method familiar to professional decorators, industrial finishers and the general public. In brief, the types are as following.

Primers are, with a few exceptions, the first coats applied and are formulated to meet the requirements of the surface. Primers for steel, for instance, are required to meet an entirely different set of conditions from primers for wood, and the formulations differ considerably.

Sealers are used on surface which is porous, absorption of paint medium can upset the pigment/binder ratio of the paints applied and sealers are therefore used to eliminate the suction. In some cases the formulation of the primer can be modified to enable it to function as a sealer also.

Stoppers and fillers. When surfaces contain holes or deep indentations, they are treated with paste stopper after application and drying of the primer. Stoppers are very highly pigmented so that they dry hard without shrinking and can be rubbed down to a smooth surface before application of further coats of paint. If the surface contains merely shallow indentations or irregularities, these are corrected by the application of filler. This is liquid and can be applied by spray or brush. Like the stopper, it dries hard and can be rubbed down to a smooth finish. Both stoppers and fillers are porous when dry and require treatment with sealer before further painting.

Undercoats are applied over the primer or filler. They are fairly highly pigmented to give good obliterating power and to give build or thickness to the paint film. They usually dry to an eggshell finish which is suitable for good adhesion by the finishing coat.

Finishing coats can be designed to dry to films which exhibit a high gloss, semi-gloss, eggshell or matt finish.

2.2.0 Decorative and Building Paints

2.2.1 History

For many years, linseed oil in one or other of its various forms was the standard binder for practically all paints. These oil paints were slow-drying, possessed poor initial gloss and gloss retention, and showed poor levelling. Nevertheless, they afforded reasonably good protection. The introduction of oleoresinous varnishes led to shorter drying times and harder films with, in the case of finishes, greater gloss and gloss retention. They gave rise to the so-called hard gloss paints. In gloss finishes oleoresinous varnishes have been replaced by alkyds, but they are still used in undercoats and primers.

Paints for decorative and building work are generally applied by brush or hand-roller, but on the new work, and especially on prefabricated sections, spraying is used. Generally, decorative paints are slow drying (4 to 16 hours according to type) and contain long media and slow-evaporating solvents. This combination allows large areas to be painted in sections without difficulties in joining up.

2.2.2 Sealers

The types of surface likely to be encountered are roughcast, stucco, concrete, asbestos sheeting, and brickwork. All these, when new, are highly alkaline (brickwork through the pointing) and porous, but the degree of alkalinity decreases on exposure to weather. Painting can be required on new surfaces or on old surfaces the condition of which may vary considerably. The latter is not difficult (provided the surface is properly prepared) but the former needs alkali resistance and sealing properties of a high order. The treatment will be determined by the nature of the following coats and the following primers are in use:-

- i) Vinyl co-polymer and acrylic emulsions. These are used under emulsion finishes and some of the proprietary masonry finishes.

- ii) Solution types based on styrene-acrylic type co-polymers. These are employed in some masonry paints and are alkali-resistant.
- iii) Chlorinated rubber is highly alkali-resistant and is used on very alkaline surfaces such as new asbestos sheeting and concrete. The application of chlorinated rubber paint is the usual treatment for concrete swimming pools where high resistance to water and alkali is required.

2.2.3 Undercoats

Undercoats are highly pigmented paints which follow the primer and any filler or stopper and provide the necessary ground for the finishing coat. An ideal undercoat would possess the following properties:-

- i) good adhesion to primer
- ii) satisfactory opacity
- iii) good flow and levelling, i.e. the dry film should show no brushmarks.
- iv) fairly rapid set to avoid sagging and pulling away from sharp edges, yet remain open long enough to be joined up to other areas.
- v) an eggshell finish to the dry film so that the finishing coat can adhere satisfactorily
- vi) a colour similar to, but preferably a little lighter than the finishing coat.

It is extremely difficult to embody all these desirable properties in any one undercoat and it is usually necessary, as with most paints, to produce the best compromise. The main difficulty is to produce the desired flow properties with the high pigmentation required to produce an eggshell finish. Pigmentation and flow properties are closely interrelated and merit brief discussion before considering undercoat formulation. (Morgans, 1969)

2.3.0 Paint Testing

2.3.1 Purposes of Paint Testing

Paint testing is important to at least four different groups of people involved in the making and using of paint:-

- i) the paint manufacturer, who should test paint as a routine part of paint manufacture and the development of new paints.
- ii) the professional applicator and the large-scale user, who should evaluate the test results of the paint manufacturer. They should also do a somewhat different type of paint testing of their own.
- iii) the specifier of paint, who should understand the purposes and principles of paint testing and the significance of the test results.
- iv) the agencies and authorities that issue paint specifications.

Paint testing is performed to develop distinct information related to objective, important properties, blueprint and application methods. For example, are the properties of paint (ornamental, protection, particular functions) adequately performed by the test paint? Does the test paint possess the essential properties of paint (adhesion, film integrity, ease of application, consistent quality) ⁴ and the necessary specific properties for the intended use? Does the paint meet the specifications issued by the person or agency specifying the paint? Is the paint being applied so as to bring out the properties built into it by the manufacturer? Does the freshly dried paint film have the properties specified for the particular end use?

2.3.2.0 Quantitative and Qualitative Testing

Paint testing is both quantitative and qualitative. Quantitative tests give numerical answers. Colour matching by eye is a qualitative test, while colour matching by instrumental colour measurement is a quantitative test.

2.3.2.1 Standard Test Methods

Standard test methods are those issued by an agency or an authority. An agency issues test methods and paint specifications for its own use in procuring paint. An authority issues test methods and specifications for use by anyone who wishes to employ standardized test methods and specifications. The American Society for Testing and Materials (ASTM) is a well-known authority that issues test methods.

2.3.2.2 Paint Specifications

Paint specifications are of two principal types, performance and composition. Performance specifications specify the test methods that the paint must pass; composition specifications give the required composition of the paint. Paint tests are conveniently grouped in to three classes:-

- i) Evaluation tests, which are conducted before paint is adopted as a standard product.
- ii) Manufacturing control tests, which are conducted during the manufacturing process.
- iii) Application control tests, which are conducted during the application of the paint.

2.3.2.3 Evaluation Tests

Evaluation tests should be made by the paint manufacturer, the professional applicator and the large user of paint. A summary of their differing reasons for making evaluation tests follows.

- i) To gather needed information about an experimental coating during the process of development.
- ii) To determine whether an experimental coating is ready for adoption as a standard product.

iii) To evaluate new raw materials, new ways to combine familiar raw materials, or new or different compounding procedures.

iv) To evaluate the results of changes made in accordance with the rulings of a government regulatory agency.

The applicator or the user makes these tests for the following reasons:-

i) To evaluate the suitability of the coating for the applicator's or the users particular needs.

ii) To verify or disprove the manufacturer's claim for any product when the claims seem unfamiliar or lavish.

iii) To avail himself or herself of new advances in coatings technology by small-scale testing before risking large-scale application of an unfamiliar coating or application procedure.

iv) To evaluate the quality control of the paint manufacturer.

2.3.2.4 Manufacturing Control Tests

Manufacturing control tests are made by the paint manufacturer during the manufacturing process to acquire certain necessary information quickly:-

i) *Composition*. Whether the paint appears to contain the proper ingredients in the correct amount.

ii) *Procedure*. Whether the paint appears to have been compounded in accordance with the standard manufacturing procedure.

iii) *Specifications*. Whether the paint meets established manufacturing control specifications, such as fineness of grind. (Weismantel, 1981)

2.3.2.5 Application Control Tests

Application control test should be performed by both the applicator and the paint manufacturer:-

i) the paint manufacturer should check the paint before canning it to make sure it has the required ease of application, which is an essential property of paint.

ii) the applicator should perform application control tests to make sure that the paint is being applied so as to bring out the properties built into it by the manufacturer.

2.4.0 Raw Materials

2.4.1 Pigments

Pigment is one of the important raw materials in paint. In non-pigmented clear coatings, no pigments are inserted. It would be essential to include a pigment or pigments to achieve crucial important characteristics of paint that distinguish it from a clear coating in the pigmented coatings line. Paints may possess both an opaque or obliterating type of pigment and a non-hiding or, as generally known as an extender type of pigment. Besides providing specialized functions, one of the important features of pigments is to hide the surface being coated. Hiding power, coverage or opacity are the terms used to describe this attribute. Some paints possess "one-coat hiding power" which simply means that only one coat of paint, normally applied, is sufficient and able to fully mask the substrate or surface which is being painted. Two or even three coats of paint may be required to coat a surface if a profound change in colour is conducted, especially if the paint lacks good opacity.

Pigments are also known for their decorative effect and it has become an important property that the industry is looking into. This defines giving the desired colour or special effects to the surface being painted. Great concern is often sounding about the colour combinations so as to make the surface as alluring as possible, whenever paint is applied. Pigments are also utilized for the protection of the surface painted, for example like Zinc Chromate pigments are used to inhibit corrosion. Red lead is often being recognized as a pigment used to prevent steel from rusting. Others such as zinc chromate, zinc dust, and lead suboxide are used in protective finish as well.

Furthermore, paint special functions are often delivered by pigments. For example, barnacles can be reduced by cuprous oxide and tributyl tin oxide which are incorporated in ship-bottom paints, and fire retardance of paint can be conveyed by using antimony oxide. The desired degree of gloss in paint can be achieved by using pigments as well. Everything being equal, high pigmentation in a paint formulation will give low gloss finishing. In addition, pigments are adopted to provide other desirable properties. Hence, desired viscosity, degree of flow or leveling, brushability of paint and etc can be achieved when pigments are employed. They are also able to give very specific properties such as fire retardance, electrical conductance or insulation, phosphorescence and etc.

2.4.1.1 White Hiding Pigments

White is able to form the basis for a wide range of shades and tints in which only a small percentage of colour is applied, besides the fact that it is a colour of its own. Thus, the industry will normally manufacture white bases to develop wide range of colours. The amount and types of essential white pigments being used by the paint industry has been declining. Thus, pigments such as leaded zinc oxides, lithopone, titanium-calcium pigment, basic lead sulfate, titanium-barium pigment, zinc sulfide, and many others have practically vanished. Titanium Dioxide is the most important white pigments used by far out of all white pigments.

2.4.1.2 Titanium Dioxide, TiO₂

There are two crystalline forms of Titanium Dioxide. Anatase form possesses about 75 percent higher of the opacity, compared to the present rutile form. Interior and exterior paints use both forms fairly well as they provide excellent properties. Titanium dioxide is needed in both commercial sales and chemical coatings. On the other hand, anatase is adopted only in small amount except in some coatings that require special properties. In enamels and flats for both water based and oil based coatings, the rutiles form come in handy.

Table 2.1 Relative opacity or hiding power of white pigments

Pigment	Hiding Units
Basic Lead Carbonates	15
Basic Lead Sulfate	15
Zinc Oxide	20
Lithopone	25
Antimony Oxide	28
Anatase Titanium Dioxide	100
Rutile Titanium Dioxide	125-135

2.4.1.3 Nano Titanium Dioxide



Fig.2.1 The powder form of Nano TiO_2 and the anatase structure of the material.

Titanium dioxide is a physically white pigment, which carries other names as titanium(IV) oxide or titania. It has a chemical formula, TiO_2 , and it is an oxide of titanium in nature. It is commonly known as titanium white, or CI 77891 in the colorants or pigments industries. It is found from the source of ilmenite, rutile and anatase generally. TiO_2 has become a promising and essential raw material in the constructive sector as it possesses vast form of applications, ranges from food coloring to paint. It has the E number E171 when it is used as a food colouring. (Zumdahl, 2009) It was found recently at the Ries crater in Bavaria that titanium dioxide occurs in other two high pressure forms, which are a monoclinic form

and an orthorhombic form, besides the common ones such as rutile, anatase and brookite minerals. (Goresy et.al., 2001; Ming et.al., 2001) The ilmenite ore is the most well known ore that contains titanium dioxide in wide spread form. On the other hand, rutile ore contains around 98% titanium dioxide and it is the second most abundant. During heating process, the metastable form of anatase and brookite will change to rutile due to high temperature. (Greenwood and Earnshaw, 1984)

Due to the reason that titanium dioxide contains high brightness and very high refractive index that leads to opacity, thus it is commonly to be used as white pigment. Anatase form, particularly, possesses the ability to generate free radicals under a specific wavelength of ultraviolet (UV) light and thus, it acts as a photocatalyst. This project mainly focus on the function of Anatase form of Nano TiO₂ in achieving self-cleaning purpose. Besides, titanium dioxide nanoparticles are suggested to be used to form the pixels of screen as they can generate electricity when transparent and under the effect of light. (Greenwood and Earnshaw, 1984)

With the continuing growth of nanotechnology and nanomaterials being applied more and more in consumer products, nanometric Titanium Dioxide has been noticed as a promising raw material to be studied and developed. This is because it performs best as a photocatalyst that can be utilized in antiseptic and medical field. Titanium Dioxide is able to inhibit bacterium from reproducing, it is also able to degrade the structure of cell membrane which will kill the microorganisms completely. Furthermore, titanium oxide nanoparticle will not dissolve itself when reacting with organic compounds and germs. The effect of germs-free on surface of paint film is long-lasting. Thus, it is highly affective when it is incorporated into a coating system which possesses self-cleaning ability (free from contaminants and pollutants). TiO₂ nanoparticle posseses wide range of applications, especially in the field of paint (UV resistant material), self-cleaning utensils, chemical fiber, plastics, printing ink,

coating, antibacterial material, air purification, foods packing material, sewage treatment, face washing milk, skin milk, chemical industry, cosmetics, sunscreen cream, moistening refresher, vanishing cream, skin protecting cream, powder make-up, coating for paper-making industry and etc.

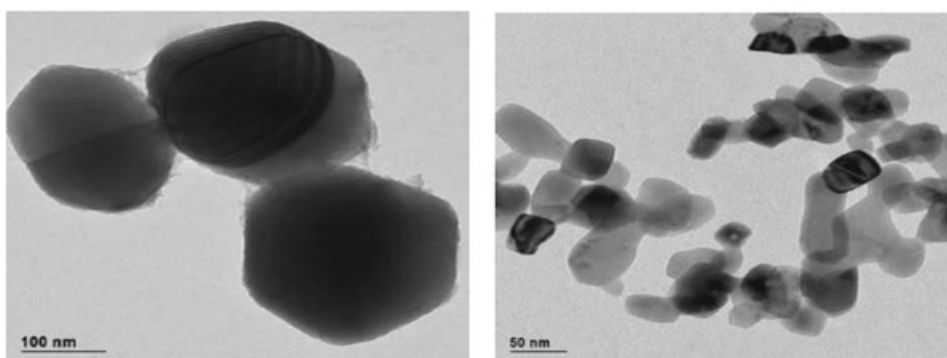


Fig 2.2 SEM image of standard TiO₂ pigments and SEM image of the nanometric phase of TiO₂.

Fig 2.2 indicates the standard TiO₂ particles, which is about 200-300nm in size. It possesses a very high refractive index, due to its structure and morphology. However, the standard-sized particles require dispersion or grinding prior incorporation into paint. Fig.4 shows the nanophase of TiO₂, which is usually less than 100nm in size. This has further contributed to its enormous specific surface area and reactivity of the particles have been multiplied. When the nanoparticles are exposed to the appropriate wavelength of Ultraviolet light, high amount of free radicals will be generated and this has enhanced its semi conductor properties, as electrons are being excited to the conduction band of the material.

2.5.0 Free Radical Generation

The oxidation process of most hydrocarbons occurs rather slowly in absence of a catalyst, which the action can be explained by kinetic arguments and contradictions. The main

function of a photocatalyst is to decrease the activation energy of a given reaction. Particles with strong oxidation and reduction ability will often be generated as the result of photoinduced processes.

Semiconductor particles (photocatalyst), which in direct contact with a liquid or gaseous reaction medium, usually exist in a heterogeneous photocatalytic system. Subsequent processes like redox reactions and transformations of molecule are able to be initiated when the catalyst is exposed to light excited states. In Fig. 2.3 a simplified reaction scheme of photocatalysis is shown. With a filled valence band (VB) and an empty conduction band (CB), semiconductors (metal oxides or sulfides as ZnO, CdS, TiO₂, Fe₂O₃, and ZnS) is able to perform as sensitizers for light-induced redox processes.

Band gap energy (E_g) actually defines the energy difference between the highest energy level of CB and the lowest energy level of VB. It correlates with the minimum energy of light required in order to make a electrically-conductive material.

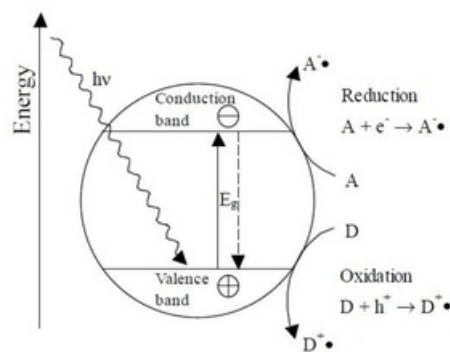
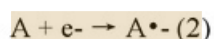


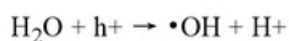
Fig 2.3 The process of a photochemical excited TiO₂ particle

An electron will be promoted from the valence band to the conduction band when a photon with an energy of $h\nu$ is beyond the energy of the band gap. Thus, this will leave a hole (h^+) behind in the lattice. The charged carriers are recombined immediately especially in

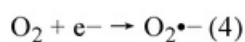
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electrically conducting materials, i.e. metals. A portion of this photoexcited electron-hole pairs will diffuse to the surface of the catalytic particle and trapped at the surface. Subsequently, chemical reaction will occur between adsorbed donor (D) or acceptor (A) molecules. The holes oxidizes the donor molecules (1) while the conduction band electrons are able to reduce adequate amount of electron acceptor molecules (2).



8
Semiconducting metal oxides are well known for its strong oxidation power of their holes h^+ . Highly reactive hydroxyl free radicals ($\bullet\text{OH}$) are produced when they react in an one-electron oxidation step with water (3). The radicals which are strong enough to oxidize most organic compounds are both holes and the hydroxyl radicals.



3
Oxygen in the air will act as an electron acceptor (4) by forming the superoxide ion in general. Superoxide ions are also extremely reactive particles, which has the ability to oxidize organic materials. (Benedix at.al., 2000)



2.6.0 Self Cleaning Principles and Properties

Air and water pollution due to massive development in this fast-paced world adversely affects human health and buildings in the urban environment. Airborne particulates in the surrounding environment can cause chronic health problems such as respiratory malfunction, degradation of visibility, cause cardiovascular concern, and damage buildings. (Zhang et.al.,

2013) Visible stains can be a massive problems for buildings and constructive materials if they occur very often on masonry and clay building façades, due to the surface build-up of external **materials of diverse nature (organic or inorganic)**. These contaminants are **mainly created from the atmospheric aerosol pollutants**, which will cause **the aesthetic properties of** the construction that leads to increase of maintenance costs. (Quagliarini et.al., 2014) Thus, the industry is highly interested in the creation of innovative and self-cleaning coating systems that curb their applicability limitation as well as the sensitivity to mechanical and chemical influences. Additives that are integrated into the coating matrix reflect the solar radiation on particles of dirt on the surface of the coating.

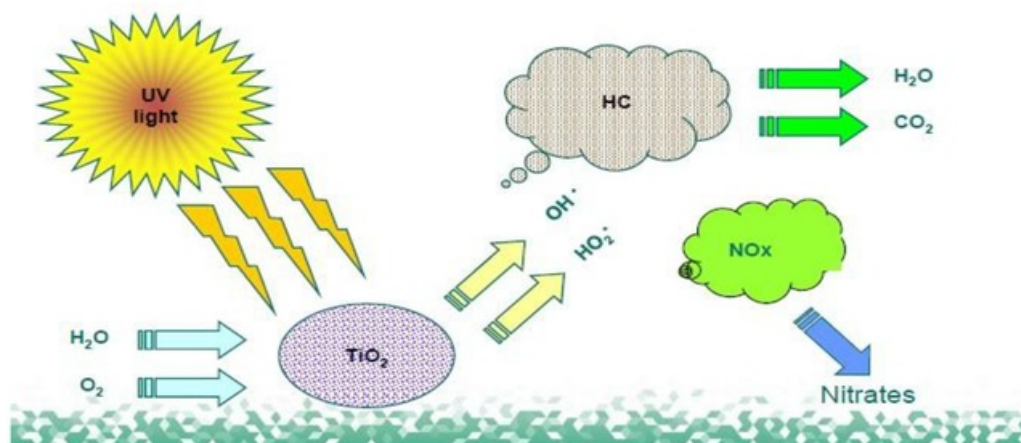


Fig. 2.4 Process of free radicals react with hydrocarbon compounds

Photocatalysis happens when nanomaterials are capable, under the effect of radiation of appropriate wavelength can initiate radical reactions with organic products. When Nano TiO₂ is exposed to the light intensity of wavelength more than 300nm, free radicals (electrons and protons) are generated when **an electron (e⁻) jumps from the valence band to the conduction band and leave a hole (h⁺) behind**. This is because **the photon of the UV possesses an energy of $h\nu$ and it exceeds the energy of the band gap in the material**. Highly reactive hydroxyl free radicals (**•OH**) are produced when they **react in an one-**

electron oxidation step with water. The radicals which are strong enough to oxidize most organic compounds are both holes and the hydroxyl radicals. Nox and Sox can then be turned into nitrates and sulphates, which these chemicals are less harmful to the environment i.e. nitrates can be used as a fertilizer for soil.

3.0 EXPERIMENTAL

3.1 Materials

Pigment Volume Concentration of the specimen will be pre-determined before a formulation is constructed in order to justify the optimal dosage of Nano TiO₂ in the coating.

- Pure acrylic Nippon Weatherbond Pastel Base obtained from Nippon Paint(M) Sdn.Bhd
- Pure acrylic Nippon Weatherbond Deep Base obtained from Nippon Paint(M) Sdn.Bhd
- Commercially available Nano TiO₂ additive (Siquest Technology) with about 98% anatase

3.2 Apparatus

- Beakers (100ml and 500ml)
- High Speed Stirrer
- Dropper
- Spatula Spoon
- Weighing Scale
- Pipette Disposable
- Measuring Cylinder
- Retort Stand
- Test Tubes (5)
- Hand coater (with 150μm thickness)

3.3 Equipment and Machines

- Scanning electron microscopy (SEM) FEI Quanta-200 instrument equipped with an energy-dispersive X-ray spectroscopy (EDS) analysis system (Oxford INCA 350)
- Viscometer
- SHEEN Gloss Meter
- ICI Cone & Plate Viscometer
- Colorimeter (Konica Minolta CM 2600d) with a 3mm aperture
- OCA 30 Contact Angle Tester
- Q-Lab, QUV® Accelerated Weathering Testers, UVA-340 lamp

3.4.0 Methodology

3.4.1 Synthesis of Pure Acrylic Exterior Coatings Incorporated with Nano TiO₂

Pure Acrylic Paint Nippon Weatherbond CC bases i.e. Pastel Base and Deep Base were obtained from Nippon Paint(M) Sdn.Bhd.. Both bases were tested in laboratory of Technical Department of the company to determine the effects of Nano TiO₂ on photocatalytic degradation of particulate contaminants. A commercially available Nano TiO₂ additive (Squest Technology) with about 98% anatase was used in this study. It was post-added into Nippon Weatherbond formulation with different composition respectively i.e. 1% Nano TiO₂ Additive and 3% Nano TiO₂ Additive. These samples were then compared with Nippon Weatherbond standard formula in order to evaluate the Dirt Pick Up Resistance, Dirt Streak Mark Resistance, QUV Resistance and other physical properties such as viscosity of the wet paint.

3.4.2 Microstructure Analysis

Microscopic analysis was conducted to study the surface's morphology and characteristics as well as to determine the composition of TiO₂ nano-particles in the dispersed form of additive solution (Siquist Technology). A thin gold layer was coated on the surface of dried samples by a gold sputter coater in order to obtain a clear signal. Scanning electron microscopy (SEM) FEI Quanta-200 instrument equipped with an energy-dispersive X-ray spectroscopy (EDS) analysis system (Oxford INCA 350) was used to observe the additive. This is to further confirm that the additive contains 98% of Nano TiO₂ particles.

3.4.3 Aesthetic Properties

In order to measure the colour of coatings with Nano TiO₂ additive incorporated, a portable colorimeter (Konica Minolta CM 2600d) with a 3mm aperture was used. As recommended in UNIEN 15886:2010 (UNI EN, 2010), nine measurements were repeated for each specimen. A daylight illuminant (D65) at 10° observer angle was used to carry out the measurements. Results were then expressed in CIELAB color space. In order to ensure specific repeated measurements on the same spots in the following tests, an 88cm reference spatial grid was used. Colorimetric analysis were conducted again on treated specimens in order to evaluate the features of the titania coatings on the visual appearance. The formula below was used to calculate the colour difference between standard specimen and Nano TiO₂-incorporated specimen.

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2}$$

Where L_0^* ; a_0^* and b_0^* are the CIELAB coordinates of untreated specimens and L^* , a^* and b^* are the CIELAB coordinates of treated specimens. By utilizing Novo Gloss Trio

apparatus (Rophoint Instruments), the gloss of each sample was measured at both 60° and 85° as standard geometries. (Quagliarini et.al., 2012) The results were averaged after measurements were repeated five times for each sample. Results were expressed in gloss units (GU).

3.4.4 Panels Preparation

Panels made of fiber cement board of size 31cm x 35cm were painted with full coating system for exterior paint which starts from Nippon Vinilex 5100 Wall Sealer as a primer (1 coat of 150µm) and NanoTiO₂ incorporated coating (2 coats of thickness 150µm each) as a topcoat. Panels were painted with Nano TiO₂ Additive incorporated coating with different composition respectively i.e. 1% Nano TiO₂ Additive, 3% Nano TiO₂ Additive and standard (with no Nano TiO₂ additive). Panels were then cut into different sizes to evaluate the Dirt Pick Up Resistance, Dirt Streak Mark Resistance, QUV Resistance, Alkaline and Efflorescence Resistance as well NaOH immersion test.

3.4.5.0 Basic Paint Performance Study

3.4.5.1 Paint Film Dirt Pick-Up Resistance

The dirt pick-up resistance of the paint film was evaluated according to ASTM WK38233 - New Test Method for Dirt Pick-up Resistance for the films of Architectural Paints and Stains. A uniform test method complete with a procedure that contains a standard dirt formulation was created. A spectrometer as well as observation were carried out for the analysis of degree of dirt pick-up at Nippon Paint (M) Sdn.Bhd RnD center.

3.4.5.2 Hydrophilicity

By considering static contact angle, the hydrophilicity of the samples was determined. The samples were made with high hydrophilicity to suit Malaysia weather where rain is

abundant throughout the year. The contact angle between coated surface and water droplets (2ml) were measured using OCA 30 Contact Angle Tester. The specimens coated on the surface of fiber cement board 7.5cm x 15cm were NP Weatherbond Standard, NP Weatherbond with 1% NanoTiO₂ additive, and NP Weatherbond with 3% NanoTiO₂ additive.

3.4.5.3 Photocatalytic Effectiveness

Photocatalytic properties of Nano TiO₂ will determine the self-cleaning ability of the coating system. Degradation of organic dye (Methylene Blue-MB) which represents organic pollutants is measured by using a test adapted from the literature in order to evaluate the TiO₂ nano-coatings. (International Standard Organization, 2010; Rodamina Test Method, 2008) MB was chosen to show contrast on the white surface of painted fiber cement boards. Fiber cement board specimens 7.5cm x 15cm were stained by 0.5 mL MB aqueous solution (MB content: 100 mmol/L) using a syringe. This concentration is adequate to produce the desired color variation on coated fiber cement boards, for both treated specimen and untreated specimen and it will not be changed by natural discoloration of MB under irradiation of UV light. Thus, color discoloration due to Nano TiO₂ after being irradiated with a specific wavelength of UV can be observed from time zero to the end of durability test. Then, specimens were dried for 24 h in dark condition. Next, samples were placed on a rack and irradiated by UV light (Q-Lab, QUV® Accelerated Weathering Testers, UVA-340 lamp). Discoloration of MB was clearly observed after the specimens were irradiated in QUV machine after 1,4, and 24h of exposure.

3.4.5.4 Dirt Streak Mark Test

Dirt Streak Mark Test panels were prepared according with 2 coats of each specimens painted on each fiber cementboard (3 inch x 1 ft) respectively. Then, the panels

were exposed for 4 months on the 90° rack with slits which the panels were placed upright. Visual evaluation was done after the exposure.

3.4.5.5 Degree of Chalking

The degree of chalking of exterior paint films was evaluated according to ASTM D4214-07. The method consists of a wide range of techniques and photographic references to determine the extend of chalking of exterior paints. These test procedures cover the evaluation of the degree of chalking on white or tinted exterior paint surface. Only Nippon Weatherbond Deep Base specimens incorporated with different composition of Nano TiO₂ additive i.e. 1%, 3% and standard were evaluated. This is because degree of chalking is much more obvious in Deep Base compared to Pastel Base.

3.4.5.6 UV Radiation Aging Test

UV radiation was being provided for 2000 h by two UV lamps (Q-Lab, QUV® Accelerated Weathering Testers, UVA-340 lamp) in order to verify the degradation of the coating due to the UV exposure. The lamps were located on the lid of the chamber with a mutual separation distance from the two racks. The samples with standard size 7.5cm x 15cm were irradiated with an average UVA intensity of 26.7 W/m² as resulted from measurements made by a digital light meter (General Tools UV513AB), for 24 h/day. The glass chamber was made opaque and light reflectance by using an aluminium foil to prevent the penetration of natural light from the surrounding. Specimens were irradiated with a total UV intensity equal to 173 MJ/m² correlates to about 34 months of northern exposed façades and 15 months of southern exposed façades in Mediterranean area (Jacorides et.al., 2009; UNI, 1994), which can be achieved in an accelerated process with UV intensity and aging test duration for 2000 h. The degradation efficiency was evaluated by using spectrometer and visual observation from the expertise of Nippon Paint (M) Sdn.Bhd.

3.4.5.7 Efflorescence and Alkaline Resistance Test

Efflorescence and Alkaline Test were carried out with all specimens using the China GP method, which is equivalent to ASTM D7072. This procedure covers the determination of the degree to which a latex paint resists the formation of efflorescence and alkali burnout on the exposed paint surface. This method is customized primarily to relate efflorescence salt migrating from the inner surface of the substrate to the deposit appearing on the surface of latex paints. This standard can be applied mainly to the painting of masonry-type substrates such as mortar, concrete cement, brick, poured concrete, stucco, and similar materials.

4.0 RESULTS AND DISCUSSIONS

4.1 Microstructure Analysis

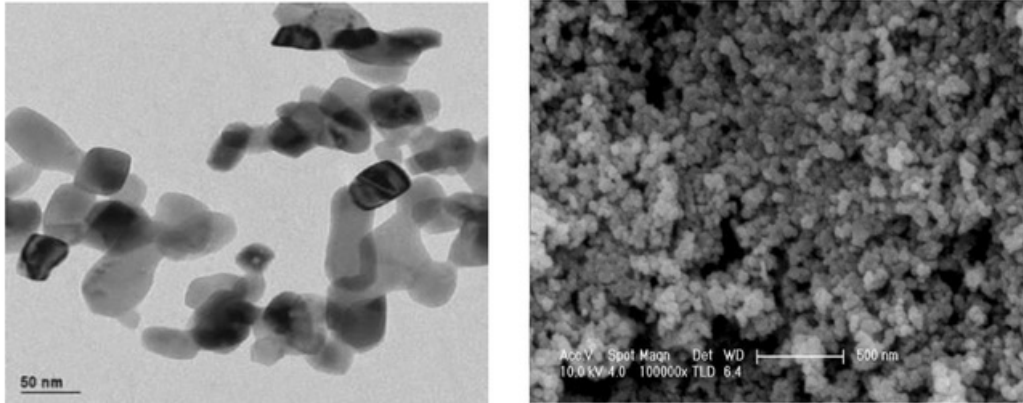


Fig.4.1 SEM micrographs of TiO₂ nanoparticles which originally in dispersed form supplied by Siquest Technology

Fig. 4.1 shows the SEM image of TiO₂ nanoparticles. Clear nanostructures can be seen having grain size of ~ 30 nm. It is clear that the nanoparticles seen by SEM image consist of a number of crystallites. This has further confirmed that the additive contains 98% of Nano TiO₂ particles.

4.2.0 Aesthetic Properties

4.2.1 Colour LAB and Gloss

The specimens will be referred as STD for NP Weatherbond Pastel Std, 1% NTA for NP Weatherbond Pastel with 1% NanoTiO₂ Additive, and 3% NTA for NP Weatherbond Pastel with 1% NanoTiO₂ Additive.

Table 4.1 Data showing colour and gloss features of all three specimens.

Paint Physical Properties		STD	1% NTA	3% NTA
Gloss 60°/85°		5.1/10.7	4.7/13.1	4.6/10.3
Opacity CIELAB standard (150µm Wet paint thickness)		94.59	95.94	94.78
Whiteness (CIELab)		83.67	83.19	83.09
Colour	L value	95.80	95.80	95.87
	a value	-0.36	-0.37	-0.40
	b value	1.30	1.41	1.46
	Δ E compared to STD	Std	0.11	0.18

Gloss level for each specimen is being evaluated by considering 60° and 85°. It is because paint will usually be applied on external flat surface wall upright and vertical. From the data shown, gloss level of all three specimens were comparable to STD, and it shows a matt finishing. It is suitable for walls especially on external surfaces as gloss finishing might affect the appearance of the wall. The specimens were casted on a crysal paper using an applicator of 150µm wet paint thickness. The thickness is set according to the paint thickness applied on wall by using brush or roller. It is conclusive that both opacity and whiteness of the paint are comparable with STD. NanoTiO₂ additive did not plays a big role in affecting the opacity and the whiteness of conventional paint. The a*, b*, L*, and Δ E* of all specimens were reported in Table 4.1. In terms of colour, L value describes the lightness of the paint film, A value describes the red colour intensity while B value tells the yellow colour intensity. We can conclude that all specimens are comparable to STD as they are all lighter, greenish toned with slight yellowish shades. Δ E measures the difference of colour among all specimens tested, and it is recommendable that the value should be <1. In this study, all trials showed value of <1, indicates that there is no significant difference in terms of colours.

4.3.0 Basic Paint Performance Study

4.3.1 Paint Film Dirt Pick-Up Resistance

Table 4.2 Dirt Pick Up Resistance for all three specimens after 2 months and 4 months of exposure on 45° rack outdoor

	Variables	STD	1% NTA	3%NTA
Out-door natural exposure on Panel- dirt pick-up resistance after 2 months exposure (Delta is compare to unexposure areas)	Appearance	not chalky	not chalky	not chalky
	ΔL	-3.86D	-2.33D	-1.22D
	Δa	0.19R	0.09R	0.04R
	Δb	0.90Y	0.53Y	0.32Y
	ΔE	3.97	2.39	1.26
Out-door natural exposure on Panel- dirt pick-up resistance after 4 months exposure (Delta is compare to unexposure areas)	Appearance	not chalky	not chalky	not chalky
	ΔL	-5.55D	-4.31D	-2.71D
	Δa	0.29R	0.22R	0.15R
	Δb	1.27Y	1.00Y	0.82Y
	ΔE	5.70	4.43	2.83

Dirt Pick Up resistance serves as a direct indication whether a paint film has a self cleaning property, where organic contaminants will not stick on the surface and be washed away by rainwater. ¹ A portable colorimeter (Konica Minolta CM 2600d) with a 3mm aperture was used in order to determine the colour of coatings with Nano TiO₂ additive incorporated compared to untreated specimen and ¹ results were expressed in CIELAB color space. As shown in Table 4.2, the values of color lightness differences (ΔL^*) do not correspond to the ¹⁵ values of total color differences (ΔE^*). Basically, with the increase of ΔL^* , the ΔE^* decreases. The results in Table 4.2 confirm the decrease of ΔE^* with increasing of NanoTiO₂ additive concentration. Generally, ΔE values were referred to determine specimen which have the most significant self cleaning property. Table 4.2 clearly shows that the higher the percentage

of nano TiO_2 particles in a paint formulation, the better it can resist to pick up dirt and other organic contaminants. Paint with 3% NTA gives the best result in terms of dirt pick up resistance compared to STD and 1% NTA after 2 months and 4 months of exposure outdoor. This can further be used as a factor to determine the optimum dosage of Nano TiO_2 additive that can be used in a paint formulation.

4.3.2 Hydrophilicity

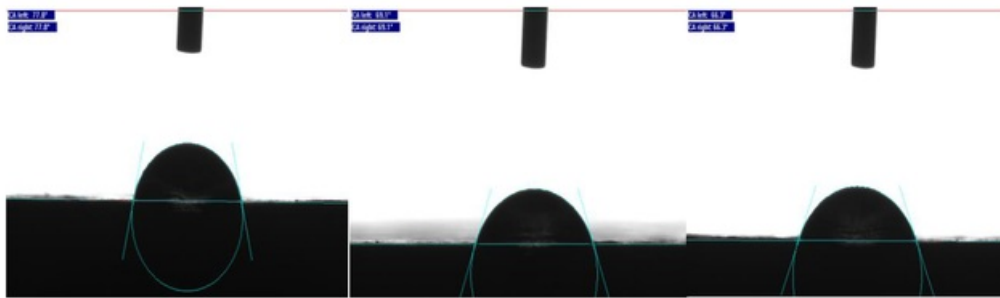


Fig. 4.2 Water contact angle measurements for coatings on a fiber cement substrate: (a) STD; (b) 1% NTA ;(c) 3% NTA

The ability for water to evenly spread out and flow on the films depends greatly on the superhydrophilicity of the film. Hence, this helps to optimize the self-cleaning property when used in outdoor applications. (Wang et.al., 1997) UV irradiation tends to induce the superhydrophilicity of anatase, rutile and amorphous TiO_2 surfaces and make them water favourable. (Sirghi and Hatanaka, 2003; Lee, 2012) The panels were exposed to UV for 24hr after coated with 2 coats of respective specimens. The result has shown that TiO_2 nanoparticles caused the water contact angles to change from 77.0° for STD to 69.1° for 1% NTA to 66.3° for 3% NTA, as shown in Fig. 4.3. A water contact angle lower than 90° is perfect for the paint film to exhibit self-cleaning properties, hence, by the incorporation of nano TiO_2 additive, surface hydrophilicity is achieved in order to get good self-cleaning effect for Malaysia weather.

4.3.3 Photocatalytic Effectiveness

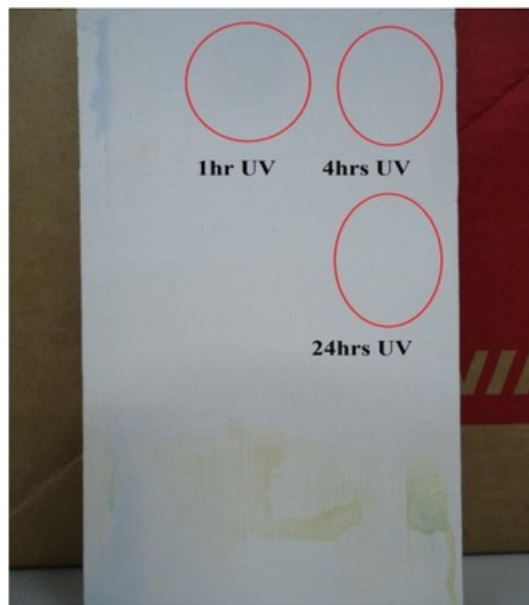


Fig.4.3 Discolouration of Methylene Blue after specimen with 3% NTA was irradiated in QUV machine after 1, 4 and 24h of exposure respectively.

Photocatalytic property possesses very much a significant impact on the effectiveness of self-cleaning properties of a paint, due to the ability of the atoms to generate free radicals that may form superoxides with water to break organic pollutants, under the appropriate wavelength of light ($>300\text{nm}$). Allen et.al (Allen et.al., 2009) reported that photocatalytic activity occurs in most frequent basis and was found that only particle with diameters less than 10 nm is efficient enough to cause the blue shift. On the other hand, due to the reason that increasing specific surface area provides more reactive sites to react with contaminants, small size effect seems to improve the photocatalytic activity of the TiO_2 . According to Benedix et.al (Benedix et.al., 2000) an electron will jump ³ from the valence band to the conduction band when an incident photon (UV) possesses ³ an energy of $h\nu$ exceeds the energy of the band gap of the nanoparticles. Generally, electrons that are no longer being bound in the lattice are known as

free radicals and they are able to react in an one-electron oxidation step with water to produce the highly reactive hydroxyl radicals ($\bullet\text{OH}$). The hydroxyl radicals are very powerful oxidants that react with most organic contaminants by oxidation process. Fig. 4.4 indicates the discolouration of Methylene Blue which is an organic dye after specimen with 3% NTA was irradiated in QUV machine after 1, 4 and 24h of exposure respectively. The discolouration is the most significant for specimen with 3%NTA. This shows the effectiveness of TiO_2 nanoparticles in destroying organic contaminations after being irradiated under UV for a specific period of time.

4.3.4 Dirt Streak Mark Resistance

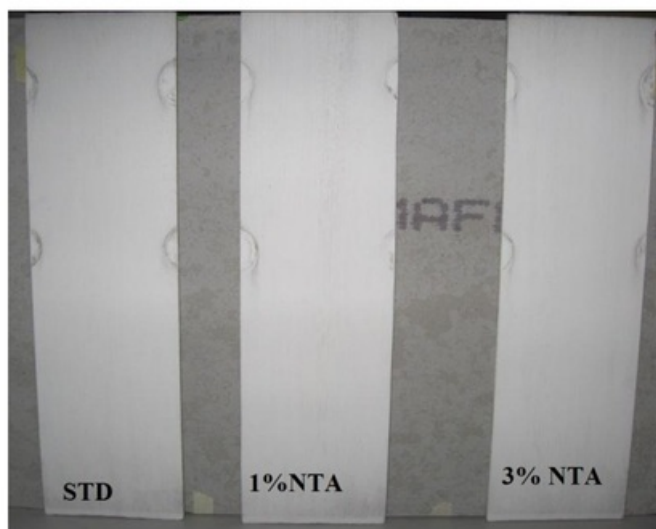


Fig.4.4 Dirt streak marks on panels painted with STD, 1%NTA and 3%NTA after 4 months exposure on 90° rack with slits.

Dirt Streak mark resistance was conducted to evaluate the ability of paint film to repel dirt streak mark under rainy condition. There are signs of dirt adhered to paint film of three samples, with 1%NTA being the obvious as given in Fig.4.5. This has indicate that addition of 1% of NanoTiO_2 additive in the paint formulation is not adequate to give the optimum

resistance to dirt streak mark. According to visual evaluation, NP Weatherbond with 3% Nano TiO₂ Additive shows better result in terms of streak mark resistance, compared to the rest of the specimens. These has further confirmed that higher percentage of Nano TiO₂ Additive should be used in order to fully deliver self cleaning property.

4.3.5 Degree of Chalking



Fig. 4.5 Degree of chalking indication for NP Weatherbond Deep Base tinted for all three specimens

The specimens were tinted with colour before painted on the panel in order to evaluate the extend of chalking issue. The fiber cement panel with 12" x 18" in size was painted with Nippon Weatherbond Deep Base specimens incorporated with different composition of Nano TiO₂ additive i.e. 1%, 3% and standard. This is because degree of chalking is much more obvious in Deep Base compared to Pastel Base. The panel was put out for exposure on a rack with orientation of 45° for 2 months. Fig.4.2 shows that there is no chalking issue for all specimens exposed. According to Zhang et. al. (Zhang et.al., 2013) it is advisable to incorporate NanoTiO₂ into silicate formulated paint as the high photocatalytic properties of anatase might cause the nanoparticles to react with acrylic binder, and causes the paint film

to chalk after exposure to UV. This study has shown favourable results for acrylic emulsion paint industry as it further proved that there is no signs of chalking on the acrylic paint films after 2 months of direct UV irradiation. This may be due to the trace amount of nanoTiO₂ used in the paint formulation which is not significant enough to cause chalkiness.

4.3.6 UV radiation Aging

Table. 4.3 UV radiation aging test result for all three specimens after 1000hrs and 2000hrs of radiation aging test respectively in Q-Lab, QUV® Accelerated Weathering Testers, UVA-340 lamp.

	Variables	STD	1%NTA	3%NTA
QUV - 1000hrs (Delta is compare to unexposure areas)	Appearance	not chalky	not chalky	not chalky
	Δ L	-0.83D	-0.77D	-0.86D
	Δ a	-0.00	0.01	0.04R
	Δ b	-0.54Y	0.49Y	0.56Y
	Δ E	0.99	0.91	1.03
QUV - 2000hrs (Delta is compare to unexposure areas)	Appearance	not chalky	not chalky	not chalky
	Δ L	-1.47D	-1.23D	-0.96D
	Δ a	0.05R	0.04R	0.06R
	Δ b	0.77Y	0.65Y	0.51Y
	Δ E	1.66	1.39	1.09

QUV is an accelerated weathering test to evaluate the chalkiness of paint film after a certain hours of exposure under intensive UV light. If paint film chalking after a certain period, this indicates that Nano TiO₂ has reacted with binder system of the paint, and this has diminish the primary function of coating which is to protect the masonry wall. According to record, NP

Weatherbond Standard Formula can withstand up to 2000 hrs of UV exposure, and still shows no signs of chalking. Delta E values indicate the differences of appearance of the specimens in terms of lightness and colour compared to initial readings before the panels were being placed in the machine. Table 4.3 depicts the different parameters obtained from this analysis. The bigger the value of ΔE , the bigger the difference compared to original fresh painted surface. After 2000hrs of UV irradiation, which is equivalent to 1.9 yrs based on a tropical warm and humid condition, indicating its super durability. (Zhang et.al, 2013) There is no signs of chalking on three specimens tested after the UV exposure. Specimen with 3%NTA shows the lowest ΔE value compared to STD and 1%NTA. This further proved that the increase of TiO_2 nanoparticles in the paint formulation plays a part in affecting the appearance of the paint film, which appears to be whiter n cleaner.

4.3.7 Efflorescence and Alkaline Resistance

Table. 4.4 Alkaline and Efflorescence Resistance Test for all specimens coated on a panel put on top of different solutions

Test Properties	STD	1%NTA	3%NTA
Alkaline resistance - (Panel put on top of 2% NaOH soln) fail at number of days	2days	1day	1day
Efflorescence resistance (Panel put on top of 5% Na_2SO_4 + 1% NaOH Soln) Fail at number of days	2days	2day	1day

Efflorescence and Alkaline Resistance Test are one of the basic paint properties to evaluate performance of a topcoat on a concrete, mortar, brick etc wall. Panels were pre-treated by immersion in water for 7 days to eliminate impurities before 2 coats of each specimens were

applied. Alkaline resistance test actually defines the ability of specimen to withstand the high level alkaline condition in a concrete wall. The specimens are considered fail when the panel starts to discolour and yellow tone appears on top of the paint film, which indicates the alkaline solution has actually seeped through. An indicator has also been applied on top of the paint film to see a clearer picture of the failure. According to the result obtained (Table 4.4), STD is able to resist alkaline solution to seep through and fail at the second day, whereas 1%NTA and 3%NTA failed on the first day itself.

Efflorescence defines the migration of solvated salt originated from the calcium carbonate compound in the cement to the atmosphere on exposure to air. Indirectly, it also indicates the loss of water (or a solvent) of crystallization from a hydrated or solvated salt when exposure under sunlight. For a topcoat to block the salt within the bricks from seeping through and arise on the surface of the paint film, it must possess a definite level of resistance. Table 4 shows that both STD and 1%NTA are able to resist the salt from arising on the topcoat for 2 days after the panels were put on top of the mentioned solution, but 3%NTA fails on the first day itself.

As a matter of fact, NP Weatherbond which perform the function as a topcoat, is unable to withstand such harsh condition, and the specimens are expected to fail after the first or second day. Therefore, it cannot be directly applied on concrete, mortar, bricks etc, where high level of alkalinity and salt are detected. A coat of wall sealer which are able to resist alkaline and salt should be applied before the topcoat. Thus, a proper coating system will actually be implemented in order to protect the wall.

5.0 CONCLUSION

This study has demonstrated preliminary investigations of incorporating Nano TiO₂ additive in acrylic paint in order to perform self-cleaning properties while not neglecting the basic paint properties at the same time. The results shown that coatings with Nano TiO₂ additive with 3% dosage is able to perform better in terms of self-cleaning, which can be significantly observed through Dirt Pick Up Resistance Test, Dirt Streak Mark Test, photocatalytic effectiveness, contact angle measurement and etc. It was found that superhydrophilicity property across the surface enables both water and oil to spread evenly, which is most suitable for Malaysia's weather. However, the research is still in preliminary stage and still unable to conclude the area that Nano TiO₂ works best, whether in acrylic or hybrid system. More developments and researches need to be done in order to further confirm on the matter. This field has been intensively investigated for its importance to buildings and constructions in future.

6.0 RECOMMENDATIONS

Research work is a never ending process which requires continuous improvement with new ideas, technologies and enhancement methods in order to achieve a new perspective and discovery. Hence, from the results obtained in this study, I would like to suggest a few recommendations to improve this study.

1. To further study the mechanical properties of Nano TiO₂ incorporated coatings.
2. To venture into a new field by incorporating Nano TiO₂ into Silicon Resin Emulsion Paint to enhance its self-cleaning performance

PRELIMINARY STUDY OF SELF-CLEANING COATING BY APPLYING NANO TITANIUM DIOXIDE ADDITIVE

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