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(54) Title: COMPOSITE PIGMENTS

(57) Abstract: There is provided a paint formulation comprising a composite pigment, said composite pigment being selected from the group consisting of metal oxide/silica, metal oxide/silicate, metal oxide/alumina, metal oxide/metal oxide and metal oxide/zirconia, wherein the size and amount of said composite pigment are selected to increase the opacity of said paint formulation.

## COMPOSITE PIGMENTS

### Technical Field

The present invention generally relates to composite pigments. The composite pigments may be used in a paint formulation so as to increase the opacity of the paint formulation.

### Background

The application of nanomaterials to various industrial uses has gathered substantial interest both industrially and academically. The main motivating force for this momentum is the ability of nanomaterials, with their near-atomic dimensions, to substantially improve the properties of final products.

For example, nanomaterials have been used in coating applications. Metal oxides like nano-titanium dioxide and silicon dioxide have been extensively used to formulate polymeric coatings to provide properties like photocatalysis and excellent abrasion resistance.

Titanium dioxide ( $\text{TiO}_2$ ) is the pervasive and unchallenged pigment in the coating industry mainly due to its excellent ability to scatter visible light. Thus,  $\text{TiO}_2$  has very high refractive index and has been commonly used to enhance the opacity of paints. However, the price of  $\text{TiO}_2$  in recent years has fluctuated very widely and increased substantially. This prevents  $\text{TiO}_2$ -based paints from being economically competitive. Furthermore, conventional paints for external architectural use often experience "yellowing" due to the exposure to solar radiation. High humidity and frequent rainfall in the tropical region also result in bacterial and algae growth on walls.

The opacity or hiding power of paints depends on numerous factors such as particle size, crystalline phase of pigment, refractive index of pigments and polymer, and the dispersion or crowding of individual pigment particles. All these factors influence the back scattering of the light by individual pigment particles. Pigment crowding of  $\text{TiO}_2$  is the most important consideration in designing of paints. This is because even though  $\text{TiO}_2$  confers opacity to the paints, by increasing the  $\text{TiO}_2$  content in the paint above a certain point, the pigment particles are brought to close proximity of each other, thereby interfering with the ability of such pigments to scatter light efficiently.

To overcome the problem of pigment crowding, extender pigments possessing smaller dimensions are used as spacer units to isolate  $\text{TiO}_2$  pigments and increase the hiding power of the paints.

The concept of using the spacer material along with  $\text{TiO}_2$  pigments to improve opacity of the paint has been known for some time. For example, there is a known product that uses differences in refractive index between the different materials to increase scattering. Other known products physically coat the  $\text{TiO}_2$  pigment to enhance the separation. Clays may also be used for such an application as they have high surface area. However, it has been difficult to practice such applications commercially due to requirement of large amount of spacer material leading to high comparative cost of the paint. Furthermore clays as spacer material also tend to decrease the gloss of the final paint film and alter rheological properties of the paint.

Alternatively commercial micron sized zinc oxide particles with a refractive index of 2.01 can be used as the pigment. However, commercial micron-sized zinc oxide

possesses larger average particle dimensions and thus, suffers from lower surface area. As a result, commercial micron-sized zinc oxide has little or negligible power to influence the opacity provided by  $\text{TiO}_2$  pigments. In addition, while nano-sized zinc oxide particles are able to increase the opacity of a paint formulation, such paint formulations have been shown to be unstable (as evidenced by the increase in the viscosity of the paint formulation to the point of gelation) when stored for long periods of time such as two to three months. In addition, formulation of water based paints using ZnO requires careful consideration of various parameters and materials. The interaction of ZnO with  $\text{TiO}_2$  is very strong under the alkaline pH range that normally prevails in water based paints. This invariably results in poor stability of the paint leading to progressive increase in viscosity and possible irreversible gelling at room temperature. The paint often fails in accelerated storage test conducted at  $60^\circ\text{C}$  for 14 days.

Further, other pigments such as white lead, zinc sulphide, lithopone and antimony oxide have also been used as alternative pigments in paints. However,  $\text{TiO}_2$  pigments are always ultimately chosen due to its higher refractive index.

There is, therefore, a need to provide paint formulations that overcomes, or at least ameliorates, one or more of the disadvantages described above. There is a need to provide stable paint formulations that overcomes, or at least ameliorates, one or more of the disadvantages described above.

#### Summary

According to a first aspect, there is provided a paint formulation comprising a composite pigment, said

composite pigment being selected from the group consisting of metal oxide/silica, metal oxide/silicate, metal oxide/alumina, metal oxide/metal oxide and metal oxide/zirconia, wherein the size and amount of said  
5 composite pigment are selected to increase the opacity of said paint formulation.

The composite pigment may have opaque properties and hence may be used to maintain or enhance the opacity of the paint or paint formulation. The composite pigment may  
10 reduce the amount of titanium dioxide that is required in the paint formulation due to the opaque properties of the composite pigment. Hence, the composite pigment may be an alternative to titanium dioxide. Due to the replacement of the more expensive titanium dioxide with the composite,  
15 the costs of producing the paint or paint formulation may be effectively reduced.

As the composite pigment enhances the opacity of the paint formulation, the composite pigment may not affect the stability of the paint formulation. Hence, the  
20 composite pigment may at least maintain the stability of the paint formulation or may increase the stability of the paint formulation. Hence, the composite pigment may be able to enhance the opacity of the paint formulation while not affecting the stability of the paint formulation, or  
25 have any detrimental effect on the stability of the paint formulation. This is compared to prior art opacity enhancing agents in which the stability of the paint formulation decreases over time.

The composite pigment may be able to maintain or  
30 enhance the stability of the paint or paint formulation when stored for a period of time. The composite may enable the paint or paint formulation to be resistant to viscosity changes. The composite may prevent or at least

reduce the gelation or agglomeration of the paint or paint formulation during storage for a period of time.

In a second aspect, there is provided a method for preparing a paint formulation comprising the step of  
5 incorporating in the paint formulation an effective amount of a composite pigment selected from the group consisting of metal oxide/silica, metal oxide/silicate, metal oxide/alumina, metal oxide/metal oxide and metal oxide/zirconia in order to increase the opacity of said  
10 formulation.

In a third aspect, there is provided a composite pigment comprising a metal oxide as a first component and a second component selected from the group consisting of silica, silicate, alumina, metal oxide and zirconia.  
15

#### Definitions

The following words and terms used herein shall have the meaning indicated:

The term "nano-sized" is to be interpreted broadly to  
20 relate to an average particle size of a particle of less than about 1000nm, less than about 300 nm, between about 200 nm to about 300 nm, between about 5 nm to about 200 nm or less than about 100 nm. The particle size may refer to the diameter of the particles where they are substantially  
25 spherical. The particles may be non-spherical and the particle size range may refer to the equivalent diameter of the particles relative to spherical particles.

The term "opacity", and grammatical variants thereof, is used to denote the impermeability of a coating to  
30 light.

The term "stable", when referring to a paint or paint formulation, refers to the ability of the paint or paint formulation to be stirred to form a homogeneous liquid even when stored at long periods of time. The viscosity of

the paint or paint formulation may be a measure of the stability of the paint or paint formulation such that a stable paint or paint formulation is considered as one in which the viscosity remains substantially constant or does not increase substantially during storage of the paint or paint formulation. During accelerated storage experiments, a stable paint is one which has a viscosity increase of about less than 20 KU units. For the avoidance of doubt, any paint or paint formulation that results in gelation or agglomeration when stored for a period of time is considered as "unstable"

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be

considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

#### Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a paint formulation will now be disclosed. The paint formulation comprises a composite pigment, said composite pigment being selected from the group consisting of metal oxide/silica, metal oxide/silicate, metal oxide/alumina, metal oxide/metal oxide and metal oxide/zirconia, wherein the size and amount of said composite pigment are selected to increase the opacity of said paint formulation.

There is also provided a composite pigment comprising a metal oxide as a first component and a second component selected from the group consisting of silica, silicate, alumina, metal oxide and zirconia. The metal oxide in said composite may be selected from the group consisting of zinc oxide, aluminium oxide, antimony oxide, magnesium

oxide, barium oxide and zirconium oxide. In one embodiment, the metal oxide is zinc oxide.

The wt% of the composite pigment in the paint formulation may be in the range of about 1 wt% to about 5 wt%, based on the total weight of the paint formulation. The wt% of the composite pigment in the composition may be in the range selected from the group consisting of about 1 wt% to about 4 wt%, about 1 wt% to about 3 wt%, about 1 wt% to about 2 wt%, about 2 wt% to about 5 wt%, about 2 wt% to about 4 wt% and about 2 wt% to about 3 wt%. In one embodiment, the wt% of the composite pigment may be about 2 wt%.

The particle size of the metal oxide in the composite pigment may be in the nano-range. The particle size of the metal oxide in the composite may be in the range selected from the group consisting of about 5 nm to about 100 nm, about 5 nm to about 80 nm, about 5 nm to about 60 nm, about 5 nm to about 40 nm, about 5 nm to about 20 nm, about 20 nm to about 100 nm, about 40 nm to about 100 nm, about 60 nm to about 100 nm and about 80 nm to about 100 nm. In one embodiment, the particle size of the metal oxide in the composite may be about 10 nm.

The surface area of the composite may be selected from the range of about 20 m<sup>2</sup>/g to about 100 m<sup>2</sup>/g, about 20 m<sup>2</sup>/g to about 80 m<sup>2</sup>/g, about 20 m<sup>2</sup>/g to about 60 m<sup>2</sup>/g, about 20 m<sup>2</sup>/g to about 40 m<sup>2</sup>/g, about 40 m<sup>2</sup>/g to about 100 m<sup>2</sup>/g, about 60 m<sup>2</sup>/g to about 100 m<sup>2</sup>/g or about 80 m<sup>2</sup>/g to about 100 m<sup>2</sup>/g.

The composite may be made either in a two-step method or in a one-step method. In the two-step method, the metal oxide particles are formed first followed by precipitation or coating with the silica or alumina on the metal oxide. Where the metal oxide is zinc oxide, the zinc oxide may be made by mixing zinc salts in a base and collecting the

precipitates of zinc oxide formed. A surfactant or dispersant may be added to reduce the particle size of the zinc oxide particles such that the formed zinc oxide particles are in the nano-range. The zinc salt used may be selected from the group consisting of zinc nitrate salt (such as zinc nitrate hexahydrate), zinc acetate and zinc chloride. The base may be selected from the group consisting of sodium hydroxide, potassium hydroxide or calcium hydroxide. It is to be appreciated that the method to make the zinc oxide is not limited to the above method and can encompass any method known to form nano-sized zinc oxide particles. Following which, an amine surfactant may be added to create a charge on the zinc oxide particles. Silica or alumina (or their precursors) is then added to form a composite with the zinc oxide. To enhance the precipitation or coating of the silica or alumina on the zinc oxide particles, a charge modifier may be added. The charge modifier may be aluminium chloride solution which functions to precipitate or coat silica on the zinc oxide particles by disturbing its residual charge.

The one step method may involve a reaction mixture comprising a metal salt, a base solution and a precursor of silica or alumina. Where the metal oxide to be formed is zinc oxide, the metal salt may be zinc salt selected from the group consisting of zinc nitrate salt (such as zinc nitrate hexahydrate), zinc acetate and zinc chloride. A surfactant or dispersant may be added to reduce the particle size of the zinc oxide particles such that the formed zinc oxide particles are in the nano-range. The base may be selected from the group consisting of sodium hydroxide, potassium hydroxide or calcium hydroxide. During formation of the composite, the pH of the reaction mixture may be adjusted appropriately. The pH of the reaction may be in the range of 7 to 10. By adjusting the

pH of the reaction during formation of the composite, uniform coating of the metal oxide particles can be achieved. The silica precursor may be sodium silicate solution while the alumina precursor may be aluminium chloride hexa hydrate, Sodium aluminate or colloidal alumina.

Once the composite is formed, the composite may be separated from the reaction mixture by filtration or centrifugation. The composite may be washed with water and dried.

The silica, silicate, zirconia or alumina may be formed as a coating that at least partially surrounds the metal oxide particle. Hence, the metal oxide component may be at least partially covered by the silica, silicate, zirconia or alumina (that is, the second component)

The metal oxide particle may be dispersed or embedded in the silica, silicate, zirconia or alumina phase. The silica, silicate, zirconia or alumina phase may be a continuous phase. The silica phase may be a continuous amorphous phase.

The composite may have a homogeneous morphology or an inhomogeneous morphology. The composite may have a multifaceted homogeneous morphology. The composite may be a mixture of nanorods and multifaceted (inhomogeneous) morphology.

Where the metal oxide in the composite is zinc oxide, the zinc oxide may have a hexagonal structure.

The composite pigment may be of the core-shell structure. The core of the core-shell structure may be hollow or empty while the shells of the core-shell structure are made up of alternating layers of the metal oxide layer (or first component layer) and silica, silicate, zirconia, metal oxide or alumina layer (or second component layer). The silica, silicate, zirconia,

metal oxide or alumina layer (or second component layer) may at least partially cover the metal oxide layer (or first component layer). The number of layers is not particularly limited.

5 In the above embodiments, the difference in refractive indices of different layered materials improves the back scattering of light. In the core-shell structure, more substantial difference in refractive index are created by forming a hollow layered inorganic  
10 composite pigment. Such a pigment upon drying leaves a hollow space that helps in better back scattering of light, leading to better opacity.

The composite may act as a substitute for titanium dioxide in the paint formulation while keeping the opacity  
15 of the paint formulation substantially the same or even increased as compared to a conventional paint formulation without the composite. The composite may maintain or enhance the stability of the paint formulation while maintaining or increasing the opacity of the paint  
20 formulation.

The composite may act as a substitute to replace up to 30% of titanium dioxide particles in the paint formulation. The composite may replace up to 29%, 28%, 27%, 26%, 25%, 24%, 23%, 22%, 21%, 20%, 19%, 18%, 17%,  
25 16%, 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2% or 1% of the titanium dioxide particles in the paint formulation.

The paint formulation may have an opacity in the range selected from the group consisting of greater than  
30 85%, greater than 86%, greater than 87%, greater than 88%, greater than 89%, greater than 90%, greater than 91%, greater than 92%, greater than 93%, greater than 94%, greater than 95%, greater than 96%, greater than 97%, greater than 98% and greater than 99%. Hence, the

substitution of conventional titanium dioxide particles with the composite may not substantially affect the opacity of the paint formulation. Accordingly, it is possible to use a lesser amount of the titanium dioxide, which is typically used to make paint coatings opaque, without compromising on the opacity and/or stability of the paint formulation.

The paint formulation may have substantially the same opacity or increased opacity as compared to another paint formulation without the composite.

The metal oxide in said composite may be selected from the group consisting of zinc oxide, barium oxide, aluminium oxide, antimony oxide, magnesium oxide and zirconium oxide. In one embodiment, the metal oxide is zinc oxide.

The composite pigment may be toxic to microbes and hence may have an anti-microbial (such as anti-bacterial or anti-fungal) effect. Hence, the composite pigment in a paint formulation may be able to enhance the opacity of the paint formulation while maintaining or enhancing the stability of the paint formulation. At the same time, the composite pigment may be able to exert an anti-microbial effect so as to increase the durability and life-time of the paint formulation. When the paint formulation is applied to a surface and dried, the anti-microbial effect of the composite pigment may also be expanded to the dried paint.

The composite having a metal oxide such as zinc oxide may function as a UV absorbent and may confer anti-microbial properties to the paint formulation. This may be due to the particle size of the zinc oxide, such as lesser than 40 nm, which result in these properties. Hence, the overall durability of the paint formulation may

be improved with the incorporation of the composite in the paint formulation.

The paint formulation may be an acrylic water based paint, a water based vinyl paint, a polyurethane paint, an alkyd paint, a thermosetting paint and a solvent based paint.

There is also provided a method for preparing a paint formulation comprising the step of incorporating in the paint formulation an effective amount of a composite pigment selected from the group consisting of metal oxide/silica, metal oxide/silicate, metal oxide/alumina, metal oxide/metal oxide and metal oxide/zirconia in order to increase the opacity of said formulation.

The effective amount of the composite pigment in the paint formulation may be in the range of 1 wt% to 5 wt%, based on the total weight of the paint formulation.

#### Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1 shows the X-Ray Diffraction (XRD) pattern of silica coated on nano zinc oxide composite formed in accordance with Example 2.

Fig. 2 shows a transmission electron micrograph (TEM) of silica coated on nano zinc oxide composite formed in accordance with Example 2. Fig. 2(a) is at low magnification, Fig. 2(b) is at a higher magnification, and Fig. 2(c) is at high resolution. The magnifications of these figures are indicated indirectly by the "line scale" corresponding to the size in nano-meter.

Fig. 3 shows a XRD pattern of alumina coated on nano zinc oxide composite formed in accordance with Example 4.

Fig. 4 shows a TEM of alumina coated on nano zinc oxide composite formed in accordance with Example 4. Fig. 4(a) is at low magnification, Fig. 4(b) is at higher magnification, and Fig. 4(c) is at high resolution. The magnifications of these figures are indicated indirectly by the "line scale" corresponding to the size in nano-meter.

Fig. 5 is a X-ray diffraction pattern of the nano zinc oxide obtained in Comparative Example 1.

Fig. 6 and 7 are scanning electron microscopy images showing the hollow silica-based composite particles.

15

### Examples

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples and a comparative example, which should not be construed as in any way limiting the scope of the invention.

20

### Example 1

#### Direct In-situ preparation of nano-ZnO-silica composite

204 grams of anhydrous zinc chloride (obtained from Mega chemicals, Singapore) was dissolved in 150 grams of water and 0.5 grams of Indoemul CO-02 was added to this solution and stirred at 1500 RPM for 5 minutes. 300 grams of 40% sodium hydroxide was added to this stirred solution for a period of 2.5 hours. The reaction mixture was then stirred for 2 additional hours. The pH of the reaction mixture was then adjusted to 7 to 7.5 using glacial acetic acid and 15.6 grams of sodium silicate solution (10% sodium oxide and 28% silicon dioxide, obtained from SD Fine chemicals Ltd, Mumbai of India) was

30

added. The pH was adjusted from 10 to 8.5 and reaction mixture was stirred for one hour until pH gradually reaches 9.5. The pH was again adjusted to 7.5 and the reaction mixture was stirred for an additional one hour.

5 The reaction mixture was then filtered and washed with water. The filtered solid was dried in an oven at 80°C for 24 hours.

The dried solid was powdered and characterised using BET surface area analysis (21.97 m<sup>2</sup>/g), XRD (see Fig. 1) and TEM (Fig. 2).

From the XRD pattern of Fig. 1, the major peaks are at about 31.76, 34.39, 36.24, 47.52, 56.59, 62.81, 66.37 and 67.92 (°2θ), which confirmed the presence of ZnO with hexagonal structure (space group- P63mc). Using Scherrer's equation, the crystalline size of 23.5 nm was calculated. The remaining peaks correspond to SiO<sub>2</sub> and Zn(OH)<sub>2</sub>. From the pattern, it is evident that the formation of SiO<sub>2</sub> was amorphous. After silica coating on ZnO, this shifted the ZnO peaks 0.02Å towards the left side which confirmed the presence of SiO<sub>2</sub>.

From the TEM image of Fig. 3(a), it can be seen that the synthesized powder had an inhomogeneous morphology, which is a mixture of nanorods and multifaceted morphology. Higher magnification (see Fig. 3(b)) showed that the nanorods consisted of ~10 nm ZnO embedded in a continuous amorphous SiO<sub>2</sub> phase. The inter-planar spacing (see Fig. 3(c)) was 3.3 Å and was close to the inter-planar spacing of (100) plane of ZnO (3.25 Å).

30

### Example 2

#### Synthesis of nano zinc oxide-silica composite

About 90 grams of nano ZnO (obtained from Example 1) was suspended and stirred in 105 ml of water with 0.1 grams of tertiary amine surfactant-Coco bis (hydroxyl

ethyl) amine (Indoemul CO-02, obtained from Indoamine Ltd, Baroda of India). 15 grams of a 30% solution of commercial Colloidal Silica (Bindzil, obtained from Akzo Nobel, Netherlands) was added to this suspension and stirred at 1500 rpm for 15 minutes. Then 0.7 grams of 10% aluminium chloride (obtained from Access Chemicals, Singapore) solution was added to the reaction moisture and stirred for 1 hour. The thick paste obtained was dried in an oven and used for characterization. The surface area of the powder was 23.43 m<sup>2</sup>/g.

### Example 3

#### Paint Formulation using nano-ZnO-silica composite

The nano-ZnO-silica composite obtained from Example 1 together with titanium dioxide (TiO<sub>2</sub>) as the main pigment was used to formulate an acrylic water-based paint. The formulation was named "N-ZnO-silica composite Formulation". The weight of the TiO<sub>2</sub> present in this formulation was reduced as compared to that present in the Standard Formulation described below. A comparative acrylic water-based paint formulation based on TiO<sub>2</sub> pigments alone was made. This formulation was named "Standard Formulation".

When the TiO<sub>2</sub> was replaced in the "N-ZnO-silica composite Formulation" with the composite, there was a decrease in the total pigment volume. This decrease in pigment volume was compensated by increasing the amount of silica and/or talc to keep the pigment volume concentration the same in the formulations shown in Table 1 below.

Contrast Ratio was measured using the ZEHNTNER Reflectometer (Zehntner Testing Instruments, Switzerland). Accelerated storage studies were made by storing the paint at 60°C for fourteen days and assessing the paint

appearance visually for any cake formation, hard  
settlement and paint flow.

Table 1: Paint formulation using Nano-ZnO-silica composite

No.	Materials	Standard Formulation (in grams)	n-ZnO-Silica Formulation (in grams)
1.	Thickener: Bermocoll E411 (Akzo Nobel, Netherlands)	0.50	0.50
2.	Anti-Microbial Agent: Zinc Omadine (Arch Chemicals, USA)	1.00	1.00
3.	Dispersing agent: Orotan 1850E-Dow Chemicals, USA)	1.00	1.00
4.	Defoamer: Dapro 7010 (Elementis Korea)	0.25	0.25
5.	Water	18.94	20.34
6.	n-ZnO-Silica composite	-NA-	2.00
7.	Titanium dioxide R900 (Dupont, USA)	23.00	16.67
8.	Calcium Carbonate	3.64	5.62
9.	Talc	1.87	2.82
10.	Fumed Silica	0.30	0.30
11.	Acrylic Resin emulsion (UCAR™ 362, obtained from The Dow Chemical Company, California, USA)	35.00	35.00
12.	ROPAQUE™ emulsion (obtained from The Dow Chemical Company, California, USA)	12.00	12.00
13.	Texanol (obtained from Eastman Chemical Company, Tennessee, USA)	0.70	0.70
14.	2-Amino-2-methyl-1-propanol + 5% water (AMP™-95 obtained from The Dow Chemical	0.30	0.30

	Company, California, USA)		
15	Mono Ethylene Glycol (Dow Chemicals, USA)	1.00	1.00
16	Tergitol NP 9 (Dow Chemicals, USA)	0.50	0.50
	<i>Contrast Ratio (Opacity) (%)</i>	95.15	95.84
	<i>Accelerated storage test</i>	Pass- Paint with slightly reduced flow	Pass-- homogeneous Paint with slightly more viscosity and reduced flow

As shown in Table 1 above, the stability and opacity of the paint formulation with the composite are comparable to that of the paint formulation without the composite. In addition, the composite can reduce the amount of titanium dioxide required by about 27%, leading to cost savings.

#### Example 4

##### Direct In-situ preparation of nano-ZnO-Alumina composite

68 grams of anhydrous zinc chloride was dissolved in 90 ml of water and 2.5 grams of anionic dispersing agent Coatex P90 (obtained from Arkema, USA) was added to this solution and stirred at 1500 RPM for 5 minutes. 100 grams of 40% sodium hydroxide was added to this stirred solution for a period of 2.5 hours. The reaction mixture was then stirred for 2 additional hours. The pH of the reaction mixture was then adjusted 8.5 using glacial acetic acid. About 12.2 grams of aluminium chloride hexa hydrate was added and pH of the reaction turns to 7. About 14 grams of 40% sodium hydroxide was added for

fifteen minutes with very good agitation. The pH of the reaction was maintained at 8.0 to 8.5 for a period of 1.5 hours. The precipitated solid was then filtered, washed with water and dried 80 degree C oven for 24 hours.

5 The surface area of the powder from the dried solid was 78.9 m<sup>2</sup>/g. The XRD pattern and TEM of nano-ZnO-alumina composited are shown in Fig. 3 and Fig. 4 respectively.

From the XRD pattern of the alumina coated on nano ZnO composite as shown in Fig. 3, the major peaks are at  
10 about 31.76, 34.39, 36.24, 47.52, 56.59, 62.81, 66.37 and 67.92 (°2θ), which confirmed the presence of ZnO with hexagonal structure (space group- P63mc). Using Scherrer's equation, the crystalline size of 25.1 nm was calculated. Along with nano ZnO, the other phases of Al<sub>2</sub>O<sub>3</sub> and AlZn<sub>7</sub>O<sub>10</sub>  
15 were formed. Form the pattern, it is obvious that the crystalline phase of Al<sub>2</sub>O<sub>3</sub> was coated on nano ZnO and which confirmed the presence of composite coating.

The TEM images (Fig. 4(a), Fig. 4(b)) showed that the synthesized powder was multifaceted phase. The inter-  
20 planar spacing (see Fig. 4(c)) was 2.5 Å and was close to the inter-planar spacing of (002) plane of ZnO (2.6 Å).

#### Example 5

##### Hollow Silica Based Composite Pigment

25 30 grams of Nano Calcium Carbonate (obtained from Nano Materials Technology Pte Ltd, Singapore) was suspended in 300 ml of rapidly stirring water. About 34.8 grams of Tetra ethyl ortho silicate (obtained from Sinopharm Chemical Reagent Company Limited, China) was  
30 added and pH was adjusted to 8.5 with ammonia. The reaction mixture was then stirred for 1 hour and pH was adjusted to 6 by slowly adding glacial acetic acid. After all the carbon dioxide evolution ceases, the sample of hollow silica was isolated by filtration and drying.

The above reaction can directly be converted into hollow silica-zinc oxide-silica composite pigment. About 408 grams of anhydrous zinc chloride was dissolved in the reaction mixture followed by Indoemul co-02 (0.25 grams).  
5 450 grams of 54% sodium hydroxide solution was added for 2.5 hours. The reaction mixture was stirred for additional 2 hours and pH was adjusted to 8-8.5 About 33 grams of colloidal silica was added to this reaction mixture and stirred for 1 hour. At the end of the  
10 reaction, hollow composite pigment was filtered and washed with water and dried in oven at 80 degree Celsius.

Table 2: Paint formulation using Hollow silica-ZnO-silica composite

No.	Materials	Standard Formulation (in grams)	n-ZnO-Silica Formulation (in grams)
1.	Thickener: Bermocoll E411 (Akzo Nobel, Netherlands)	0.40	0.40
2.	Anti-Microbial Agent: Zinc Omadine (Arch Chemicals, USA)	1.00	1.00
3.	Dispersing agent: Orotan 1850E-Dow Chemicals, USA)	1.00	1.00
4.	Defoamer: Dapro 7010 (Elementis Korea)	0.25	0.25
5.	Water	22.54	22.14
6.	Hollow Silica-ZnO-Silica composite	-NA-	2.00
7.	Titanium dioxide R900 (Dupont, USA)	23.00	16.98
8.	Calcium Carbonate	4.94	7.42
9.	Talc	1.86	2.57
10.	Fumed Silica	0.30	0.30
11.	Acrylic Resin emulsion (UCAR™ 362, obtained from The Dow Chemical Company, California, USA)	34.00	34.00
12.	ROPAQUE™ emulsion (obtained from The Dow Chemical Company, California, USA)	9.00	9.00
13.	Texanol (obtained from Eastman Chemical Company, Tennessee, USA)	1.00	1.00

14.	2-Amino-2-methyl-1-propanol + 5% water (AMP™-95 obtained from The Dow Chemical Company, California, USA)	0.30	0.30
15	Mono Ethylene Glycol (Dow Chemicals, USA)	1.00	1.00
16	Tergitol NP 9 (Dow Chemicals, USA)	0.50	0.50
	<i>Contrast Ratio (Opacity) (%)</i>	95.84	95.89
	<i>Accelerated storage test</i>	Pass- Paint with slightly reduced flow	Pass-- homogeneous Paint with slightly more viscosity and reduced flow

### Comparative Example 1

#### Synthesis of nano zinc oxide in methanol/water

32 grams of zinc nitrate hexahydrate (obtained from  
 5 Accesschem Pte Ltd, Singapore) was dissolved in 67.5 grams  
 of methanol (obtained from Accesschem Pte Ltd, Singapore)  
 and 40 grams of water.

8.7 grams of sodium hydroxide (obtained from Sigma  
 Aldrich, Missouri, United States of America) was dissolved  
 10 in 40 grams of water separately and added to the zinc  
 nitrate hexahydrate mixture slowly over a period of 1 hour  
 and 15 minutes.

After the addition, the reaction was stirred for 1.5  
 hours. Thereafter, about 120 ml of water was added and  
 15 the mixture was stirred for additional 1.5 hours.

The reaction mixture was then filtered and washed  
 with water till the filtrate showed a pH of 7. The solid

residue material obtained was dried in an oven at 80°C and grounded to get fine white powder.

#### Characterization of nano zinc oxide

5           The fine white powder was analyzed by X-ray diffraction (XRD) and the XRD pattern is shown in Fig. 5. From Fig. 5, the XRD pattern confirms that pure zinc oxide (ZnO) was obtained. Specifically, the three main 2 Theta peak values in Fig. 5 are at 31.72; 34.45; and 36.21,  
10           which correspond to standard ZnO peaks as mentioned in the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 36-1451 P6<sub>3</sub> mc space group.

          The fine white powder was also analyzed by the Brunauer-Emmett-Teller (BET) method. The BET surface area  
15           measurement showed that the ZnO obtained has a surface area of 27.8 m<sup>2</sup>/gram.

#### Paint Formulation using nano-ZnO

          The nano zinc oxide (n-ZnO) together with titanium  
20           dioxide (TiO<sub>2</sub>) as the main pigment was used to formulate an acrylic water-based paint. The formulation was named "n-ZnO Formulation". The weight of the TiO<sub>2</sub> present in this formulation was 70% of that present in the Standard Formulation described below. A comparative acrylic water-  
25           based paint formulation based on TiO<sub>2</sub> pigments alone was made. This formulation was named "Standard Formulation".

          When 30% of the required TiO<sub>2</sub> was replaced in the "n-ZnO Formulation" with nano zinc oxide, there was a decrease in the total pigment volume. This decrease in  
30           pigment volume was compensated by increasing the amount of silica and/or talc to keep the pigment volume concentration the same in the formulations shown in Table 3 below.

Contrast Ratio was measured using the ZEHNTNER Reflectometer (Zehntner Testing Instruments, Switzerland). Accelerated storage studies were made by storing the paint at 60°C for fourteen days and assessing the paint appearance visually for any cake formation, hard settlement and paint flow.

Table 3: Paint formulation using Nano-ZnO

No.	Materials	Standard Formulation (in grams)	n-ZnO Formulation (in grams)
1.	Thickener-1 (Aquaflow™ NHS 300, obtained from Hercules Inc., Delaware, USA)	0.20	0.20
2.	Thickener-2 (Aquaflow™ NHS 300, obtained from Hercules Inc., Delaware, USA)	0.10	0.10
3.	Dispersing agent (Coatex P 90, obtained from Coatex Inc, Arkema, South Carolina, USA)	0.50	0.50
4.	Defoamer (Tego® Foamex 825, obtained from Evonik Industries, Germany)	0.45	0.45
5.	Water	30.58	28.00
6.	n-ZnO	-NA-	1.50
7.	Titanium dioxide	27.00	18.90
8.	Calcium Carbonate	20.50	20.50
9.	Silica	0.98	5.00
10.	Fumed Silica	0.98	0.98
11.	Acrylic Resin emulsion (UCAR™ 362, obtained from The Dow Chemical Company, California, USA)	43.5	43.5
12.	ROPAQUE™ emulsion (obtained from The Dow Chemical Company, California, USA)	19.5	19.5
13.	Texanol (obtained from Eastman Chemical Company, Tennessee, USA)	2.76	2.76

14.	2-Amino-2-methyl-1-propanol + 5% water (AMP™-95 obtained from The Dow Chemical Company, California, USA)	0.15	0.15
	<i>Contrast Ratio (Opacity) (%)</i>	91.83	93.81
	<i>Accelerated storage test</i>	Pass-- homogeneous Paint with slightly reduced flow	Fails--paint solidified into thick mass

As can be seen from Table 3, the incorporation of nano zinc oxide, while increasing the opacity of the paint formulation, caused the paint formulation to gel and become unstable.

**Applications**

The disclosed composition advantageously enhances the stability of a paint formulation without depriving the paint formulations from being economically feasible to produce or affecting the opacity of the paint formulation.

Advantageously, the disclosed composition permits a lower amount of expensive raw material required in paint formulations without depriving the paint formulations of the properties required. In embodiments, the composite of the present disclosure can be used as a partial replacement for the relatively more expensive titanium dioxide pigment in paint formulations. Furthermore, the disclosed composition possesses improved durability against the natural elements.

Advantageously, the disclosed composite confers anti-bacterial properties to the composition.

Advantageously, the disclosed composite improves the ultraviolet resistance of the composition, thereby conferring durability to the composition.

Advantageously, the disclosed composite does not  
5 leach out of the composition.

Advantageously, in embodiments, the disclosed composite of the present disclosure can be used as a partial replacement for conventional ZnO in the vulcanization of rubber.

10 In embodiments, the disclosed composite of the present disclosure can be used as a wide band width semiconductor in certain electronic applications.

In embodiments, the disclosed composite of the present disclosure can also be used to improve abrasion  
15 and wear resistance in polymer composites whether alone or in combination with other nanomaterials such as clay.

In embodiments, the disclosed composite of the present disclosure can be dispersed in organic solvents and polymers to improve the durability of organic polymer  
20 composites to the natural elements.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of  
25 the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

## Claims

1. A paint formulation comprising a composite pigment, said composite pigment being selected from the group consisting of metal oxide/silica, metal oxide/silicate, metal oxide/alumina, metal oxide/metal oxide and metal oxide/zirconia, wherein the size and amount of said composite pigment are selected to increase the opacity of said paint formulation.

2. The paint formulation of claim 1, wherein the wt% of said composite pigment in said formulation is in the range of 1 wt% to 5 wt%, based on the total weight of said formulation.

3. The paint formulation of claim 1 or claim 2, wherein said metal oxide is selected from the group consisting of zinc oxide, aluminium oxide, antimony oxide, barium oxide, magnesium oxide and zirconium oxide.

4. The paint formulation of any one of the preceding claims, wherein the particle size of said metal oxide in said composite pigment is in the range of 5 nm to 100 nm.

5. A method for preparing a paint formulation comprising the step of incorporating in the paint formulation an effective amount of a composite pigment selected from the group consisting of metal oxide/silica, metal oxide/silicate, metal oxide/alumina, metal oxide/metal oxide and metal oxide/zirconia in order to increase the opacity of said formulation.

6. The method of claim 5, wherein said effective amount of said composite pigment is in the range of 1 wt% to 5 wt%, based on the total weight of said paint formulation.

5

7. A composite pigment comprising a metal oxide as a first component and a second component selected from the group consisting of silica, silicate, alumina, metal oxide and zirconia.

10

8. The composite pigment of claim 7, wherein said metal oxide as the first component is at least partially covered by said second component.

15

9. The composite pigment of claim 7 or 8, wherein said composite pigment has a core-shell structure.

10. The composite pigment of claim 9, wherein said core-shell structure is a hollow core with alternating layers of first and second components.

20

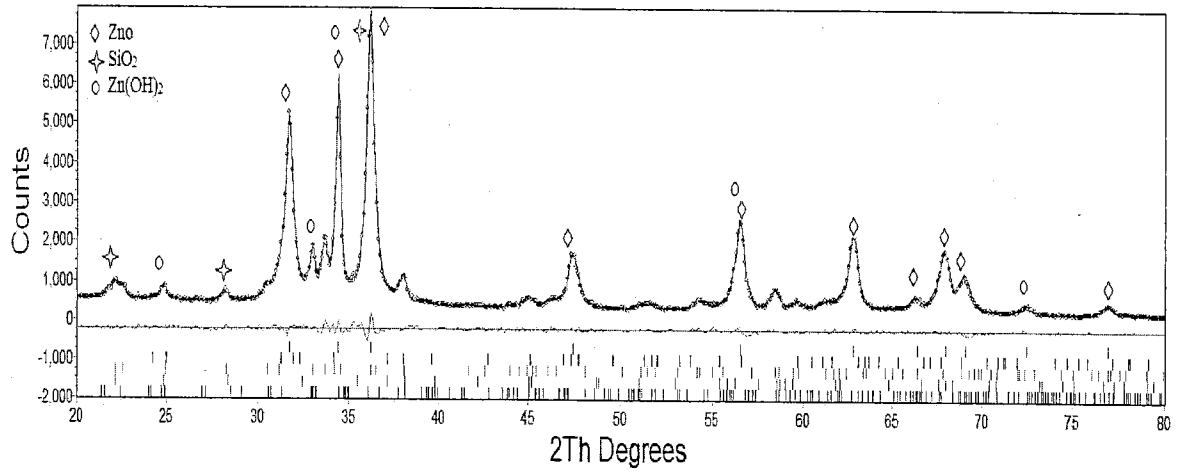


Fig. 1

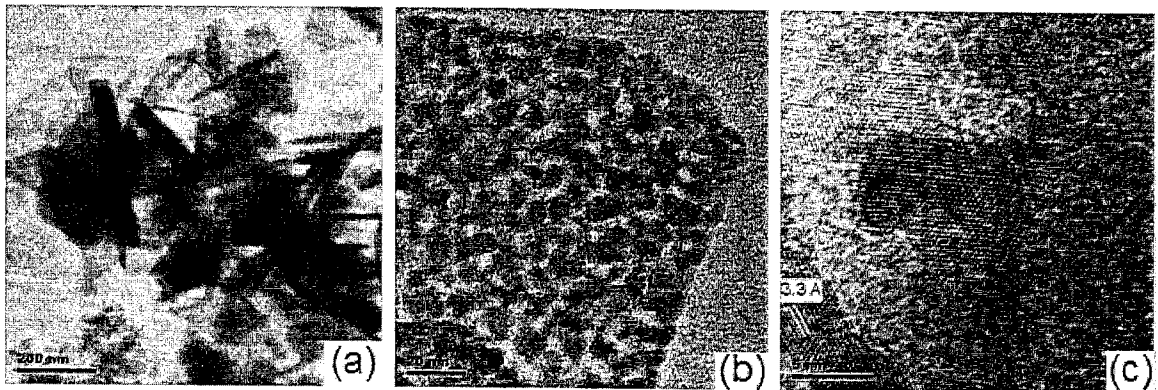


Fig. 2

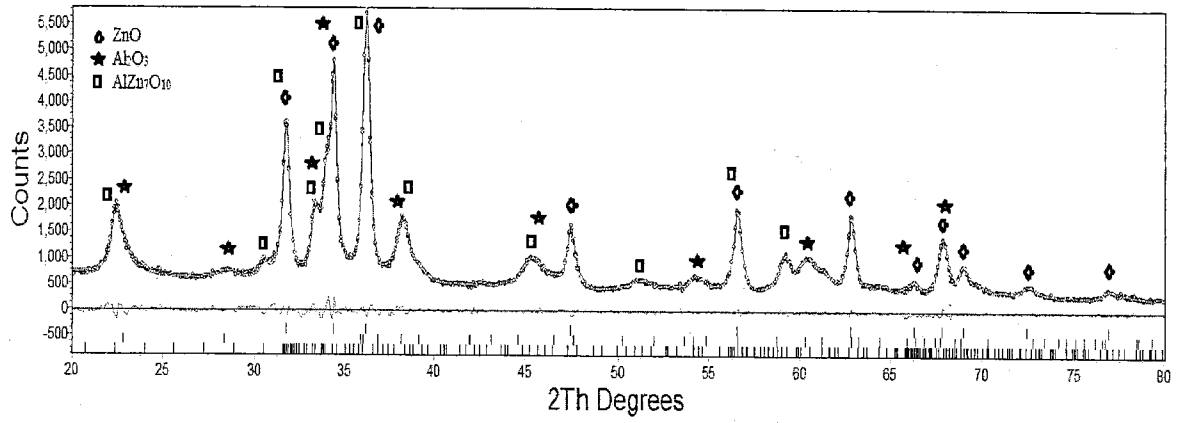


Fig. 3

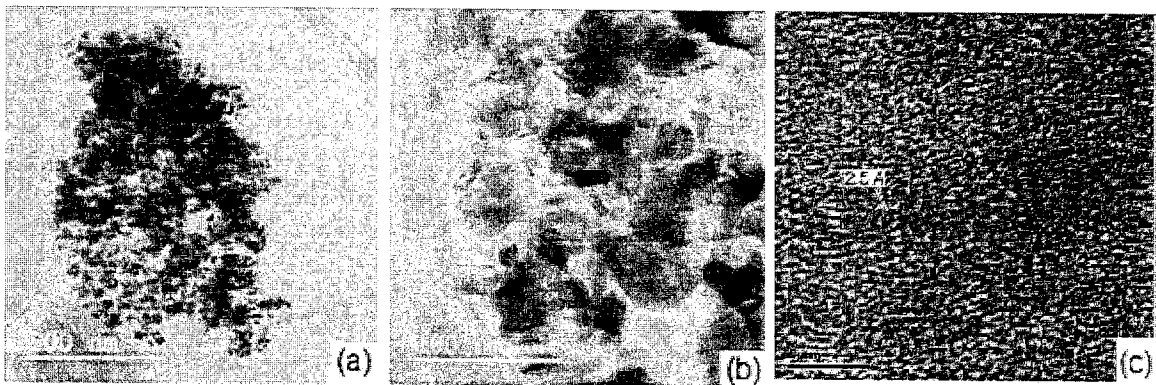


Fig. 4

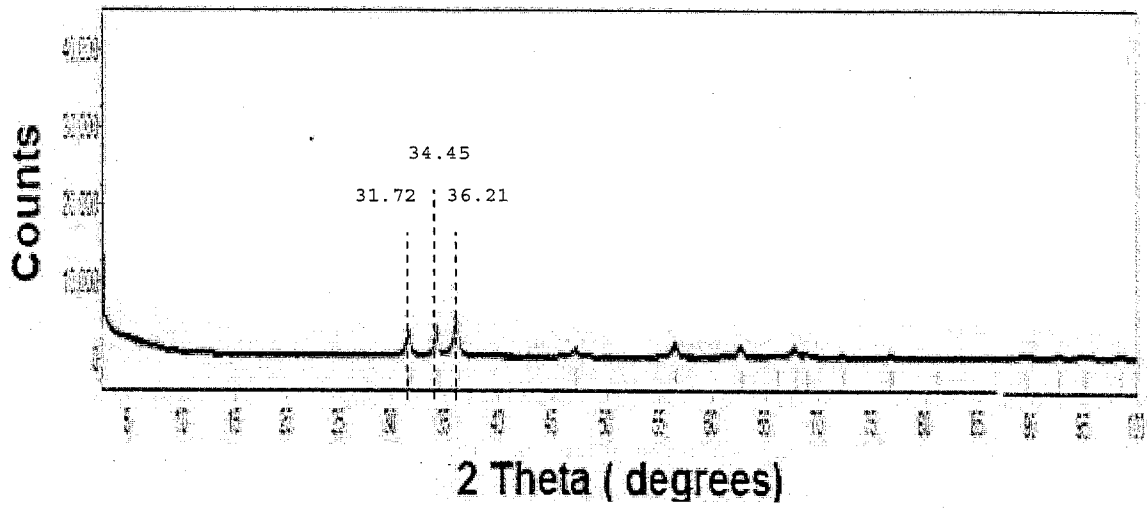


Fig. 5

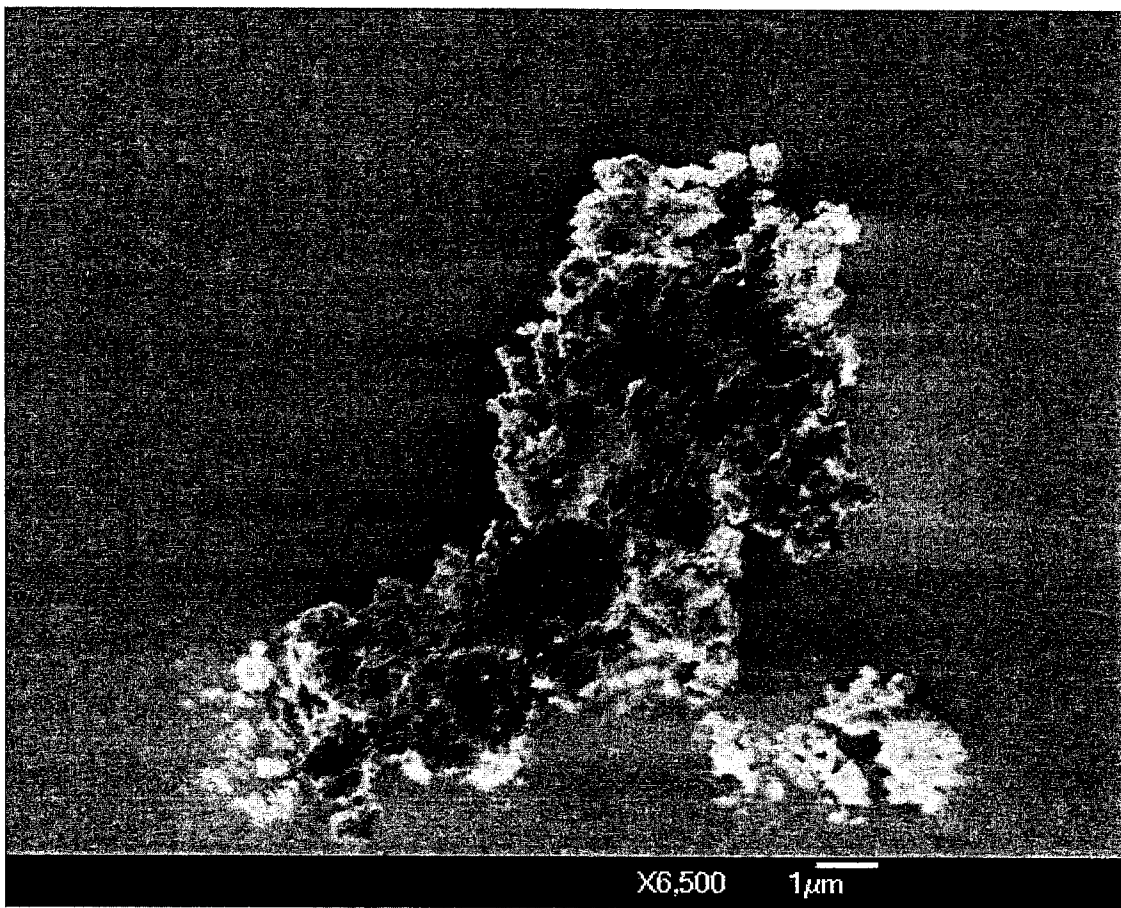


Fig 6

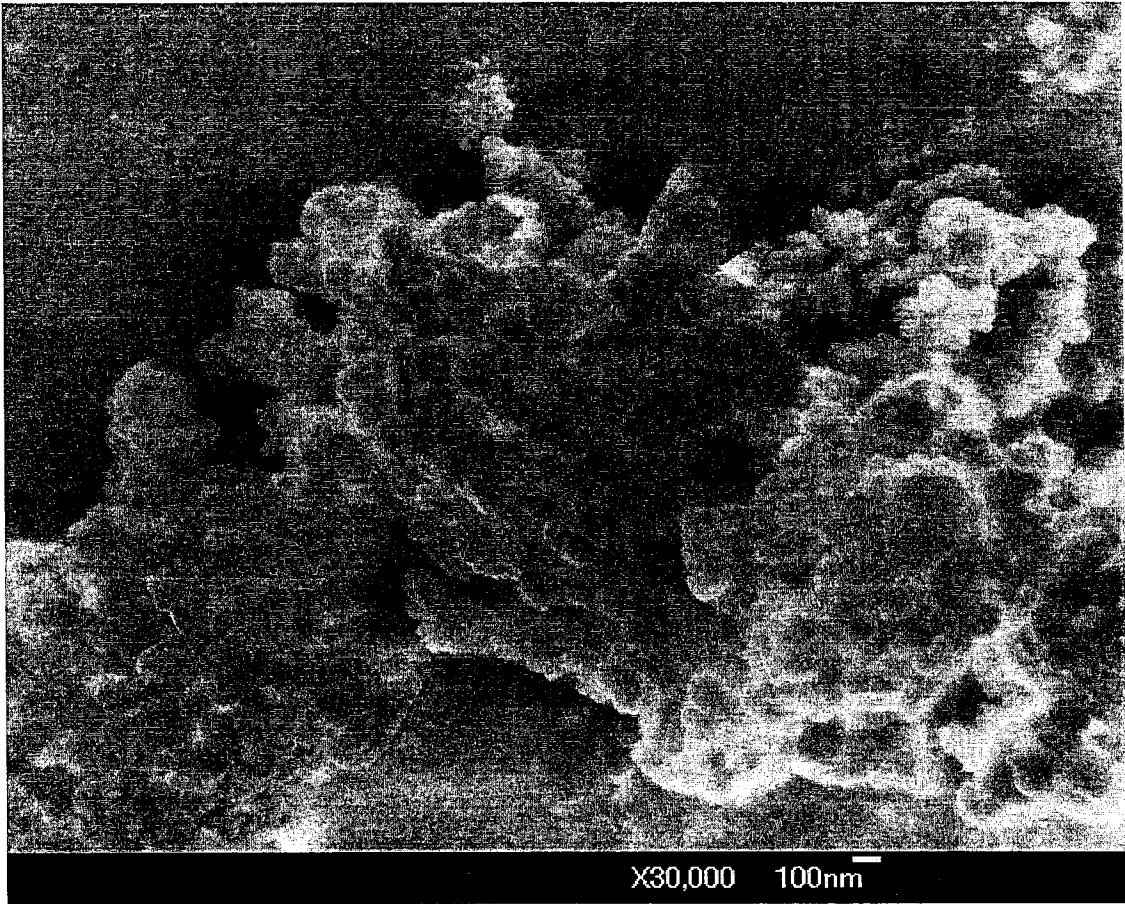


Fig 7

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2014/000432

## A. CLASSIFICATION OF SUBJECT MATTER

*C08K 3/22 (2006.01) C08K 3/34 (2006.01) C09D 1/00 (2006.01) C09C 1/04 (2006.01) C09C 1/28 (2006.01)*  
*C09C 1/40 (2006.01) C09C 1/36 (2006.01) C09C 1/02 (2006.01) B82Y 30/00 (2011.01)*

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS, CAS REG, WPI, EPODOC, Google, Google Patents (Advanced), Google Scholar, Espacenet (Advanced)

IPC & CPC marks: C08K3/22 B82Y30/00 C09C1/0081 OR C09C3/063

Keywords: paint, composite, pigment, (the claimed metal oxides), silica, silicate, core, shell, hollow

CAS registry numbers: (for each of the claimed metal oxides)

Google Patents and Google Scholar: Applicant/Inventor search

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 3 November 2014	Date of mailing of the international search report 03 November 2014
<b>Name and mailing address of the ISA/AU</b>  AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	<b>Authorised officer</b>  Andrew Davis AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262104067

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:  
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

**See Supplemental Box for Details**

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

International application No.

C (Continuation).

DOCUMENTS CONSIDERED TO BE RELEVANT

**PCT/SG2014/000432**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1532521 A (LAPORTE AUSTRALIA LIMITED) 15 November 1978 p. 1, ln. 45-81; p. 2, ln. 78-79; p. 6, ln. 30-35; Examples 1-5; Table 2	1, 4-5, 7-8
X	JP S63199275 A (UBE INDUSTRIES. ) 17 August 1988 Abstract	1, 3-5, 7-8
X	US 6200680 B1 (TAKEDA et al.) 13 March 2001 Claims 6-7; col. 42, ln. 34 – col. 45, ln. 5	7-10
X	WO 2008/019905 A1 (EVONIK DEGUSSA GMBH) 21 February 2008 Abstract; p. 3, ln. 21 – p. 4, ln. 31; p. 6, ln. 6-11; p. 12, ln. 13-35; p. 13, ln. 16-19; Examples 7-9	1-9
X	WO 2008/079758 A1 (AVON PRODUCTS, INC.) 03 July 2008 Claims 1-3	7-9

**Supplemental Box****Continuation of: Box III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-10 (in part) are directed to a paint formulation, a method for preparing a paint formulation and a composite pigment, comprising a composite pigment of metal oxide and silica.
- Claims 1-10 (in part) are directed to a paint formulation, a method for preparing a paint formulation and a composite pigment, comprising a composite pigment of metal oxide and silicate.
- Claims 1-10 (in part) are directed to a paint formulation, a method for preparing a paint formulation and a composite pigment, comprising a composite pigment of metal oxide and alumina.
- Claims 1-10 (in part) are directed to a paint formulation, a method for preparing a paint formulation and a composite pigment, comprising a composite pigment of metal oxide and metal oxide.
- Claims 1-10 (in part) are directed to a paint formulation, a method for preparing a paint formulation and a composite pigment, comprising a composite pigment of metal oxide and zirconia. The feature of a composite pigment featuring a metal oxide is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is a composite pigment featuring a metal oxide.

However this feature does not make a contribution over the prior art because it is disclosed in: each of D1-D5 (see Box C of the search report for each of the specific references).

Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/SG2014/000432**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

<b>Patent Document/s Cited in Search Report</b>		<b>Patent Family Member/s</b>	
<b>Publication Number</b>	<b>Publication Date</b>	<b>Publication Number</b>	<b>Publication Date</b>
GB 1532521 A	15 November 1978	None	
JP S63199275 A	17 August 1988	None	
US 6200680 B1	13 March 2001	EP 0768277 A1	16 Apr 1997
		EP 0768277 B1	02 Oct 2002
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		EP 0893409 B1	03 Sep 2003
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		DE 102006038518 A1	21 Feb 2008
		EP 2051937 A1	29 Apr 2009
		JP 2009545509 A	24 Dec 2009
		US 2010008872 A1	14 Jan 2010
WO 2008/079758 A1	03 July 2008	AR 064460 A1	01 Apr 2009
		TW 200846027 A	01 Dec 2008

**End of Annex**

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(July 2009)