Low Carbon Footprint TiO₂ Substitutes in Paint: A Review

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Abstract—Titanium dioxide (TiO₂) is one of the most efficient light scattering pigments known to man, and as a result it is widely used to deliver opacity, especially in paint formulations. However, due to the cost of TiO₂, dwindling resources, and an energy intensive manufacturing process which produces undesirable by-products, substitutes are required to maintain a source of white pigment in the future and to comply with changing sustainability legislation. Many substitutes exist, including kaolin (both untreated and calcined), and hollow latex spheres. These, along with other alternatives, are reviewed.

Index Terms-Opacity, paint, pigments, titanium dioxide.

I. INTRODUCTION

White pigments are used extensively in many applications to give a clean, crisp, white color, and their applications include foodstuffs, plastics, paints, and other coatings [1]. Pigments give paint its color and opacity, with white pigment specifically giving opacity to the paint, whilst a tinter gives the color. Black and certain darker colored paints are an exception to this. A highly opaque pigment will lend desirable properties to a paint formulation, allowing the paint to completely hide a substrate with a thin film. To be an effective white pigment, the pigment needs to be; stable, safe (to produce, as a product, and as waste), almost colorless (or white), a solid, insoluble in water and solvents, have a high refractive index, and be suitable for production in an optimized colloidal particle size [2].

Paint films and coatings have many qualities that are the factors of the properties of the paint components. These qualities can be divided into; appearance, environmental resistance, mechanical and adhesive, and special effects. With respect to appearance, qualities such as color, depth of color, gloss, film brightness, opacity and texture are important, whilst for environmental resistance, the qualities desired will include resistance to; temperature (heat, cold, and changes between the two), microbes, moisture (rain and humidity), and ultraviolet (UV) radiation. Mechanical and adhesive qualities in paints are often complementary, and this is because paints need to adhere to the substrate that they are applied to in order for properties such as flexibility to be examined. For instance, a highly flexibly paint film that does

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not adhere to a substrate will have limited use as a paint. Mechanical properties will also include; drying times, rheology, tensile strength, thixotropy, abrasion, and attrition resistance. The latter of which is often determined by scrub tests. Finally, paint formulations can also be designed to deliver special effects, such as; conductivity, infrared reflectance, and photvoltaicty [3]-[9]. Many of these factors will be influenced by different properties, for example, scrub resistance is dependent upon binder type and pigment volume concentration [8], whilst gloss is a factor of surface roughness, and as a result, the greater the particulate content of a coating, the less glossy it will be [2]. Of these properties, opacity is one of, if not the, most important.

II. OPACITY THEORIES

Opacity is the level of how opaque a substance is, it is also referred to as hiding power, and is often measured using contrast ratios. Contrast ratios are usually measured using a spectrophotometer, where Y_B , and Y_W are the lightness of the paint, using the XYZ color system, over a white and black background, respectively (Equation (1)). Opacity occurs when light is refracted, with the level the light is refracted being quantified by the refractive index (Equation (2) [10]).

$$Contrast \ ratio \ = \ 100 \times Y_B / Y_W \tag{1}$$

$$Refractive index = \frac{Speed of light in vacuum}{Speed of light in substance}$$
(2)

Particles that have a higher refractive index will refract light to a greater degree than particles with a lower refractive index. The scattering occurs at the interfaces of two substances that have different refractive indices, and as such, this scattering will occur multiple times within a paint film, as the scattered light will come into contact with multiple pigment particles, and therefore many interfaces. This can lead to complete reflection before the light reaches the substrate, resulting in an opaque film (Fig. 1). It also means that a paint containing a pigment with a higher refractive index will have a greater probability of this happening. Because of this, film thickness plays a large role in film opacity, with the target for manufacturers to engineer a film that will give complete opacity with as thin a film as possible to save resources and reduce costs.

A. Mie theory

Mie theory explains light scattering through the entire spectrum of light, from infrared, through the visible spectrum, to UV. It does this by using two complex scattering amplitudes for two orthogonal directions of incident polarization, extinction and scattering efficiencies, an asymmetry factor, and two Mie coefficients [11].

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Fig. 1. Light (arrows) scattering within a film, containing particles with high (left) and low (right) refractive indices. Subsequently, the low refractive index particles will not give an opaque film, as the light reaches the substrate.

Consequently, Mie theory is used to define the scattering of individual particles or dilute systems. Paint however, is not a dilute system, it is a concentrated film, and consequently the Kubelka-Munk (KM) theory is used. This is only a brief overview of Mie theory, and more detailed explanations can be found in the literature, including van de Hulst, 1957 [12].

B. Kubelka-Munk (KM) Theory

Originally developed by Kubelka and Munk in 1931, the KM theory looks at light scattering and opacity in a film. The KM theory is a model, where a film of known thickness (*L*) has an incident light intensity (*I*), and reflectance *R*, with the substrate having reflectance R_g . Light that has undergone scattering and transmission, and is exiting the film is denoted as *J*, and at distance *x* from the substrate there is a thin lamina, with thickness *dx*, which has flux *j*(*x*) travelling upwards and flux *i*(*x*) travelling downwards (Fig. 1; [13]). The KM theory makes the following assumptions:

- 1) The film has a known, finite thickness, but is infinitely long in width and length to eradicate boundary effects.
- 2) The incident light hitting the surface is perfectly homogenous and diffuse.
- 3) Fluorescence and polarisation are ignored.
- 4) No surface reflectance occurs internally or externally.
- 5) Scattering and absorption constants do not vary with film thickness.
- 6) The film is homogenous, isotropic, and contains small particles that are able to disperse light.



Fig. 1. The path of light in a film as defined by the KM model.

The KM theory has been used to study all manner of films, including paints, soils, porcelain, and human teeth [14]-[17].

III. AIR VOIDS FOR OPACITY

Other than using pigment particles with high refractive indices, air voids are also used to increase opacity in paint films. Air voids are pockets of air within the paint film, and there are three types of air void that can aid opacity [4]:

- 1) Intraparticle voids air voids within pigment particles.
- 2) Intraresin voids air voids within the resin.
- 3) Intercoating voids air voids at the pigment particles-resin interface.

In turn, air voids can aid opacity within paint films via three mechanisms [2]:

- 1) Air voids that scatter light.
- Very small air voids which reduce the refractive index of the binder/air mixture, which increases the light scattering ability.
- 3) Foams which scatter light at the air-polymer interface.

It is counterintuitive to think that pockets of colorless gas can aid opacity; however air voids are able to do this because it leads to increased scattering occurring at the pigment-air void interfaces [18]. It is because of this that foams, and white water rapids, appear white, and there are a number of patents that have exploited micro- and nano-voids to aid opacity [19]-[25].

The optimal size of a spherical air void to aid opacity has been empirically calculated to have a diameter of 250-300 nm [26]. This is because it is close to the wavelength of visible light, and therefore is more efficient at scattering visible light. Hence, if air voids of this size can be accurately produced with a high level of monodispersity, and incorporated into a paint formulation, it would be an efficient way of increasing opacity.

The opacity of a paint film varies with the pigment volume concentration (PVC; Fig. 3). As the PVC increases, so does opacity, to a point, after which, the opacity decreases with increasing PVC. This is due to crowding of the pigment particles which leads to multiple particles acting as one larger particle which is not as effective at scattering light [27]. When the PVC increases, another point of interest is reached, where the opacity begins to increase again with increasing PVC. This point is called the critical PVC (CPVC). The CPVC is the point at which there is not enough binder to completely wet all the pigment particles, and as a result, when the paint film dries, intercoating air voids are left between the paint component particles and the resin, which increases the film's opacity. The CPVC was first described by Asbeck & Van Loo in 1949 [28].



Fig. 2. Effect of TiO_2 volume concentration (PVC) on total film hiding (opacity), indicating where the CPVC lies.

Because most air voids form as pockets of solvent or water evaporate as the paint dries, the added opacity occurring from the air voids is only apparent once the paint has been applied and has had time to dry. This means that a fresh, wet, coating of paint may be slightly translucent and as a result lead to the substrate being partially visible. The person applying the paint may then apply an unnecessary additional coat if they are unaware that the paint will increase in opacity as it dries. If however air voids of the right size can be incorporated in an impermeable particle, it would increase the wet opacity and not affect the dry opacity of the paint. Consequently the PVC used in a paint formulation has a large impact on the properties of the paint produced [29].

Benefits to incorporating air voids into paint films include reduced raw material and transportation costs [30], and improved product sustainability, since air is essentially an inexhaustible resource. The adverse effect to incorporating air voids into paint formulations however include poor stain resistance, since air voids can be filled with external liquids.

IV. TITANIUM DIOXIDE (TIO₂)

Titanium dioxide (TiO₂), also known as titania, titanic anhydride, titanium white, Pigment White 6, CI 77891, and E171 [31]-[33] has usurped the former, traditional white pigments of lithopone, white leads, zinc oxide, and zinc sulfide to become the most common white pigment used across all industries, including paint. This is due to TiO₂ being relatively cheap to produce, nontoxic, and giving a far greater performance than other competitor pigments [2], [4], [34].

There are four naturally occurring sources of TiO₂; rutile (TiO₂), anatase (TiO₂), ilmenite (FeTiO₃) and leucoxene (TiO₂/FeTiO₃), the latter of which is a weathered form of ilmenite. Only rutile and anatase are used as pigments, with rutile being approximately 20% better than anatase at scattering light. Although rutile and anatase have the same chemical composition, they vary in their densities, lattice structure and refractive indices [2], [35]. Anatase was the first form of TiO₂ to be used as a white pigment in paints in the 1920's, with rutile being first used in the 1940's. Modern grades of TiO₂ are surface treated to alter their properties, to give better performance in a variety of ways [36].

There are two routes to producing TiO₂ pigment for paint [2]; the sulfate route and the chloride route, and production is ever increasing, with estimates of annual production predicted to be approaching 2.5 $\times 10^{12}$ T by 2026 [37]. In the sulfate route, the ore is dissolved in sulfuric acid, the aqueous solution of titanyl sulfate is then purified, a hydrous titania gel is precipitated and calcined to crystallize the TiO₂ which then requires grinding. This technique is labor intensive and a batch process. The chloride route on the other hand is more modern, and considered to be a more environmentally friendly method than the sulfate route. The ore is chlorinated, then distilled and chemically treated to purify the titanium tetrachloride (TiCl₄). The TiCl₄ is then flame oxidized to TiO₂ and chlorine, the latter of which is recycled. This technique is largely automated and a continuous process which produces a purer, and therefore better performing, product.

Waste from both TiO_2 manufacturing processes (sulfate and chloride routes), includes dilute acids, soluble iron compounds, and various inorganic compounds that are present in the ore, all of which are potentially damaging to the environment, and as a result, treating these waste products before discharge is mandatory, and the cost of this can be high. The chloride method does however produce less, hazardous by-products [35].

The reason TiO₂ is used in preference to other opacifiers

and fillers is because the refractive indices of rutile and anatase are higher than other white powders, with rutile TiO_2 having a refractive index of 2.6-2.9, depending upon the crystal axis [38]. This high refractive index is due to the crystal structures, and by grinding the TiO_2 particles to 250 nm particles, the light scattering effects are maximized, making the particles more efficient opacifying agents [2], [4], [39]. As well as high levels of opacity, TiO_2 properties also give protection to polymers from UV degradation [40].

There are two main issues with TiO_2 ; its cost, and its carbon footprint. In 2000, TiO_2 cost approximately $US2.20 \text{ kg}^{-1}$ [41] and in 2012 the cost exceeded US\$3.75 kg⁻¹ [42]. This is an increase in cost of 70% over 12 years. This trend in rising cost is likely to continue, due to the limited global resources of rutile and anatase, and because of the way TiO_2 is processed. Moreover, these resources and processes are liable to come under pressure for environmental reasons. As a result, more cost effective and sustainable alternatives are required.

V. TITANIUM DIOXIDE ALTERNATIVES

 TiO_2 alternatives can be separated into three different classes; direct replacement with natural materials, top-down products, and bottom-up products. Top-down alternatives are opacifying agents that have been created by altering an existing structure or product, whilst bottom-up alternatives are created by building a structure or product from raw materials, e.g. through precipitating mineral structures. This is often undertaken by empirical methods, but particles can be analyzed using computational models to determine whether they will have the desired properties [43].

Reducing crowding can also improve TiO_2 scattering efficiency (Fig. 2), meaning that less TiO_2 is required in a paint formulation to give the same opacity. Dow produces EVOQUETM which is a prime example of a product that does this. It works by binding to the TiO₂ particles and physically stops the TiO₂ particles from getting too close to each other, and therefore reduces crowding [44]. This review however, is focused on TiO₂ substitution, and not products which only deal with reducing crowding.

A. Direct Replacements

Direct substitution with another mineral is the easiest was of replacing TiO_2 . Most minerals however will still have to be mined, milled and/or ground (comminution), processed, and transported, which means that they may still have a high carbon footprint.

1) Zinc oxide (ZnO)

ZnO has been widely used in a number of applications, including; brass production [45], medicinal uses [46], rubber production [47], and as a white pigment [48], [49]. With regards to its use as a white pigment, ZnO has a refractive index of roughly 2.00 [50], which is lower than TiO₂, and why it has been largely usurped by TiO₂ as the most commonly used white pigment in paints. ZnO is still used for certain applications however, most notably as an antifouling agent in maritime applications [51]-[53].

There are a number of different ways to produce ZnO, including; as by-products, decomposition of hydrozincite, hydrometallurgical processes, spray pyrolysis, as well as

other minor production routes. Traditionally however, ZnO has been made by two different pyrometallurgical routes; direct, and indirect. The indirect route, also known as the French process, works by heating zinc before oxidation with the atmosphere, whilst the direct route, also known as the American process, works by vaporizing the zinc, before oxidation in a combustion chamber [54].

ZnO cannot however be used in conjunction with TiO_2 in a paint formulation as there are interactions between the two particles that occur, causing instability, and resulting in the formation of a gel complex. This is thought to be a result of one of three mechanisms, depending on a variety of different parameters in the formulation, such as pH, dispersants used, and the grade of materials used [55]:

- 1) Solubilisation of the zinc and subsequent chelation onto the dispersant.
- 2) Co-flocculation of the TiO_2 and ZnO.
- 3) A conglomeration of the binder used and the ZnO.

This lack of stability between the two particles means that ZnO is not widely used in paint formulations as an opacifying agent. This fact combined with its refractive index being significantly lower than that of TiO₂, means that it is not used nearly as much as it could be in the paint industry.

B. Top-down

Top-down strategies refer to strategies where existing particles or structures are altered to produce opacifying agents. A number of different strategies are outlined below.

1) Calcium carbonate (CaCO₃)

 $CaCO_3$, in the form of calcite, is the most commonly used mineral filler in paints due to its low cost, abundance and relatively high refractive index of 1.601-1.677 [56]. Although the scattering efficiency of CaCO₃ is not as high as TiO₂, it can be improved by creating ground CaCO₃ (GCC).

GCC is produced by grinding CaCO₃ into a fine powder; however the process of comminution will produce a polydispersed product, which would then have to be screened if a specific size range was required. Even though GCC gives a higher opacity than raw CaCO₃, it comes at the cost of grinding and milling, which is a very inefficient process that requires huge amounts of energy, especially to reach finer particle sizes. Therefore, although grinding improves the opacity of raw CaCO₃, it does so at a huge energy cost. Moreover GCC is not as efficient at scattering light as precipitated CaCO₃ (PCC; discussed later). The only way to improve GCC as an opacifying agent would be to improve the efficiency of the grinding and milling processes.

2) Clay minerals

Clay minerals are widely used as cheap extenders, and TiO_2 substitutes due to their relative abundance, low cost and reasonable opacifying properties. This is due to their often platy structure, which can form many air voids in a formulation that is above the CPVC, however they will often give a rough surface and be prone to flaking, which limits their uses.

a) Kaolin

Kaolin has exchangeable cations on its external surfaces, and the external charge varies depending on pH. As a result, there is a large variety in the chemistry of kaolins and this will affect many properties, including opacity and rheology [57]. For example, at high solid concentrations, kaolin, in certain forms, has a relatively low viscosity which is important for its use in paints as the paint needs to be fluid enough to easily be spread over a substrate [41].

Kaolin particles that are $\leq 2 \mu m$ have a pseudo-hexagonal plate structure [58], and this geometry, coupled with kaolin's opacifying properties (refractive index = 1.57 [59]) means that it is fairly efficient at preventing light from reaching the substrate beneath a paint film, and can form air voids when the paint formulation is above the CPVC. Consequently, kaolin is widely used as a partial TiO₂ substitute in paints [60]. Kaolin is often calcined, flux calcined [61], or flash calcined to increase its opacity as described later.

b) Perlite

Perlite is an inorganic, glassy rock of volcanic origins, which can be expanded through heating to create a porous structure [62]. This can be used in a paint to reduce weight, but also, if the air voids are of the right dimensions, to increase opacity [63]. Perlite can also be used as a flame retardant in paint formulations [64], [65].

c) Talc

Talc is a mineral that naturally occurs in a number of different forms, including an exfoliated flaky structure, with a refractive index of 1.586 [66]. The flaky structure of talc gives it similar properties to kaolin plates and is typically used as particles of $\approx 5 \ \mu m$ [67]. However talc is not as efficient at scattering light as kaolin, and therefore cannot be used to replace as much TiO₂, and is therefore not used as commonly.

d) Vermiculite

Vermiculite is a clay mineral which can be expanded by heating at temperatures of 1000-1200 $^{\circ}$ C to produce low density particles [68], and larger pieces of expanded vermiculite are commonly used as protective packaging filler. Vermiculite can also be exfoliated to produce extremely thin single sheets of vermiculite. Vermiculite in the exfoliated form is used as a paint opacifying agent, with the plate-like structure having similar properties as kaolin. The refractive index of vermiculite is however, not as high as that of kaolin, and vermiculite is more often used in paint formulations for its fire retardant properties [69].

With all of the aforementioned minerals, heating is generally used to exfoliate, expand, or promote air voids within them. This is usually done by calcination.

e) Calcined clays

Clay calcination is the process of heating clay minerals at high temperatures (>1000 °C), keeping the clays at high temperature for up to several hours and then cooling the clays to room temperature [70]. Calcined kaolin has a higher opacity compared to hydrous kaolin, and as a result, calcined kaolin is being increasingly used as a filler in paints due to the cost of rutile TiO₂ [41], [71]. Calcined clays have been found to be so efficient at scattering light, that they are able to replace TiO₂ by up to 20% without having a detrimental effect on the paint formulation [5]. This makes calcined clays a powerful partial substitute for TiO₂, however the calcination process requires a large amount of energy, and the resultant product will have a high carbon footprint.

f) Flash calcined clays

Flash calcination works in the same way as calcination

(described above), however it is done far more quickly, with flash calcination taking <1 s whilst traditional calcination can take hours [70], [72]. The flash calcination of kaolin particles results in pockets of air forming from the quick evaporation of water molecules, and thus expansion within the mineral and subsequently the resultant air voids give an increase in opacity.

The process of flash calcining kaolin has already been proven to be economically viable on a commercial scale by Imerys, who trademarked their product as OpaciliteTM [73]. The process of (flash) calcination requires a large amount of energy (temperatures being in the region of 400-1300 °C), and therefore has a large carbon footprint. If the results of flash calcination could be achieved in a much more energy efficient way, then the product could make an attractive TiO₂ substitute [41], [74].

3) Cenospheres

Cenospheres are naturally occurring hollow spheres that are filled with air or other gasses. One source is from fly ash; a by-product from coal burning electricity generating power stations [75], [76]. Fly ash cenospheres come in a variety of sizes but generally have a diameter between 20-200 μ m and a wall thickness of 2-10 μ m [75]. Due to the hollow nature of cenospheres, they can be easily extracted from the bulk of fly ash by a sink/float process [77] and a specific size range can easily be separated by screening. The hollow nature of the cenospheres also means that they have a low density, and as a result, if cenospheres could be incorporated into a paint formulation, then the net weight of the paint would be reduced, resulting in cheaper transportation, and a more sustainable product.

The primary issues with using cenospheres are their size and color. If an abundant source could be found with air voids of 200-300 nm, or if they could be synthesized at this size then they would have a very high potential to be a paint opacifier. Cenospheres can be anything from near-white to black in color, which could be an issue, however the cenospheres could potentially be bleached or coated, which may increase the opacity even more.

With regards to the carbon footprint of cenospheres, it would be very high to produce them as they are formed by burning coal, and other fossil fuels and biomaterials [78], however as they are a waste by-product from the energy industry, using cenospheres as an opacifying agent in paints would be a form of recycling, and therefore cenospheres would be a sustainable solution whilst fossil fuels are used for power production.

C. Bottom-up

Bottom-up strategies refer to strategies where opacifying agents are produced from raw materials. A number of different strategies are outlined below.

1) Hollow spheres

Hollow spheres offer a great structure for opacifiers because they are uniform in their geometry, meaning that the light scattering effect will be the same regardless of particle orientation. Hollow spheres also work well as a colloidal particle in a paint formulation, as they will flow without hindrance, and therefore are unlikely to have a detrimental effect on rheology. There are a large number of ways to produce hollow spheres on the nano- and micro-scales, and these are used for a number of different applications including superconductors and batteries [79]-[87]. Some of the many methods of producing hollow spheres that do, or could, have applications in paints as opacifying agents are discussed in more detail below.

a) Hollow latex spheres

Kowalski and Vogel were the first to develop hollow latex spheres for use as opacifiers in 1984 [21], [22], and what they produced is now sold commercially as ROPAQUETM by Rohm & Haas Company [88], [89]. ROPAQUETM can be used to replace in excess of 35% of TiO₂ in a paint formulation (formulation depending), and is the primary partial substitute for TiO₂ for many paint manufacturers [89]. As well as increasing opacity, hollow latex spheres can also have a significant effect on other parameters, such as gloss [26].

There are a number of different ways to produce hollow latex spheres, including; encapsulation of a non-solvent hydrocarbon for the polymer being synthesized, incorporation of a blowing agent, osmotic swelling, phase separation of two polymers in a common solvent, solvent swelling, and water in oil in water emulsion methods [26]. The formulation used in producing hollow latex spheres is critical as the spheres are prone to rupturing during production, rendering them less effective as opacifiers.

The predominant method of producing hollow latex spheres is by osmotic swelling [26]. This is where an acidic core is coated with latex that has a high glass transition temperature (T_g), and is introduced to a basic solution. The acidic core reacts with the basic solution causing the latex shell to expand and create a water-filled sphere. As the water-filled sphere dries, the water inside the latex sphere evaporates, creating a hollow latex sphere (Fig. 3). This technique for making hollow latex spheres can produce highly monodisperse particles.



Fig. 3. Diagram outlining the production of hollow latex spheres via acid core neutralisation (osmotic swelling).

The primary issue with hollow latex spheres is that they are susceptible to rupturing if burnished, and once ruptured they lose a lot of their opacifying properties. Therefore, if hollow latex spheres could be made stronger, they would be a more robust and beneficial paint opacifier.

Void containing inorganic pigments have also been made from zirconia and yttria, however both of these required calcinations, which requires a large amount of energy and therefore has a large carbon footprint. Calcium phosphate microcapsules have also been produced at temperatures as low as 37 °C; however, the particles produced were 20-70 μ m in size, rendering them too large for paint applications [90], [91].

b) Armored hollow latex spheres

As mentioned previously, the primary issue with hollow latex spheres is that they are prone to burnishing, and once ruptured, they no longer act as an opacifying agent as they no longer contain an air void. This could be minimized by coated hollow latex spheres with a hard external armor coating to give them extra resistance to burnishing.

Hollow latex spheres have been coated with various different chemistries, including gold nanoparticles [92] and clay particles [93], proving that hollow latex spheres can be coated with a hard exterior. Graphene coated latex spheres have also been made via miniemulsion polymerization, however traditional miniemulsion polymerization techniques require high energy mixing. Low energy miniemulsion polymerization methods have been developed which will reduce the carbon footprint and possibly make this a viable option in the future [94], [95].

Although armoring hollow spheres would make the hollow spheres more durable and possibly give them wet opacity, it would also increase the carbon footprint as further treatment is required, using more ingredients, each of which will have their own environmental impact. Because of this, a cost-benefit analysis would need to be undertaken to determine whether the strengthening effects would justify the extra cost, and environmental impact incurred.

c) Hollow glass spheres

Hollow glass spheres are often used in paint formulations for insulation purposes [96], and can be created by using a propane/oxygen flame to convert irregular glass frits into the hollow spheres [97]. Due to the impermeable nature of glass, hollow glass spheres would give both wet and dry opacity to paints; however the yield of hollow spheres produced by this method is low, with the majority of the spheres being completely solid. The hollow spheres are also prone to cracking when they cool and the size of the spheres produced were far too large for use in paint formulations, however this could possibly be addressed by using smaller glass frits [97].

2) Non-spherical hollow structures

There are a plethora of structures other than spheres which, if hollow and with the optimal geometries, could work as opacifying agents. Some of these possible structures are discussed below.

a) Flat air particles

Flat air particles were first theorized by Ross in 1971, and are particles that contain sheet like, planar air voids, which if parallel to the substrate have been theorized to greater opacity than rutile TiO₂ [98]. Due to this potential for extremely high opacity, if this theory is correct, and flat air molecules could be produced in an economically viable manner and applied in a way that ensures that they are parallel to the substrate, it could have a significant impact on the entire paint and coatings industry as it would largely replace TiO₂ as the primary opacifier and white pigment. This would also allow coatings to be engineered to be thinner, without losing opacity. As far as the author can ascertain, there is nothing in the literature that has been able to prove or disprove this theory, and as a result the high opacity of flat air particles remains theoretical.

b) Rods and tubules

Hollow rods and tubules can come in an almost infinite variety of lengths and widths, and they can either be circular or angular (e.g. hexagonal) in their cross section, which will affect how they pack. There is a profusion of different ways to synthesize micro- and nano-rods and tubules from a variety of different materials and chemicals available in the literature [99]-[103].

When tubes are put into a formulation however, they can have a large effect on rheology as the tubules can interact with each other, intertwine and essentially flocculate [104]. This can lead to shear thickening, and this is the opposite of what is required in a paint formulation. A paint formulation wants to be shear thinning, as when the shear force of the brush or roller on the wall is applied, the painter wants the paint to flow and therefore spread more easily on the substrate that is being painted. When the force from the brush or roller, along with the shear force, is removed, the painter wants a paint that thickens, so that it does not sag or drip. Because of this, incorporating rods and/or tubules into paint formulations could have rheological limitations.

3) Precipitation

There are a number of different routes through which precipitation can be used to produce opacifying agents. PCC is used commercially and methods of precipitating hollow structures by spray precipitation are discussed below.

a) Precipitated CaCO₃ (PCC)

PCC is produced by precipitating $CaCO_3$ from solution, and the resultant PCC can come in a large variety of structures, including cuboids, spheres, and other structures [105]-[107]. The structure of the PCC is determined by the conditions under which it is precipitated, such as pH, temperature and the presence of other substances. It has been shown that up to 8% of TiO₂ in a water-borne paint formulation can be replaced with PCC without impacting on the more important paint properties [107]. Generically, PCC is formed by subjecting natural limestone to three processes; calcination, hydration and precipitation (Equation (3)).

$$CaCO_{3} \xrightarrow{Heat} CaO + CO_{2}$$
(3)

$$CaO + H_{2}O \rightarrow Ca(OH)_{2}$$

$$Ca(OH)_{2(aq)} + CO_{2} \rightarrow CaCO_{3} + H_{2}O$$

Because the natural limestone undergoes calcination, it means that PCC production will have a large carbon footprint, however if the calcination step could be removed, then PCC would have a far lower carbon footprint. Tier *et al.* [108] looked at using slags from steel production, instead of calcined lime, and found that PCC could be produced, but that further filtering was required. If this technique could be optimized, then it could add value to a waste product and possibly become a commercial product.

b) Spray precipitation

Spray precipitation can be used to make hollow structures, and Chou *et al.* [109] produced hollow spheres of Al_2O_3 , TiO₂ and ZrO₂ using this route. This technique involves spraying precursor solutions into a precipitation agent which results in the polymerization of the precursor agent by acid-base neutralization or dehydration, depending on the chemistry. The size of the droplets in the spray will determine the size of the hollow spheres, which can be difficult to control, and thus results in a polydispersed array of hollow spheres.

4) Spindrift[™]

Developed by Dulux Australia, SpindriftTM particles are spherical honeycomb structures (containing multiple air voids) based around a TiO_2 core, and are produced by emulsion polymerization [110].

The benefits of SpindriftTM are that it adds spacing to the TiO_2 particles, which reduces clustering, it is resistant to burnishing and relatively light due to the air voids, which will also aid opacity. However, SpindriftTM is not as good an opacifier as other commercial products, such as RopaqueTM due to the small size of the air voids, and the polydispersity of the product.

5) Nanorattles

Nanorattles are hollow latex spheres that contain loose TiO_2 particles within the air voids. Nanorattles were developed by Nguyen *et al.* [111] with DuluxGroup (Australia), using reversible addition fragmentation chain transfer (RAFT) techniques. They were created by dispersing TiO_2 particles in amphiphilic macro-RAFT copolymers before being encased in a water-swellable hydrophilic layer. This in turn, was encapsulated in a hard hydrophobic layer which is expanded by swelling in a basic solution. The outermost, hard polymer shell is then strengthened by crosslinking. Due to their design, each nanorattle should give opacity because of three factors:

- 1) The TiO₂ particle
- 2) The air void
- 3) Increased spacing created by the outer layer

Kerker *et al.* [112] modelled this system, however, in their model, the TiO₂ particle was suspended in mid-air within the microvoid, however this is not realistic as it defies gravity. In the studies by Auger *et al.* [113], [114] however, eccentrically positioned TiO₂ particles within the air voids were modelled using a T-matrix approach. These studies suggest that nanorattles will not be as efficient at scattering light, as if the TiO₂ particles and air voids were separate. Consequently, this may limit the use of nanorattles in paint formulations.

6) Biomimicry

White pigments occur in nature, with studied examples including the Small White Butterfly, *Pieris rapae* [115], and the *Cyphochilus* beetle [116]-[118]. Biomimicry is involved in anthropogenically reproducing natural structures to harness their properties. In this instance, it would be to reproduce white pigments.

Hallam *et al.* [117] looked at the *Cyphochilus* beetle and found that the whiteness of its scales is due to an optimized packing density of scattering centers. Analysis of SEM and TEM images found the scales have a structure of irregularly packed fibrils, with a mean size of 250 ± 50 nm, and the mean spacing between the fibrils was found to be 600 ± 260 nm. Therefore, if the irregularly packed mass of air void containing fibrils structure of the beetle scales can be copied, it can be used as an efficient way to produce very thin films that have high opacity [117]. This could however have rheological complications, as outlined in the 'rods and tubules' section previously.

Diatoms are a major and extremely diverse type of phytoplankton that are found in marine and aquatic environments and have siliceous exoskeletons [119], [120]. When the diatoms perish, the organic matter decomposes, leaving the hollow siliceous exoskeleton, which sink to the bottom of the body of water, collect and form diatomaceous deposits.

Diatom exoskeletons are very diverse and generally 2-2000 μ m in size [121]. Many are porous and there are a variety of structures, including discs, rods, and spheres. If a species could be found that is of the optimum size and their exoskeletons made synthetically, or if deposits of their exoskeletons could be found in sufficient abundance, then the diatom exoskeletons could be used directly as opacifying agents. Diatomaceous silica is used as a TiO₂ extender; however this is not species/structure specific [5].

Another potential strategy for utilizing these natural structures would be to farm the creatures and harvest scales of the *Cyphochilus* beetle, or collect deposits of diatom exoskeletons. However, this strategy is extremely inefficient and is unlikely to be economically viable.

D. Summary of current research issues

Of all of the research that has, and continues to be undertaken, it has shown that it is incredibly difficult to produce a product that will be able to completely replace TiO_2 in a paint formulation, whilst possessing similar or better performance properties at an economically feasible cost. Consequently it is yet to be achieved. One of the biggest issues is producing a product that will allow for the reduction in TiO_2 in paints to be achieved but with a low carbon footprint, as a lot of current, and potential, products involve comminution, and/or calcination, both of which require a huge amount of energy, and increase the carbon footprint of the product.

VI. CONCLUSION

In conclusion, TiO_2 has been the primary white pigment and opacifier used in paints for a long time, however due to its cost, dwindling resources, and environmental impact, an alternative is required and sought after. This paper examines current and potential TiO_2 alternatives and shows that there are viable alternatives for partial TiO_2 substitution available. However, none of the current alternatives are comparable to TiO_2 at scattering light as there are still obstacles to oversome. Continued research into low carbon footprint alternatives to TiO_2 is important to the future sustainability of the paints industry.

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