Cureus Journal of Engineering

Open Access Original Article

Effective Utilization of Anchored Pigment/Extender Composite to Reduce TiO2 Crowding in High Pigment Volume Concentration Water-Based Paints

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Received 02/17/2025
Review began 02/27/2025
Review ended 03/26/2025
Published 04/08/2025

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DOI:
https://doi.org/10.7759/s44388-025-03351-3

Abstract

Over the years, the usage of titanium dioxide (TiO_2) as an opaque pigment has exploded into many fields specifically in paints and coatings, due to its high refractive index. Theories of light scattering clearly reveal that the highest level of whiteness and opacity is achieved with certain particle size distribution and a definite physical separation between two TiO_2 particles. With increased interest, there are attempts to maximize its opacity through chemical and physical modification of surface of TiO_2 particle. Unlike conventional spacer technologies, we have reported an approach through anchoring the TiO_2 on an inert extender thereby avoiding any crowding of the particles during paint film formation. The composite and paint film modified with composite are characterized by Scanning Electron Microscopy and particle size analysis.

Categories: Advanced Materials, Architectural Design and Innovation, Nano Materials
Keywords: opaque pigment, spacing, crowding, water based paint, titanium dioxide

Introduction

From coated fabrics to printing inks, cosmetics to toothpaste, pharmaceuticals to food colorants titanium dioxide (TiO_2) is one of the most commonly used pigment [1-3]. Owing to its high refractive index, TiO_2 show high opacity making it one of the important raw material in paint and coating industry. Increased popularity of TiO_2 in other fields has pushed up its demand in world market resulting in spiraling price rise [4]. In order to offset the price rise, paint formulators have been employing innovative strategies to reduce TiO_2 consumption without compromising the film opacity. In general, pigments tend to agglomerate during film formation as finer TiO_2 particles tend to fill in the interstices of larger particles, like $CaCO_3$ and clay resulting in crowding. Such "particle crowding" will result in poor dispersion of pigments compromising the light scattering efficiency and hence contributing for lower opacity of the dried paint [5,6]. Thus, controlling the spacing arrangement of TiO_2 pigment in dried paint is key for efficient usage of TiO_2 while maintaining the film opacity. Size of TiO_2 particles too is known to affect light scattering. Conventional paint is made with TiO_2 particles in the size range of 100 to 400 nm; however, most efficient light scattering occurs at size range of 200 to 300 nm of particles [7], which are uniformly spaced out.

Among various strategies employed for controlling the spacing arrangement of TiO_2, utilizing certain pigments to act as "spacer" or "extender" has gained traction as they are cheaper and work by mechanically spacing the TiO_2 pigments in the film. In a recent review, Ruszala and co-workers have examined current as well as potential low carbon footprint alternatives for TiO_2 replacement in paints industry [6]. Dietz has studied the effect of fine particle-sized extenders such as flash calcined china clays and entrapped air on utilization of TiO_2 in emulsion paints [8]. The study concludes that although some small improvements in TiO_2 utilization were possible using these extenders, the claims of 20% to 30% saving in TiO_2 could not be substantiated. Reduction of up to 7.4% of TiO_2 content in architectural semi-gloss waterborne interior paint formulation without any adverse effect on paint properties has been reported by Karakaş et al. [9] by using calcined clay and calcite. Emek et al. [10] have attempted to partially substitute TiO_2 with low particle size huntite, calcite, and Neuburg siliceous earth; results indicated that replacement of TiO_2 with up to 30% of huntite increased hiding power, whiteness, and gloss values of paint formulations. Effect of precipitated calcium carbonate on optical properties of waterborne paints at different pigment volume concentrations (PVCs) as against ground calcium carbonate and calcined Kaolin is studied by Karakaş et al. [11]. The team deduced that optimum formulations could be developed by substituting TiO_2 with the

How to cite this article
Raghavendra V B, Shreepathi S (April 08, 2025) Effective Utilization of Anchored Pigment/Extender Composite to Reduce TiO2 Crowding in High Pigment Volume Concentration Water-Based Paints. Cureus J Eng 2 : es44388-025-03351-3. DOI https://doi.org/10.7759/s44388-025-03351-3

precipitated calcium carbonate without any adverse effects resulting in higher film toughness and cheaper formulation. As for comparison between the extenders, precipitated calcium carbonate showed better opacity and gloss as compared to ground calcium carbonate and calcined Kaolin [11].

To develop theoretical understandings on the dispersion stability of TiO_2 pigment, a typical latex and an extender within a liquid paint, Croll [12] applied Derjaguin, Landau, Verwey and Overbeek theory. The study estimated the spacing between particles in a random dispersion from their particle sizes, their concentrations, and the characteristic packing fraction assigned to the dispersion. The theory works well only when details on particle composition and polymer adsorption are incorporated in the calculations. However, the theory cannot be applied to systems having non spherical particles like clay platelet [12]. Researchers at DuPont Titanium Technologies [13] have applied optical theory and concluded that optimal scattering of TiO_2 in paints can be achieved by (1) introducing air voids into coating by higher pigment loading or through addition of hollow opaque polymers, (2) replacing large extender particles with small extender particles, and (3) by using highly coated TiO_2 products. Among these, application of hollow opaque polymers as light scattering pigment to supplement the use of TiO_2 has been explored well. The air voids inside the hollow opaque polymers create refractive index difference with outer polymer shell there contributing for better hiding not just to waterborne paints but also for solvent-borne architectural paints [14,15]. An interesting way for improving the scattering of TiO_2 particles by creating air voids in paint is suggested in work by Diebold [5] as air voids themselves can scatter light to certain extent; however, such paint system may lead to other issue such as loss of film integrity, adhesion, etc.

Though several attempts have been made to optimize spacing of TiO_2 in paints and coatings through introduction of extenders or spacers, uncontrolled distribution and segregation of TiO_2 and extenders particles during film formation pose greatest challenge. As these particles can move freely, they tend to aggregate limiting their applicability. If one need to take advantage of better separation of TiO_2 particles, then it is necessary to tag these particles to the surface of a relatively larger extender particle, either chemically or physically. In this work, we have adopted an approach of physical attachment of TiO_2 particle to a micron size ground calcium carbonate particle with the help of a polyol/dispersant type organic moiety. Such an anchoring helps to greatly reduce the crowding of TiO_2 particles in higher pigment volume concentration paint and maximizes the opacity.

Materials And Methods

Materials

Styrene acrylic terpolymer emulsion with 50 wt% solid, having particle size (d_{50}) of 120 nm, was used to prepare all the water-based paints. The glass transition (Tg) and minimum film formation temperature of the polymer was in the range of 16°C to 19°C; viscosity was 600 cP (measured using Brookfield viscometer). Rutile grade of TiO_2 with average particle size of 300 nm and coated with silica and alumina was procured from DuPont (India), calcium carbonate extenders, and calcined clay, sodium salt of polyacrylic acid dispersing agent, glycols, preservatives, and high viscosity hydroxy ethyl cellulose thickener were of commercial grade and procured from local manufacturers. Exact grade name of the material and manufacturer is not disclosed to prevent product promotion arising out of this study. Coalescing solvent, i.e., 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate, was from Eastman Chemical Company (India), and Opaque polymer was from Dow Chemical Company (India).

$TiO_2/CaCO_3$ composite

Commercially available composite of TiO_2 and $CaCO_3$ was used for the study where in the ratio of TiO_2:$CaCO_3$ was 15:85 prepared through a dry mixing process where a polyol was used as anchoring agent.

Preparation of TiO_2 slurry

Generally, two types of TiO_2 are used in the manufacturing of architectural latex paint: (i) predispersed slurry and (ii) dry powder. It is therefore important to understand the differences in performance between rutile used as (i) slurry and (ii) physical anchoring on to $CaCO_3$ (current work, detailed in "TiO2/CaCO3 composite" section). Slurry was prepared by charging the required amount of TiO_2 and $CaCO_3$ powders into a mixture containing water and other additives in a twin shaft high-speed disperser. The slurry contents, having typical composition mentioned in Table *1*, were mixed thoroughly to get a finish of 5 on a Hegmann gauge.

Raw materials	Concentration (wt%)
Titanium dioxide (Rutile grade)	55
Calcium carbonate	12
Water	16
Other additives (glycols, thickeners, biocides)	17

TABLE 1: Typical composition of TiO2 slurry

Preparation of paint

The high PVC paint batches were processed [16] on a custom-built tabletop high-speed disperser. In general, the paint processing includes four stages: (i) premixing stage, (ii) grinding stage, (iii) stabilization stage, and (iv) let down stage. In the premixing stage, cellulosic thickener, water, dispersant, defoamer, biocide, and glycols were mixed at slow speed (400 rpm). In the grinding stage, pigment and extender were added slowly to the container and mixing continued at higher speed (1500 rpm) for 40 minutes. The mixture was then cooled to room temperature and was stabilized by adding a non-ionic surfactant. It was mixed thoroughly for 10 minutes followed by the addition of emulsion, coalescing agent, organic opacifier, and other ingredients, which were then mixed at low speed (700 rpm) for 15 minutes, then cooled to room temperature (let-down stage). The paint batches thus processed were stored for further testing and analysis. The generalized paint formulation, referred to as the standard paint formulation, is detailed in Table *2*.

Ingredients	Concentration (wt%)
Water	39.15
Dispersing agents	0.75
Cellulosic thickener	0.60
Titanium dioxide	5.5
Calcined clay	16.00
Calcium carbonate	9.00
Styrene acrylic emulsion	11
Opaque polymer	16
Biocide	1.00
Coalescing agent	1.00

TABLE 2: Standard paint formulation

Series of other paint formulations were prepared by replacing TiO_2 in the standard paint formulation with a known amount of $TiO_2/CaCO_3$ composite (either 2 times or 2.5 times) as tabulated in Table *3*. In another attempt, TiO_2 powder from the standard formulation was completely replaced by TiO_2 slurry (Formulation-7) containing an equivalent amount of TiO_2. Any difference in weight % were compensated by adjusting $CaCO_3$ content.

Sample name	Reduction in TiO_2 (%)	Addition of $TiO_2/CaCO_3$ composite (%)	Effective TiO_2 content (%)	Net decrease of TiO_2 (%)
Standard formulation	0.00	0.00	5.50	0.0
Formulation-1	5.00	10.00	5.31	3.45
Formulation-2	5.00	12.50	5.33	3.10
Formulation-3	10.00	20.00	5.12	6.91
Formulation-4	10.00	25.00	5.16	6.18
Formulation-5	15.00	30.00	4.92	10.54
Formulation-6	15.00	37.50	4.98	9.45
Formulation-7 (slurry)	100.00	100.00	5.50	0.0

TABLE 3: Paint formulations post replacement of TiO2 with TiO2/CaCO3 composite

Characterization

Thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA1 under nitrogen purge in the temperature range of 30°C to 1000°C at a heating rate of 10°C/min. Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray (EDX) analysis of raw materials and coatings were carried out using the JEOL 7100F microscope. The samples were stuck on the double-sided tape and sputter-coated with platinum for 30 seconds at 20 mA. The samples were imaged at varying magnification using Scanning Electron Microscopy (SEM), and EDX analysis was performed to determine the elemental composition. Particle Size Analysis (PSA) was conducted using Malvern PSA 3000 Hydro MV instrument. The powder samples were mixed with 0.1% sodium hexametaphosphate to make a paste, which was dispersed in deionized water by sonicating for 1 min using an internal sonicator at 100% power. Analysis was performed under continuous rotation at 3000 rpm.

Paint evaluation

Various paint parameters were evaluated as described below.

Contrast ratio, yellowness, whiteness: Paint was applied on lacquered LANETA paper (3B) with 6 mil and air dried for 24 hours. Measurements were carried out using Xrite Model CI 7800 spectrophotometer.

Reducing strength: White paint was mixed with green colorant by volume in a ratio of 100:2. It was applied on a white panel with a 6 mil applicator and air-dried for 24 hours at ambient conditions. The reflectance value was measured at 660 nm and reducing strength was calculated by the Saunderson equation [17] using the Xrite Model CI 7800 spectrophotometer.

Viscosity: Viscosity was measured in KU on Stormer Viscometer at temperature of 30 ± 1°C, using Brookfield Stormer Viscometer KU2.

Results

As the study is aimed at optimizing the distribution of TiO_2 particles within paint film in the presence of extender particles, both materials have been subjected to analytical characterization. The basic pigment properties like whiteness and oil absorption value of TiO_2, $CaCO_3$, and $TiO_2/CaCO_3$ composite are measured prior to evaluation in paint as detailed in Table *4*.

Name of material	Whiteness	Oil absorption* (g) /100 g
TiO_2	>100	25.0
$CaCO_3$	97.0	27.0
$TiO_2/CaCO_3$ composite (Formulation-1)	99.7	27.0

TABLE 4: Properties of TiO2, CaCO3, and TiO2/CaCO3 composite

* Tested according to ISO 787 with a minor modification. Acid value of the linseed oil in this work is <2 mg KOH/g

The size and morphology of TiO_2 and $CaCO_3$ particles are studied by SEM along with $TiO_2/CaCO_3$ mixture and composite to understand the relative distribution of TiO_2 and $CaCO_3$ particles (Figure *1*). The presence of roughly spherical particle morphology is observed for TiO_2 with sizes varying from 200 to 400 nm as shown in Figure *1A*. Micron-sized irregular shaped particles along with much smaller submicron-sized particles are observed in $CaCO_3$ sample (Figure *1B*). A physical mixture of TiO_2 and $CaCO_3$ particles in the similar ratio as the composite was prepared by simple dry mixing of both particles and their images are shown in Figure *1C*. The image clearly shows the presence of aggregated areas of nanometer-sized TiO_2 and micron-sized $CaCO_3$ particles along with a few areas where both particles are present together. This is expected as there is no interaction expected between both the particles. Interestingly, the $TiO_2/CaCO_3$ composite (Formulation-1) displayed in Figure *1D* shows very different particle morphology. TiO_2 particles are found to be uniformly deposited on the surface of $CaCO_3$ particles, indicating that it is merely not a physical mixture. Though $CaCO_3$ particles are aggregated, no such aggregation was observed with respect to TiO_2 particles. Since TiO_2 particles appear to be bound on the $CaCO_3$ particles in the composite, it would be interesting to see if the morphology is still maintained in paint, albeit after going through rigorous processes employed during paint making.

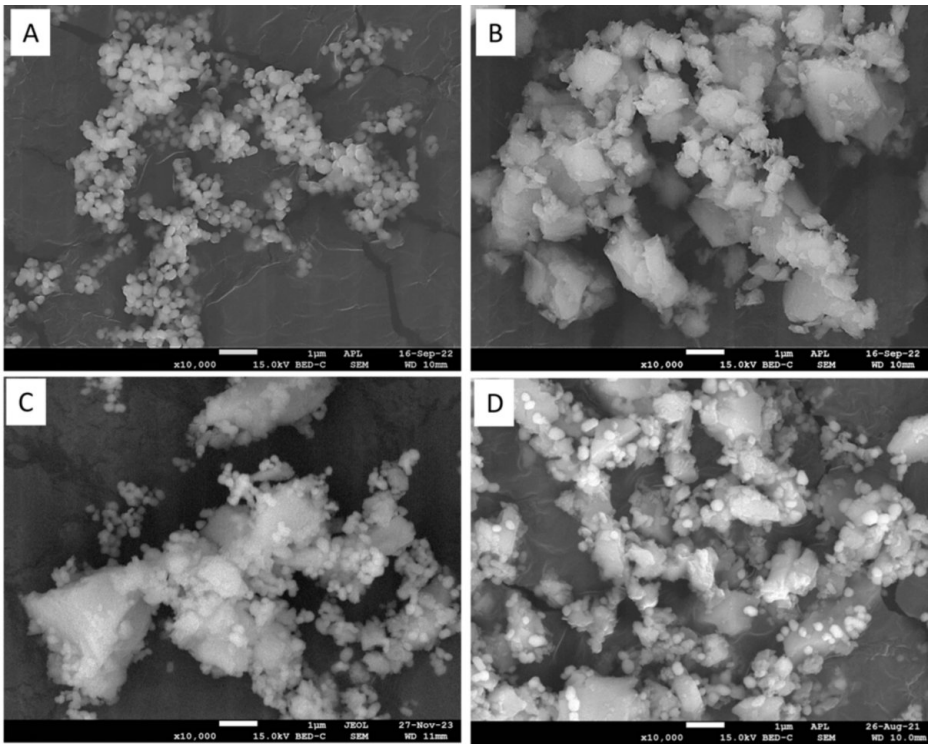


FIGURE 1: SEM images of (A) TiO2, (B) CaCO3, (C) TiO2/CaCO3 physical mixture, and (D) TiO2/CaCO3 composite

SEM, Scanning Electron Microscopy

The thermal decomposition profiles of TiO_2, $CaCO_3$, and $TiO_2/CaCO_3$ composite (Formulation-1) are shown in Figure 2. As expected, TiO_2 shows insignificant weight loss of ~3%, maybe from surface-treated material. In the case of $CaCO_3$, a single-step weight loss of 40% centered around 750°C is observed due to decarbonation. The decomposition profile of $TiO_2/CaCO_3$ composite is similar to $CaCO_3$ except that the weight loss is around 37%, which is to be expected due to the presence of TiO_2 in the composite.

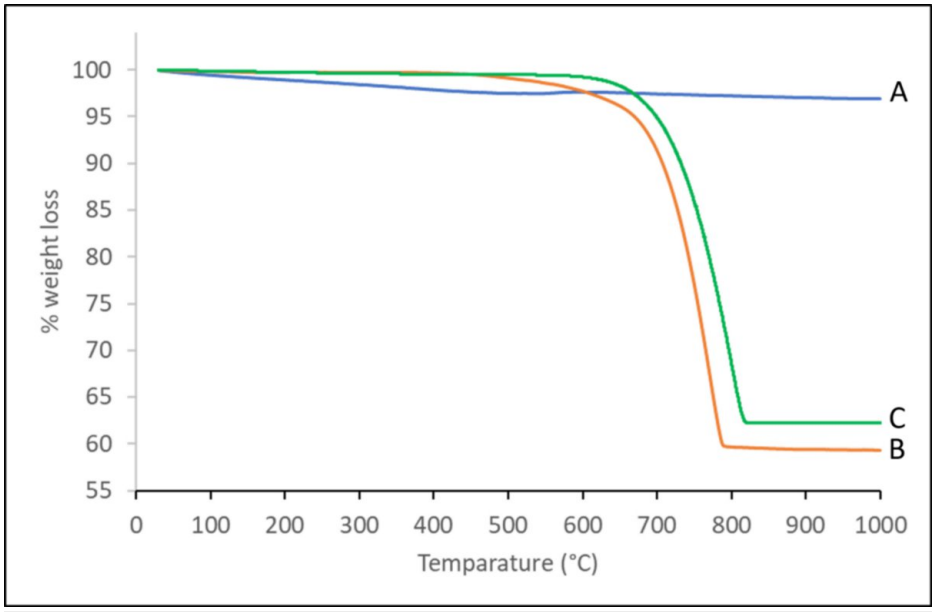


FIGURE 2: TGA profiles of (A) TiO2, (B) CaCO3, and (C) TiO2/CaCO3 composite

TGA, thermogravimetric analysis

The particle size distribution of TiO_2, $CaCO_3$, and $TiO_2/CaCO_3$ composite (Formulation-1) is as shown in Figure 3. A monomodal distribution with d_{50} around 560 nm is observed for TiO_2 particles (Figure 3A) calculated with refractive index (RI) of 2.760. The d_{50} for $CaCO_3$ particles, calculated with RI of 1.569, is 1.6 µm as shown in Figure 3B, which is one order higher than TiO_2 particles. One important factor which affects the particle size measurement is the RI of material under observation. Calculation is simple when only one type of material is studied; complications arise when mixture or composite of two or more materials is being studied [18]. In such cases, the RI of material having smaller particle size or higher RI among the mixture is considered. Hence, the RI of TiO_2 was used for calculating the particle size of $TiO_2/CaCO_3$ composite as displayed in Figure 3C. It is evident from the graph that the particle size of the composite is in the range of $CaCO_3$ particles though it contains TiO_2 particles as well. Such an observation is also reinforced from SEM study discussed earlier (Figure 1C), though the particle sizes are lower compared to PSA study. This inconsistency is due to the fact that the particles are completely dried when studied under SEM, while particles are suspended in an aqueous surfactant solution when studied under PSA.

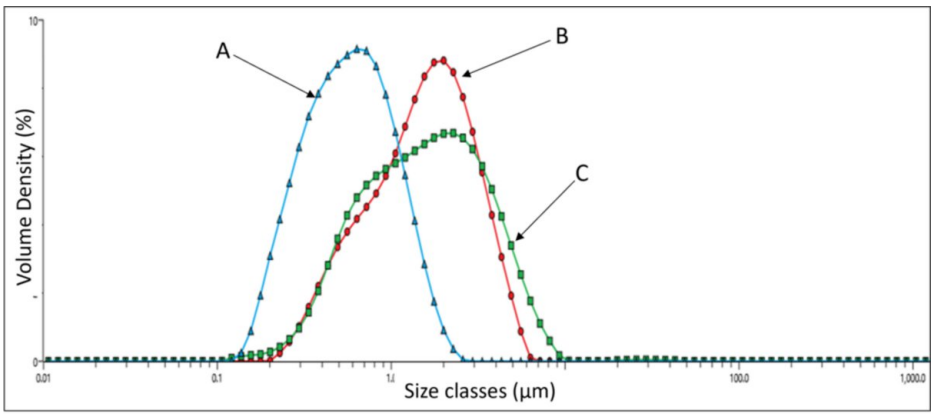


FIGURE 3: PSA profiles of (A) TiO2, (B) CaCO3, and (C) TiO2/CaCO3 composite

PSA, Particle Size Analysis

As the opacity of the paint film depends on the effective spacing of TiO_2, a series of formulations, as detailed in Table *3*, are made to achieve optimal dosage of TiO_2 without altering the performance of the base paint. The paint film properties (viscosity, yellowness, whiteness, contrast ratio, and reducing strength), tabulated in Table *5*, clearly indicate that most of the parameters of the modified formulations based on $TiO_2/CaCO_3$ composites are on par with the standard formulation. Among the optical properties of the film studied, contrast ratio and reducing strength are critical. Contrast ratio is a direct measure of opacity of paint film, expressed as the ratio of the reflectance of a paint film from a black substrate to that of a white substrate [19]. Reducing strength is a measure of whiteness imparted by TiO_2 upon tinting the paint, determined by the absorption and scattering coefficients of the trial and reference standard [20]. Reducing strength is severely impacted by the amount of TiO_2 and its spacing in the paint film. Considering the errors associated with measurement of reducing strength, differences up to +/- 2 units are acceptable. Interestingly, all the TiO_2 reduced designs (Formulation-1 to 7) show similar contrast ratio (Table *5*), indicating the possibility of achieving similar hiding at significantly lower TiO_2 content. However, reducing strength is decreased in line with reduction in TiO_2 content. Absorption of light by $TiO_2/CaCO_3$ composite might be one of the probable reasons for this observation. As optical properties of pigments are the result of combinations of light absorption, reflection, and transmission, contributions of each of these phenomena to contrast ratio and reducing strength of paint films depend on pigment type and concentration. Any absorption of light by $TiO_2/CaCO_3$ composite also contributes to opacity of the film while it reduces the reducing strength. On replacing 5% of TiO_2 in the standard formulation with 2 times (Formulation-1) and 2.5 times (Formulation-2) of $TiO_2/CaCO_3$ composite, the reducing strength is lowered slightly but within acceptable limits. Reducing higher quantities of TiO_2 (10% and 15%) with $TiO_2/CaCO_3$ composite (Formulation-3 to Formulation-6) resulted in lowering of reducing strength beyond the acceptable limit of 2 units. Within Formulations 1 and 2, the net decrease in TiO_2 is higher for Formulation-1, hence it can be concluded that it is the optimal formulation.

Sample name	Viscosity on stormer (KU)	Yellowness (ASTM E313)	Whiteness (Hunter 60)	Contrast ratio	Reducing strength
Standard formulation	106	1.1	94.7	98.6	100.00
Formulation-1	107	1.0	94.7	98.7	98.41
Formulation-2	106	1.0	94.7	98.9	98.49
Formulation-3	106	1.0	94.7	98.9	97.44
Formulation-4	105	0.9	94.8	98.9	97.91
Formulation-5	106	1.0	94.8	98.8	96.38
Formulation-6	105	0.9	94.9	98.7	97.31
Formulation-7 (slurry)	132	1.3	94.2	98.3	91.6

TABLE 5: Properties of paint formulations

The interaction between TiO_2 and $CaCO_3$ particles in standard formulation as well as in optimal composite formulation (Formulation-1) is further studied by SEM, as shown in Figure *4*. The bright particles in the size range 200 to 400 nm are TiO_2 particles, the circular grey particles are opacifiers [16], and micron-sized irregularly shaped particles are $CaCO_3$ particles. Since only TiO_2 and $CaCO_3$ are changed across the formulations, we have focused our study only on these particles. Both low and high magnification images of standard formulation, Figure *4A* and C show highly flocculated TiO_2 particles. There are many $CaCO_3$ particles without any TiO_2 particles deposited on them, as well as free TiO_2 particles not anchored on $CaCO_3$ particles, indicating the nature of interaction as physical blending. A very different kind of particle interaction is observed between TiO_2 and $CaCO_3$ in the composite, as shown in Figure *4B* and D (from Formulation-1). TiO_2 particles appear to be present along with $CaCO_3$ particles and no free TiO_2 particles are observed, indicating close interaction between the particles in paint film. These interactions appear to have led to better spacing of TiO_2 particles across the paint film, resulting in opacity comparable to the standard formulation, though their TiO_2 content is less.

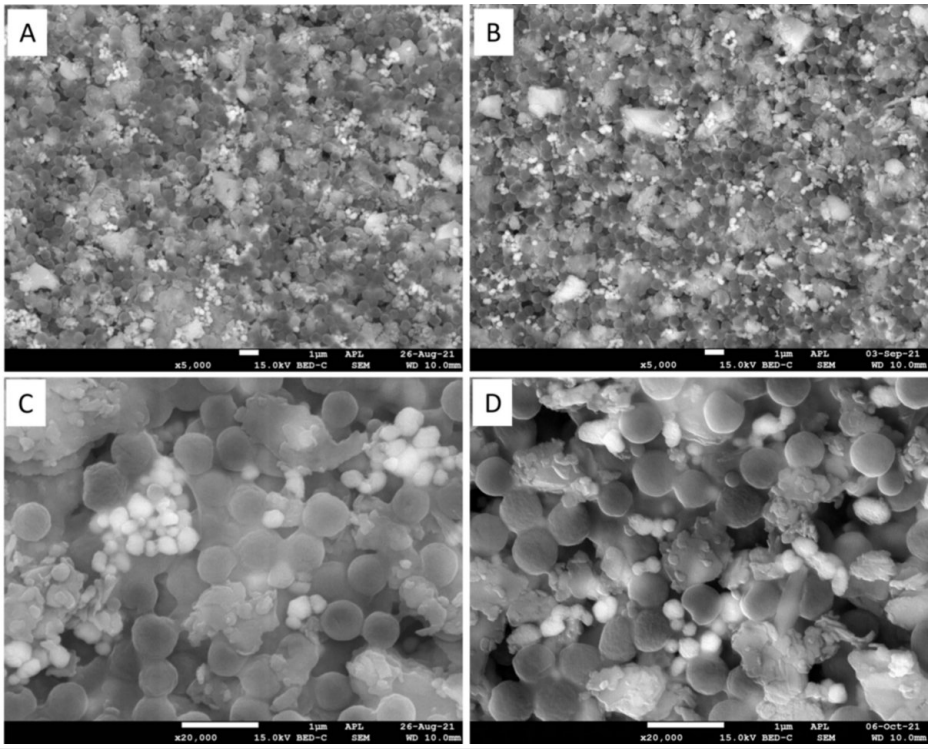


FIGURE 4: SEM images of standard formulation (A and C) and TiO2/CaCO3 composite (B and D) at low and high magnifications

SEM, Scanning Electron Microscopy

In an effort to understand the difference in TiO_2 dispersion in paint when introduced in slurry form, TiO_2 from the standard formulation was replaced completely with TiO_2 slurry (Formulation-7 in Table *3*). The paint made from slurry showed much higher viscosity than standard formulation (Table *5*), along with drastic decrease in the reducing strength to 91.6. SEM images (Figure *5*) support this observation. Here too, aggregation of TiO_2 particles, as well as $CaCO_3$ particles, is observed indicating no advantage in following this route for paint making.

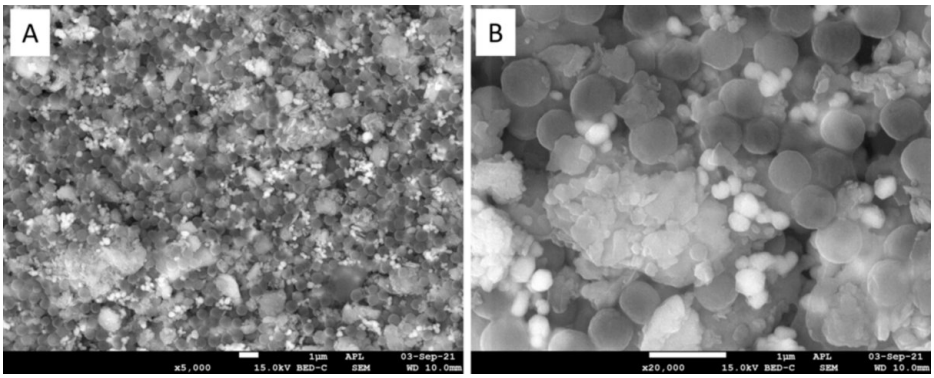


FIGURE 5: SEM images of TiO2/CaCO3 composite (Formulation-7 using slurry) at low and high magnifications

SEM, Scanning Electron Microscopy

Discussion

It is evident from the results that it is important to disperse the TiO_2 particles within the binder without aggregation to achieve optimal opacity. The degree of dispersion depends on the strength of anchoring of TiO_2 on $CaCO_3$. Though the anchoring agent discussed here gives the best results, it would be interesting

to study the effect of different anchoring agents on the efficacy of TiO_2 dispersion in $CaCO_3$.

Conclusions

An unconventional approach of anchoring TiO_2 to a filler particle to achieve maximized scattering is discussed in this work. Through a commercially available TiO_2-anchored composite of calcium carbonate, we have demonstrated the possibility of achieving the same opacity and reducing strength with lower effective TiO_2 in the paint. The efficacy of such TiO_2-anchored $CaCO_3$ is impacted by the strength of adhesion between TiO_2 and $CaCO_3$. In the current study, we are able to achieve a net reduction of 3.45 % of TiO_2 by effective dosing of TiO_2 by partial replacement with TiO_2-anchored $CaCO_3$. This reduction is due to effective spacing of TiO_2 in high pigment volume concentration-based paint, which otherwise crowds between the interstices of larger filler particles. SEM imaging was effectively used to demonstrate the spacing of TiO_2. This work will open up several opportunities for researchers and industries to look for diverse types of anchoring agents that can significantly improve the adhesion of TiO_2 onto the filler, thereby enabling superior control over spacing of TiO_2.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

Concept and design: Venugopal B. Raghavendra, Subrahmanya Shreepathi

Acquisition, analysis, or interpretation of data: Venugopal B. Raghavendra

Drafting of the manuscript: Venugopal B. Raghavendra

Critical review of the manuscript for important intellectual content: Venugopal B. Raghavendra, Subrahmanya Shreepathi

Supervision: Subrahmanya Shreepathi

Disclosures

Human subjects: All authors have confirmed that this study did not involve human participants or tissue. **Animal subjects:** All authors have confirmed that this study did not involve animal subjects or tissue. **Conflicts of interest:** In compliance with the ICMJE uniform disclosure form, all authors declare the following: **Payment/services info:** All authors have declared that no financial support was received from any organization for the submitted work. **Financial relationships:** All authors have declared that they have no financial relationships at present or within the previous three years with any organizations that might have an interest in the submitted work. **Other relationships:** All authors have declared that there are no other relationships or activities that could appear to have influenced the submitted work.

Acknowledgements

The authors would like to thank the Asian Paints Management for their support to publish this work, and Modern Instrumentation Laboratory, Asian Paints R&T Centre for providing the analytical facilities. The authors are also thankful to Mr. Dinesh Tanna and Dr. Amit Joshi for useful technical discussions.

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