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The effect of tin dioxide (SnO_2) on the anatase-rutile phase transformation of titania (TiO_2) in mica-titania pigments and their use in paint

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ABSTRACT

The synthesis of mica-titania special effect pigment and the effect of rutile promoting additive, tin dioxide (SnO_2), on the phase transformation of titanium dioxide (TiO_2) were investigated. SnO_2 coating with variable thicknesses on sieved and pre-treated muscovite mica prior to TiO_2 coating yields a pearlescent pigment with higher rutile-to-anatase ratio. Different than what is reported in a few cases, not the co-deposition of SnO_2 and TiO_2, but the coating of SnO_2 before TiO_2 was found critical in obtaining TiO_2 coatings consisting of 95% rutile phase at 1073 K. A calcination temperature as low as 1073 K resulted in the preservation of substrate's structural integrity. Scanning electron microscopy analyses showed that SnO_2 promotes TiO_2 growth at certain nucleation points rather than random nucleation points. Mica-titania pigments were incorporated in the acrylic based paints and gloss and hardness characteristics of the paint specimens were measured. Specimens with increased rutile content showed improved gloss.

1. Introduction

A pearlescent pigment is a kind of luster pigment which exhibits a pearl-shine effect due to angle-dependent optical effects driven from layers of particles with different refractive indices [1]. Currently, they have found very broad utilization in decorative and functional applications such as automotive top coatings, plastics, printing inks, industrial coatings, and cosmetics because of their eye-catching effects, angle-dependent interference colors, pearl luster, or multiple reflection [2]. The most widely used effect pigments consist of mica flakes coated with TiO_2.

Mica-titania pigments can be synthesized by several techniques. The most common technique is the heterogeneous nucleation in solutions. It is widely used and the best controlled process [3]. This technique consists of two alternatives, homogeneous hydrolysis and titration methods [4]. It is easier to control the process in titration method than in hydrolysis method. Moreover, the adhesion of the TiO_2 is better when this method is employed [4,5]. Mica-titania pigment is prepared by precipitation of titanium hydroxide on the surface of mica via hydrolysis of $TiCl_4$ by the addition of a suitable base. Calcination is carried out to convert titanium hydroxide to crystalline titanium dioxide. During the coating process, the pH should be adjusted and kept constant by simultaneous addition of a base [6]. In all methods, TiO_2 that coats mica is mostly in anatase crystalline form because muscovite mica, which is used as substrate, is known to have a template effect (i.e. muscovite mica promotes anatase formation) [7]. This behavior is believed to be due to the migration of Al^{+3} ions out of muscovite mica into the anatase layer leading to the inhibition of phase transformation [8]. However, rutile, thermodynamically stable phase of TiO_2, is preferred in coating applications due to many reasons. The refractive index of rutile (2.903) is higher than that of anatase (2.488) [9]. Thus, if the rutile form of TiO_2 is coated on mica, this results in a product with better luster and reflectivity, better color and color homogeneity [10]. In other words, phase transformation between anatase and rutile, and their ratio in titania layers have a significant influence on the pearlescent appearance of mica-titania pigments [9]. Furthermore, rutile is known to have a lower photocatalytic activity than anatase, implying that rutile transformation is more desirable to achieve prevention against oxidation of binder in outdoor weathering [7]. If rutile crystalline form is desired, generally a layer of hydrous tin dioxide (SnO_2) is first precipitated on the surface of mica followed by precipitation of a layer of hydrous TiO_2 by titration method. SnO_2 influences TiO_2 to crystallize in rutile form on mica

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substrate during calcination [10]. The mechanism by which the tin compound treatment of mica substrate facilitates the formation of rutile coatings is not fully understood. One possibility is that the amorphous hydrated tin compound deposited on mica changes into cassiterite, the only crystal form of SnO_2. Since cassiterite is isomorphous with rutile, it promotes the crystallization of the TiO_2 in the rutile form upon calcination [11]. The use of SnO_2 is the method of choice and is used universally in commercial rutile TiO_2 coated mica pigments [12].

There are only few studies reported in the literature on anatase-to-rutile transformation with the effect of SnO_2. In this study, titania coated mica pigment was synthesized by titration method and the effect of SnO_2 on anatase-to-rutile phase transformation was investigated. Mica substrate was pre-treated to cleave out its layers and to improve its surface properties.

2. Experimental

2.1. Materials

The ground muscovite mica used as a substrate in this study was supplied by Kaltun Mining Co. in Çine, Aydın, Turkey. Analytical grade sodium bicarbonate ($NaHCO_3$), titanium tetrachloride ($TiCl_4$), stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were used in the experiments.

2.2. Preparation method

2.2.1. Mica-titania synthesis

Dry ground mica flakes were sieved through 270 mesh (i.e., 53 μm) to obtain narrow size distribution. Then, the thickness of mica platelets was reduced by sodium bicarbonate treatment and the surface characteristics of the mineral were improved by decantation. Mica was first heated to 1073 K, and then, quenched into saturated sodium bicarbonate solution as quickly as possible. 5% HCl solution was added into this mixture that was stirred by a mechanical stirrer. This causes carbon dioxide evolution. After about an hour of stirring, mixture was washed and filtered to remove the excess salts [13]. Later on, the particles smaller than 10 μm were removed by decantation process.

For the production of mica-titania pigment, $TiOCl_2$ precursor was used in titration method. $TiOCl_2$ was obtained from the hydration of $TiCl_4$. It is important to note that concentrated $TiCl_4$ gives a sudden reaction with water at room temperature and, the undesired phase, $Ti(OH)_4$ forms. In order to prevent its formation, $TiCl_4$ was added dropwise into the concentrated HCl solution which was kept at 268 K in an ice bath; the resulting product is then $TiOCl_2$. The synthesis of TiO_2 (anatase) coated mica was carried out with the following procedure: 3 g pre-treated mica was suspended in distilled water and was heated to 348 K. The pH value of solution was adjusted to 2.0 by 5% HCl. Next, a $TiOCl_2$ solution was introduced into the agitated slurry at a rate of 0.8 ml min^{-1}. The pH value of the slurry was kept constant by simultaneous addition of 1 M NaOH solution. After the addition was completed, the slurry was aged for 10 min and then allowed to settle and cool to room temperature. The particles were separated, washed with distilled water, and dried at 333 K for 24 h. The final product was calcined at 1073 K for 2 h [9].

The introduction of SnO_2 in order to obtain rutile phase of TiO_2 onto mica substrate was done by using $SnCl_4$ solution. First, mica was dispersed in water and heated to 348 K, and then, pH was adjusted to 1.8 by using HCl. Then, $SnCl_4$ solution was added drop wise while pH was held constant through the simultaneous addition of NaOH. After aging the slurry for 10 min, the titania coating was done as described above. The process was repeated by using different amounts of SnO_2 such as 0.22%, 0.44%, 0.66%, and 0.88% g SnO_2/g of pigment.

2.2.2. Paint preparation

In order to characterize the optical properties gained in the paint, two separate batches were prepared. The first one was prepared with mica-titania pigment with anatase being the main phase whereas the second one with rutile being the main phase. The main formulation of the batches is given in Table 1. The acrylic resin was first dissolved in a solvent mixture, and then, the pigment was added. It was then mixed at 500 rpm for half an hour by using a mechanical stirrer. The paint thus prepared was applied onto glass plates by a paint applicator. The thickness of the wet film was 40 μm. The specimens were dried at room temperature for about a week before carrying out the tests.

2.3. Analyses

Particle size analysis (Sympatec PM-Tour, 2000) was performed to get information about the size distribution of mica flakes. It measures particle sizes in the range of 0.1 μm–8.75 mm and the measuring technique comprises analyzing diffraction patterns when laser beam passes through a dispersion of particles in air. SEM analysis (Quanta 400F Field Emission) was done to inspect the surface of mica particles before and after the decantation and precipitation processes. The measurements were done in high vacuum mode of the instrument and the samples were coated with 10 nm thick Au/Pd layer prior to SEM observation. Single-point BET analysis (Quantachrome Corporation, Autosorb-1-C/MS) was carried out by nitrogen gas adsorption to find the specific surface area of the mica substrate before and after sodium bicarbonate treatment. Mica particles were outgassed in flowing nitrogen gas with an adsorbate temperature of 350 K for 6 h. XRD analysis (RIGAKU – D/Max-2200/PC) was done by using CuKα ($\lambda = 0.154$ nm) radiation operated at 40 kV and 20 mA for the crystal structure determination of TiO_2 on mica. XRD patterns were recorded in the 2θ range from 25° to 50° with a step size of 0.02°.

Gloss of the paint samples was measured using a glossmeter (Rhopoint, Novo-Gloss) which directs light at a specific angle to the sample surface and simultaneously measures the amount of reflection. Since the angle of incidence of light is important on the impression of color, three different incident angles, namely 20, 60, and 85°, were used in gloss measurements. The 20°, 60°, and 85° angles were used for high, medium, and low gloss measurements, respectively. Hardness of the samples was determined by Persoz Pendulum Hardness Tester (Braive Instruments Hardness Tester, Model 3034). This method evaluates hardness by measuring the damping time of an oscillating pendulum which rests with two steel balls on the coating surface. The viscoelastic behavior of the coating determines the oscillation times.

3. Results and discussion

3.1. Mica pre-treatment

Table 2 shows the results of the BET analyses of the untreated and $NaHCO_3$ treated samples. Approximately 1.5 fold of increase

Table 1
Acrylic based paint recipe.

Formulation	Weight % (w/w)
Acrylic resin	63.6
Toluene	10.0
Acetone	5.6
Ethyl Methyl Ketone	8.3
Butyl acetate	2.5
Mica-titania pigment	10.0

Table 2
BET analysis of mica samples.

Sample	Specific surface area (m^2/g)
Mica (sieved + decantated)	4.54
Mica (sieved + decantated + $NaHCO_3$)	6.69

in specific surface area was obtained by $NaHCO_3$ treatment. Decantation process decreased the number of particles with sizes below 10 μm as seen from Fig. 1.

SEM micrographs (Fig. 2) also showed that tiny and broken particles on mica surfaces were successfully removed through decantation and smooth mica surfaces were obtained. Tiny particles scatter light and diminish pearlescence. Their removal improves gloss property of mica-titania pigment.

3.2. Mica-titania pigment

XRD analysis was performed to observe the phase transformation of TiO_2 on mica surfaces at different amounts of SnO_2 deposition. In Fig. 3, it can be observed that with increasing amount of SnO_2, the most intense peak of rutile at $2\theta = 27.49°$ progressively intensifies by splitting a peak of mica that is located at $2\theta = 27.85$ while the intensity of most intense peak of anatase at $2\theta = 25.36°$ tends to decrease. This can be interpreted as the promoted transformation of anatase phase to rutile by SnO_2. Also, the disappearance of the second intense peak of anatase ($2\theta = 48.14°$) and the appearance of second intense peak of rutile ($2\theta = 36.15°$) with increasing amounts of SnO_2 confirmed this phase transformation.

In Fig. 3a, the diffraction pattern for untreated mica trace is given. Upon treatment at 800 °C, due to a slight dehydration in mica, the main mica peaks in traces that belong to the coated mica particles show certain shifts with respect to the untreated mica. This combined with the fact that the most intense peaks of anatase and rutile at $2\theta = 25.36°$ and 27.49° interfere with mica peaks and make a semi-quantitative interpretation from intensities impossible. Therefore, in order to calculate the percentages of anatase and rutile phases, corresponding parts of the patterns were analyzed by deconvolution (Peakfit, v. 4.11). Since final crystallite sizes of the coatings were on the order of several tens of nanometers, there was a considerable broadening in the peaks. Therefore, the areas underneath the corresponding peaks were considered in calculations rather than the intensities. The volume-based data collected from XRD patterns were converted to mole percentage by using the equations given below:

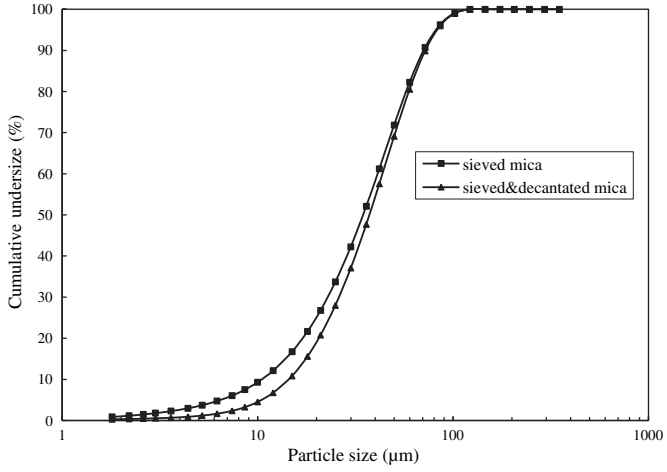

Fig. 1. The particle size distribution of sieved only and sieved & decantated mica.

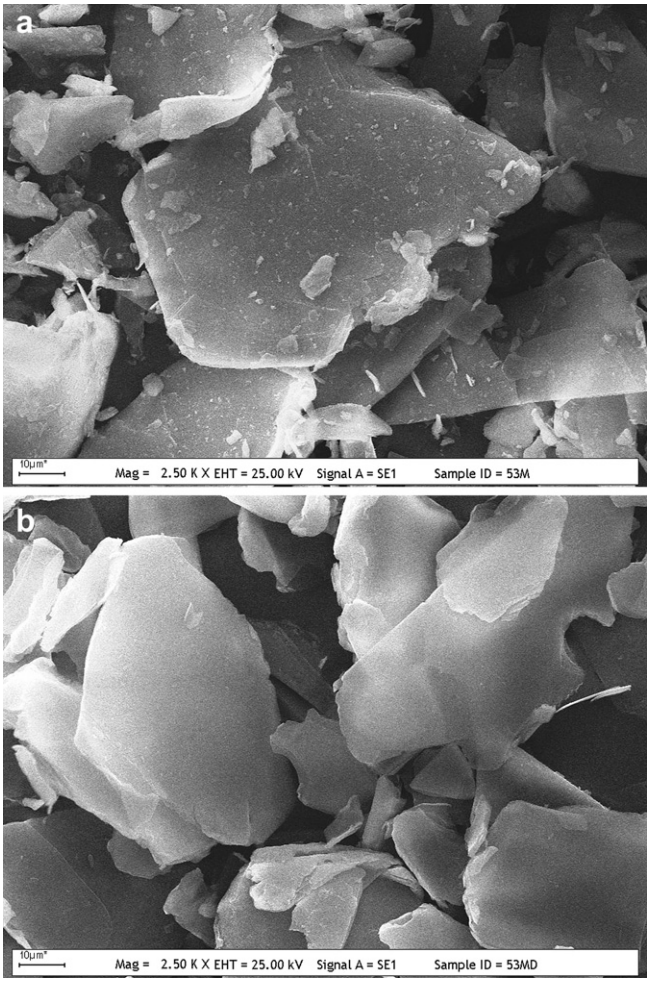

Fig. 2. SEM micrographs of (a) sieved only mica (×2500), (b) sieved & decantated mica (×2500).

$$V_r(\%) = [A_r/(A_r + A_a)] \times 100 \quad (1)$$

$$M_r = (V_r \times \rho_r)/MW_t \quad (2)$$

$$M_r(\%) = [M_r/(M_r + M_a)] \times 100 \quad (3)$$

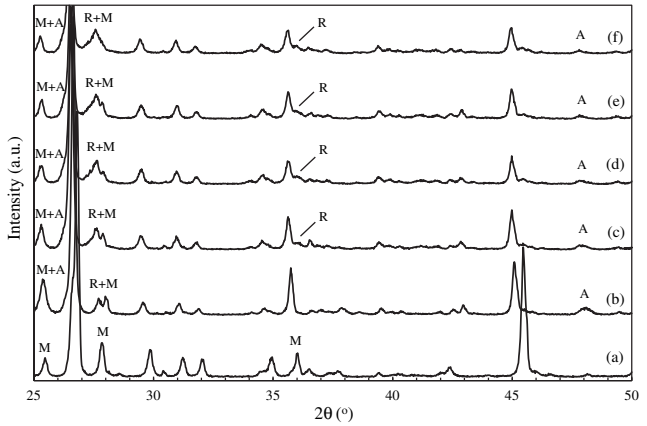

Fig. 3. XRD analysis results of mica-titania pigments having varying amounts of SnO_2 (M:mica, A:anatase, R:rutile): (a) muscovite mica, (b) TiO_2/mica, (c) 0.22% SnO_2/TiO_2/mica (d) 0.44% SnO_2/TiO_2/mica, (e) 0.66% SnO_2/TiO_2/mica, (f) 0.88% SnO_2/TiO_2/mica.

Table 3
Rutile and anatase mole percent in mica-titania pigments.

Sample	Rutile (Mole %)	Anatase (Mole %)
Mica-titania	2.55	97.45
Mica-titania (0.22% SnO_2)	24.55	75.45
Mica-titania (0.44% SnO_2)	71.28	28.72
Mica-titania (0.66% SnO_2)	95.64	4.36
Mica-titania (0.88% SnO_2)	91.64	8.36

where V_r (%) is the volume percentage of rutile, A_r and A_a are the analytical areas of rutile and anatase peaks, respectively, M_r is the mole of rutile, ρ_r is the theoretical density of rutile, MW_t is the molecular weight of TiO_2, and M_r (%) is the mole percentage of rutile.

The mole percentages of rutile and anatase phases determined by the equations above are given in Table 3. The sample in which 0.66% SnO_2 was used had the highest rutile content of 95% as seen from Table 3.

Fig. 4 shows the graphical illustration of the change in the crystalline form of TiO_2 on mica with varying amounts of SnO_2. It is clear that the mole percent of anatase phase decreases with the increasing quantity of SnO_2, except for 0.88% SnO_2, while the mole percent of rutile phase increases significantly. The mica-titania pigment with 0.88% SnO_2 displayed little decrease with respect to the pigment with 0.66% SnO_2. This implies that the excessive SnO_2 has an adverse effect on anatase-to-rutile transformation.

Song et al. studied the deposition of TiO_2 on muscovite flakes and the effect of doping coatings with different metal ions (Al^{3+}, Sn^{4+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+} or Cu^{2+}) on anatase-to-rutile transformation. Their XRD analysis revealed that Al^{3+}, Co^{2+}, or Cu^{2+} retarded the anatase-to-rutile transformation of TiO_2 whereas Sn^{4+}, Fe^{3+}, Zn^{2+}, Mn^{2+} promoted the transformation. They introduced the ions during TiO_2 hydrolysis, and achieved 63% conversion with SnO_2 at 1073 K [9]. Higher rutile conversions were achieved at 1173 K (69%) and 1273 K (91%), but mica can withstand only up to 1173 K, and then, begins to transform into feldspar above this temperature [1]. They have used co-precipitation method in their work. In our work SnO_2 was deposited onto mica surface before TiO_2 deposition. This sequential change turned in much higher anatase-to-rutile conversion even at a calcination temperature as low as 1073 K.

SEM micrographs of anatase (TiO_2) and rutile (0.66% SnO_2/TiO_2) coated mica pigments are given in Fig. 5. It is clearly seen from

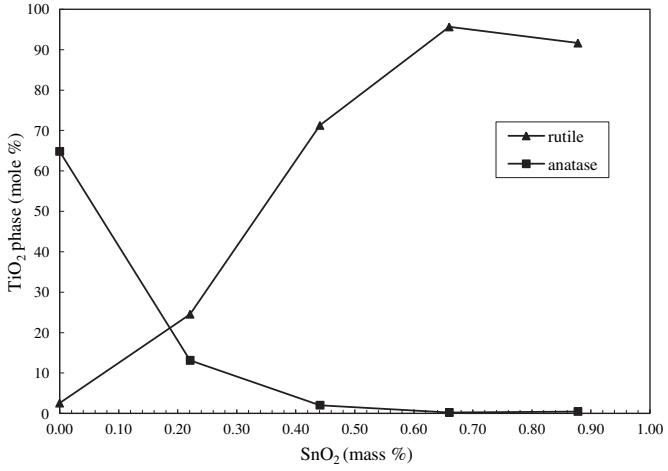

Fig. 4. Mole percents of anatase and rutile crystalline phases of the mica-titania pigments with varying SnO_2 amount.

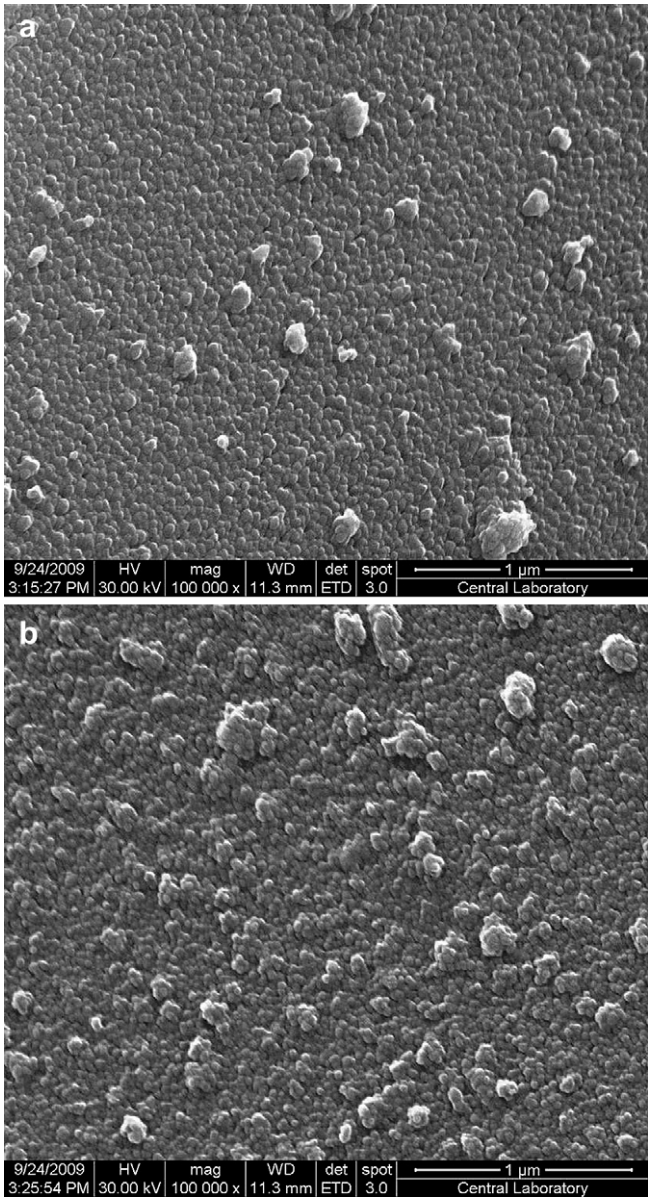

Fig. 5. SEM micrographs of mica-titania pigments; (a) TiO_2/mica, (b) 0.66% SnO_2/TiO_2/mica.

Fig. 5a that TiO_2 deposited homogenously onto mica surfaces. However, the presence of SnO_2 seems to cause more grainy deposition on the surface as seen from Fig. 5b.

In order to see the effect of SnO_2 from SEM analysis more clearly, TiO_2 amount that was coated the mica surfaces was doubled with a base coating of 0.88% SnO_2. In Fig. 6a rather smoothly grown TiO_2 is seen on mica surfaces, while in Fig. 6.b, discrete hemi-spheres of TiO_2 can be noticed more clearly. This result can be interpreted as a proof for the positive effect of SnO_2 in controling the growth of TiO_2 in rutile form.

In order to understand how SnO_2 affect anatase-to-rutile transformation of TiO_2, crystal structures of the phases can be examined (Table 4). It can be seen that anatase, rutile, and cassiterite structures have the same point group symmetry. However, while the lattice parameters of rutile and cassiterite phases are strikingly close to each other along both a and c axes, anatase has an elongated unit cell along c-axis and a slightly smaller unit cell along a-axis. Furthermore, the corresponding oxygen positions'

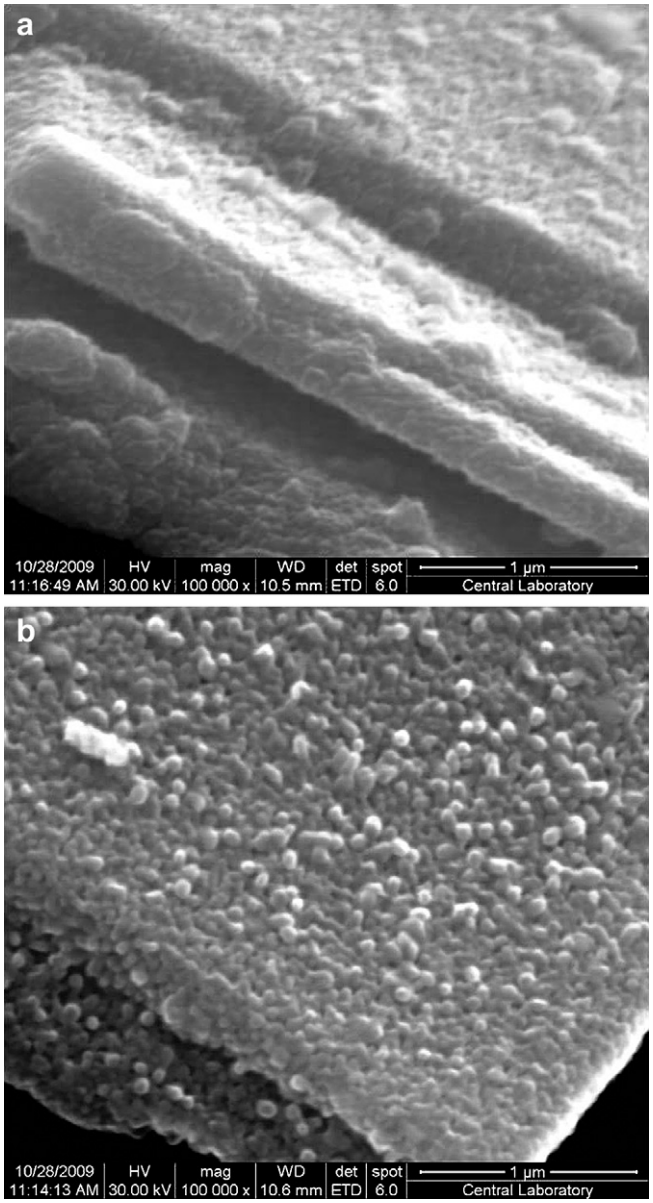

Fig. 6. SEM micrographs of mica-titania pigments; (a) TiO_2/mica, (b) 0.88% SnO_2/TiO_2/mica.

similarity in rutile and cassiterite provide the basis of a perfect epitaxial relationship between the oxygen polyhedra of both structures. Therefore such an epitaxial match probably manifests itself as a promoter for rutile phase, either during heterogeneous nucleation from the solution or the following heat treatment at 1073 K.

Table 4
Point group symmetry, lattice parameters, and oxygen positions of anatase, rutile, and cassiterite.

Phase	Point group symmetry	Lattice parameters		Oxygen positions		
		a	*c*	*x*	*y*	*z*
Anatase (TiO_2)	4/m 2/m 2/m	3.7845	9.5143	0	0.25	0.0816
Rutile (TiO_2)	4/m 2/m 2/m	4.5937	2.9587	0.304	0.304	0
Cassiterite (SnO_2)	4/m 2/m 2/m	4.7382	3.1871	0.387	0.387	0

Table 5
Gloss values of paints.

Sample	Gloss value (SGU)		
	20°	60°	85°
Mica-titania pigment (TiO_2)	37.0 ± 1.2	84.0 ± 1.7	62.0 ± 1.8
Mica-titania pigment (0.66% SnO_2/TiO_2)	50.0 ± 1.3	115.0 ± 1.4	79.0 ± 1.4
Percent increase (%)	35	37	27

Table 6
Hardness values of paints.

Sample	Persoz hardness (s)
Mica-titania pigment (TiO_2)	102.0 ± 3.5
Mica-titania pigment (0.66% SnO_2/TiO_2)	100.0 ± 3.7

3.3. Acrylic based paint formulations

The gloss values of the paints measured at different angles are given in Table 5. It was found that the sample with highest rutile content (i.e., the one with 0.66% SnO_2) showed improved gloss by 35, 37, and 27% at low, medium, and high angles of incident light beam, respectively. This is an expected result because rutile form of TiO_2 has higher refractive index than anatase, so it should impart higher gloss. Such a high increase in gloss values due to anatase-to-rutile transformation by using only 0.66% SnO_2 during pigment synthesis is a very significant achievement.

The hardness values of the paints measured by Persoz pendulum (reference: damping time on glass is 430 s) are given in Table 6. The hardness of the samples were determined according to ASTM D 4366. The differing anatase and rutile contents yielded same hardness values implying that the crystal phase of titania did not affect hardness. The hardness of a composite material is usually controlled by the matrix phase which is polymer in this case.

4. Conclusion

By using titration method and heterogeneous nucleation mechanism, TiO_2 was coated onto pre-treated mica substrates. Under normal circumstances, anatase is the crystalline phase of TiO_2 deposited. Incrementally varying amounts of SnO_2 deposited onto the mica substrates prior to TiO_2 coatings, promoted a quantitatively detectable increase in the amount of rutile phase in the coatings with respect to anatase. Use of only 0.66 wt% SnO_2 with respect to pigment weight was found to be adequate to provide a coating that consists of about 95% rutile phase. Precipitation of SnO_2 precursor prior to that of TiO_2 was found indispensible in attaining this high rutile percentage even at calcination temperatures as low as 1073 K, at which also mica substrate remain unaffected. The remarkable epitaxial match in between the unit cell dimensions of SnO_2 and rutile phases provides a plausible explanation on how a prior SnO_2 coat layer renders the substrate surfaces selective for rutile phase. When the gloss properties of the acrylic based paints that were prepared by using anatase and rutile mica-titania pigments were compared, the gloss values of paints with rutile pigment were found to be higher than those of the ones with anatase pigment as expected.

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