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ARTICLE

Synthesis and characterization of blue TiO₂/CoAl₂O₄ complex pigments with good colour and enhanced near-infrared reflectance properties

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Blue TiO₂/CoAl₂O₄ complex pigments were prepared through calcination of precursors from the precipitation of Al³⁺ and Co²⁺ on TiO₂ particles in sequence. The synthesized powders were characterized by colorimetry, near-infrared diffuse reflectance spectroscopy, X-ray diffraction, scanning electron microscopy and ultraviolet-visible spectroscopy. The pigments were found to have composite phases composed of rutile TiO₂ and spinel CoAl₂O₄. The bright blue pigments having good color properties could be obtained via calcination of the precursors at 1000 °C. As the mass of CoAl₂O₄ increased to 40 wt. % of TiO₂, the pigments presented good color properties (L* = 53.43, a* = -4.75, b* = -41.78) and the results showed little variation with an increase in the CoAl₂O₄ content. In comparison to the pure CoAl₂O₄ pigments, the as-prepared pigments with a CoAl₂O₄/TiO₂ mass ratio of 0.4 exhibited an enhanced near-infrared reflectance and also showed better color properties relative to the mixed pigments of TiO₂ and CoAl₂O₄.

Introduction

Cobalt aluminate (CoAl₂O₄), which is commonly known as Thenard's blue, has an impressive optical effect. It is characterized by a spinel-type of structure and has unique properties. Some of these unique properties are high refractive index, chemical reactivity, colour and good thermal stability¹. Cobalt aluminate is widely used in the production of ceramics, plastics, paint, rubber and glass. Various processes have been developed for the synthesis of cobalt blue. Some of these processes are solid-phase reaction², sol-gel²⁻⁷, co-precipitation⁸, sonochemical synthesis⁹, hydrothermal synthesis^{4, 10}, complexation¹¹ and combustion¹. With the recent development of material synthesis technology, nano-sized cobalt blue pigments can also be prepared via a number of special methods¹²⁻¹⁴. The pigments resulting from these methods can be transparent¹³ and highly stable in different media¹⁵. These new methods can help find new applications for the cobalt blue. One example of such development and application is of using cobalt blue in the production of the ceramic ink-jet printing ink¹².

In order to enhance the aesthetics of the built environment, dark-coloured pigments are often combined with the surface coatings for their applications to the buildings as paints^{16, 17}. Most of the solar energy (52% of the irradiance) lies in the near – infrared region (700 - 2500 nm)^{16, 17}. Since most of the dark pigments have low near – infrared (NIR) reflectance, therefore the surface temperature of the built environment

increases under solar irradiation due to the NIR absorption. The increase in temperature decreases the comfort in the inner rooms and hence results in an increase in the energy consumption due to a higher use of air conditioning. On the other hand, preferring cool pigments over the traditional pigments, results in a dramatically lower heat build-up in the surface of the roofs¹⁸⁻²⁰. In one of our previous works²¹, it was demonstrated that the application of the cool NIR reflection pigments can reduce the surface temperature by about 10 °C. In addition, under low wind conditions, the average air temperature on a road can be reduced by 5 °C by replacing the conventional asphalt with cool pigments²². Thus, various synthesis methods have been adopted to enhance the NIR reflectance of pigments or to develop novel colour pigments having similar characteristics. One of the methods is to dope the pigments with different metal ions in order to enhance their NIR reflectance²³⁻²⁷. The NIR reflectance of Cr₂O₃ green pigments can be improved from 55% to 85% by doping it with lanthanum (La) and praseodymium (Pr) ions²³. The NIR reflectance of BiVO₄ yellow pigments can also be improved from 50% to 88% by applying the doping technology²⁴⁻²⁶. In addition, due to low toxicity^{28, 29} and high NIR reflectance, several rare metal-based pigments have been proposed as viable alternatives to the traditional toxic pigments. The NIR reflectance of such pigments can exceed the value of 90%. Y₂BaCuO₅³⁰ and BaCr₂(P₂O₇)₂³¹ were developed as green pigments having 90% NIR reflectance. Moreover, SrCuSi₄O₁₀ doped with Fe, La and Li not only exhibit high NIR reflectance, but also show better colour properties relative to the cobalt blue³².

Due to its high reflectance in the short NIR region, cobalt aluminate can also be used as a cool pigment³³. However,

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cobalt is scarce and expensive. Furthermore, serious environmental problems may arise from the manufacture of Co-based ceramic pigments³⁴. Cobalt blue also exhibits an undesirable absorption band in the 1200–1600 nm range³³. Hence, NIR reflectance of the cobalt blue must be improved while the use of cobalt in the development of the cool cobalt blue pigment should be reduced. Rutile TiO₂ is a white pigment having a high NIR reflectance. When it is used in mixed pigments, it has the ability to further improve the NIR reflectance^{35,36}. Rutile TiO₂ also decreases the use of CoAl₂O₄ which is used in both the mixed pigments and in colour enhancing schemes for the pigments, but the mixture with high NIR reflectance tend to be light in colour due to the diluting effect of TiO₂³⁵⁻³⁷. The doping technology can enhance the NIR reflectance of pigments²⁴⁻²⁶, but the colour hues of CoAl₂O₄ probably are changed³⁸. A two-layer process has been proposed as an alternative to the mixed pigment coatings^{17,37}. The coatings resulting from the two-layer process exhibit high NIR and have the same visible aspects as those of the common building surfaces. In the present study, a complex pigment consisting of TiO₂ core and CoAl₂O₄ outer layer was also prepared for the cool products. Complex pigments with low cobalt consumption are expected to exhibit not only improved NIR reflectance but also good colour properties.

Experimental

Materials. CoCl₂·6H₂O, Al(NO₃)₃·9H₂O and NH₃·H₂O (25%-28%) were purchased from the Chuandong Chemical Co., Ltd., China. All reagents were analytically pure. Other reagents, such as polyethylene glycol (PEG 10000), titanium tetrachloride (TiCl₄, Sinopharm Chemical Reagent Co. Ltd., China.) and polyurethane (PU) paint (Dü Fang, Acryl PU-Klalack) were used as received.

Synthesis of complex pigments. TiO₂ powder was synthesized according to a process similar to the one reported in the references^{21,39}. In a typical synthesis, 20 mL of TiCl₄ was added to the ice blocks along with vigorous stirring. Once the ice blocks melted completely, the solution was diluted to a volume of 178 mL. Subsequently, 1 wt. % of PEG 10000, which acted as a dispersant, was added to the solution. After refluxing the solution at 100 °C for 4 h, the pH of the suspension was adjusted to about 6 by using 10% aqueous ammonia. The TiO₂ powder was obtained by filtering and washing the suspension several times followed by a drying process at 90 °C for 3 h.

About 2 g of the as-prepared TiO₂ powder was re-dispersed in 50 mL of the distilled water under vigorous stirring. Aluminum nitrate was dissolved in this suspension and a 10% aqueous ammonia solution was used to adjust the pH to a value which lied in the range of 6–7. Subsequently, 1M cobalt chloride was added to the suspension drop by drop and the pH of the suspension was adjusted to a value of around 9–10 by adding 10% aqueous ammonia solution. The precipitate was obtained after several cycles of filtering and washing processes. The resulting powder was obtained by drying the precipitate at 90 °C for 4 h. The colour products were obtained

by calcination of the powder at different temperatures ranging from 700 °C to 1000 °C. For all pigments, the ratio of Al³⁺ to Co²⁺ was kept constant at 3:1. This value has been reported as the optimum value for the Al³⁺ to Co²⁺ ratio². The contents of cobalt chloride were determined by the contents of theoretical CoAl₂O₄ which was used in mass ratios of 0.2, 0.4, 0.6, 0.8 and 1.0 relative to TiO₂. Pure CoAl₂O₄ pigments were obtained by calcining the precipitates of Al³⁺ and Co²⁺ without TiO₂ powder at 1000 °C. The mixed pigments of CoAl₂O₄ and TiO₂ were acquired by direct mixing of CoAl₂O₄ and TiO₂ powder. The CoAl₂O₄ content was measured from the CoAl₂O₄/TiO₂ ratio which had a value of 0.4.

Coloration of plastics and paints. Approximately 0.2 g of the pigments was mixed with 10 g of PU paint under ultrasonic treatment for 2 min. The mixture was then placed in a 9 cm petri dish and allowed to solidify. Coloured paint was obtained after solidification.

Characterization techniques. The phases of the products were characterized by X-ray diffraction (XRD) using Cu-K α radiation in an XD-3 diffractometer (Beijing Pgeneral). Morphological analyses were performed by scanning electron microscopy (Quanta x50 FEG). Ultraviolet-visible (UV-vis) NIR spectra were recorded on a spectrophotometer with an integrated sphere (Hatachi U-4100). For UV-vis analysis, BaSO₄ was used as the reference sample. The colour of the pigments was evaluated by measuring the L*, a* and b* parameters by using a Konica-Minolta spectrophotometer CM-700d. Near-infrared diffuse reflectance spectroscopy was conducted to confirm the optical properties of the samples. The micrographs were obtained using an Olympus CX31 instrument. Thermogravimetry and differential scanning calorimetry (TG-DSC) of the pigments were carried out in air with a heating rate of 10 °C/min by using Netzsch instruments (NETZSCH STA 409 PC/PG).

Results and discussion

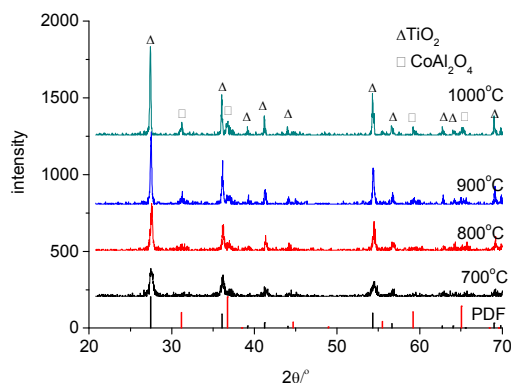


Fig.1 XRD patterns of the samples with 0.4 mass ratios of CoAl₂O₄/TiO₂ at different temperatures. The vertical lines in the PDF represent the relative peak intensities at respective 2 θ values corresponding to the spinel CoAl₂O₄ (red), rutile TiO₂ (black) phases

The phase composition and morphology of the as-prepared pigments. The obtained TiO₂/CoAl₂O₄ complex pigments were

expected to show blue colour and an enhanced NIR. Therefore, the expected phase composition for these pigments was rutile titania and spinel cobalt aluminate. As shown in Fig. 1, the rutile TiO_2 phase with the representative peaks at around 27.4, 36.1 and 54.3° was observed for all products, which were calcined in the range of 700 - 1000 °C. As the calcination temperature was increased, the peaks became more intense and sharper, indicating improved crystallinity. The calcination temperature is also a key factor in the formation of spinel cobalt aluminate. During its formation, a higher temperature resulted in the formation of more cobalt aluminate. Fig. 1 shows that the spinel CoAl_2O_4 phase with the representative peaks at around 31.2 and 36.8° was distinctive only above 900 °C. The most intensive peak occurred for the sample which was calcined at 1000 °C. However, the products, which were calcined at 700 °C and 800 °C, did not show any spinel cobalt aluminate phase. No peaks corresponding to the cobalt oxides and alumina were observed. This indicated that the resulting oxides might be amorphous in nature. Similar results have also been reported in a previous study⁴⁰. The cobalt aluminate phase can be obtained by heating the samples above the formation temperature of the blue CoAl_2O_4 . Zayat et al.² observed that the formation of the CoAl_2O_4 phase occurred only when the temperature was above 800 °C. Alternatively, Cava et al.⁴⁰ found that the cobalt aluminate phase was formed at a temperature above 1050 °C.

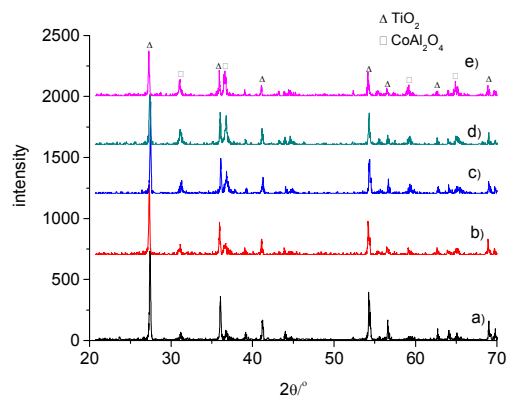


Fig. 2 XRD patterns of the samples with different mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ at 1000 °C. a):0.2, b):0.4, c)0.6, d)0.8, e)1.

The existence of spinel CoAl_2O_4 determined the coloration of the complex pigments. The phase compositions of the pigments with different CoAl_2O_4 contents are shown in Fig. 2. The sample having a $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ mass ratio of 0.2 showed a significant spinel CoAl_2O_4 phase. An increase in the CoAl_2O_4 content resulted in more intensive peaks for the CoAl_2O_4 phase. These results indicated an increase in the CoAl_2O_4 phase in the pigments. On the other hand, the peaks for the rutile TiO_2 phase decreased. In addition, no phases other than the spinel CoAl_2O_4 and rutile TiO_2 phases were detected. Typically, precipitates of Co^{2+} would react with Al^{3+} precipitates to form CoAl_2O_4 above the formation temperature of CoAl_2O_4 ². However, the same reaction can occur between the precipitates of Co^{2+} and TiO_2 to form cobalt titanate. Two of such examples include CoTiO_3 ^{41,42} and Co_2TiO_4 ⁴¹. Sales et al.⁴³ observed the formation of the CoTiO_3 phase for gels with Co, Al and Ti. Cobalt titanate exhibited a dark green colour^{16,42}, which deteriorated the colour properties of the pigments. However, no cobalt titanate was detected in all of the samples (as shown in the XRD patterns

presented in Fig. 2). These results indicate the isolation of a rich aluminum coating from the TiO_2 and the precipitates of Co^{2+} . Therefore, the expected phase composition of the obtained pigments showed good colour properties and high values of reflectance.

The dispersion and grain size of pigment particles can be detected by SEM. Fig. 3 shows SEM image of the complex pigment with 0.4 mass ratio of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$. The pigment particles were granular in nature and presented a homogeneous grain size. The grain sizes were distributed from 1 μm to 5 μm. Compared with the pigments in precious report²¹, these pigment particles have bigger particle size and present irregular morphology. And some smaller particles anchored on the surface of these irregular particles. All these differences of morphology and grain size plausibly come from the formation of spinel Co_2AlO_4 .

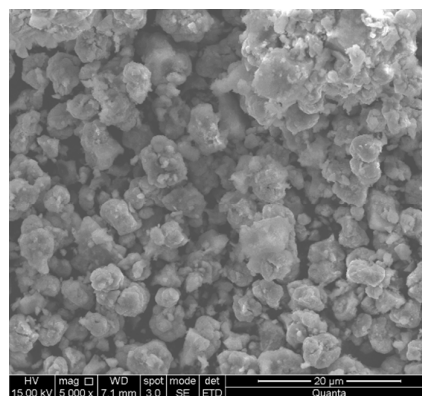


Fig. 3 SEM results the complex pigment with 0.4 mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$

The optical and colour properties of pigments. Different phase compositions may result in different absorptions in the visible region. The pigments showed different hues. Optical properties of the as-prepared complex pigments were studied by measuring the UV-vis spectra. Results from the analysis of UV-vis spectra of various samples, which were calcined at different temperature, showed that with an increase in the calcination temperature, the CoAl_2O_4 phase became more evident (as shown in Fig. 4a). The energy level for Co^{2+} (3d7 configuration) in both octahedral and tetrahedral ligand fields has three spin-allowed transitions^{2,13}. The spectra showed a band absorption pattern at around 546, 584 and 624 nm. The triple band was attributed to a Jahn–Teller distortion of the tetrahedral structure^{13,40,44}, which is responsible for the blue coloration. The spin-forbidden transition was observed as small peaks or shoulders around 479 nm and was attributed to transitions between the octahedral and tetrahedral sites⁴⁴. The observed absorption bands became more intense as the calcination temperature increased, thereby indicating that the CoAl_2O_4 phase increased with an increase in the temperature. This behaviour was consistent with the XRD results. Certainly, the above finding hinted that the blue hue value of the pigments would increase with the calcination temperature.

In addition, the absorption bands between 400–500 nm and above 700 nm were also analysed. These absorption bands corresponded to the samples which were calcined at lower temperatures, especially for the sample calcined at 700 °C. The absorption bands were due to the Co^{3+} component of Co_3O_4 ^{45,46}, which would result in a dark green colour of the obtained pigments 2. Indeed, the sample, which was calcined at 700 °C, showed a grey green colour. The bands decreased and disappeared with an increase in the calcination temperature. Simultaneously, the

observed colour of the pigments changed from green to bright blue. These findings suggested that the preparation temperature determined the coloration of the pigments. This was due to the CoAl_2O_4 and Co_3O_4 , both of which depend upon the calcination temperature.

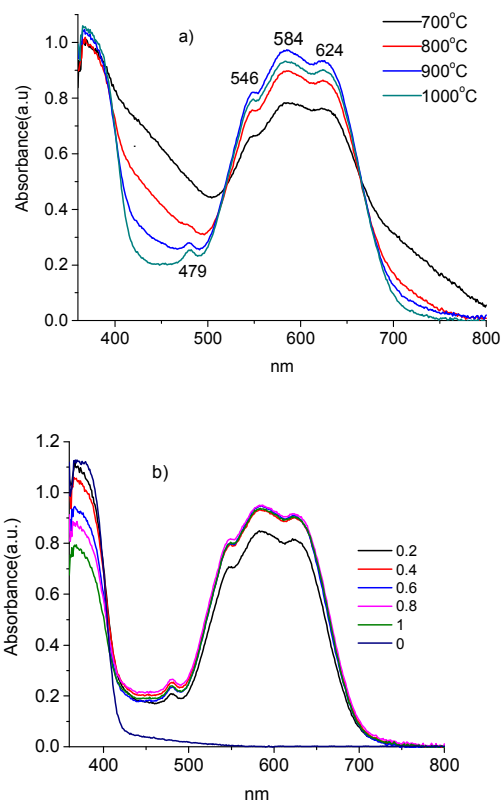


Fig. 4 The UV-vis spectra of the samples with 0.4 mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ by the calcination of different temperatures (a) and with different mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ by calcination of 1000 °C (b).

To obtain the CoAl_2O_4 phase, pigments must undergo calcination at 1000 °C. The optical spectra of the pigments with different CoAl_2O_4 contents are presented in Fig. 4b. Fig. 4b showed that all samples exhibited the characteristic absorption band of CoAl_2O_4 phase only, indicating that the pigments exhibited the expected bright blue colour. The absorption band at 350–400 nm was attributed to the absorption of TiO_2 in complex pigments, which decreased with an increase in the CoAl_2O_4 contents. This band was located in the ultraviolet region, so the difference did not result into a different colour. In general, the visible absorption of the complex pigments depends on the CoAl_2O_4 phase content, in which the pigments having lesser CoAl_2O_4 content show lower absorption. Indeed, the pigment with a $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ mass ratio of 0.2 showed much lower visible absorption compared to other pigments. These results suggested that this pigment demonstrated the lowest intensity of colours. Interestingly, when the CoAl_2O_4 content increased above 0.4, the differences in absorption intensity were hardly distinguishable. Thus, the visible absorption intensity of pigments was not always as heavily dependent on the CoAl_2O_4 content as expected.

The colour properties of the pigments were investigated further by colorimetry. Fig. 5 shows the colorimetric parameters of the obtained pigments. As shown in Fig. 1 and 4a, the calcination

temperature determined both the phase composition and the visible absorption of the obtained pigments. Therefore, the calcination temperature played a critical role in the colour properties of the pigments. Fig. 5a shows that the luminosity L^* increased slightly with an increase in the calcination temperature. All samples exhibited green ($-a^*$) and blue ($-b^*$) hues. The green component ($-a^*$) decreased as the temperature increased, whereas an opposite trend (between the hue and the temperature) was observed for the blue component ($-b^*$). As shown in Fig. 5a, the sample which was calcined at 700 °C presented a nearly pure dark green colour ($L^* = 46.46$, $b^* = -1.75$, $a^* = -15.15$) while the sample, which was calcined at 1000 °C, had a bright blue colour and showed the highest luminosity ($L^* = 53.43$), blue component ($b^* = -41.78$) and the lowest green component ($a^* = -4.75$). High calcination temperature enhanced the occurrence of the blue components and the elimination of green hue. This could be attributed to the formation of CoAl_2O_4 and the exhaustion of Co_3O_4 respectively. These findings were consistent with the results of both the XRD and the optical absorption.

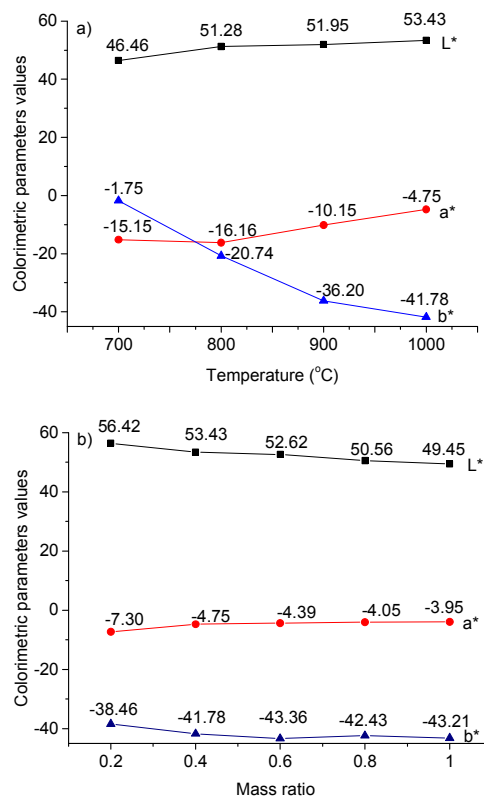


Fig. 5 Colourimetric parameters of pigments with 0.4 mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ calcined at different temperatures (a) and with different mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ by calcination of 1000 °C (b).

The CoAl_2O_4 phase is responsible for the blue hue of the pigments. The results in XRD and optical absorption indicated that the CoAl_2O_4 phase occurred for all pigments which were calcined at 1000 °C. Therefore, as shown in Fig. 5b, pigments with good colour properties could be obtained with as low as 20 wt% CoAl_2O_4 relative to TiO_2 . As the CoAl_2O_4 content increased, both the luminosity L^* and the green component ($-a^*$) decreased while the blue component ($-b^*$) showed an increasing trend. However, compared to the calcination temperature, the effect of the CoAl_2O_4 content on

the colour properties was considerably less significant, especially when the CoAl_2O_4 content increased above 0.4. This finding was consistent with the results of the optical absorption presented in Fig. 4b. For blue CoAl_2O_4 pigments, Zayat et al.² observed that the formation of white Al_2O_3 from excess Al in the pigments results in a loss of colour intensity. In comparison to the pure CoAl_2O_4 pigments ($L^* = 30$, $a^* = 9.52$, $b^* = -48.61$), the mixed pigments with a $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ mass ratio of 0.4 presented much lower colour intensity ($L^* = 65.97$, $a^* = -2.31$, $b^* = -28.11$). This result was attributed to the dilution effect of white TiO_2 in the mixed pigments^{35, 36}. Similarly, in comparison to the pure blue pigment, the complex pigments with a mass ratio of 0.4 presented slightly lower colour intensity ($b^* = -41.78$). However, even though the complex pigments and the mixed pigments contained equal contents of CoAl_2O_4 , yet the intensity of the complex pigments was much higher than that of the mixed pigments. In comparison to the pure pigment, the complex pigments showed much higher luminosity L^* . More importantly, the complex pigments with good properties ($L^* = 53.43$, $a^* = -4.75$, $b^* = -41.78$) effectively contained 28.5% CoAl_2O_4 . This meant that the mass ratio of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ was 0.4. Therefore, the complex pigments with good properties could reduce the use of Co.

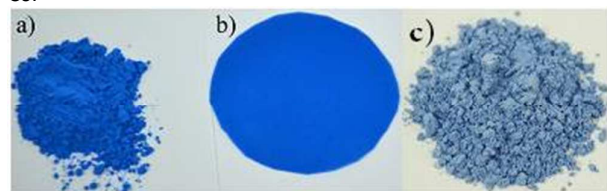


Fig. 6 Photos of complex pigment (a), PU coloured with the complex pigment (b) and the mixed pigments with the same contents of CoAl_2O_4 .

As shown in Fig. 5, the obtained complex pigments exhibited good properties. The vivid bright blue colour of the complex pigment with a $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ mass ratio of 0.4 is shown in Fig. 6. However, the mixed pigment with the same CoAl_2O_4 content showed a light blue colour. This visual difference was consistent with the results of the colorimetric parameters. The complex pigments showed high tinting strength. A film of PU paint coloured with the complex pigments exhibited a similar colour. No further processing was implemented for the complex pigment. The coloured PU film exhibited a homogeneous colour, indicating that the complex pigment was homogeneously dispersed in the organic matrix.

The thermal stability and chemical resistance of the pigments. The thermal behaviour of the complex pigment was studied for a temperature change ranging from room temperature to 900 °C (as shown in Fig. 7a). The TG curve illustrated a slight loss of 2.3%, which could be attributed to the release of physically adsorbed water. No endothermic peak was observed from the DSC curve, indicating that no phase transition occurred for the complex pigment. We also analysed the chemical stability of the complex pigment via comparative acid-corrosion experiment in 1M HCl for 96 h. Fig. 7b shows the absorbance curves of 0.01M CoCl_2 and 1M HCl solution with complex pigment. The CoCl_2 solution presented absorption at 511 nm, but no absorption was observed for HCl solution with the complex pigment. This indicated that the complex pigment had high chemical resistance to HCl solution. Obviously, the good thermal behaviour and high chemical resistance of the complex pigments are beneficial for their potential applications.

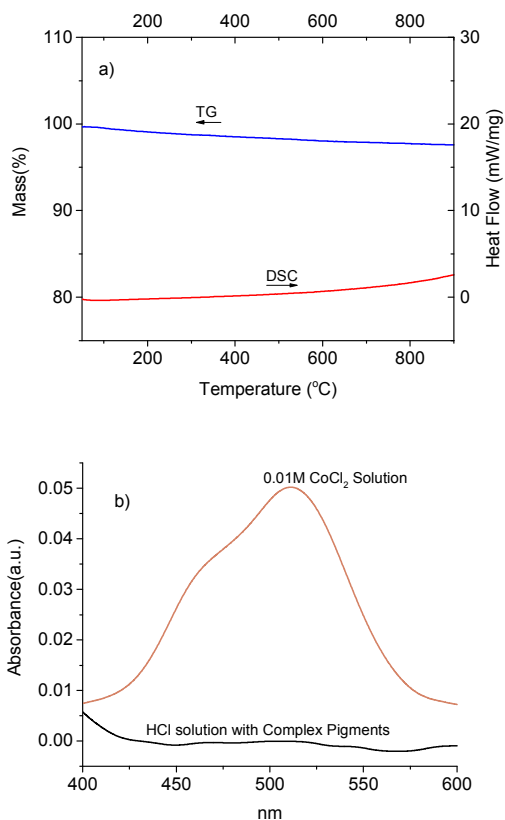


Fig. 7 TG-DSC curves of the complex pigment with 0.4 mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ (a) and the absorbance curves of CoCl_2 solution and HCl solution with complex pigment (b).

The NIR reflectance of the pigments. Around 52% of the energy in the solar irradiance spectrum is from near infrared irradiation (700–2500 nm)^{16, 17}. For the cool nonwhite pigments, this part of solar energy is expected to be reflected as much as possible. Doping is often used to enhance the NIR reflectance of nonwhite pigments^{23–27}. Another method to enhance the NIR reflectance is to colour the white pigments with high NIR reflectance by the coloured pigments and hence, prepare mixed pigments^{35, 36}. As shown in Fig. 8, a visible improvement in the NIR reflectance was observed for the mixed pigments, which could be attributed to the high reflection of rutile TiO_2 . However, the Fig. 6 and the results of the colorimetric parameters show that this enhancement was at the expense of colour intensity, which can be confirmed by the results presented in the Fig. 8. The mixed pigment had the highest reflectance in the range of 500 - 700 nm. Other published reports have also presented similar findings^{35, 36}. Therefore, the deep colour coating could not be obtained by using the mixed pigments, but the advantage lies in acceptable aesthetics of the dark colours⁴⁷. The above results showed that the complex pigments exhibited good properties and enhanced reflectance (as shown in Fig. 8). In comparison to the pure CoAl_2O_4 , the complex pigment showed at least 10% enhancement in the NIR reflectance. At the characteristic absorption band (1200–1600 nm) of CoAl_2O_4 ³³, the complex pigment showed around 15% enhancement and ultimately increased to 30% in the range of 1700–2500 nm. Furthermore, the reflectance of the complex pigment was observed to be 10% lower than that of the mixed pigment. However, the energy of the observed band accounted for 17% of the solar energy³³, which

demonstrated that the solar reflectance of the complex pigment was only 1.7% lower than that of one of the mixed pigments. Therefore, the complex pigments exhibited good colour properties and high NIR reflectance.

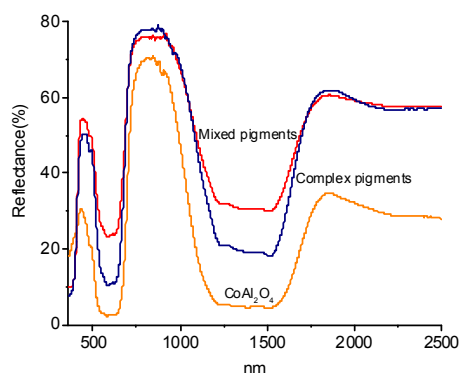


Fig. 8 UV-Vis-NIR reflection spectra of the pigments with 0.4 mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$.

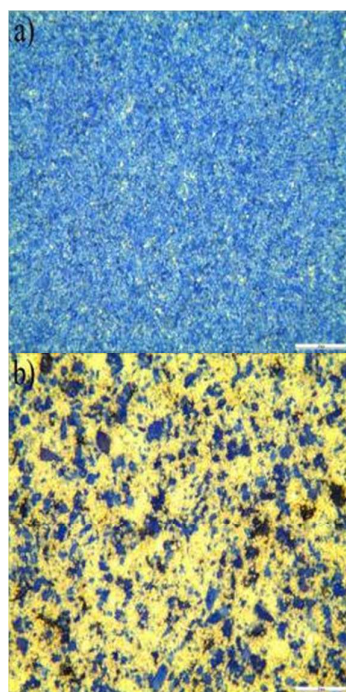


Fig. 9 Micrograph of the samples. a) Complex pigments with 0.4 mass ratios of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ and b) mixed pigment with the same content of CoAl_2O_4 . The bar represents 20 μm .

The above results indicated that the complex pigments exhibited a higher NIR reflectance and better colour properties relative to the pure cobalt blue pigments and mixed pigments with the same compositions. In this work, the CoAl_2O_4 phase was precipitated on the surface of rutile TiO_2 . Therefore, the complex pigment consisted of CoAl_2O_4 on the surface and rutile TiO_2 in the inner core. The CoAl_2O_4 phase on the surface resulted in the blue hue of the complex pigment particles. As shown in Fig. 9a, the micrograph of the complex pigment exhibited an almost uniform blue hue. However, for the mixed pigments with the same compositions, a completely different micrograph was observed (see Fig. 9b). The mixed pigments consisted of the blue CoAl_2O_4 aggregates and yellow rutile TiO_2 . The vast majority of the rutile TiO_2 could shield

part of the CoAl_2O_4 to absorb some visible light and NIR. Therefore, a lighter blue hue and a higher NIR (1200–1600 nm) reflectance were observed for the mixed pigments (as shown in Fig. 6c and 8 respectively). Some similar conclusions have been reported in previous studies^{35, 36}. Jiang et al.³⁵ mixed white rutile TiO_2 and cobalt aluminate blue to obtain a colourful cool coating having high solar reflectance. However, the coating Jiang et al.³⁵ prepared was light blue grey in colour. A grey coating with high solar reflectance could be obtained by mixing black pigments and TiO_2 ³⁶.

A two-layer coating process has recently been used to prepare both colourful and darker coatings with high NIR reflectance^{17, 37}. Libbra et al.¹⁷ coated the colour coating on the NIR-reflective basecoat to prepare cool colour red clay tile having higher solar reflectance. The cool colour pigments prepared by Libbra et al.¹⁷ yielded similar visible aspects as those of common building surfaces. Levinson et al.³⁷ also generated cool coloured concrete tiles and asphalt shingle roofing products having a dark appearance. For the complex cobalt aluminum blue pigments, a similar two-layer structure was obtained, which meant that the outer CoAl_2O_4 would render pigments with a bright blue colour. The outer CoAl_2O_4 would also render inner rutile TiO_2 core, which was one of the pigments, with over 80% NIR reflectance²¹, hence enhancing the NIR reflectance of complex pigments. The unique microstructure of the complex pigment provided pigments with good properties and high NIR reflectance. The optical properties must be obtained by using only 28.5% cobalt aluminate blue, which would substantially reduce the use of cobalt and hence, lead to a decrease in the cost of pigments. This would potentially reduce the environmental problems.

Conclusions

The complex pigments were obtained by calcination of the precursors with the precipitates of Al^{3+} and Co^{2+} on the surface of rutile TiO_2 . The resulting complex pigments consisted of rutile TiO_2 and spinel CoAl_2O_4 . The complex pigments exhibited good colour properties due to the visible absorption of the outer CoAl_2O_4 layer. These showed enhanced NIR reflectance because of the high NIR reflection of the inner rutile TiO_2 core. The complex pigments may help reduce the use of cobalt. Furthermore, the complex pigments are environmentally friendly and can be produced at a relatively lower cost.

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