Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 2029–2035
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Synthesis of white pearlescent pigments using the surface response method of statistical analysis

Nooshin Bayat [a], Saeid Baghshahi [b,*], Parvin Alizadeh [c]

[a] *Materials and Energy Research Center, Meshkin Dasht, Iran*
[b] *Department of Materials Science and Engineering, Faculty of Engineering, Imam Khomeini International University, Qazvin, Iran*
[c] *School of Engineering, Tarbiat Modares University, Tehran, Iran*

Received 15 February 2007; received in revised form 18 June 2007; accepted 24 July 2007
Available online 24 August 2007

Abstract

White pearlescent pigments were synthesized by coating mica flakes with a thin layer of TiO_2. To this aim a chemical bath deposition method was used. Deposition was conducted through homogeneous hydrolysis of $TiCl_4$ solutions in a highly acidic environment (pH < 2). To control the hydrolysis process and to study the effect of influencing factors, a statistical method of design of experiment named as ''response surface method'' was used. Scanning electron microscopy, X-ray diffractometery and spectrophotometery were used to characterize the pigments. It was found that among the factors investigated, temperature and time had the least and the highest effects on the coating quality, respectively. The optimal solution, i.e. concentration, temperature and time for coating was found to be 122 g L^{-1}, 43 °C and 55 h.

Keywords: A. Films; B. Platelets; B. Spectroscopy; C. Colour; D. TiO_2

1. Introduction

Pearlescent pigments consist of flaky particles of high reflectance. These flakes are either consisted of single crystals or a multilayer structure, in which each layer has a different refractive index and absorption properties [1–3]. When these flakes are dispersed in a transparent matrix of lower refractive index, an optical effect similar to that of natural pearls and shells will be demonstrated. This effect is due to the specular reflection of visible light by the flakes, which are oriented in parallel in the matrix. When light is irradiated on the flakes present in the matrix, the flakes on the surface reflect part of the light specularly and transmit the rest. The transmitted light is reflected by the flakes deeper in the matrix and so on. The higher the aspect ratio of the flakes and the smoother their surface, the intensity of the specular reflected light is higher, and that of the diffused one is lower, causing the luster effect of the pigments [3–5].

In contrast to common pigments, which function by selective absorption and scattering of visible light, pearlescent pigments function based on the interference or reflection of light from the interface of the layers or the surface of the flakes. According to the rules governing thin layers of optical solids, the wavelength of the light which is amplified by interference depends on the thickness and the refractive index of the layers. Hence in pearlescent pigments it is possible to obtain white to iridescent colours in visible range [2]. Also, combining a transparent layer and an adsorbing layer, the so called flop effect (change of colour by changing the view angle) may be demonstrated. In theses pigments interference colours are seen in specular view angle and adsorbing colours are observed in diffused view angle. Thus, the flop effect is observed [1,4].

Pearlescent pigments are being used in decorating plastics, glasses, glazes, etc. Some have also been used due to such properties as electrical conductivity, magnetic properties, sensitivity to laser and IR reflection, and so on [1,4,6–8].

Among the pearlescent pigments, those made of mica/TiO_2 which are synthesized by coating TiO_2 on thin layers of mica, are of high importance. Being a type of interference pigments, they are also used as the basis for many technical pigments. According to Fresnel law, to introduce strong interference colours, the thickness of the TiO_2 coating on mica flakes should be in the range of 20–100 nm. Also to achieve the highest lustrous effect, the width and thickness of the mica flakes

* Corresponding author. Tel.: +98 21 77841175; fax: +98 281 3780073.
E-mail address: baghshahi@ikiu.ac.ir (S. Baghshahi).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.07.034

should be in the range of 10–50 μm and less than 70 nm, respectively (an aspect ratio of at least 150) [2,3].

There are various ways for depositing TiO_2 on mica flakes, including homogeneous hydrolysis, titration and CVD, in all of which $TiCl_4$ may be used as the precursor for TiO_2 [1,4,9,10]. In this work homogeneous hydrolysis was used, in which, the control of the rate of hydrolysis is difficult. To circumvent this problem, recently thermohydrolysis has been used. In this method unstable compounds such as urea is used in the solution. These compounds are gradually decomposed during heating and by creating a basic environment, the rate of hydrolysis can be controlled. The coating which is formed in this way is usually amorphous, which is subsequently heat treated to convert to rutile, the favorite polymorph of TiO_2 which has a high refractive index [11,12]. However, for the first time, we used a highly acidic environment for better control of the process, which caused the formation of rutile phase without any need for further calcinations.

2. Experimental procedure

The mica used in this work was supplied by Hansco Co. To obtain a suitable particle size distribution, the mica was first fast milled for 3 h in water. The flakes were dried at 100 °C for 1 h and passed through a 270 mesh sieve. The particles size distribution (equivalent sphere size) was measured using a laser particle size analyzer (Fritsch Analyset Model 22, Germany) and the specific surface area was measured by BET method (Micromeretic Gemini 2360, USA). The thickness of the flakes was measured by a scanning electron microscope (Stereo Scan 360 Leica, Cambridge).

Deposition was conducted in one step by homogeneous hydrolysis of titanium tetrachloride ($TiTCl_4$) solution in a highly acidic condition (pH < 2).

In this work, among the most important factors, three of them, i.e. the solution concentration, temperature and time were studied (Table 1). To study the effect of these factors, a statistical method of design of experiments named as ''response surface method'' (RSM) in a ''face centered composite'' was used.

As seen in Table 1, the factors were studied at three levels. Hence, according to the face centered composite, sixteen experiments were conducted (Fig. 1 and Table 2). As indicated in Fig. 1 and Table 2, samples 9 and 10 are the same. This repetition is done to check the reproducibility of the results.

For each experiment 2 g sieved mica was dispersed in 50 mL of $TiCl_4$ solution, the concentration of which is given by Tables 1 and 2. The temperature of the solutions was adjusted by a hot plate. During the deposition process, the suspension was agitated by a magnetic stirrer for the defined period of time (Table 2), and TiO_2 was allowed to deposit on the surface of mica flakes. Subsequently, the mica flakes were centrifuged for 3 min with a speed of 1500 rpm and then were separated by a paper filter, washed by distilled water and dried at 100 °C for 1 h.

Table 1
The levels used for concentration, temperature and time

Factors	Levels		
	1	0	−1
X_1: Concentration (g L^{-1})	200	150	100
X_2: Temperature (°C)	60	45	30
X_3: Time (h)	75	40	5

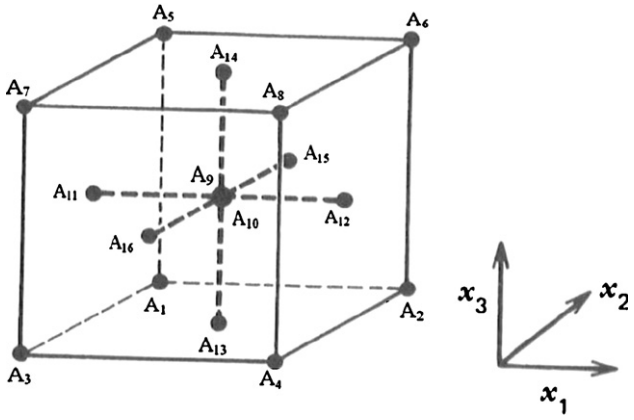

Fig. 1. A face-centered central composition design.

To study the uniformity of the coatings and their thickness, scanning electron microscopy (SEM) was conducted. The formation of rutile phase was investigated using XRD (Philips PW 3710), using Cu Kα radiation.

To investigate the optical properties of the coatings, a glass plate was coated by a nitrocellulose lacquer containing 2% of the prepared pigments. Then the glass was laid on a black background and its reflection spectrum was obtained by a guniophotometer (Macbeth CE 760 GL) at 20° angle. A white tile was used for calibration. Colour characteristics also were measured and the colour difference with a reference pigment (Zhejiang Aoke Pearlescent Pigment Co. Ltd., China) was obtained using the following equation:

$$\Delta E = (\Delta a^* + \Delta b^* + \Delta L^*)^{1/2} \quad (1)$$

Table 2
The conditions for homogeneous hydrolysis

Samples	X_1	X_2	X_3
B_1	−1	−1	−1
B_2	1	−1	−1
B_3	−1	1	−1
B_4	1	1	−1
B_5	−1	−1	1
B_6	1	−1	1
B_7	−1	1	1
B_8	1	1	1
B_9	0	0	0
B_{10}	0	0	0
B_{11}	−1	0	0
B_{12}	1	0	0
B_{13}	0	0	−1
B_{14}	0	0	1
B_{15}	0	−1	0
B_{16}	0	1	0

3. Results and discussion

Laser particle size analysis revealed that the mean particle size of the mica flakes was 40 μm and the majorities (95%) of them were less than 75 μm. SEM observations confirm the measurement (Fig. 2). The mean thickness of the flakes was about 1.5 μm (Fig. 3). These dimensions are in the range recommended [1]. The BET specific surface area of them was 3.74 $m^2\ g^{-1}$.

The colour characteristics of the samples and their difference with the reference pigment (ΔE) which was measured by the spectrophotometer is given in Table 3.

For determining the optical conditions matrices "x" and "y" (below) were constructed using Tables 2 and 3, and the regression model was written using Eqs. (2) and (4) [14].

$$x = \begin{bmatrix} 1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & -1 & 1 & -1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & 1 & -1 & -1 & 1 & 1 & 1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 \\ 1 & 1 & -1 & 1 & -1 & -1 & 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & -1 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix},$$

$$y = \begin{bmatrix} 45.97 \\ 43.43 \\ 43.67 \\ 43.19 \\ 33.23 \\ 30.36 \\ 30.01 \\ 42.10 \\ 18.50 \\ 20.00 \\ 30.66 \\ 32.66 \\ 39.73 \\ 14.07 \\ 25.64 \\ 15.89 \end{bmatrix}, \qquad \beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_k \end{bmatrix}$$

x is an $(n \times p)$ matrix of the levels of the independent variables, y an $(n \times 1)$ vector of the observations and β is a $(p \times 1)$ vector of the regression coefficient. The vector of least squares estimators $(\hat{\beta})$ is given by:

$$[\widehat{\beta}] = [x'x]^{-1} \cdot [x'y] \tag{2}$$

$x'x$ is a $(p \times p)$ symmetric matrix and $x'y$ is a $(p \times 1)$ column vector. x' is a matrix the same as x, but with rows and columns changed and x^{-1} is the inverse of x. An inverse matrix is a matrix that $x'x = 1$. $x'x$ and $x'y$ are used to obtain the least square results.

The fitted regression model is:

$$\hat{y} = x\hat{\beta} \tag{3}$$

or in scalar notation:

$$\hat{y}_i = \beta_0 + \sum_{i=1}^{k} \hat{\beta}_i x_{ij}, \quad i = 1, 2, \ldots, n \tag{4}$$

where k is the number of factors and x_{ij} is the interaction of the factors. Hence:

$$\widehat{y_i} = 19.75 + 0.82x_1 - 0.38x_2 - 6.62x_3 + 11.65x_1^2 + 0.76x_2^2 + 6.89x_3^2 + 2.13x_1x_2 + 1.38x_2x_3 + 1.53x_1x_3 \tag{5}$$

x_1, x_2 and x_3 are the solution concentration, temperature and time, respectively, and their coefficients determine half of the effect of each one in the results (ΔE). The symbols x_1x_2, x_2x_3 and x_1x_3 are the interactions of the factors, and their coefficients

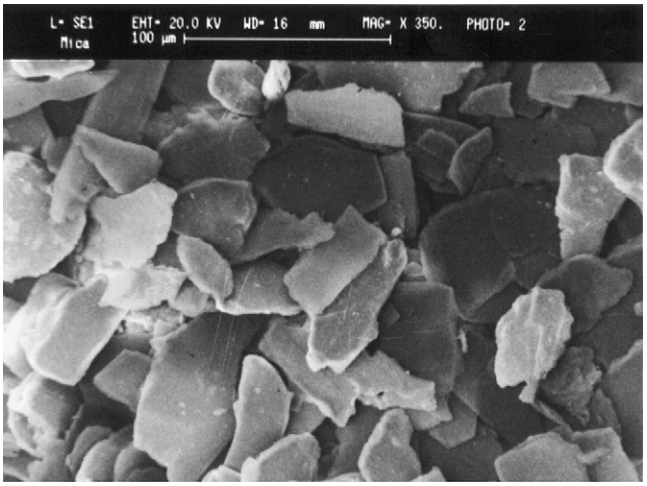

Fig. 2. SEM micrograph of the sieved mica.

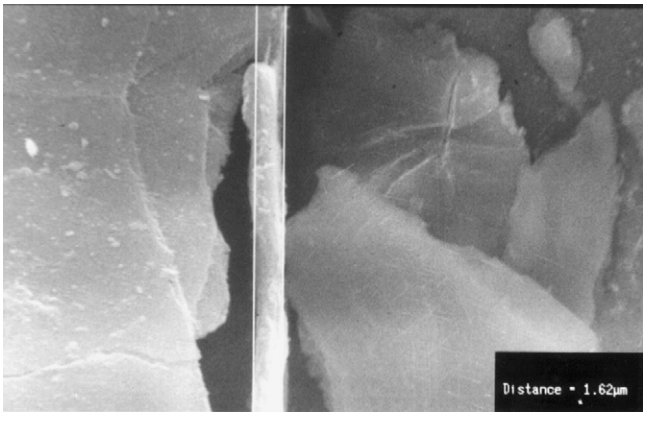

Fig. 3. SEM micrograph, showing the thickness of the mica flakes.

Table 3
The colour characteristics of the samples and their difference with the reference pigment (ΔE)

No.	L^*	a^*	b^*	Measured ΔE
Ref.	58.2	−1.527	−2.776	0
B_1	12.395	0.846	0.268	45.97
B_2	17.308	5.604	9.991	43.43
B_3	17.227	2.538	11.925	43.67
B_4	17.425	4.36	10.21	43.19
B_5	25.41	−0.56	2.508	33.23
B_6	28.76	0.636	4.311	30.36
B_7	29.137	0.409	4.452	30.01
B_8	18.772	1.835	11.582	42.10
B_9	40.43	−0.82	2.324	18.50
B_{10}	38.991	−0.918	2.765	20.00
B_{11}	28.52	0.422	4.679	30.66
B_{12}	26.875	0.587	6.211	32.66
B_{13}	20.488	1.637	9.323	39.73
B_{14}	44.904	−0.618	1.731	14.07
B_{15}	33.238	0.004	2.873	25.64
B_{16}	43.249	−1.02	2.582	15.89

also determine half of the effect of each one in the results (ΔE). Using Eq. (4), the values of predicted ΔE $(\widehat{y})$ for each factor level and each point in the determined space shown in Table 1 may be calculated. Obviously, any point in the space which makes ΔE minimum is considered as the optimal. For confirming the model, the following equations may be used to calculate the difference between the experimental and predicted ΔE, and also the standard deviation.

$$e_i = y_i - \widehat{y_i} \tag{6}$$

$$\mathrm{SS_E} = y'y - \beta' x' y \tag{7}$$

$$\widehat{\sigma}^2 = \frac{\mathrm{SS_E}}{n - p} \tag{8}$$

$$d_i = \frac{e_i}{\widehat{\sigma}} \tag{9}$$

Table 4
The measured and anticipated ΔE values, together with the values for the residuals and the standard errors

No.	Measured (ΔE)	Anticipated (ΔE)	Residuals (e_i)	Standard error (d_i)
B_1	45.97	50.30	4.33	0.81
B_2	43.43	44.58	1.15	0.22
B_3	43.67	42.53	−1.14	−0.21
B_4	43.19	45.32	2.13	0.405
B_5	33.23	31.19	−2.04	−0.39
B_6	30.36	31.68	1.32	0.25
B_7	30.01	28.94	−1.07	−0.20
B_8	42.10	37.94	−4.16	−0.78
B_9	18.50	19.76	1.26	0.24
B_{10}	20.00	19.76	−0.24	−0.05
B_{11}	30.66	30.59	−0.07	−0.01
B_{12}	32.66	32.23	−0.43	−0.08
B_{13}	39.73	33.27	−6.46	−1.21
B_{14}	14.07	20.03	5.96	1.12
B_{15}	25.64	20.89	−4.35	−0.82
B_{16}	15.89	20.14	4.25	0.80
B_{opt}	11.18	18.10	6.92	1.30

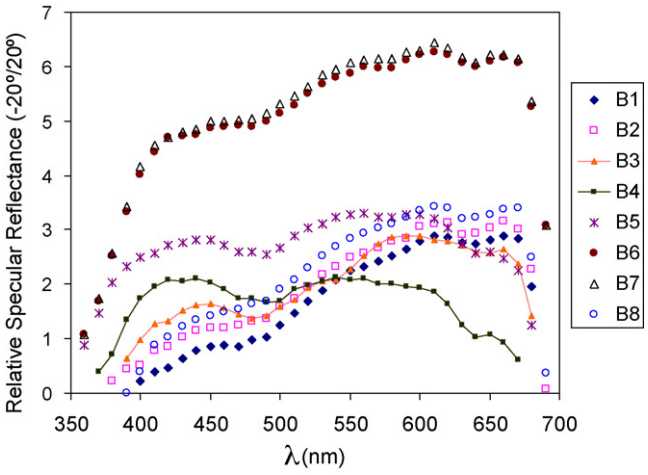

Fig. 4. The relative specular reflectance of the samples B_1–B_8.

Where, e_i is the difference between the actual observation y_i and the corresponding fitted value $\hat{y}_i$ and is called the residual values, $\mathrm{SS_E}$ is called error or the residual sum of the squares, $\hat{\sigma}^2$ the standard deviation, n and p the number of rows in matrices y and x', respectively, and d_i is the standard error. The results are shown in Table 4. As seen the standard error is in the acceptable range, i.e. between −3 and 3.

3.1. The effect of concentration, temperature and time

Based on the model used, the effect of concentration on ΔE (twice the coefficient of x_1 in Eq. (5)) is 1.64. This shows that by decreasing concentration, ΔE decreases. Hence, in the concentration range used in this experiment the lowest level (100 g L^{-1}) is the best concentration for coating.

With the same rationale, it may be said that the negative value for the effect of temperature (−0.76) indicates that by increasing temperature, ΔE decreases. Hence, the highest temperature in the range (60 °C) favors the formation of the coating. Finally, it can be deduced that time has the most pronounced effect with a value of −13.2. Therefore, the best time in the range used is 75 h. The samples synthesized using the lowest level of time, have the

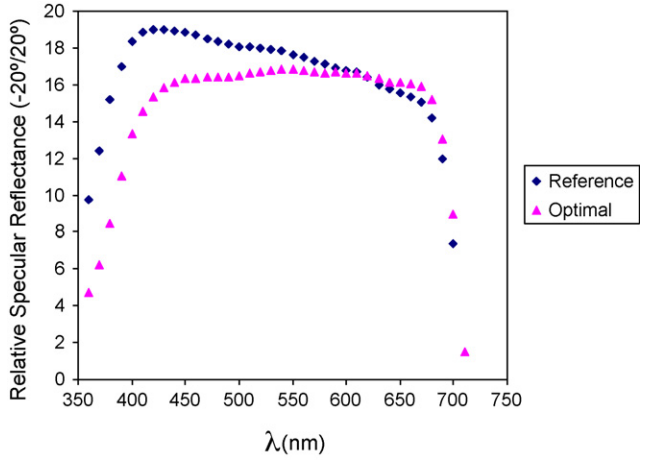

Fig. 5. The relative specular reflectance of the reference and the optimal samples.

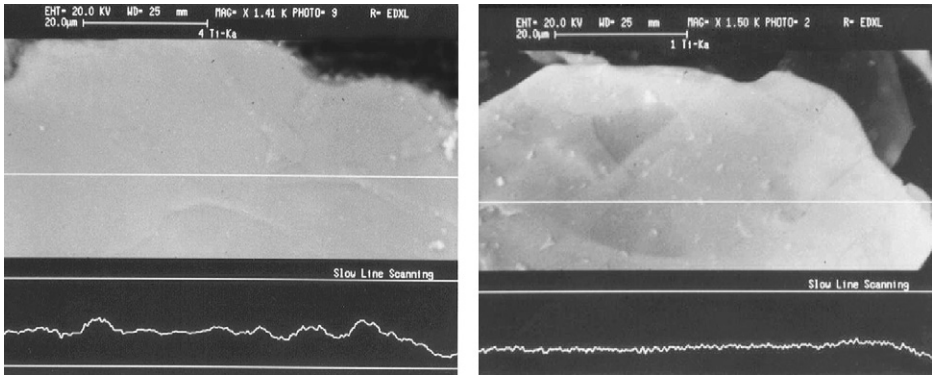

Fig. 6. The Ti line scan of the optimal (left) and reference (right) samples.

highest difference with the reference pigment, since they did not have enough time for deposition of the flakes.

3.2. Interaction of the factors

From the results, it can be observed that the interaction of concentration–temperature (twice the coefficient of x_1x_2 in the same equation) is 4.26. This indicates that with concurrent increase or decrease of these two factors, ΔE increases. Hence, to obtain the best results, these two factors should change in opposite directions, since increasing or decreasing both deteriorates the uniformity and optical properties of the coating.

3.3. The spectrophotometery results

Fig. 4 shows the relative specular reflectance for the samples B_1–B_8, which have been synthesized using the higher and lower levels of concentration. As seen the samples B7, B6, B5 and B8 have the best reflectance, respectively. The level of time for all of these samples is 1 (the longest time used in these experiments). Therefore, it may be concluded that the other samples did not have enough time for deposition to be completed. On the other hand, comparing samples B7 and B8 it may be concluded that concentration has the least effect on the reflectance. Note that the time and temperature for both of these samples are identical and the only different factor is concentration.

Therefore, based on the present regression analysis and the experimental results, it was found that during deposition of rutile on mica flakes, the reaction time with an effect of −13.24 and temperature with an effect of −0.76 have the highest impact on the colour difference with the reference pigment. The least colour difference was obtained on solution concentration of 122 g L^{-1}, at 43 °C and after 55 h.

The optimal condition and the highest yield may be calculated using the following equations:

$$x = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}, \quad b = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_9 \end{bmatrix}, \quad B = \begin{bmatrix} \beta_{11} & \beta_{12/2} & \beta_{13/2} \\ \beta_{12/2} & \beta_{22} & \beta_{23/2} \\ \beta_{13/2} & \beta_{23/2} & \beta_{33} \end{bmatrix}$$

$$x_{\max} = -\tfrac{1}{2}B^{-1}b \tag{10}$$

$x_1 = -0.056 \Rightarrow$ concentration $= 121.85\ \mathrm{g\,L^{-1}}$

$x_2 = -0.128 \Rightarrow$ temperature $= 43.08\ ^\circ\mathrm{C}$

$x_3 = 0.499 \Rightarrow$ time $= 54.97\ \mathrm{h}$

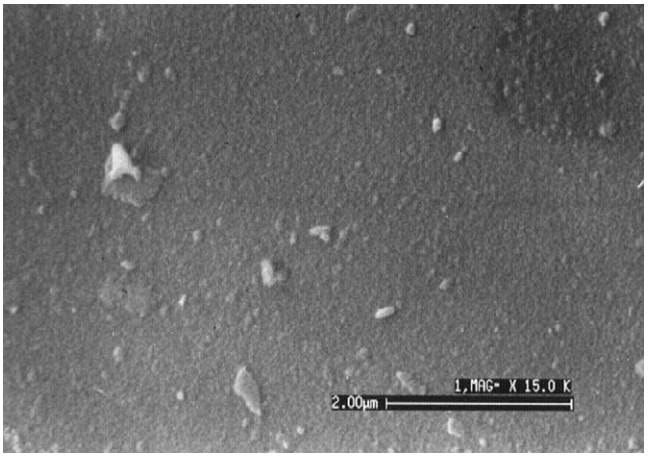

Fig. 7. SEM micrograph of the coated mica (sample 7), which indicates the uniformity of the coating.

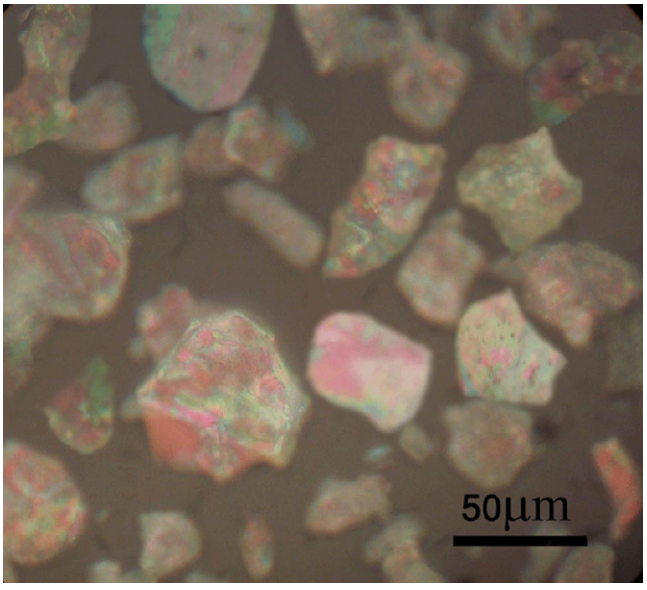

Fig. 8. Optical micrograph of sample 7, showing a high reflectivity.

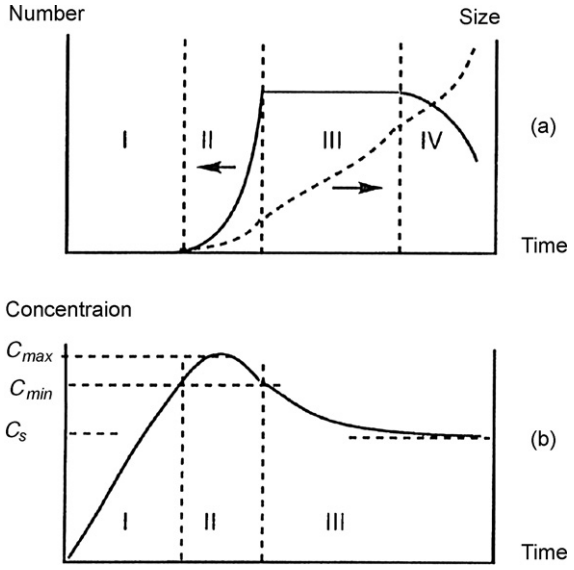

Fig. 9. The change of (a) the number and size of the nuclei and (b) the concentration of monomers with time. The condensation rate is zero when $c < c_{min}$ and considerable when $c > c_{min}$. c_s is the solubility limit of the solid phase.

The results shows that the optimal conditions occurred at the medium levels of all the factors studied. Fig. 5 shows the relative specular reflectance of the optimal and reference samples.

Fig. 6 shows the Ti line scan of the optimal and reference samples, indicating the deposition of TiO_2 on the flakes. Fig. 7 is a SEM micrograph of the coated mica (sample 7), which indicates the uniformity of the coating. Fig. 8 is an optical micrograph of the same sample, showing the high reflectivity of it.

Depending on the concentration, time and temperature, hydrolysis and surface adsorption may occur concurrently or separately [15]. During hydrolysis of $TiCl_4$ solution, in the first step, cationic complexes of $[Ti(OH)_2(OH_2)_2]^{2+}$ are formed, due to acid–base reactions. By joining these complexes $[Ti(OH)_4(OH_2)_2]$ monomers of zero charge are

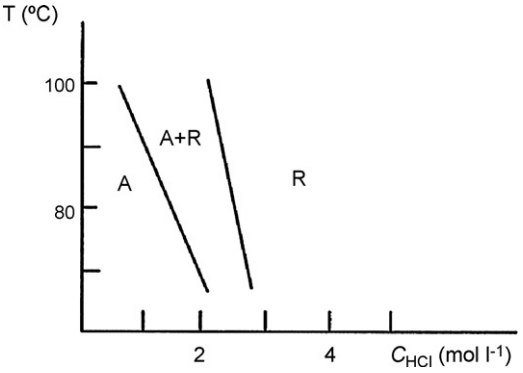

Fig. 11. The formation of rutile (R) and anatase (A) phase with pH (HCl) and temperature.

formed. During the second stage, when the concentration of monomers is minimum (c_{min}), monomers of zero charge join through olation reactions and the first TiO_2 nuclei are formed (Fig. 9). During the third stage, the nuclei start to grow until c_{min} is reached again.

The best condition for nucleation is achieved when the concentration of monomers is close to c_{min}. Therefore, the concentration and temperature should be adjusted appropriately. Therefore, by increasing the concentration, the pearlescence effect is deteriorated, since the concentration is more than c_{min}, the rate of nucleation and growth is high and the agglomerates are formed.

One of the interesting results of the present work is that the grown phase on the flakes is rutile (Fig. 10), the high refractive index favorable phase, and therefore no extra heat treatment is required. In the other samples the TiO_2 peaks were absent or very short, so we and the XRD pattern of the reference sample was similar to the one we obtained.

It is observed from Fig. 11 that the formation of rutile is highly dependent on pH and by increasing the acid concentration, formation of rutile rather than anatase is favored [13].

Fig. 12 shows that in this condition, monomers share apexes rather than faces and rutile is directly formed during hydrolysis [13].

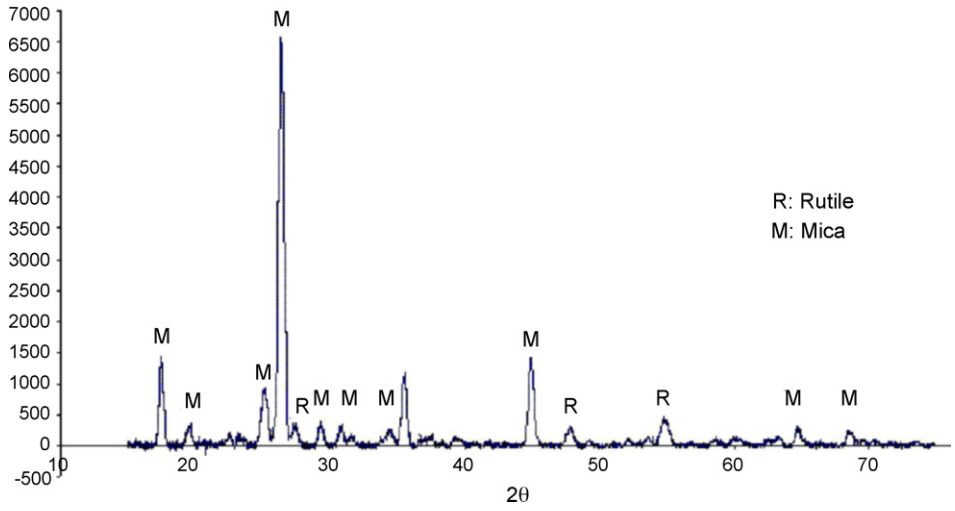

Fig. 10. XRD pattern of the optimal sample.

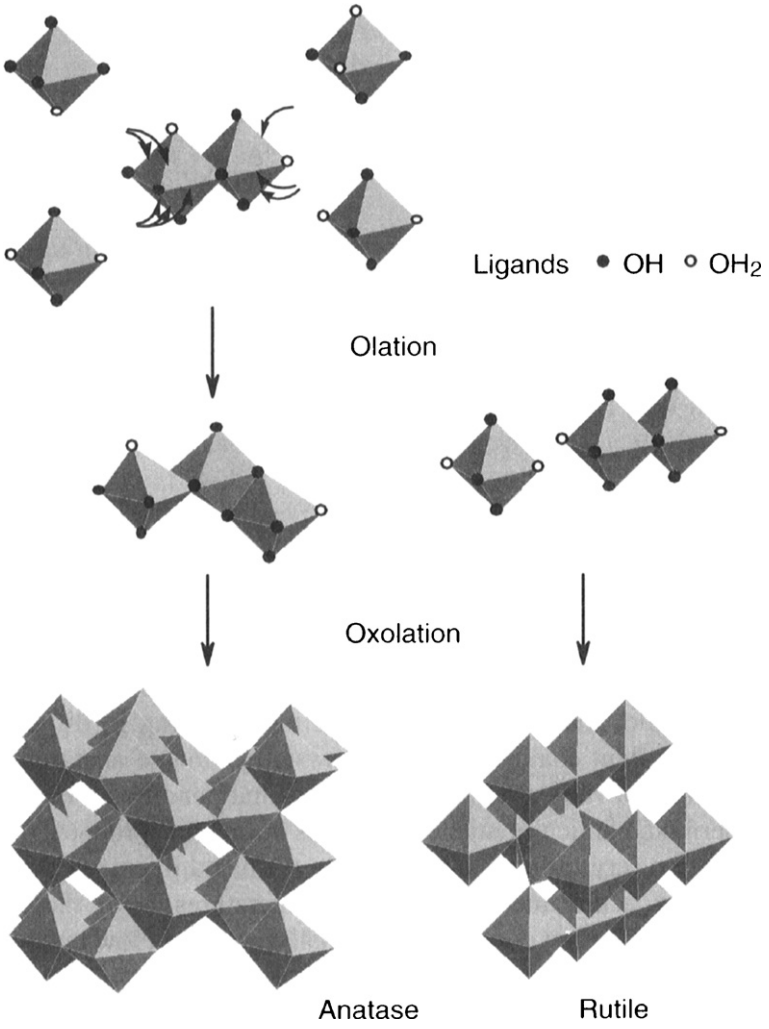

Fig. 12. The stages in formation of rutile.

4. Summary

White pearlescent pigments were synthesized by coating mica flakes with a thin layer of TiO_2. Based on the present regression analysis and the experimental results, it was found that during deposition of rutile on mica flakes, the reaction time with an effect of −13.24 and temperature with an effect of −0.76 have the highest impact on the colour difference with the reference pigment. The least colour difference was obtained on solution concentration of 122 g L^{-1}, at 43 °C and after 55 h. The optimal concentration, temperature and time were 121.85 g L^{-1}, 43.08 °C and 54.97 h, respectively. Interestingly, using highly acidic solutions, rutile was directly deposited, without need for further calcinations.

References

[1] G. Buxbum, Industrial Inorganic Pigments, Wiley-VCH, Weinheim, 1998 (Chapter 5).
[2] S. Hanchisu, Nacreous Pigments, Prog. Org. Coat 3 (1975) 191–220.
[3] L.M. Greenstein, Pigment Handbook, vol. 3, John Wiley and Sons, 1998 (Chapter I-G).
[4] H.M. Smith, High Performance Pigments, Wiley-VCH, Weinheim, Germany, 2002 (Chapter 7).
[5] L.M. Greenstein, Pigment Handbook, vol. 1, John Wiley and Sons, NY, 1998 (Chapter III-D-d-2).
[6] J.F. Van Ness, et al., Glass Composition and Method of Manufacture and Article Produced Therefrom, U.S. Patent 4,353,991 (1982).
[7] A. Rau, et al., Pearl Luster Pigments Stable to Glaze and Enamel, U.S. Patent 5,022,923 (1991).
[8] J. Tan, et al., Preparation and conductive mechanism of mica titania conductive pigment, Dyes Pigments 62 (2004) 107–114.
[9] H.R. Linton, et al., Nacreous Pigment Compositions, U.S. Patent 3,087,828 (1963).
[10] M.H. Gutcho, Inorganic Pigments Manufacturing Processess, Noys Data Corporation, 1980.
[11] H.J. Tan, et al., The preparation and characteristics of cobalt blue mica coated titania pearlescent pigment, Dyes Pigments 52 (2002) 215–222.
[12] J. Tan, et al., The preparation and characteristics of a multi-cover-layer type, blue mica titania, pearlescent pigment, Dyes Pigments 56 (2003) 93–98.
[13] J.P. Jolivet, Metal Oxide Chemistry and Synthesis, John Wiley and Sons, 2000 (Chapter 3).
[14] D.C. Montgomery, Design and Analysis of Experiments, John Wiley and Sons, 1997 (Chapter 13).
[15] J.P. Jolivet, Metal Oxide Chemistry and Synthesis, John Wiley and Sons, 2000 (Chapter 2).