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Pigmentation of Vat Blue RS by ball milling in solvents

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Abstract

Pigmentation of Vat Blue RS by ball milling in the presence of organic solvents or water was carried out and the effects of ball milling time, characteristics of solvent used and two-step ball milling on the transformation of crystal phase and the resulting pigment properties were studied. Experimental results showed that the α-phase of C.I. Pigment Blue 60 can be obtained by ball milling 2 h in the presence of xylene and NaCl. The rate of transformation to the α-phase was improved with an increase in the proportion of aromatic solvents in the medium employed. By milling in an aqueous medium without organic solvents, the original pigment crystal phase was destroyed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Vat Blue RS; C.I. Pigment Blue 60; Pigmentation; Ball milling

1. Introduction

As a vat dye, Vat Blue RS (C.I. Vat Blue 4) exhibits good fastness to light, acid, alkali, and solvents, and is mainly used in dyeing cotton fibres. Transforming it to C.I. Pigment Blue 60 (PB60) gives a bright, reddish blue colorant with excellent all-round fastness properties. The pigment has very good heat fastness and is fast to overspray. It has excellent durability in both solid and metallic finishes, showing little fading in pale shades, and has much less tendency to bronze upon exposure of full and strong shades, compared to competitive phthalocyanine blues.

The major use of PB60 is in automotive coatings, where it is used both as a self-shade and in combination with phthalocyanine blues to produce a very wide range of solid and metallic reddish-blue shades. It is occasionaly used also in security printing inks, decorative coatings and thermoplastics [1].

Vat Blue RS (VBRS), when synthesized as crude pigment by the alkaline condensation method cannot be directly used as a finished pigment because of its lower color strength, dull shade, and unstable crystal form. Therefore, the crude pigment must be conditioned (or pigmented), by optimizing its properties with well-known procedures [2,3]. The pigmentation of crude VBRS by dry or wet grinding method, has been studied, but not with respect to the crystal transformation during the grinding step [4,5]. A study of the pigmentation of VBRS is important because the experimental methods employed are suitable for evaluating other vat pigments.

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In this paper, VBRS was subjected to ball milling in the presence of organic solvents and aqueous media. The crystal phase transformation of VBRS and other pigment properties were assessed as a function of solvents properties, ball milling time, and two-step ball milling. The pigment products obtained were characterized by evaluating particle size, X-ray data, color strength, hiding power, and SEM data.

2. Experimental

2.1. Ball milling treatment

VBRS dry powder (5 g), xylene or other solvents (80 ml) and NaCl (40 g) were mixed in a 200 ml stainless steel tank, together with 30 ceramic spheres ($\bar{d}$ = 0.5 cm). The tank was fixed in a planetary motion ball milling machine and the contents milled for a predetermined amount of time. The ceramic spheres were then removed, the solvents and inorganic salt washed by water and ethanol, and the pigment slurry filtered and dried under vacuum pressure.

2.2. Determination of pigment properties

Color strength, flowability and shade comparisons were determinated according to Chinese National Standard GB1708-79, GB1719-79, and GB1864-89, respectively. The mean diameter and distribution of pigment particles were measured using a LKY-1 type microparticle diameter analyzer equipped with a centrifugal settler. The settling medium was 20% aqueous glycerine at room temperature. The surface and shape of the pigment particle was assessed using a Hitachi X-650 Scanning Electronic Microanalyzer (SEM). X-ray diffraction patterns were recorded on a Japan Rigaku 2038 X-ray powder diffractometer, using CuK_α radiation: 30 KV, 15 mA, $T_c = 2\ 1$ K×44/min, at 40 mm/min.

3. Results and discussion

Ball milling methods have been widely used in the pigmentation of crude pigment and the formation of various crystal phases. Using this technique, a pigment can be converted to the desired crystal phase, particle size and distribution, and surface characteristics. This is achieved with the aid of the strong shear forces in the presence of solvents and inorganic grinding aids. Thus, crude VBRS (δ-form) can be transformed to the desired α-phase, giving improved color strength, brilliance and dispersibility.

3.1. Effects of ball milling time on properties of pigment

When crude VBRS was ground in the presence of xylene, the properties of the final pigment (PB60) varied with ball milling time, as shown in Table 1 and Fig. 1.

From Table 1, it can be seen that the δ-form of crude VBRS has changed significantly when ground for 1 h, with diffraction peaks exhibited in $2\theta = 5.5°$, 26°, which means that the crystal phase has been partially transformed to the α-form. When ground for 2 h, however, the δ-crystal phase is completely transformed to the α-phase. Further milling, for 5 and 10 h, does not affect the crystal

Table 1
Effects of ball milling time on the properties of C.I. Pigment Blue 60

Sample no.	VBRS (g)	Xylene (ml)	NaCl (g)	Time (h)	Flowability (mm)	Color strength (%)	$\bar{d}$ (μm)
Untreated	–	–	–	–	23.6	100	0.52
B63	5	80	40	1	23.0	105	0.46
B62	5	80	40	2	24.2	110	0.22
B3	5	80	40	5	26.0	110	0.24
B6	5	80	40	10	28.5	105	0.46

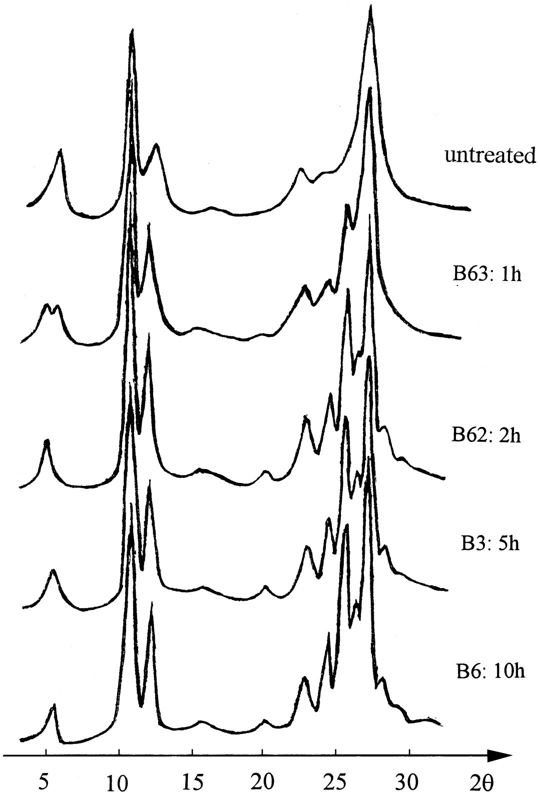

Fig. 1. X-ray diffraction patterns of VBRS treated by ball milling at different time with xylene and NaCl.

phase. Following transformation to the α-phase, the pigment aquires a more brilliant shade and higher color strength and hiding power.

After the crude pigment has been fully transformed to the α-phase, further ball milling does not change the crystal phase, but flowability and particle size do change. The use of xylene normally makes the crystals grow larger, but the shear force of ball milling reduces the particle size when ball milling in the presence of xylene and NaCl [6,7]. The resultant pigment properties are derived from a complex combination of these two actions. Results of Table 1 also suggest that ball milling action mainly determines PB60 properties because as particle size increases, flowability also increases and color strength is reduced when ball milling time is extended from 2 to 10 h. Therefore, the optimal pigmentation of VBRS can be obtained using a ball milling time of 2–5 h.

A similar impact of ball milling time on pigment properties is observed when xylene is replaced by chlorobenzene and $Al_2(SO_4)_3$, the results of which are shown in Table 2. The irregular δ-crystal phase of VBRS is transformed to α-phase, giving the well-defined rod-like crystal shown in Fig. 2.

3.2. *Effects of solvent properties on pigmentation*

Besides reducing the particle size and increasing the surface area of a crude pigment to the required dimensions, transformation to the required crystal phase is equally important, and can be achieved by the use of phase-directing solvents during the milling process. The variables used in this aspect of our study and the results obtained are shown in Table 3.

The results in Table 3 show that pigment properties and crystal phase transformation are closely related to the solvents used. With polar watermisible solvents, such as methanol, ethanol and ethylene glycol, the crystal phase of the pigment is unchanged, and flowability and shade are nearly the same as that of crude VBRS. When a solvent such as dichloroethylene is used, the pigment is partially transformed to the α-phase. When weakly polar aromatic solvents such as dichlorobenzene, toluene, chlorobenzene and xylene are used, the pigment is completely transformed to the α-phase,

Table 2
Effect of the ball milling time in the presence of chlorobenzene and $Al_2(SO_4)_3$

Sample no.	VBRS (g)	Chlorobenzene (ml)	$Al_2(SO_4)_3$ (g)	Time (h)	Flowability (mm)	$\bar{d}$ (μm)
Untreated	–	–	–	–	23.6	0.52
B1	5	80	40	1	24.0	0.38
B2	5	80	40	3	25.5	0.23
B58	5	80	40	10	25.7	0.28
B59	5	80	40	16	26.9	0.44

giving a well-defined crystal form, higher flowability and a brighter reddish-blue shade.

The above results suggest that for water-miscible solvents, there are significant differences between the polarity of the pigment and the solvents, which leads to an unchanged crystal phase. For solvent molecules that do not contain an aromatic moiety, there is an appreciable difference in molecular planes, and the pigment is not completely solvated. Therefore, only part of the pigment is transformed to the α-phase. For weakly polar aromatic solvents that resemble the structure of the pigment molecule, solvation-precipitation of the pigment occurs during ball milling, giving complete transformed of VBRS to the α-phase. Similarly, while ethanol alone does not convert VBRS transformation to the α-phase, ethanol mixtures containing a solvent such as chlorobenzene work well.

The experimental conditions employed, and the resulting X-ray diffraction patterns are shown in Fig. 3. Under conditions A, pigment is not completely transformed to the α-phase; however, under conditions B, complete transformation to the α-phase occurs, showing that the chlorobenzene content in the mixture is sufficient. The SEM of pigment treated under conditions B is shown in Fig. 4. When compared with the results

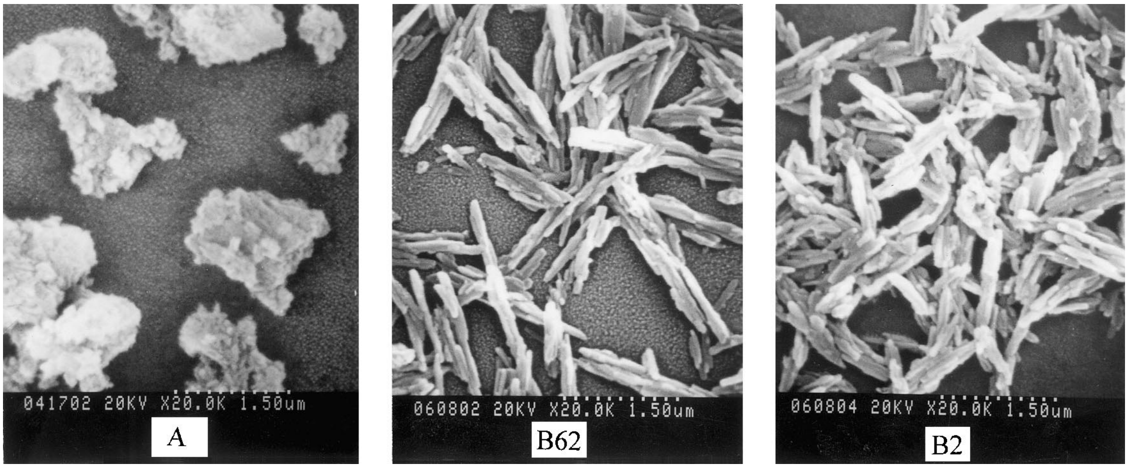

Fig. 2. SEM of crude VBRS and PB60. A = untreated; B62 = VBRS milled with xylene and NaCl for 2 h; B2 = VBRS milled with chlorobenzene and $Al_2(SO_4)_3$ for 3 h.

Table 3
The effects of ball milling in the presence of different solvents

Sample no.	NaCl (g)	Solvent	Amount of solvent (ml)	Time (h)	Flowability (mm)	Shade[a]
B52	40	*o*-Dichlorobenzene	80	16	33.6	Somewhat reddish-blue, brighter
B49	40	Benzene	80	16	32.4	Somewhat reddish-blue, brighter
B32	40	Chlorobenzene	80	16	29.6	Somewhat reddish-blue, brighter
B45	40	Toluene	80	16	29.5	Somewhat reddish-blue, brighter
B4	40	Xylene	80	16	29.4	Somewhat reddish-blue, brighter
B53	40	Dichloroethylene	80	16	27.4	Slight reddish-blue, duller
B38	40	Methanol	80	16	23.7	Nearly same
B39	40	Ethanol	80	16	23.7	Nearly same
B11	40	Glycol	80	16	23.8	Nearly same

[a] Versus crude VBRS.

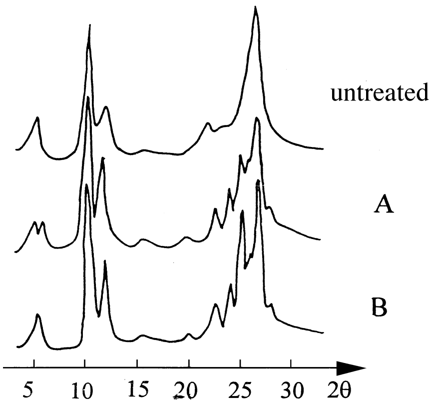

Fig. 3. X-ray diffraction patterns of crude VBRS milled in mixed solvents. A = crude VBRS milled with chlorobenzene (60 ml) and ethanol (40 ml) for 3 h; B = crude VBRS milled with chlorobenzene (20 ml) and ethanol (40 ml) for 3 h.

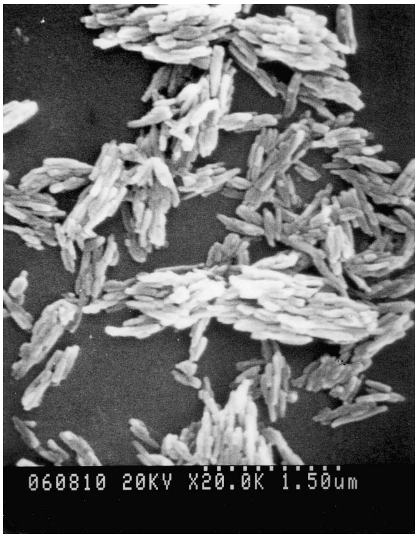

Fig. 4. SEM of crude VBRS milled with chlorobenzene and ethanol for 3 h.

in Fig. 4. When compared with the results in Fig. 2, it is clear that the two pigments have similarity particle shapes, but the particle size in Fig. 4 is smaller. This would indicate that increasing the chlorobenzene content accelerates the transformation to the α-phase, whereas increasing the ethanol content reduces the transformation rate.

3.3. Pigmentation via two-step ball milling

When exposed to xylene without ball milling, crude VBRS can also be transformed to the α-phase, but the pigment obtained has a larger particle size and lower color strength. This shows that pigment particle size may be reduced and the properties of the resultant pigment improved by aqueous ball miling the α-phase pigment produced by xylene pre-treatment. Nonionic surfactant OS-15 was added to the ball milling mixture to improve pigment dispersibility. In the solvent transformation of crude VBRS to the α-phase, a mixture of VBRS (5 g) and xylene (170 ml) was kept for 0.5 h at 90–95°C. The experimental data obtained following grinding the product in an aqueous medium are shown in Table 4.

In the absence of OS-15, the resultant pigments have larger particle sizes and higher flowability (see X16 and X18). When OS-15 is added to the ball milling mixtures, the pigments obtained have smaller particle sizes, lower flowability, and higher color strength (see X21 and X22). Since the surfaces of pigment particles can absorb OS-15 molecules, this may prevent pigment particles from aggregating. At constant ball milling time, increasing

Table 4
Experimental results of PB60 from grinding (α-form) in aqueous medium

Sample No.	α-Form VBRS (g)	Water (ml)	OS-15 (%)	Time (h)	Flowability (mm)	$\bar{d}$ (m)
X16	5	80	0	2	30.6	0.34
X18	5	80	0	6	39.5	0.73
X17	5	80	2	2	29.5	–
X19	5	80	2	6	31.5	–
X21	5	80	5	2	29.0	0.32
X22	5	80	5	6	30.5	0.53
X24	5	80	10	2	26.5	–
X25	5	80	10	6	28.5	–

the OS-15 level leads to lower flowability, smaller particle size, and higher color strength (see X16, X17, X21 and X24; X18, X19, X22, and X25).

On the other hand, when the amount of OS-15 is constant but the ball milling time is varied, increasing ball milling time gives a larger particle size, higher flowability and lower color strength. This means that ball milling in an aqueous medium does not retain a suitable crystal phase. In fact, we found that the α-phase is transformed to an amorphous product as shown in Fig. 5. It is clear that the intensities of diffraction peaks are substantially reduced by ball milling for 2 h, and that peak intensity is further reduced and nearly disappears after 6 h. Fig. 6 shows that the crystal phase of the pigment is destroyed by ball milling. This indicates that ball milling in aqueous media can not be carried out for an extended period, without transforming the pigment to an amorphous product, reducing color strength, and dulling the shade.

In the other studies, a second two-step ball milling process was carried out: In step 1, crude VBRS was ground in the presence of xylene, transforming to the α-phase pigment. This step employed crude VBRS (5 g), xylene (80 ml), NaCl (40 g), and a 2 h ball milling time. In step 2, the pigment produced in step 1 was ground in an aqueous medium to modify the crystal phase or particle size.The step employed, α-phase PB60 (5 g), water (80 ml), OS-15 (0.25 g), ball milling times of 2 and 6 h. After the two-step sequence, the pigment had higher flowability, duller shade and lower color strength. X-ray diffraction patterns of these products are shown in Fig. 7. The α-phase pigment has a clear peak at $2\theta = 5.5°$ but no peak at $2\theta = 31.5°$. After milling for 2 h, peak intensity of the diffraction pattern is reduced, and a strong peak is produced at $2\theta = 31.5°$. After milling for 6 h, the peak at $2\theta = 5.5°$ nearly disappears, and the intensities of other diffraction peaks are clearly reduced, including the peak at $2\theta = 31.5°$. These

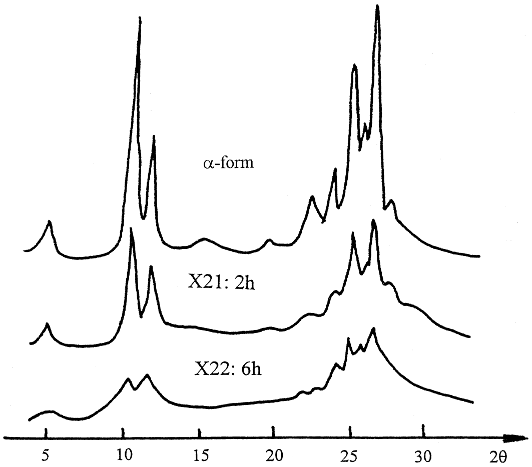

Fig. 5. X-ray diffraction patterns of PB60 milled in aqueous medium. X21 = α-PB60 milled with water and OS-15 for 2 h; X22 = α-PB60 milled with water and OS-15 for 6 h.

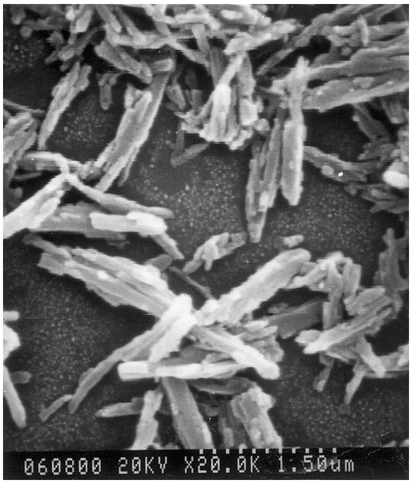

Fig. 6. SEM of α-PB60 milled in water and OS-15 for 6 h.

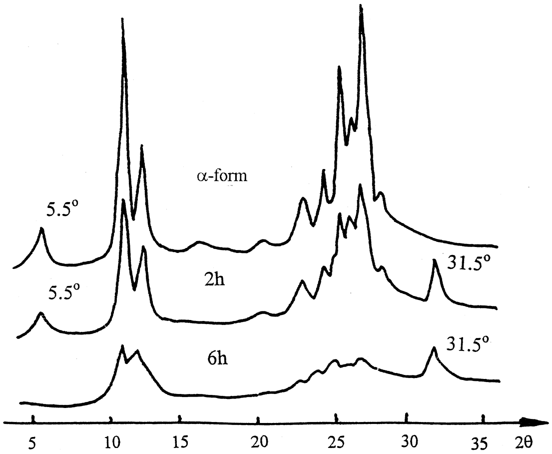

Fig. 7. X-ray diffraction patterns of α-PB60 following two-step ball milling in water and OS-15 2 and 6 h.

observations show that the strong shear force produced by ball milling in aqueous medium not only destroys the crystal phase, but also transformation of the pigment to a new crystal phase. The new crystal phase appears to be different from crude VBRS (δ-form) and the α-, β-, γ-phases [8], and exhibits the weaker X-ray diffraction peaks and inferior tinctorial properties.

4. Conclusion

The pigmentation of crude Vat Blue RS can be carried out by ball milling in the presence of organic solvents and inorganic salts. Crystal phase transformation and tinctorial properties of pigment treated by ball milling correlate with ball milling time and solvent properties. α-Phase C.I. Pigment Blue 60 with superior coloring properties can be obtained in the presence of either xylene and NaCl or chlorobenzene and $Al_2(SO_4)_3$. Weakly polar aromatic solvents facilitate the transformation of crude Vat Blue RS to the α-phase. Transformation to the α-phase is accelerated by increase in aromatic solvent content in mixed solvent media. Milling in an aqueous medium destroys the α-phase, producing a new crystal form.

References

[1] Lewis PA. Pigment handbook, vol. 1, 2nd ed. John Wiley & Sons Inc., 1988. p. 651.

[2] Zhang Tianyong, Zhou Chunlong. Pigmentation of vat pigments based on vat dyes. Dyestuff Industry 1995; 32(1): 6–13

[3] Chromy L, Kaminska E. Relationship between the optical properties of coloured pigments and their morphology and crystallinity. Progress in Organic Coatings 1978;6:31–48.

[4] Arai Y, Lizaka K. Pulverization of organic crude pigments. Jpn. Kokai Tokkyo Koho JP 04122778, 1992

[5] Seki Y, Tanemura K, Ogawa H. Manufacture of indanthrone blue or carbazone dioxazine violet pigments. Jpn. Kokai Tokkyo Koho JP 09165528,1997

[6] Smith FM, Easton JD. Phthalocyanine pigments — their form and performance. Journal of the Oil and Colour Chemists' Association 1966;49:614–30.

[7] Wanser CC. Physical and chemical considerations on copper phthalocyanine. Journal of Coating Technology 1985;57(729):57–62.

[8] Honigmann B. Crystal properties of organic pigments. Journal of Paint Technology 1966;38(493):77–84.