ESTABILITY OF THE PINK PIGMENT (Cr)CaSnSiO$_5$. INTERACTION WITH CERAMIC MATERIALS

A. Escardino[*], S. Mestre[*], A. Barba[*], M. Monzó[*], P. Jodar[**], L. Díaz[**]

[*]Instituto de Tecnología Cerámica (ITC)
Asociación de Investigación de las Industrias Cerámicas
Universitat Jaume I. Castellón. Spain
[**]Itaca, S.A. (Spain)

ABSTRACT

The pink pigment (Cr)CaSnSiO$_5$, whose crystalline structure corresponds to malayaite, is characterised by generating a very wide range of glaze colours depending on the type of frit used. The study carried out with different types of frit, selected among those commonly used in the ceramic sector, has identified three possible phenomena that could affect the arising colour: pigment dissolution, crystallisation from the glaze of other species different from the pigment, and immiscible glassy phase separation in the glaze.

1. INTRODUCTION

According to some authors, the use of pink pigments of chromium-calcium-tin-silica in ceramics goes back to the XIII century [1], and was kept as an alternative to CdSeS to produce pink and reddish tones, while the glazes were based on the system SiO$_2$-PbO. When the development of lead-free glazes began, it was found that in many cases this pigment did not produce the desired colours [2], even though the pigment was stable up to very high temperatures [3].

The crystalline structure of the pigment is known as malayaite, with theoretical formula CaSnSiO$_5$, which is similar to sphene, (whose theoretical formula is CaTiSiO$_5$, with monoclinic symmetry) [4]. The reddish colour stems from the inclusion of Cr as a dopant in the structure [5].

Numerous studies have been devoted to pigment synthesis, to define the most favourable production conditions, varying pigment composition to achieve other colours or synthesising it by non-conventional methods [4,6,7,8]. However, studies analysing the variations in the arising colours when the pigment is incorporated into glazes are relatively scarce.

The poor colouring power of the pigment in certain glazes was in principle assigned to its instability on exposure to attack by the glassy phase forming from the glaze during firing. Blachere considers the presence of Zn or other bivalent cations in the glaze to favour Cr extraction from the pigment to form the corresponding spinel, causing pigment break-up [2]. On the other hand, Stefani et al. indicate that the substitution of Ca in the pigment structure by Ba or Sr from the glaze is responsible for the loss of colour [4].

Studies using several types of frit, such as those of Byrne, et al. [10], show that in some cases the structure of the pigment is broken up, while in others lack of colour is not associated with the disappearance of malayaite, so that other phenomena must be involved. In these studies, although the effect of heat treatment peak temperature on the stability of the colour generated is partly analysed, the influence of its residence time at peak temperature or of the type of cooling is not considered, which can be of decisive importance when the pigment is used to decorate single-fire tiles.

In view of the above, this work analyses the effect of the interaction between the pink chromium-calcium-tin-silica pigment with several frits, in order to identify the mechanisms responsible for the arising colours, when heat treatments with the structure of the single-fire cycles are used.

2. EXPERIMENTAL PROCEDURE

The tests were carried out with samples of industrial frits and pigment, so that the results are comparable with those found in an industrial plant. The characteristics of the selected frits, type, maturing temperature (Tm) and compositional details are set out in Table 1.

frit	type	Tm (°C)	Composition (mol%)			
			Al_2O_3	M_2O	MO	ZrO_2
F1	Fast twice fire	1000	7	9	12	-
F2	Porous single fire	1110	5	4	23	-
F3	Traditional twice fire	940	8	13	10	-
F4	Fast twice fire	980	5	5	18	-
F5	Porous single fire	1090	4	5	24	-
F6	Porous single fire	1100	4	4	24	4
F7	Traditional twice fire	870	3	4	38	-
F8	Fast twice fire	1060	5	9	10	7
F9	Porous single fire	1120	5	2	27	-

Table 1. Characteristics of the frits used in the study

The frit-pigment mixtures were appropriately proportioned by weight and wet milled in a planetary mill with acetone for 9 minutes. The suspension was dried under infrared lamps and the powder was sieved on a 600 μm mesh. The sieved material was moistened to 6% (kg H_2O/kg dry solid), and cylindrical test specimens were formed in a laboratory press, at a pressure of 400 kg/cm^2. The test specimens were dried in a laboratory oven and fired in an electric laboratory kiln, with a typical floor tile cycle (fast heating up to 500°C, heating at 25°C/min to Tm of the test frit, holding the specimens at peak temperature followed by forced fan cooling, except in the quartz inversion stretch, in which natural cooling was used). The fast cooling experiments were carried out using the same heating scheme, with a 6-min hold at Tm, allowing the specimens to cool in the kiln with a fan until reaching the chosen fast cooling start temperature (Ter), when the test specimens were withdrawn from the kiln and allowed to cool in ambient air.

The determination of the spectrophotometric curves and the CIELab chromatic co-ordinates of the resulting test specimens were carried out on a Macbeth, Colour-eye 7000, spectrophotometer with a standard CIE C illuminant and CIE 2° standard observer. (In the CIELab system, L* is the lightness or white-black axis, a* is the red-green axis, and b* is the yellow-blue axis).

The evolution of the pigment in the glazes was monitored by identifying the crystalline phases present in the glazes by means of X-ray diffraction (XRD), with a Phillips PW 1840 instrument using the random powder method. For this, the test specimens were previously ground in a ring mill with a tungsten carbide beaker.

Test specimen microstructure was determined on a Phillips X50 scanning electron microscope. To enhance the differences in composition, the samples in which the differences were more difficult to appreciate were lightly etched with diluted HF.

3. RESULTS

3.1 COLOUR DEVELOPMENT

As a reference of actual frit colour, Table 2 details the chromatic co-ordinates of the frits, each fired with a 6-min hold at Tm. The chromatic co-ordinates of the colours produced on adding 5 wt% pigment to the different frits, fired at the respective Tm with four different hold times, are listed in Table 3.

	F1	F2	F3	F4	F5	F6	F7	F8	F9
L*	85.60	92.44	87.68	91.32	96.75	97.44	93.94	96.99	94.19
a*	-3.39	-3.64	-3.01	-2.54	-0.79	-0.89	-2.88	-1.16	-2.51
b*	5.82	-2.96	3.37	3.24	2.56	2.60	4.05	1.02	-0.83

Table 2. Chromatic co-ordinates of the frits fired for 6' at their Tm.

t (min)	frit	L*	a*	b*	frit	L*	a*	b*	frit	L*	a*	b*
0.1	F1	46.99	25.63	4.28	F2	47.55	24.70	-9.74	F3	62.15	19.28	2.98
6		45.69	25.96	4.64		48.63	23.21	-13.27		62.71	19.64	2.92
15		45.33	25.90	4.70		50.20	22.17	-13.77		61.95	20.28	3.06
30		45.19	25.82	4.77		52.05	20.94	-13.67		61.72	20.62	3.12
0.1	F4	48.36	24.43	3.76	F5	66.98	19.00	-0.09	F6	67.61	18.53	0.09
6		49.71	24.70	3.79		68.83	17.65	0.15		69.02	17.61	0.21
15		51.11	25.01	3.78		69.64	17.09	0.11		70.61	16.64	0.22
30		51.67	25.08	3.79		70.30	16.85	0.18		71.49	16.10	0.18
0.1	F7	76.43	11.52	2.00	F8	68.76	19.53	0.96	F9	50.37	24.75	-9.36
6		76.55	12.64	2.20		71.26	18.71	1.53		51.82	23.00	-12.92
15		76.26	13.15	2.33		72.51	18.11	1.53		53.74	22.11	-12.67
30		75.59	14.52	2.15		73.26	17.55	1.55		55.13	21.44	-12.34

Table 3. Chromatic co-ordinates of specimens with 95% frit + 5% pigment, fired for different residence times at their Tm.

The tables show that the frits produce white glazes with high lightness, and a greenish and a yellowish component, except in two cases, F2 and F9, which have a slightly bluish tinge. However on incorporating the pigment, three different groups can be clearly distinguished as a function of resulting colour chromaticity:

I. F1 and F4 give rise to intense reddish colours (a*>24, 3<b*<5), which remain quite stable on increasing the hold at Tm.

II. F3, F5, F6, F7 and F8 yield pinkish colours (10<a*<21, 0<b*<3), whose behaviour on increasing residence time is variable, though in most cases a tendency is detected toward a decrease of the red component, while the yellow one remains stable (F7 is the most notable exception).

III. F2 and F9 produce purple colours (a*>20, b*<-9), but they reduce the red component and increase the blue one as the hold at Tm rises.

These differences indicate that the behaviour of the glaze+pigment combination is subject to the effect of various phenomena that modify the final colour, and that their intensity also depends on residence time.

3.2. CHARACTERISATION OF THE CRYSTALLINE PHASES

The crystalline phases identified in each test specimen, as well as the intensities of the most characteristic diffraction peaks of each specimen are detailed in Table 4. With regard to the pigment, the study was conducted using the pigment's most intense peak (I_{100} and I_{50} of malayaite), not overlapped by any other crystalline phase peak.

frit	crystalline phase	peak (I)	time at Tm (min)			
			0.1	6	15	30
F1	malayaite ($CaSnSiO_5$)	100	269	292	286	272
F2	malayaite ($CaSnSiO_5$)	50	259	199	144	172
	wollastonite ($CaSiO_3$)	100	172	-	-	-
F3	malayaite ($CaSnSiO_5$)	50	303	299	331	335
	cristobalite (SiO_2)	100	0	34	161	23
F4	malayaite ($CaSnSiO_5$)	100	328	324	306	292
	hardystonite ($ZnCa_2Si_2O_7$)	100	0	146	353	493
F5	malayaite ($CaSnSiO_5$)	50	256	246	193	199
	petedunnite ($ZnCaSi_2O_6$)	100	790	655	524	506
F6	malayaite ($CaSnSiO_5$)	50	243	222	222	213
	petedunnite ($ZnCaSi_2O_6$)	100	502	576	462	506
F7	malayaite ($CaSnSiO_5$)	100	581	480	515	416
	willemite (Zn_2SiO_4)	80	303	2323	2381	2323
	$Zn_{1.7}SiO_4$	100	590	-	-	-
F8	malayaite ($CaSnSiO_5$)	50	335	216	174	204
	zircon ($ZrSiO_4$)	45*	388	581	807	807
	baddeleyite (ZrO_2)	100	320	62	42	0
	cristobalite (SiO_2)	100	161	-	-	-
F9	malayaite ($CaSnSiO_5$)	50	246	253	159	146
	wollastonite ($CaSiO_3$)	100	380	335	222	202
	cristobalite (SiO_2)	100	286	339	259	207

*Overlapping with reflection I5 of malayaite.

Table 4. XRD results.

The evolution of characteristic peak intensity of the crystalline phases present in the test specimens (of malayaite, as well as of devitrified phases), allows interpreting the variation of lightness and the red component observed in the colorimetric study. This enables distinguishing the groups below (in the figures the chromatic co-ordinates a* and L*-45 have been represented on one axis to fit them to the same range of values, while crystalline phase peak intensity, detected by XRD, has been plotted on the second axis. Residence time at Tm has been plotted on the abscissas).

a) The quantity of pigment remains constant and other crystalline phases do not appear. As is to be expected in this case, the red component hardly varies, and its absolute value depends partly on the transparency of the glassy phase. This is the case of frit F1 (see Figure 1). The small reduction in lightness can be assigned to the increase in glass homogeneity with longer heat treatment time.

b) The quantity of pigment remains practically constant and other crystalline phases appear. In this case the red component also shows no appreciable variation in the frits exhibiting this behaviour (F3 and F4, see Figures 2 and 3), although the absolute value of a* is lower in the former. This can be due to the lesser transparency of the glassy phase developed by F3, which is consistent with the minor variation of lightness that this frit exhibits when it begins to devitrify cristobalite, while F4 lightness rises as the devitrified hardystonite fraction increases.

c) The quantity of pigment decreases and other crystalline phases appear. In this case the expected behaviour is a decrease in the red component and rise in lightness, as residence time increases, due to the combined effect of the disappearing colorant and rise in opacifiers. This behaviour is clearly observed in frits F5, F6 and F8, since the first two devitrify petedunnite and the third zircon and baddeleyite (see Figure 4 to 6).

Frits F2 and F9 can also be included in this group, although the former with certain reservations because wollastonite, which initially devitrifies, has already dissolved after a 6′ hold at Tm (see Figure 7 and 8). In both cases a clear decrease is appreciated in pigment quantity as residence time rises, with an ensuing decrease of the red component. The rise in lightness can be assigned to the presence of crystalline phases, but it is also necessary to keep in mind the immiscible glassy phase separation phenomenon, which is set out below to interpret the appearance of the blue component.

Finally, frit F7 departs from expected behaviour, since the decrease in the quantity of pigment is small, and is also masked by the important quantity of crystalline phases that devitrify in the glaze (Figure 9). In this case lightness falls a little, and the red component increases slightly as residence time rises, which can be related to a rise in transparency of the residual glassy phase.

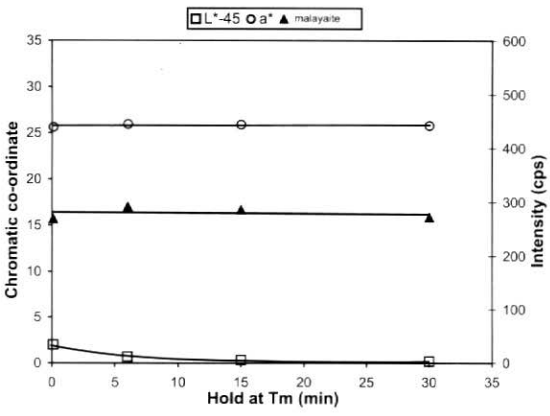


Figure 1. Results of frit F1.

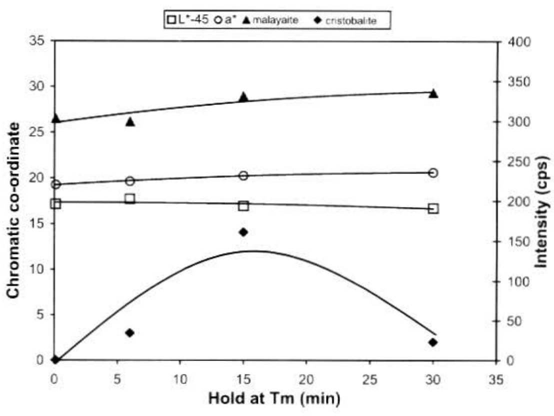


Figure 2. Results of frit F3.

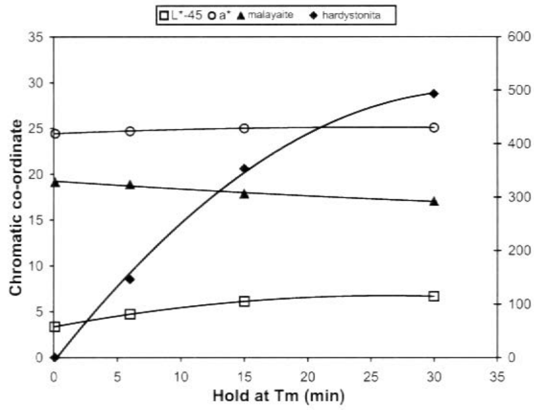
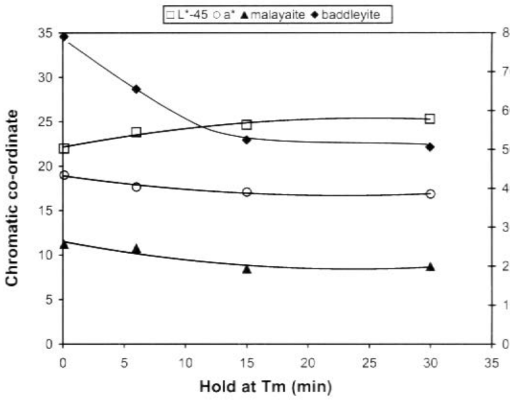


Figure 3. Results of frit F4.



.Figure 4. Results of frit F5.

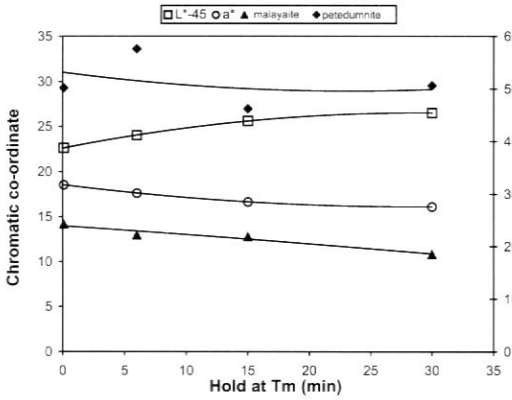


Figure 5. Results of frit F6.

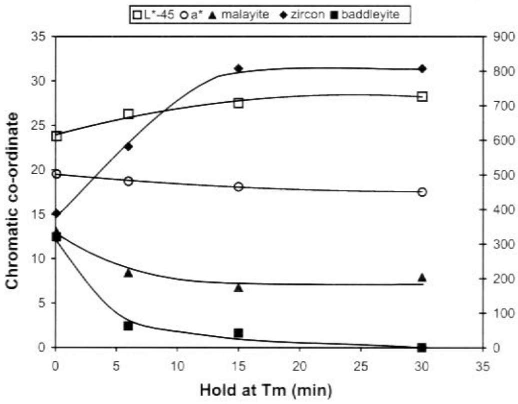


Figure 6. Results of frit F8.

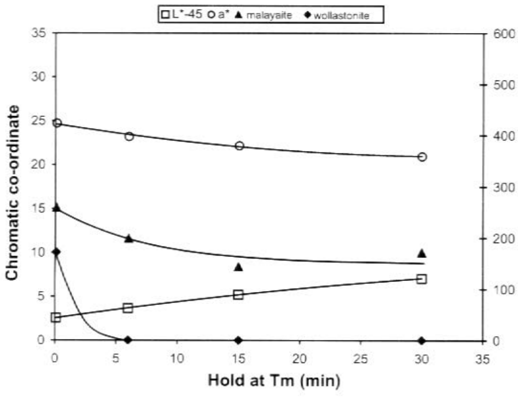


Figure 7. Results of frit F2.

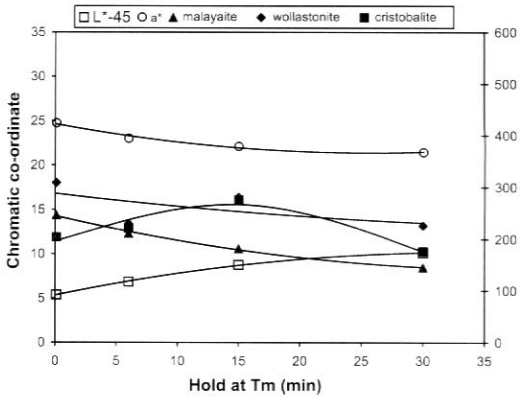


Figure 8. Results of frit F9.

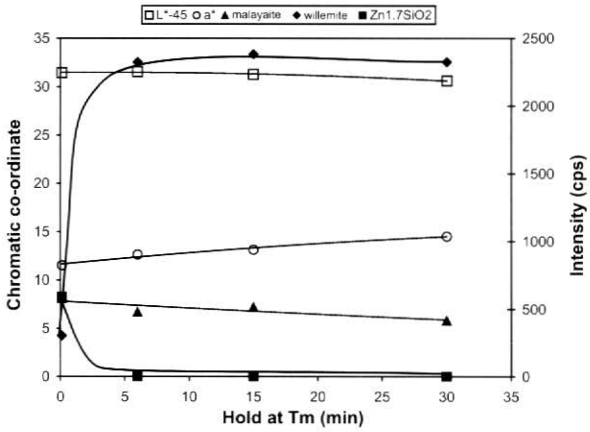


Figure 9. Results of frit F7.

The diffraction results have in no case shown the presence of mixed MCr_2O_4 spinels, which can arise from the extraction of Cr contained in the pigment by the glaze, or of $BaSnSiO_5$ phases, indicating that these pigment break-up mechanisms do not appear in these specific glazes, or that the quantity of these phases lies below the detection limit.

When relating the chemical composition of the different frits to pigment lack of stability in the arising glassy phase during firing (frits F2, F5, F6, F7, F8 and F9), this phenomenon seems to be mainly related to frits rich in calcium, since the frits in which pigment decomposition is not observed have in common, from a compositional point of view, a CaO molar below 8.5%. However it cannot be discarded that pigment stability is a complex function of the glaze composition, which varies as the various detected crystalline species devitrify.

3.3. EXPERIMENTS TO VISUALISE POSSIBLE IMMISCIBLE GLASSY PHASE SEPARATION

Glazes from frits F2 and F9 differ from the rest because of their notable blue component, which transforms the expected reddish colour into an intense purple. The appearance of blue tinges in the glasses is a clear indication of phase separation or at least of some heterogeneities in the composition, which are reflected in the refractive index, of an appropriate size to cause visible light scattering (less than 0.3 microns) and hence the appearance of a blue tinge (according to the Rayleigh theory, dispersed light intensity is inversely proportional to the fourth power of its wavelength, and therefore preferentially disperses the radiation belonging to blue and violet in the spectrum [11]). As phase separation usually takes place during glaze cooling, different experiments were carried out modifying the cooling stretch of the cycle used to make the test specimens, in order to verify whether the component found was due to this phenomenon.

Since frits F2 and F9 are very similar from a chemical composition and colorimetric behaviour point of view, the tests were conducted with frit F2, both by itself and with a 1 wt% pigment addition. The results of the experiments with fast cooling are detailed in Table 5.

Ter	F2			F2 + 1% pigment		
(°C)	L*	a*	b*	L*	a*	b*
1110	79.17	-3.39	2.32	60.55	19.75	1.57
1000	80.56	-3.78	2.96	59.68	20.09	2.33
950	80.25	-3.10	0.75	61.01	20.54	-5.41
900	85.66	-2.53	-3.72	64.21	19.47	-9.87
850	85.42	-3.95	-5.24	64.93	18.81	-11.14
800	86.11	-4.32	-4.64	67.41	17.47	-11.27
600	86.05	-4.44	-4.81	67.60	17.37	-11.65

Table 5. Chromatic co-ordinates of the test specimens fast cooled from Ter.

The results show that a critical range exists between 800 and 1000°C, in which lightness rises (Figure 10), while the red component alters to a smaller extent (Figure 11), and the blue tinge of the glaze appears (Figure 12). This effect is apparently more intense in the glaze with pigment, due to selective absorption by the pigment in the central area of the visible spectrum, which reinforces the visual appreciation of the blue component, as the spectrophotometric curves show (Figure 13).

To verify the assumption, the microstructure was determined of F2 test specimens with a 1 wt% pigment addition, made with the standard heating cycle, with a 6′ hold at Tm, and three types of cooling from this temperature: fast cooling, standard cooling and slow cooling (v = 5°C/min). The chromatic co-ordinates of these test specimens (see Table 6) indicate that on reducing the cooling rate, lightness increases, the red component decreases and b* goes from a lightly positive value to a clearly negative one, moving later to almost neutral. This behaviour is consistent with the appearance of glassy phase separation during cooling.

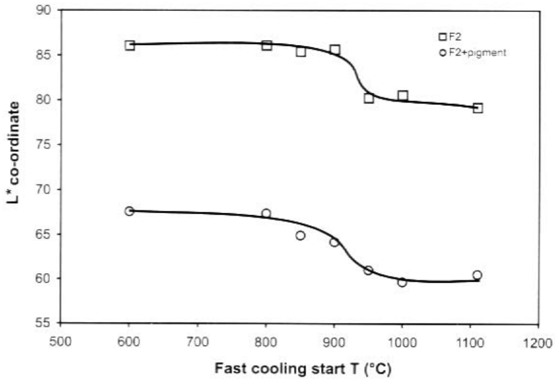


Figure 10. Evolution of L with Ter.*

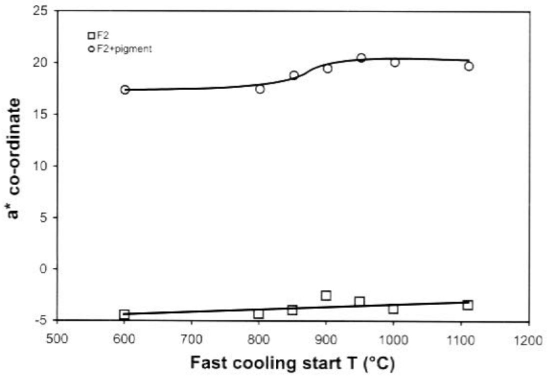


Figure 11. Evolution of a with Ter.*

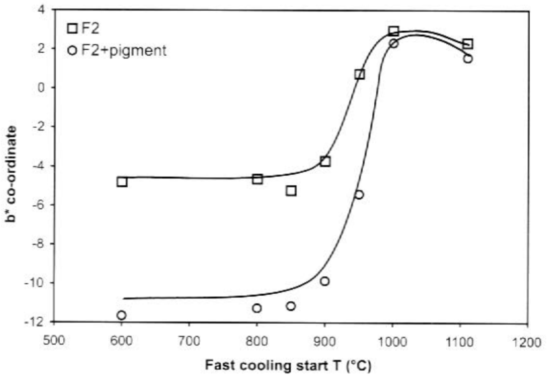


Figure 12. Evolution of b with Ter.*

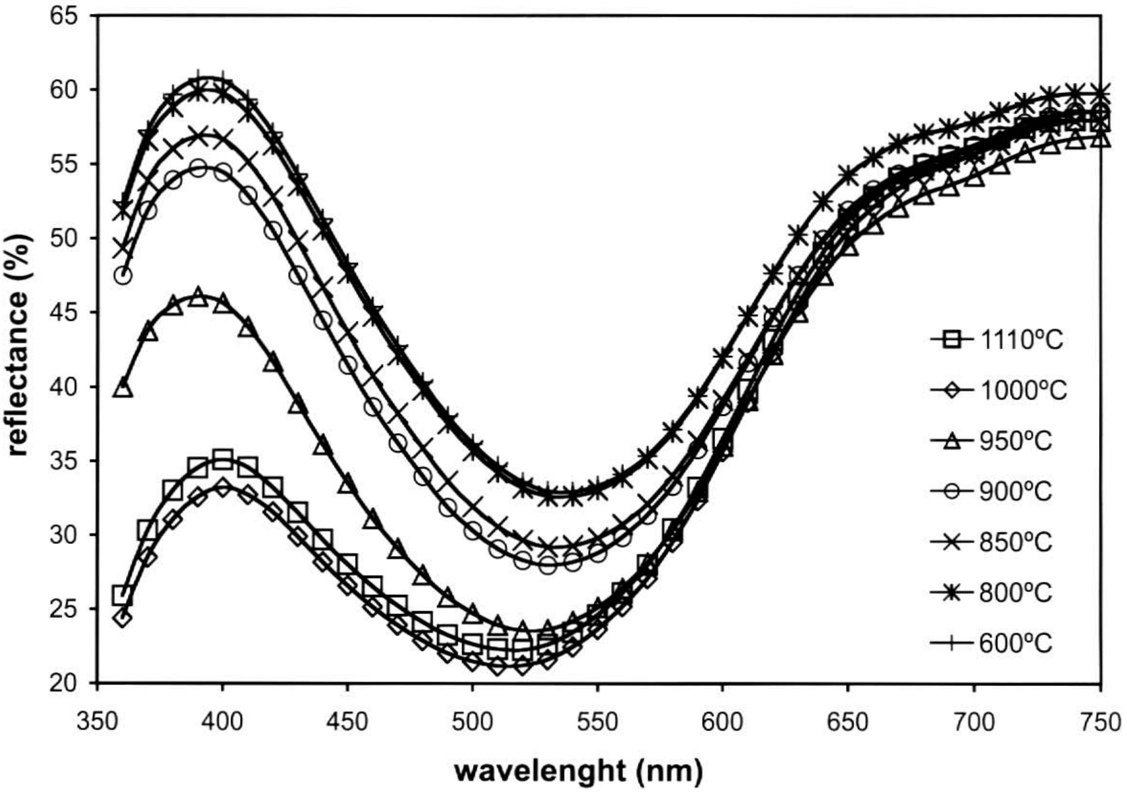


Figure 13. Spectrophotometric curves.

cooling	L*	a*	b*
Fast	60.55	19.75	1.57
Standard	68.63	16.30	-12.58
Slow	81.46	11.17	-0.14

Table 6. Chromatic co-ordinates of the specimens with F2 + 1% pigment, held at 6' a Tm and subjected to different cooling.

The microstructure of the test specimens, observed by SEM, shows that the glaze subjected to fast cooling is very homogeneous and shows no microstructure (Figure 14). However, the glaze subjected to standard cooling presents a slight heterogeneity in the composition, without exhibiting the typical interfaces of well developed phase separation (Figure 15), but with adequate size to generate radiation scatter in the blue range. Finally in the glaze subjected to slow cooling, phase separation is fully developed (Figure 16). These results are consistent with the phenomenon proposed as the cause of the blue component in the purple hue that these glazes exhibit. The cooling phase is therefore critical to the colour produced by this pigment in this type of frit, and must be carefully controlled to keep shades from appearing in the finished product.

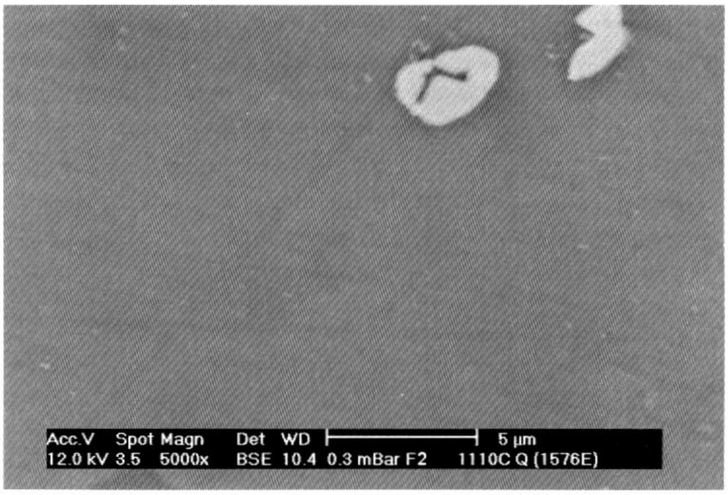


Figure 14. Microstructure of a specimen of frit F2 + 1% pigment produced with fast cooling

Figure 15. Microstructure of a specimen of frit F2 + 1% pigment produced with standard cooling .

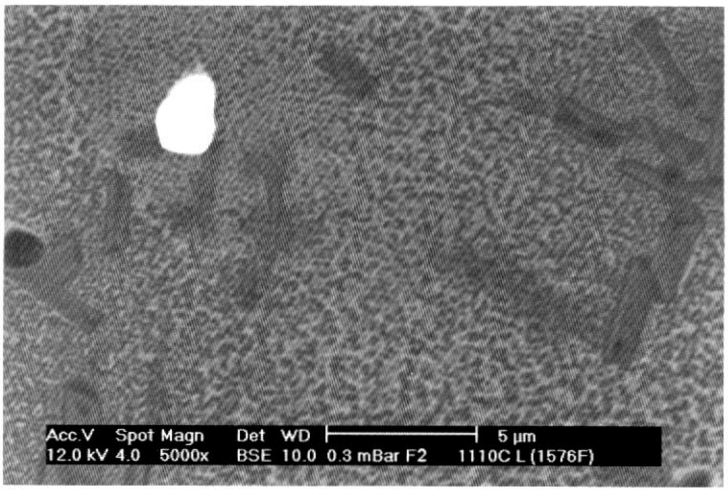


Figure 16. Microstructure of a specimen of frit F2 + 1% pigment produced with slow cooling.

4. CONCLUSIONS

The interaction of the pink pigment (Cr)$CaSnSiO_5$ with the glazes has demonstrated that several phenomena exist, as a result of which optimum colour development is not achieved in the final glaze. Besides the total or partial dissolution of the pigment in the glassy phase, which is the mechanism indicated most frequently in the literature, the presence of other crystalline phases and even the appearance of microheterogeneities in the composition during cooling, which are phase separation precursors, also have an important effect. Therefore, this pigment's conditions of use must be strictly controlled, if reproducible results are to be obtained, both with regard to the glaze composition to which it is added and to the heat treatments it undergoes.

REFERENCES

[1] HURD, B.M. Chrome-tin pink and maroons. *Am. Ceram. Soc. Bull.*, 40 (1), 11-12, 1961.

[2] BLACHERE, S.T. Chrome-tin pink glazes. *Am. Ceram. Soc. Bull.*, 68 (1), 81-84, 1989.

[3] EPPLER, R.A. Selecting ceramic pigments. *Ceram. Eng. Sci. Proc.* 8 (11-12), 1139-1149, 1987.

[4] STEFANI, R.; LONGO, E.; ESCRIBANO, P.; CORDONCILLO, E.; CARDA, J.B. Developing a pink pigment for glazes. *Am. Ceram. Soc. Bull.*, 76 (9), 61-64, 1997.

[5] EPPLER, R.A. and EPPLER, D.R. *Glazes and glass coatings*. Westerville: American Ceramic Society, 2000.

[6] SANGHANI, D.V.; ABRAMS, G.R.; SMITH, P.J. A structural investigation of some tin-based coloured ceramic pigments. *Trans. J. Br. Ceram. Soc.*, 80, 210-214, 1981.

[7] ESCRIBANO, P.; GUILLEM, C.; ALARCÓN, J. Cr-SnO_2-CaO-SiO_2-Based ceramic pigments. *Am. Ceram. Soc. Bull.* 63 (12), 1492-1494, 1984

[8] CORDONCILLO, E.; DEL RÍO, F.; CARDA, J.; LLUSAR, M.; ESCRIBANO, P. Influence of some mineralizers in the synthesis of sphene-pink pigments. *J. Eur. Ceram. Soc.*, 18, 1115-1120, 1998.

[9] REN, F.; ISHIDA, S.; TAKEUCHI, N.; FUJIYOSHI, K. Chromium-based ceramic colours. *Am. Ceram. Soc. Bull.* 71 (5), 759-764, 1992.

[10] BYRNE, C.J.; KUTNEY, S.G.; PIPOLY, R.A. The effect of glaze composition on the colour and stability of chrome tin pink pigments. *Ceram. Eng. Sci. Proc.*, 15 (1), 206-223, 1994.

[11] NASSAU, K. *The physics and chemistry of colour: The fifteen causes of colour*. New York: John Wiley & Sons, 1983.