Thermochimica Acta, 218 (1993) 229–245
Elsevier Science Publishers B.V., Amsterdam

Aesthetic parameters of highly feldspathic porcelain

Wafa I. Abdel-Fattah[a], F.M. Tera[b] and F.A. Nour[a]

[a]Ceramic Department, National Research Centre, Tahrir Street, Dokki, Giza (Egypt)

[b]Physical Standards Department, National Institute of Standards, Tahrir Street, Dokki, Giza (Egypt)

Keywords: Translucency measurements, feldspathic porcelain, mineralizers, surface topography.

ABSTRACT

Parian porcelain (80% feldspar and 20% Kaolin) or (80% feldspar, 10% Kaolin and 10% quartz) and those containing $BaCO_3$, $Al(OH)_3$ or $ZrSiO_4$ in 5, 10 and 15% were prepared and matured.

Optical measurements were performed according to the tristimulus values C.I.E. system (see Annex) and x, y and z were obtained from the reflection and transmission data of parian porcelain with mineralizers. The translucency and brightness of the specimens were calculated after normalizing with the sensitivity of human eye (the ordinary observer).

Results proved increased transmittance with higher wavelength and with mineralizers. Both translucency and whiteness improved substantially with $BaCO_3$ while $ZrSiO_4$ raised opacity. The results were discussed in terms of porosity and surface topography. Resulted bodies are comparable to the transmittance-reflectance plot of some American and British porcelains.

INTRODUCTION

A unique property of this high feldspathic parian porcelain is its translucency which could be defined as the relative amount of light

0040-6031/93/$06.00

transmission of diffuse reflectance from a specimen surface through its turbid medium (Macadam, 1981). The optical properties of parian porcelain has not yet been dealt with inspite of its use in ableware and porcelain teeth (Southan, 1987).

Optical measurements of porcelain unadequately varied between visual appearance to single transmission wavelength. Correlation of translucency evident to human eye, which varies along the visible spectrum, is very seldom. Methods of studying translucency are: 1) direct transmission (very low), 2) total transmission (including scattering) and 3) spectral reflectance. The last two methods are chosen, in the present work, to define comprehensively the optical characteristics of the porcelain bodies and to obtain the tristimulus values of the C.I.E. system x, y and z to simulate human eye sensitivity.

Whiteness and translucency were indicated to be dependent on the microstructure of the body, light absorbed and to the presence of coloring oxides (Levin and Nikulina, 1974). The influencing factors are the alkali concentrations and firing temperatures which in turn affect sintering and not the pigment oxides (Danute et al., 1972). Lekareva et al. (1966) denoted improved whiteness upon decreasing the alkali content although high potash ions were reported to guarantee high translucency especially in high alkali system (Slosarczyk, 1983). Dietzel (1969) attributed the whiteness of porcelain to the acidic nature of the glassy phase which dissolves Fe_2O_3 giving FeO, masking the rest of Fe_2O_3 and shielding its yellow color.

In the present work, parian porcelain bodies were prepared using local raw materials. The effect of incorporating mineralizers in the form of $BaCO_3$ or $Al(OH)_3$ or $ZrSiO_4$ at the level of 5, 10 and 15% on their aesthetics in relation to microstructure are studied. Various approaches for measuring were assessed.

EXPERIMENTAL

Porcelain bodies

Porcelain specimens were prepared using the semidry pressing technique. Local raw materials used are potash feldspar (F), Quartz (Q) and Kalabsha Kaolin (K) (Aswan). Specimens were vitrified and true density as well as bulk density were used to calculate sealed porosity (ASTM C-329-75). Chemical composition of the mature base-bodies are quoted from the chemical analysis of their raw materials. Chemically pure

$BaCO_3$ or $Al(OH)_3$ or $ZrSiO_4$ were incorporated separately at the level of 5, 10 and 15% in each base body (FK) or (FKQ).

TABLE 1

Chemical constitution of porcelain base-body

Body composition			Body notation	Calculated oxide % on fired base							
F	K	Q		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
80	20	-	FK	62.06	23.94	0.43	0.73	0.45	0.14	10.01	2.61
80	10	10	FKQ	67.95	19.68	0.22	0.64	0.44	0.11	10.00	2.60

Surface topography

Specimens were examined after careful polishing, cleaning and evaporating thin layer of gold (500 A). Scanning electron microscope (Nano Lab. 7 SEMCO, Canada) was used.

Optical properties

A double beam recording Spectrophotometer (Schimatzu UV 300) with an integrated sphere assembly was used. Before measuring the reflection, the zero and 100% setting are made according to the ordinary UV 300 procedure. MgO powder pressed as specimens having 2.4 mm diameter are used as standard white.

For the total transmission measurements, an alumina specimen holder with the sample at the entrance part of the sphere was used. Freshly prepared MgO reflectance standard was used to complete the integrated sphere. The intensity of the beam passing through a rectangular specimen (2.4 x 1.6 mm) was continuously recorded. Both measurements were performed on one and the same specimen to insure same thickness and surface polish. The average thickness of each samples was obtained from five measurements along the diameter of the specimens using travelling microscope.

The normalized translucency values (y_{tn}) according to the C.I.E. are obtained by multiplying the previously obtained values (y_t) from transmission curves by the relative spectral power distribution of the

C.I.E. illuminant (A), ($s_\lambda.y_\lambda R_\lambda$) specific for wavelength at intervals of 10 nm which are available in standard tables (Judd and Wyszecki 1965).

The actual translucency relative to the sensitivity of the human eye within the whole spectrum (y_{Ti}) and the integrated tristimulus values after normalization (y_{tni}) are related to the relative thickness of the respective sample x_0/x as included in the equation:

$$y_{Ti} = y_{tni}^{x_0/x}$$

where x_0 is the thickness of the sample with 1 mm thickness and x is the thickness of any measured sample. The translucency % (y_{Ti}%) is then obtained by dividing the integrated normalized y_{Ti} by the standard illuminant (A) which is equal to 1078.9 and multiplying by 100.

To calculate the brightness, y_{rn}; the y_r values from reflection curves were multiplied by the relative spectral power distribution ($s_\lambda.y_\lambda R_\lambda$) of the C.I.E. illuminant (A). The brightness % (y_{ri}%) was obtained by dividing the normalized integrated (y_{rn}) by 1078.9 which is the standard illuminant (A) and multiplying by 100.

RESULTS AND DISCUSSION

The incorporation of the mineralizers retarded maturing to higher temperature with wider firing range especially the barium carbonate in group I and group IV with quartz as in Table 2.

Optical properties

Reflection

The spectral reflectance obtained is exemplified by those of group I containing $BaCO_3$, Figure 1a. The absorption band in the blue region (about 400 nm) is fairly marked on the original body as well as those of low concentrations of the mineralizers denote the presence of iron impurities at 380-460 nm. Its fainting proves the role played by the mineralizers especially at the high concentrations. The relative brightness

TABLE 2

Constitution and ceramic properties of mature parian porcelain at their respective firing temperatures

Group No.	Specimen constitution	Mineralizer (%)	Specific notation	Firing temperature (°C)	Water absorption (%)	Density g/cm³	Porosity (%)	Shrinkage (%)
	FK	-	FK	1150	0.11	2.37	0.27	12.88
I	$BaCO_3$	5	FKBI	1225	0.38	2.47	0.94	2.39
		10	FKBII		0.27	2.55	0.70	2.39
		15	FKBIII		0.28	2.53	0.70	2.39
II	$Al(OH)_3$	10	FKAII	1175	0.31	2.44	0.76	2.38
		15	FKAIII		1.84	2.31	4.25	2.36
III	$ZrSiO_4$	10	FKZII	1175	0.43	2.39	1.03	2.42
	FKQ	-	FKQ	1175	0.19	2.33	0.45	11.66
IV	$BaCO_3$	5	FKQBI	1225	0.27	2.47	0.65	2.43
		10	FKQBII	1200	0.22	2.39	0.52	2.40
		15	FKQBIII	1175	0.24	2.37	0.58	2.39

FK = 80% F and 20% K
FKQ = 80% F, 10% K and 10% Q
F: feldspar, K: Kaolin and Q: quartz

(y_r), which is obtained from reflection curves and denotes brightness, when plotted as a function of the measured wavelength elucidates the achieved improvement due to mineralizers. Optimum brightness is recorded around λ = 580–600 nm, Table 3, and represented by Figure 1b for group I. The variation of maturing temperature being 1225 or 1250 °C has more pronounced effect at low levels of mineralizers as FKBI which diminishes with high concentration. The diffusely reflected light has two components, one resulting from the reflection at the phase boundaries on either surfaces of the specimen and the other from light scattered by scattering centres inside the specimen.

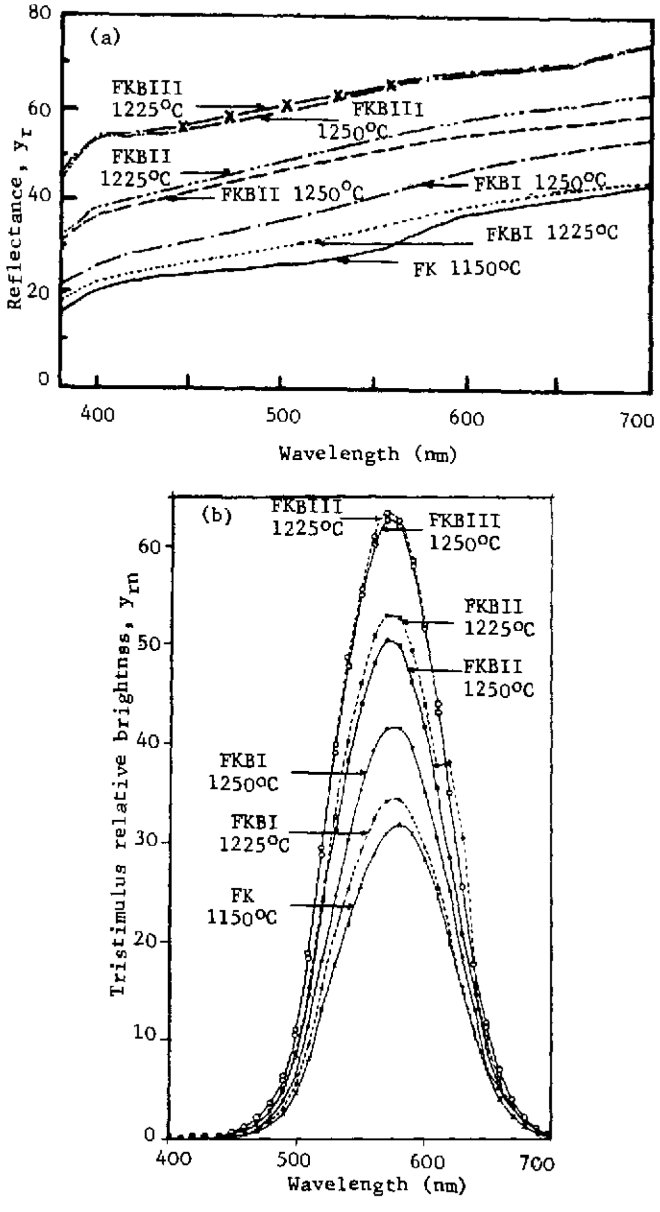

Fig. 1. a. Reflectance, y_r curves for porcelain FK and of group 1 containing $BaCO_3$ matured at 1225 and 1250 °C as a function of wavelength.

b. Tristimulus Relative brightness, y_{rn} for porcelain FK and of group 1 containing $BaCO_3$ matured at 1225 and 1250 °C as a function of wavelength.

TABLE 3

Values of transmittance % (y_t), reflectance % (y_r) and absorbance % (A) from the spectral transmission, reflection and absorption curves at λ = 555 nm.

Group No.	Specimen notation	Firing temperature (°C)	Spectral values (%)		
			y_t	y_r	A
	FK	1150	0.6	30.5	68.9
I	FKBI	1225	2.4	34.8	62.8
	FKBII		6.1	54.4	39.5
	FKBIII		11.5	65.4	23.0
II	FKAII	1175	1.1	48.4	50.5
	FKAIII		3.3	55.4	41.3
III	FKZII	1175	0.0	65.6	34.4
	FKQ	1175	3.6	32.2	64.2
IV	FKQI	1125	9.6	42.4	48.0
	FKQII	1200	16.6	57.1	26.3
	FKQIII	1175	18.3	60.3	21.4

Transmission

The amount of light transmitted which is the sum of directly transmitted light and diffuse transmitted light by scattering varied between 0.6% for the original body (FK) to 11.5% for the improved one containing 15% $BaCO_3$ (FKBIII), Table 3. Figure 2a is an example of these curves for group I. The total transmission of the specimens have similar spectra showing increasing transmittance with wavelength from 400 to 700 nm which is coinciding with Rayleigh's scattering equation (Macadam, 1981). The presence of additives including quartz seems to act as scattering centres which resulted an improved translucent appearance by diffuse transmission and scattering similar to the role of Tin oxide opacifier in dental porcelain (Hahn and Teuchert, 1980). Multiple scattering of light in porcelain was denoted to be the main factor of its translucency (Brodbelt et al., 1980). Plotting the y_t parameter of the tristimulus values from transmission curves versus wavelength (λ) as exemplified by those of group I. Figure 2b shows optimum values at $\lambda \approx$

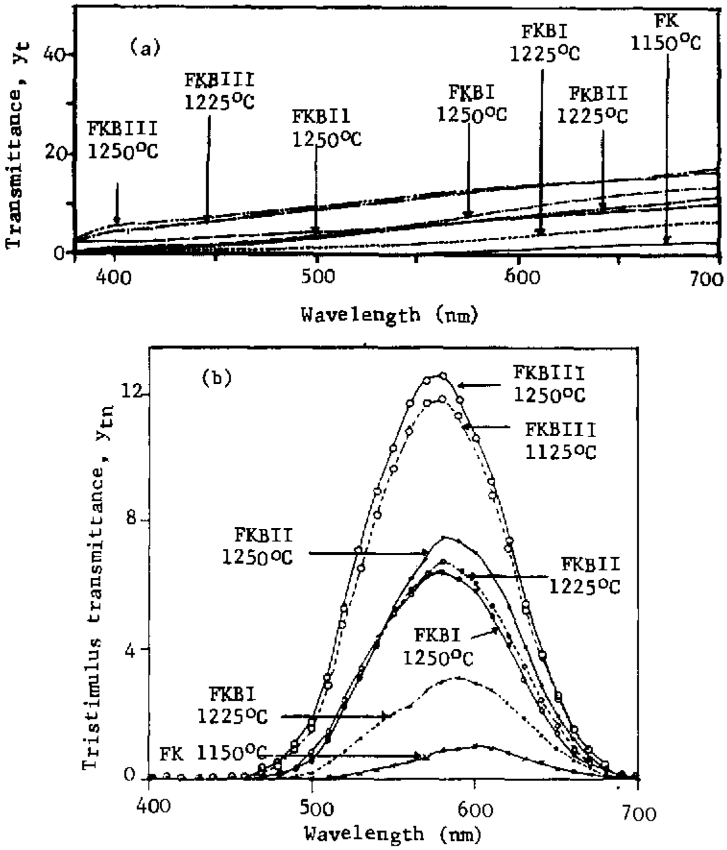

Fig. 2. a. Transmittance, y_t curves for porcelain FK and of group I containing $BaCO_3$ matured at 1225 and 1250 °C as a function of wavelength.

b. Tristimulus transmittance, y_{tn} for porcelain FK and of group I containing $BaCO_3$ matured at 1225 and 1250 °C as a function of wavelength.

580 to 600 nm which is higher than maximum sensitivity of human eye being at $\lambda \approx 555$ nm as reported by Judd and Wyszecki (1965).

Absorption

The absorption curves originated from the percentage of light absorbed (calculated by subtracting the sum of transmitted and reflected lights from 100) at each wavelength interval, Table 3. The high absorbance %

(A) of the original specimen (65.8%) was reduced substantially with $ZrSiO_4$ and $Al(OH)_3$ and both are inferior to $BaCO_3$. With highest concentration of $BaCO_3$ (15%) absorbance % was reduced to one third of the base-body, Figure 3.

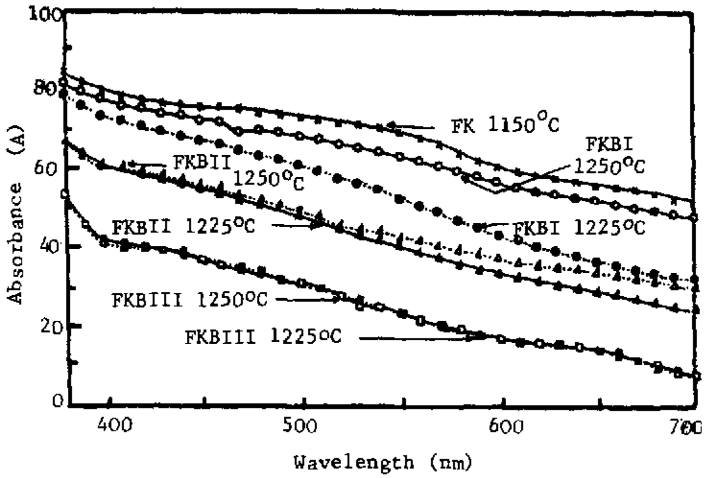

Fig. 3. Absorption curves for porcelain FK and of group 1 containing $BaCO_3$ matured at 1225 and 1250 °C as a function of wavelength.

Analyzing the tristimulus translucency, Figure 1b and those of brightness, Figure 2b, at various wavelengths proves that their optimum values do not coincide with that relative to human eye ($\lambda \approx 555$ nm), Table 4.

It can be realized that normalized relative values or even the integrated % values have higher values than when calculated at $\lambda = 555$ nm only. The latter although at maximum sensitivity of human eye, yet normalized and integrated values are more realistic. Therefore, one cannot depend on one or two values at $\lambda = 555$ nm or at optimum wavelengths within the spectrum to characterize the optical properties. Consequently, the ideal values should be normalized and integrated values relative to the standard respective illuminant (Macadam, 1981) and taking the sample thickness into consideration.

TABLE 4

Normalized transmittance (y_{tn}) and normalized reflectance (y_{rn}) at λ = 555 nm; their optimum wavelengths, y_{tno} and y_{rno} after normalization and the normalized integrated transmittance, Y_{Ti}%, reflectance, Y_{Ri}% and absorbance, A%, relative to standard illuminant (A).

Specimen notation	Normalized values					Normalized integrated % values (400-700 nm)		
	at λ = 555		Optimum wavelength					
	y_{tn}	y_{rn}	λ (nm)	y_{tno}	y_{rno}	Y_{Ti}%	Y_{Ri}%	A%
FK	0.48	-	600	0.98	-	0.9	33.3	65.8
FKBI	2.09	30.5	590	3.17	34.4	3.1	36.9	60.0
FKBII	5.4	48.4	580	6.73	52.8	6.8	53.7	37.5
FKBIII	10.4	58.2	580	11.80	63.2	12.3	66.3	21.4
FKAII	9.81	42.9	600	2.1	47.8	1.9	50.6	47.5
FKAIII	2.87	49.7	580	3.8	53.9	2.4	57.2	40.4
FKZII	0	58.3	570	-	63.8	0.5	67.5	32.0

Effect of firing temperature

When the specimens were fired at two successive maturing temperatures 1225 and 1250 °C for group I containing $BaCO_3$ mineralizers as an example, the lowest concentrations (5%) has pronounced improving effect with harder firing. Higher concentration of $BaCO_3$ (10 and 15%) have insignificant further improvement, Table 5.

TABLE 5

Effect of maturing temperatures on aesthetic parameters porcelain containing $BaCO_3$

Specimen notation	1250 °C				1225 °C			
	Sealed pores	Y_{Ri}%	Y_{Ti}%	A%	Sealed pores	Y_{Ri}%	Y_{Ti}%	A%
FKBI	1.19	43.9	7.6	48.5	1.21	36.9	3.1	66.0
FKBII	1.10	49.7	6.7	43.6	0.31	55.7	6.8	37.5
FKBIII	0.19	66.0	12.9	21.1	0.29	66.3	12.3	21.4

Effect of quartz

When quartz replaced half the amount of Kaolin used in the original batch as in group FKQ, its brightness and translucency are improved. Further, the inclusion of $BaCO_3$ helped more improvement and enhanced better aesthetic as given in Table 6 and Figure 4a,b.

TABLE 6

Effect of quartz replacing Kaolin and $BaCO_3$

Specimen notation	Firing temperature (°C)	Y_{Ri}%	Y_{Ti}%	A%	Sealed pores
FKQ	1175	35.1	4.9	60.0	1.40
FKQBI	1225	42.7	10.4	46.8	1.29
FKQBII	1225	61.2	11.7	27.1	1.20
FKQBIII	1175	61.8	19.2	19.0	0.17

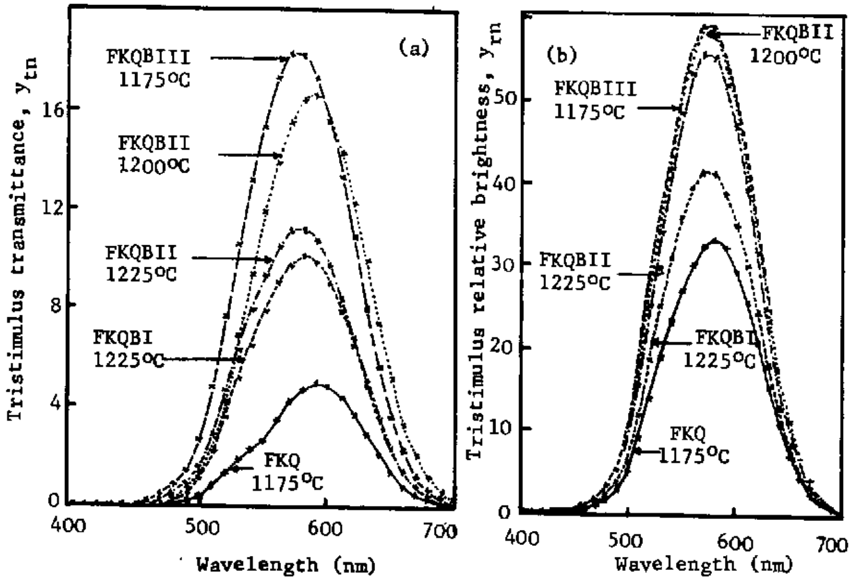

Fig. 4. a. Tristimulus transmittance, y_{tn} from transmission curves (a) and tristimulus relative brightness, y_{rn} from reflection curves (b) for FKQ and FKQ containing $BaCO_3$ fired at different temperatures as a function of wavelength.

The effect of mineralizers on aesthetics are due to reflections from crystallinity of the specimens, grain size of these crystals, porosity and sealed pores, Tables 5 and 6.

For the bodies containing $BaCO_3$, whose translucency increases by a factor of 10 and brightness is doubled, possess high crystallization of leucite as proved by X-ray diffractograms, Figure 5b, and minimum porosity, Table 5, compared to that of base-body, Figure 5a.

Their scanning electron micrographs show uniform and square leucite crystals, Figure 6b. It is obvious that $BaCO_3$ inclusion served to suppress unusual crystal growth which interferes with light transmission and minimized differences in reflection between phases. The inclusion of $Al(OH)_3$ affected improved parameters and catalized leucite formation but to a lower extent as shown in their XRD, Figure 5c, and SEM, Figure 6c. The X-ray diffraction tracings of bodies containing various percent of $ZrSiO_4$ demonstrate enhanced leucite crystallization, Figure 5d. Their surface topography (SEM), Figure 6d, reveals numerous crystal habits and sizes. Therefore, $ZrSiO_4$ acted as nucleating agent similar to the role of TiO_2 in dental porcelain (Pishch and Kazachenok, 1977). This crystal environment along with comparatively higher porosity, Table 5, should have affected light to be diffusely reflected rather than transmitted similar to $ZrSiO_4$ role in glazes. The inclusion of quartz, Figure 5e, results richer silica melt, affected more crystallinity and rounded aggregates of uniform sizes. Inclusion of $BaCO_3$ increased the illuminated leucite squares as found in SEM, Figure 5f and X-ray diffraction, Figure 6f, respectively. The incorporation of $BaCO_3$ could have reduced refractive index (RI) mismatch of the present heterogeneous system. Feldspathic glasses ware reported to have RI 1.31 and low leucite has 1.30 (Hahn and Teuchert 1980) compared to those reported for Al_2O_3 and $ZrSiO_4$ being 1.78 and 1.95 respectively.

Plotting the translucency % versus brightness % of the present parian porcelain containing various mineralizers and containing quartz and $BaCO_3$, Figure 7, demonstrates the achieved improved aesthetics in comparison with base-bodies FK and FKQ compared to the some American, Continental and British porcelains.

CONCLUSION

1. Optical parameters should be measured throughout the visible spectrum and normalized to the standard illuminant to simulate the vision of human eye. Factors influencing translucency are various

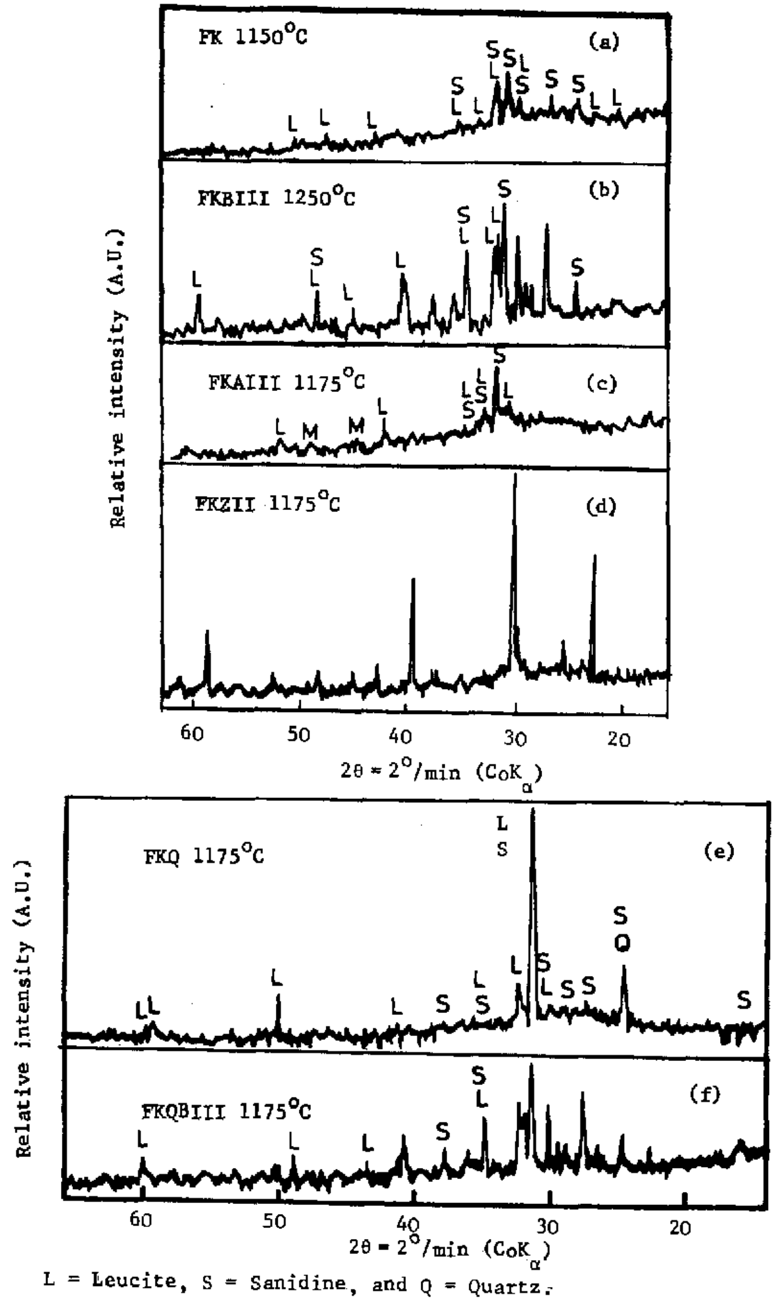

Fig. 5. X-ray diffraction tracings for porcelain FK (a), FK containing: $BaCO_3$ (b), $Al(OH)_3$ (c), $ZrSiO_4$ (d); and FKQ (e), FKQ containing $BaCO_3$ (f).

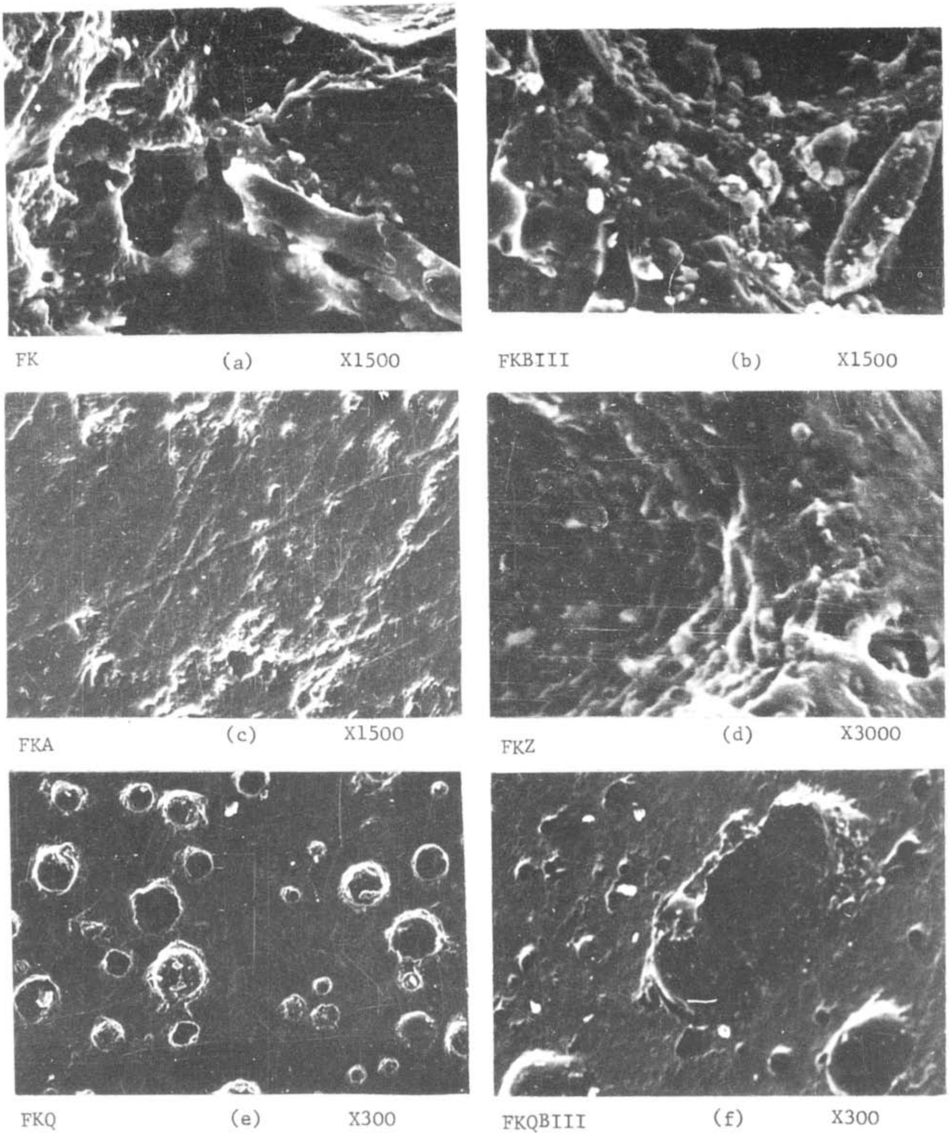

Fig. 6. The scanning electron micrographs for porcelain FK (a), FK containing: $BaCO_3$(b), $Al(OH)_3$ (c), $ZrSiO_4$ (d); and FKQ (e), FKQ containing $BaCO_3$ (f).

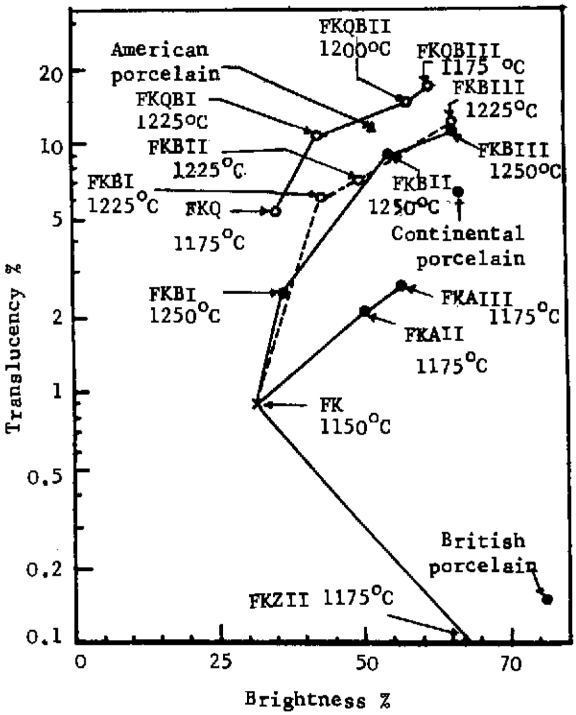

Fig. 7. Translucency % versus brightness % of porcelains FK and FKQ containing: $BaCO_3$, $Al(OH)_3$ and $ZrSiO_4$, in comparison with American (Δ), Continental (•) and British (O) porcelains.

phases, including porosity, their particle sizes, shapes and volume concentration.

2. For high translucency, light should be scattered so that transmission is diffuse and large fraction of the incident light should be transmitted more than reflected with minimum absorption. This was exhibited by $BaCO_3$ inclusion which acted as strong mineralizer resulting more homogeneous grain morphology.
3. The low solubility of $Al(OH)_3$ and fine dissemination of $ZrSiO_4$ in glassy phase yield an environment of improved parameters but still inferior to $BaCO_3$ mineralizer although $ZrSiO_4$ proved its nucleating power.
4. Mineralizers including quartz enlarged the firing range and high concentrations are more effective at low firing temperature.

REFERENECS

Brodbelt, R.H.W., Drien, W.J.B. and Fan, P.L., 1980. Translucency of Dental Porcelain. *J. Dent. Res.* 59(1):70-75.

Danute, K., Maria, K. and Ewa, S., 1972. Effect of Kaolin on the Whiteness of Porcelain. *Steklo i Keram.* 23, V.2:364-367 (Russian).

Dietzel, A., 1969. The Whiteness of Porcelain. *Ber. Deut. Keram. Ges.* 46(9):467-468.

Dinsdale, A. 1960. Translucency of Tableware bodies. *Bull. Am. Ceram. Soc.* 55(11):993-995.

Goodman, G., 1950. Relation of Microstructure to Translucency of Porcelain Bodies, *J. Am. Ceram. Soc.* 33(2):66-72.

Hahn, C. and Teuchert, K., 1980. Importance of the Glass Ceramic System K_2O-Al_2O_3-SiO_2 in Dental Porcelain. *Ber. Deut. Keram. Ges.* 57(9-10):208-214.

Judd, D.B. and Wyszecki, G., 1965. *Color in Business, Science and Industry.* 2nd Ed., John Wiley and Sons Inc.

Lekareva, T.S., Smitievo, L.M. and Kholodok, N.L., 1966. Porcelain of High Whiteness and Translucency on the Basis of Gusev Stone. *Steklo i Keram.* 23(4):27-30 (Russian).

Levin, D.I. and Nikulina, L.N., 1974. Relation Between Whiteness and Translucency of Porcelain. *Steklo i Keram.* (9):31-32 (Russian).

Macadam, D.L., 1981. *Color Measurements Theme and Variation.* Springer, Heidelberg.

Pishch, T.V., Kazachenok, P.S., 1977. Effect of Certain Additives on the Whiteness of Porcelain. *Steklo i Keram.* (8):29-30 (Russian).

Slosarczyk, A., 1983. The Behaviour of Some Polish Silica Raw Materials in the Process of Manufacturing Hard Porcelain. *Sprechsaal* 116(7):578-583.

Southan D.E., Factors Affecting Translucency of Dental Porcelain. *Quintessence Int.* 18(3):197-202.

ANNEX

Tristimulus values x, y and z

The C.I.E. (Commission International d'Eclairage) symbols x, y and z represent fraction of 3 colors. x is a fraction of red, y is a fraction of green and z is a fraction of blue. The tristimulus values x, y and z contain part of the standard spectral value corresponding to reflection of a specimen. They are calculated by multiplying together the numerical values of the reflectance curve with the spectral distribution curve and the values of energy radiation (S_λ) falling on the specimen of definite intervals of wavelength (10 nm) and integrating the results over the whole of the visible spectrum. The following equation is used for x, y and z.

$$Y = \int_{400}^{700} (S_\lambda . R_\lambda . Y_\lambda)$$

where: x, y and z, the tristimulus values,

400-700 nm is the visible spectrum range,

X_λ, Y_λ and Z_λ are the tristimulus values of equal energy spectrum,

S_λ is the energy distribution of the illumination falling on the color at a given wavelength, and

R_λ is the reflectance of the color at a given wavelength.

The products of $S_\lambda . R_\lambda . Y_\lambda$ are calculated for certain standard illuminants and are available in Table DIN 5033 (Judd and Wyszecki, 1965). The standard illuminant used in this work is 'A'.