CERAMICS EFFECT OF DIFFERENT GLAZE-BASE SYSTEMS ON GENERATION OF COLOUR

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ABSTRACT

Three different Glaze-Bases, namely KNaO, CaO-ZnO and CaO Systems, were prepared and fired at their respective maturing temperatures. Two pigments of M.81 ($CaSnSiO_5^{(CR)}$), 5% and R.50 ($ZrSiO_4$), 5% and Copper Oxide, (CuO), colouring oxide 1% were used.

It was found that there is a remarkable influence of Base on the colouration, using these pigments and colouring oxides. The differences of L, a* and b* values of colour hue, chroma, lightness or darkness, were remarkable and interesting. This studies throws more light on the importance of Glaze-Bases and colour effects.*

KEYWORDS: *Colour Tree, Glaze Base, maturing temperature, ceramics, pigments, colouring oxide, L*, a*, b* values*

INTRODUCTION

Definition of Glaze: Glaze is a thin layer composed of the molten silicate mixture, like glass, on a ceramic body and it is nearly homogeneous. Its physical and chemical properties are similar to glass, i.e. insoluble, except in strong acid and strong alkali, or slightly soluble. It is erodable by hydrofluoric acid, impervious to gas and liquid. It is not a chemical compound composed of specific composition like glass, but an intricate mixture.

Glazes with high gloss reflect light strongly. Reflection with matt glazes is low, and there are many glazes with medium reflection. It is not characteristic of glaze for crystal to be found macroscopically, but matt glazes with crystals and crystalline glazes are exceptional.

Seger Formula: Glazes are expressed by the Seger Formula. The essential component in the pottery and porcelain glaze is silica. Silica is an acidic component. Alumina is also one of the important components of almost all glazes; it is a neutral component. In addition to these, more than one alkaline or alkaline earth substances, like soda, potash, lime and zinc oxide, and lead oxide are in frequent use in glaze formulation. The basic ingredients are usually two or more, and sometimes much more. These are integrated into one component expressed as RO or R_2O.

The Seger Formula is as follows:

$RO_1\ R_2O_3\ RO_2$

R_2O

RO

$R_2O\ XAl_2O_3\ YS_1O_2$

The reason why this formula is widely and conveniently used is not only that it shows chemical compositions, but also that it expresses the property of glazes to some extent. Thus Seger Formula can tell roughly the firing temperature (number of Seger cone), and the after-firing appearance: brightness, mattness, transparency, and opacity.

It is important to pay attention to the following points in order to understand the glaze properties from the Seger Formula:

- Basic component, RO, R_2O constituent
- Content of Silica (RO_2 constituent), Y value; that is the amount of Silica to basic components.
- Ratio of Alumina (R_2O_3) to Silica, that is, x/y

Glaze Base and Colour: The colour and shade of any glaze is important in the marketing of ceramic products. In ceramics, pigments and colouring metal oxides are used in getting our desired colour results.

Table-2 shows the three glaze compositions, and their raw materials indicated have been worked out per mass percent, as shown.

The Process of Recognizing Colour: This experiment will not be fully understood without a mention of the process of colour-recognition and the Colour Tree.

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Colour cannot be recognized in darkness. Neither can it be recognized with the eyes closed. An object must be present within the range of sight for its colour to be seen or recognized. The process of our recognizing the colour of an object involves a beam of light from a light source hitting the object and entering the eye. The light stimulates the retina of the eye, which enervates nerves that convey this message to the brain for the sense of colour to form, and thus recognizing the colour of the object. Any colour recognized in this manner is referred to as **the colour of an object**.

As can be seen in Figure-1, the coloured glaze acts like a filter – absorbing some colours and releasing the colour of the filter when light is passed through it. The wavelengths of the incident beam and the scattered reflection indicate the colour to the eye.

Note that if the eye faces a light source, the emanating light-rays directly enter the eye and are recognized as the colour of the light source. Colour that is recognized in this manner is referred to as **light source colour**. The process of colour recognition is illustrated in Figure-1(a), 1(b), 1(c).

The Colour Tree: The next important issue to make the experiment more clear is the mention of Colour Tree developed some years ago in the USA. Colour Tree is a three-dimensional object in which the three attributes of hue, value and chroma are schematically arranged in a prescribed form, which emanates from a colourless axis as the centre.

Figure - 1: Process of Recognising Colour

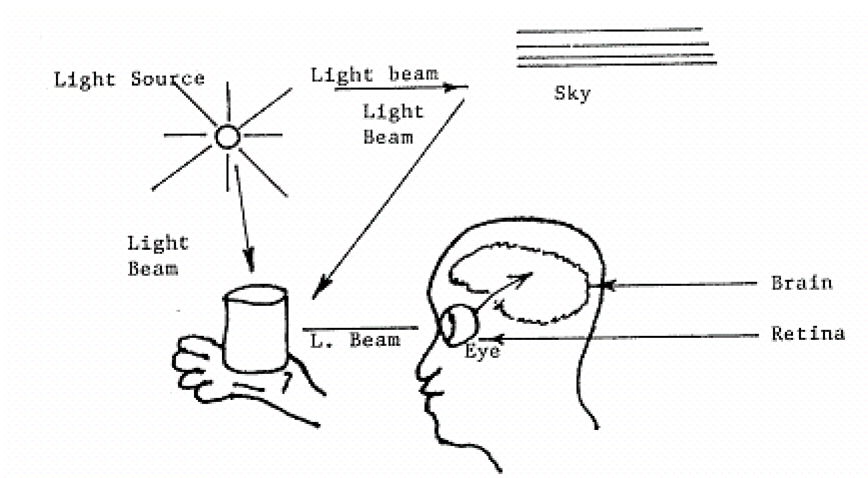

Figure - 1(a): Wavelength and Incedent of Beam

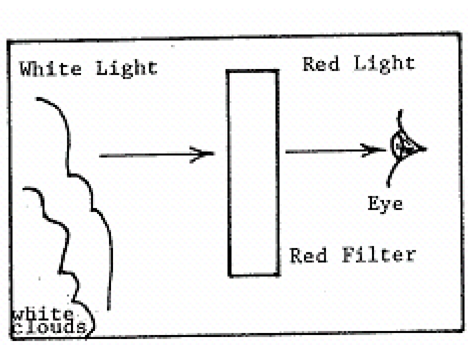

Figure - 1(b): Filter and Action of White-Light

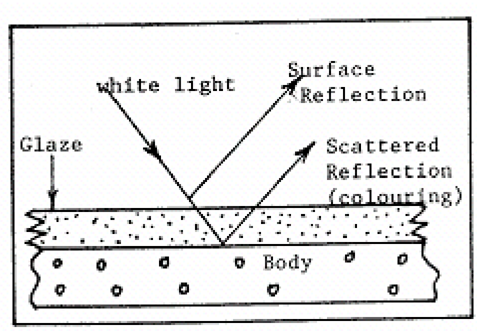

Figure - 1(c): How a Coloured Glaze Acts Like a Filter

The Colour Tree is a cylindrical or sometimes spherical shape, which is a representative form of any single colour. Any single colour is defined by the position of a dot or point on this form, which is recorded in the order of hue, value or chroma, (H.V.C.), and L*, a*, b* values.

L*, a*, b* values are graduated and are very important for this experiment. These L*, a* and b* can be summed up as follows:

+L* 1-100 means more light or colour paleness
-L* 1-100 means more darkness of colour
+a* 0-60 means towards vivid red
-a* 0-60 means towards blue
+b* 0-60 means towards yellow
-b* 0-60 means towards green

All colours belong to these parameters, and their intensity, tone, lightness or darkness depends on their L*, a*, b* values. Minus 100 L value means total darkness and no colour can be recognized.

Procedure

In the present study, two pigments were used, in addition to a colouring oxide. These are M.81 and R.50, and one colouring oxide, CuO. Attempt has been made to find out the effect that the three different base glazes (KNaO system, ZnO-CaO system and CaO system) have on them. The firing temperatures were 950 ^{o}C, 1200 ^{o}C, and 1230 ^{o}C, respectively, and a soaking time of 30, 30 and 60 minutes, respectively.

EXPERIMENTAL PROCEDURE

Materials

Base glaze (Seger Formula)

113 KNaO		
0.472 CaO	0.236 Al_2O_3	1.887 SiO_2 (CaO-ZnO system)
0.415 ZnO		
0.940 KNaO		
0.057 CaO	0.236 Al_2O_3	1.892 SiO_2 (KNaO system)
0.003 ZnO		
0.108 KNaO		
0.889 CaO	0.236 Al_2O_3	1.892 SiO_2 (CaO system)
0.003 ZnO		

X-ray was used to find out the various mineral assemblages of the glazes after firing.

RESULTS AND DISCUSSION

M.81 and KNaO, CaO-ZnO and CaO Systems: As can be noticed from Figure-3, the curves of the graph behave quite differently. At 950^{o}C, in KNaO system, a* value is very high, followed by L* value and then b* value. However, at 1200 ^{o}C, L* value is the highest followed by a* value and then b* value. This is the CaO-ZnO system. At 1230 ^{o}C, in CaO system, a* value rises highest followed by L* and b*.

At 950, the mineral assemblages are Malayaite, 4.0 peak and Feldspar, 3.5. This is partly an unmelted condition of the pigments, and CuO atoms are suspended in the crystals. Thus a* value is high.

Table - 1: Experimental Raw Materials

Pigment	Main Component	Crystalline Structure	Weight (%)
M. 81	$CaSnSiO_5$ (Cr)	Sphene	5
R. 50	$ZrSiO_4$	Zircon	5
Metal Oxide	CuO	-	1

Table - 2: Glaze Preparation (Mass %)

Materials	KNaO System Mass (%)	CaO-ZnO System Mass (%)	CaO System Mass (%)
Feldspar	37.9	-	-
Gaerome Clay	5	6.1	4.9
Sodium Carbonate (Na_2CO_3)	16.1	-	-
Alumina	0.3	5.9	6.2
Potassium Carbonate (K_2CO_3)	20.7	-	-
Silica Sand	-	32.8	33
Limestone	-	18.3	35.6
Zinc Oxide	-	14.8	-
Frit	20	22.6	20.3

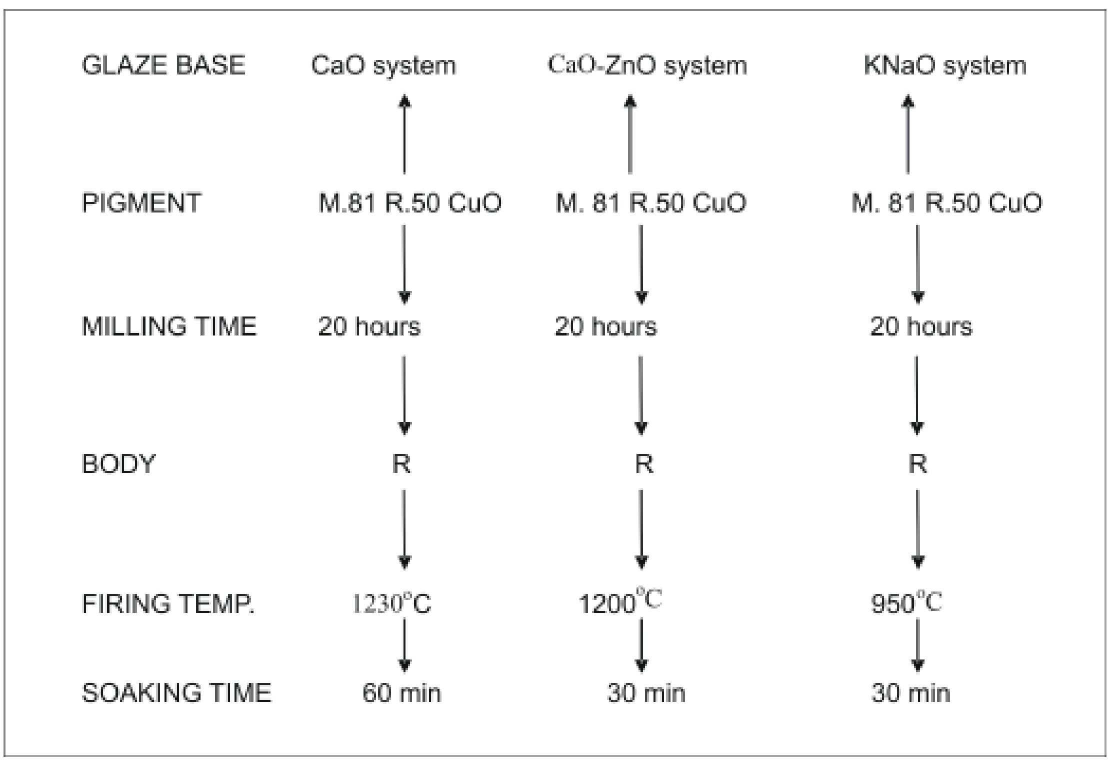

Figure - 2: Schematic Flow of Colouration Test

Table - 3: Average Data of Test

Base glaze	Body	Pigment	DW	CO	SA	GS	CD	MA
CaO-Zno system (1200°C ,30min)	R	M-81	+0.44	L* 72.2 a* 8.0 b* 6.9	-	96.9	0K(0K)	$Cs_{3.0}$
		R-50	+0.49	L* 64.1 a* 19.2 b* 20.2	Pn	84.3	0K(0K)	$Zr_{2.0}$
		Cu0	+0.40	L* 69.2 a* -13.0 b* 10.1	-	94.4	0K(0K)	G
KNa0system (950°C, 30min)	R	M-81	-0.25	L* 56.9 a* 31.4 b* 3.5	roughly Pn,um crazing	14.3	0K(0K)	$Ma_{4.0}$ $Fe_{3.5}$
		R-50	-0.21	L* 62.2 a* 23.2 b* 9.5	roughly Pn,um crazing	18.2	MD(0K)	$Zr_{6.0}$ $Fe_{2.5}$
		Cu0	-0.28	L* 74.6 a* -3.8 b* -7.4	roughly crazing um	7.6	0K(OK)	$Fe_{3.5}$
Ca0 system (1230°C, 60min)	R	M - 81	+0.21	L* 60.0 a* 16.2 b* 9.6	crazing	94.3	0K(0K)	G
		R - 50	+0.23	L* 74.2 a* 2.3 b* 14.2	crazing boss	93.9	OK(MD)	G
		CuO	+0.16	L* 65.8 a* -12.4 b* 8.3	crazing	94.5	0K(0K)	G

DW: Difference of warpage
CO: Colour
SA: Surface appearence
GS: Glossiness
CD: Chemical durability
MA: Mineral assemblages
R: White tile body

DW:+...(mm)
......-....(mm)
SA:Pn.....pin hole
um..............Unmelted

CD:MD........middle damage
OK.........no problem
MA:Cs.........cassiterite (SnO_2)
Zr..........zircon($ZrSiO_4$)
Ma........malayaite($CaSnSiO_5$)
Fe.........feldspar

G.... glass

However, at 1200 °C, in the CaO-ZnO system, the only mineral is Cassiterite (SnO_2) with 3.0 peak value. This is because the Zinc Oxide reacts with the Malayaite, forming the mineral Cassiterite that is Tin Oxide and an opacifier and therefore lowering the colour intensity. At 1230 °C, the CaO system melts and there is no crystal formation but glass. This glasssification decomposes the atomic structure of the colouring agents, making the glaze colour pale or lowering the intensity. However, the interesting thing about the graph is that b* value increases with the increase in temperature, that is, the colour moves towards yellow. The colour of M.81 with KNaO system is deep maroon, with CaO-ZnO, pale maroon and with CaO, the colour is very light maroon, or almost no colour.

R.50 with KNaO, CaO-ZnO, and CaO Systems: Like the M.81, the R.50 behaves interestingly with the three different Base Glazes, as shown in Figure-4. With the KNaO, a* value is the highest followed by L* and then b* value. However, for CaO-ZnO system, the trend of the curve (at 1230 °C) for a* and b* is opposite to that of L*. In this case, a* and b* values decrease, while the L* value increases. Another interesting thing is that the value of a* decreases with increase in temperature. KNaO system at 950 °C, has Zircon 6.0, and Feldspar 2.0 crystals and a* value is the highest. At 1200 °C, which is CaO-ZnO system, there is only a Zircon crystal with peak of 2.0. The CaO system at 1230 °C, has glass and no crystals.

With the KNaO system, the colour of R.50 is “Salmon maroon”, the CaO-ZnO system has a ‘yellow ochre’ colour and the CaO system has a very pale salmon brown/maroon.

CuO with KNaO, CaO-ZnO, and CaO systems: The metal oxide colourant of Copper Oxide (CuO) also revealed an interesting and unique feature – Figure-5. The trend is similar to KNaO and CaO-ZnO at 1200 °C. Their L* and a* values slope downwards. However, b* value moves gently and steadily upwards, in fact, reaching +10.1. Interestingly, all the three systems have negative a* values. This means that the colours are moving towards green.

By adding 1% of CuO, the KNaO system gives Blue colour, CaO-ZnO bluish green and CaO system, green colour. KNaO system had Feldspar mineral at 950 °C. However, CaO-ZnO and CaO systems, at 1200 °C and 1230 °C respectively have no crystal but glass, and therefore negative a* values and some negative b* values at 950 °C. The CaO-ZnO system has an opacified bluish green, i.e. colour not very clear. Temperature did not seem to have had any influence with the CuO colouring oxide.

Glossiness: One of the advantages of the Seger Formulae is that it gives an impression about the state of the glaze before firing (i.e. matt, opaque, etc). In this case, the Alumina to Silica ratio is very important. From the Seger Formulae the experiment revealed that the Alumina to Silica ratio (x/y) of the three Base Glazes of KNaO system, CaO-ZnO system and CaO system is 1:8. This range can give high glossiness to the three Base Glazes. It was also observed that there was high glossiness for the CaO-ZnO system and CaO system. Both systems have much glass formation and glassification, which can be linked with glossiness to some extent. However, the KNaO system has a remarkably low glossiness. In fact, while CaO-ZnO systems have glossiness of over 84%, that of KNaO is under 19%. Perhaps this is due to the fact that the KNaO system did not completely melt, as can be noticed by the mineral assemblages. However, the same system fired to 1000°C and a little beyond did not show any significant difference in the glossiness.

Surface Appearance: There were pinholes, rough surface appearance, and unmelted condition with all the KNaO system (with the three colouring agents). The rough surface may be due to incomplete melting, while the crazing is due to the difference of co-efficient of expansion of the body and that of the glaze, as shown in Figure-6.

There were pinholes with CaO-ZnO system, using R.50 pigment. But, with the other two colourants, there were no problems with their surface appearances.

The CaO system with M.81, R.50 and CuO showed crazing. There was also “boss” on CaO with R.50 and this is illustrated in Figure-7. Table-3 shows the details of glossiness, warpage, colour, chemical durability and mineral assemblages. All the experimental data are summarized in Table-7.

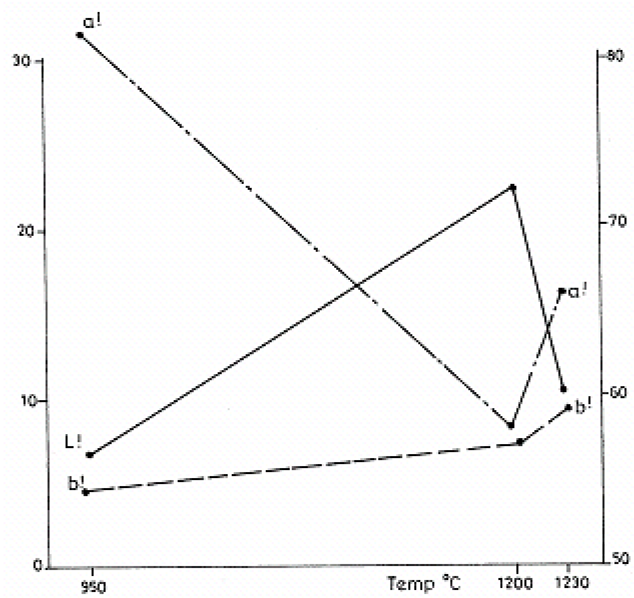

Figure - 3: Graph of Temp/ L*, a*, b* value for M.81 Pigment

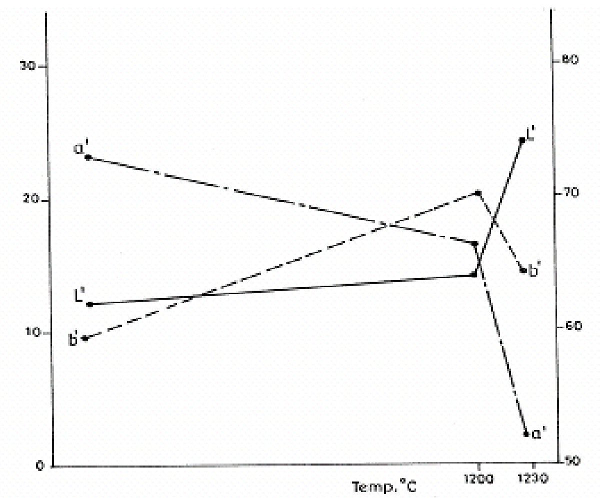

Figure - 4: Graph of Temp/ L*, a*, b* values for R.50 Pigment

Table - 4: L*, a*, b* values for M.81 Pigment

Glaze	Pigment	L'value	a:Value	b: Vlaue	Temp. °C	Mineral Assemblage
KNaO	M.81	56.9	31.4	3.5	950	Malayaite 4.0 Feldspar 3.5
CaO-ZnO	M.81	72.2	8.0	6.9	1200	Cassiterite (Sno2) 3.0
CaO	M.81	60.0	16.2	9.6	1230	Glass

Table - 5: L*, a*, b* values for R.50 Pigment

Glaze	PIGMENT	L'value	a:value	b:value	Temp oC	Mineral Assemblage
KNaO	R.50	62.2	23.2	9.5	950	Zircon 6.0 Feldspar 2.5
CaO-ZnO	R.50	64.1	19.2	20.2	1200	Zircon 2.0
CaO	R.50	74.2	2.3	14.2	1230	Glass

Table - 6: L*, a*, b* values for CuO

GLAZE	COLOUR PIGMENT	'L'. Value	'a' Value	'b' Value	Temp °C	Mineral Assemblage
KNaO	CuO	746	-3.8	-7.4	950	Feldspar
CaO-ZnO	CuO	69.2	-13-1	10.1	1200	Glass
CaO	CuO	65.8	-12.4	8.5	1230	Glass

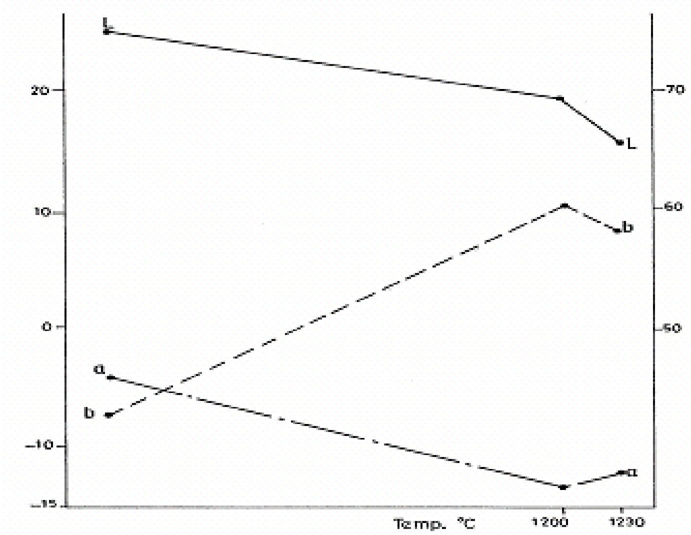

Figure - 5: Graph of Temp/ L*, a*, b* for CuO (Copper Oxide)

SURFACE APPEARANCE CHART

Pinhole: Pinhole prevention: make maturing temperature longer. Also slow cooling is sometimes necessary.

Crazing: difference of co-efficient of expansion between glaze and body.
Prevention: checking the expansion of body and glaze to match.

Rough Surface: This is caused by incomplete melting.
Prevention: probably increasing the temperature (950 – 1050^{o}C)

UNMELT OF GLAZE: This in not a defect

BOSS

Prevention: by constant cleaning of spraying booth.

CONCLUSION

It is a known fact that in the atmosphere, the amount of pigment or colouring oxide, thickness of glaze, type of body, etc, give colour-variations in glazes with colourants. This research work has shown that the composition of a Base Glaze plays a very important role in the resultant colours and their shades (i.e. L*, a*, b* values).

It is imperative therefore to consider the relationship between Base Glazes and colour effect when designing coloured glazed products in Ceramics Industry.

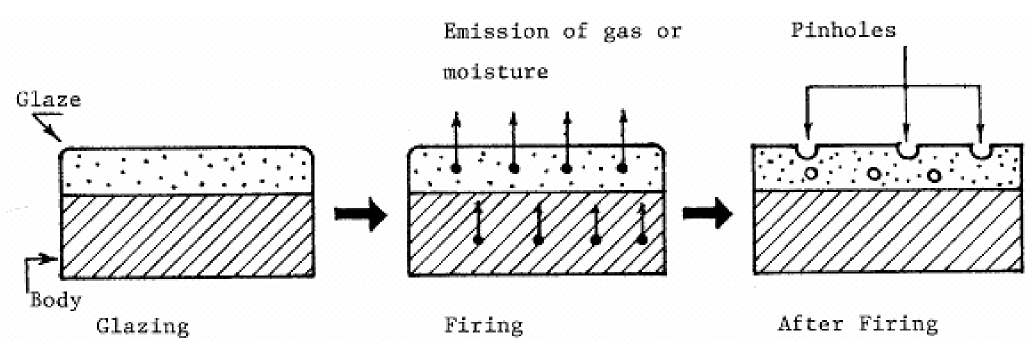

Figure - 6: Formation of Pinhole

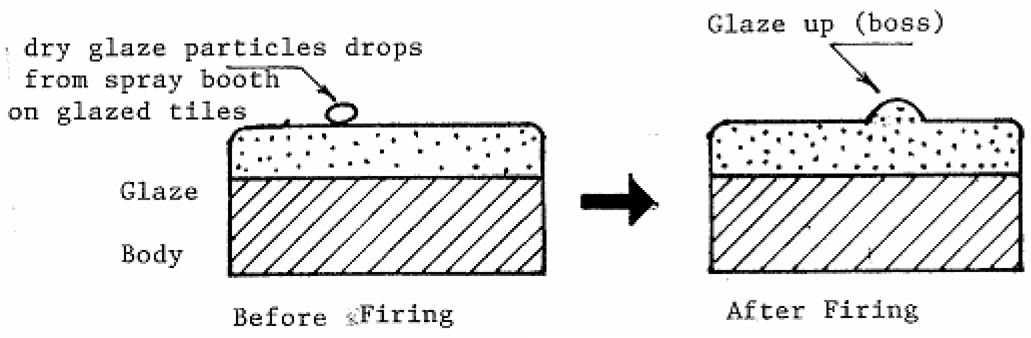

Figure - 7: Formation of Boss

Table - 8: Summary of Experimental Results

M.81 PIGMENT – 5%							
Glaze	**Temp(°C)**	**Mineral Assemblage**	**Glossness**	**Surface Appearance**	**L***	**a***	**b***
KNaO	950	Malayaite 4.0	14.3	Rough UM Pinholes CR	56.9	31.4	3.5
CaO-ZnO	1200	Cassiterite (SnO_2) 3.0	96.9	O.K	72.2	8	9.6
CaO	1230	Glass	94.5	CR	60	16.2	9.6

R.50 PIGMENT – 5%							
Glaze	**Temp(°C)**	**Mineral Assemblage**	**Glossness**	**Surface Appearance**	**L***	**a***	**b***
KNaO	950	Zircon 6.0 Feldspar 2.5	18.2	Rough UM Pinholes CR	62.2	23.2	9.5
CaO-ZnO	1200	Zircon	84.3	Pinholes	64.1	19.2	20.2
CaO	1230	Glass	93.9	CR. Boss	74.2	2.3	14.2

Glaze	Temp(°C)	Mineral Assemblage	Glossness	Surface Appearance	L*	a*	b*
KNaO	950	Feldspar 2.5	18.2	Rough UM Pinholes CR	74.6	-3.8	-7.4
CaO-ZnO	1200	Glass	94.4	O.K.	69.2	-13.1	10.1
CaO	1230	Glass	94.5	CR	65.5	-12.4	8.5

Glaze	Temp(°C)	Firing Time (mins)
KNaO	950	30
CaO-ZnO	1200	30
CaO	1230	60

CR - Crazing
UM - Unmelt

RECOMMENDATIONS

- Using different glaze-base systems, very interesting colour-ranges could be obtained.
- The Colour Tree is a reliable source for colour in ceramic systems; therefore it is an important guide for the Ceramists and the Ceramics Industry.
- For a particular type of colour that is needed, one must pick a point within demarcation of the Colour Tree, which is a percentage (%).
- Colours must always be picked to match the environment where, for example, ceramic tiles would be mounted.
- In using the Colour Tree in Ceramics, colour stability at elevated temperatures must be observed critically, because the number of stable colours diminishes with increasing temperature.
- For repetitive use, especially in mass production, the Colour Tree is the best option.

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