Leadless glazes for redware

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Abstract

Low fired red ware with high iron content is the most common clay species in Finland. Traditionally red ware have been glazed using lead glazes. Because of high iron content in clay surface alkaline and boron glazes have caused blue lilac colour effects and also disturbing milky coloured effect as white crystals have been formed in cover of the glaze surface. The using of low-solubility lead glazes have been a better selection than alkali boron glazes. In this research have been developed leadless glazes using calcium borate-compounds together with other typical glaze minerals as kaolin, feldspar and whiting. Testing results are giving surfaces with high the translucency and glossy in the low fired temperature 1020°C. There is good ecological point to start the new millennium using none of the lead raw materials. There should not been used any more lead oxide in the ceramic field. The use of local materials and low energy firing methods with leadless glazes will increase the ecological design with both the cultural and traditional purpose.

Introduction

The use of lead gazes has behind it a long history of development in the manufacturing of ceramics in different parts of the world. The use of lead glazes has continuously been controlled and specified [1]. Lead content raw materials for glazes are still used in the manufacturing of ceramic products, because of the high glossiness and low viscosity it is difficult to obtain by leadless raw materials. Although the drawbacks of lead glazes are realised, the colours of the low solubility lead glazes have had a great esthetical impact on the production of ceramics [2]. The awareness and responsibility of the mankind for the environment as a total process makes it necessary to move towards the use of leadless glazes. Ecological and esthetical demands have in addition made it necessary to approve the use of leadless glazes [3].

The aim of the investigation is to develop mixtures of leadless raw materials, which melt to glossy and transparent glazes on the iron-containing (9 %) red ware. The glaze should melt at a temperature of 1020°C, when the colour of the clay is red brown. The thickness and burning temperature of the glaze layer should be considered for, according to the quality of the clays with greater care than when using raw materials containing lead. When raw materials for the leadless glazes are selected different colour alternatives are considered for in addition to the transparency. The utility of leadless glazes and the alternatives of colours on different engobes produce a new world of colours.

Glaze materials and testing

Frits produced by Potterycrafts from England were chosen. In the samples the same amount (72 %) of two boron frits, P2953 and P2954, and two alkaline frits, P2961 and P2962. In the mixtures earth alkalis, chalk and strontium carbonate, were tested as complements for each other. Both alkaline earth metals were tested in all mixtures and the viscosity were tested at an angle of 45° at a temperature of 1020 °C. Potash feldspar FFF from Kemiö containing 8% of K_2O was used. All the glass forming material was obtained from the frit, feldspar and china clay, without the addition of any pure quartz; the glaze mixtures were named as L-series and are given in Table 1. The glaze L2 was tested using other amount of raw materials in glaze L2.1 and L2.2.

Table 1. Leadless glaze compositions L1, L2, L2.1, L2.2, L3 and L4.

Raw-material	**L1**	**L2**	L2.1	L2.2	**L3**	**L4**
Borax frit (P2953)*	**72**	-	-	-	-	-
Borax frit (P2954)*	-	**72**	71	71	-	-
Alkali frit (P2961)*	-	-	-	-	**72**	-
Alkali frit (P2962)*	-	-	-	-	-	**72**
Whiting / Strontium carbonate	3	3	2	2	3	3
China clay**	10	10	8	6	10	10
Potash feldspar ***	15	15	19	22	15	15

*Potterycrafts frit, **Standard Porcelain, ECCI, ***Feldspar FFF (K8), SP Minerals

The glaze mixtures were tested over the red earthenware clay (Fe_2O_3 9w-%), which has a total shrinkage of 16% when fired at 1020 °C. The glaze ware tested over two testing tiles, when one third of the tile ware covered with white engobe including the same weight percent of china clay Standard porcelain and ball clay Hyplas 71, both from ECCI. Tiles were fired in an oxidation atmosphere in the electric kiln using the following firing temperature program; step 1: 80°C/h to 250°C, step 2: 100°C/h to 600°C, step 3: 100°C/h -> T3 1020°C and then soaking for 5 minutes at that temperature before cooling.

Table 2. Colour metal oxides used in glaze testing

Colour oxide	A	B	C	D
SnO_2	4	8	12	16
TiO_2	2	5	8	10
MnO_2	2	4	6	8
CuO	2	4	6	8
CoO	1	2,5	4	7
Cr_2O_3	1	2	3	4
Fe_2O_3	2	5	8	11

Table 3. Engobes

Raw material	White engobe	Pink engobe
China clay*	45%	40%
Ball clay**	45%	40
Borax frit P2953	10%	10
Soapstone***	-	10

* Standard porcelain

**Hyplas 71

***Clacined stone powder, high iron content

Coloured glazes and engobes.

The colour metal oxides were mixed into the glazes given in Table 1. For each colour metal oxide colour tones were tested separately (Table 2). The coloured glazes were tested separately both on a white and pink engobe. The white and pink engobe were in addition coloured green by copper (II)-oxide (CuO 5%, 10% and 15%) and blue by cobalt (II) -oxide (2%, 5% and 10%).

Results

The empirical formula (molar ratios) of the glaze is given in Table 4. After firing the test pieces melted and showed a glossy surface. From the fired samples is seen that chalk is more suitable than strontium carbonate as a raw material for leadless glazes at low temperatures below 1000 °C. In the glazes [4] SrO caused the formation of a non-transparent and opaque surface. When the results of the firing are compared to the empirical formula the composition of the glaze L2 seems to give the best result when placed on the red ware. It gives surface effects with high translucency and low viscosity together with other good results.

Table 4: Empirical formulas of the leadless glazes (Table 1) and ratio Al_2O_3 and SiO_2.

Oxide	L1	**L2**	L2.1	L2.2	L3	L4
*BaO	-	-	-	-	-	.091
*CaO	.555	**.935**	.919	.912	.518	.165
*Ka_2O	.101	**.035**	.043	.046	.056	.215
*Na_2O	.342	**.028**	.037	.040	.424	.528
*Fe_2O_3	.001	**.001**	.001	.001	.002	.001
B_2O_3	.716	**1.285**	1.294	1.284	.706	.091
Al_2O_3	.597	**.238**	.242	.230	.869	.227
SiO_2	2.328	**1.140**	1.231	1.239	2.990	2.019
Ratio	3.899	**4.788**	5.099	5.379	3.440	8.905

*RO-group

Glaze surfaces on low fired red ware with high shrinkage show the following results: L1 is opaque but has no cracking effect. L2 gives an excellent result, no cracking and low viscosity even compared with lead glaze of low solubility [5]. L3 is opaque and small bubbles are seen on the white engobe surface. There is a high amount of aluminium oxide (0.869) in glaze L3. In glaze L3 bubbles are seen and it is weakly opaque and low amount of cracking occur. A thicker layer gave a more opaque performance.

Table 5: The results of the colored glaze experiments used in the interpretation of the fired results of the colored glazes.

	A	B	C	D
SnO_2	LW	LW	W	W
TiO_2	*no*	*color*	*effect*	
MnO_2	LR	LR	LBr	Br
CuO	LT	T	T	DT
CoO	LB	B	DB	DB
Cr_2O_3	G	DG	DG	DG
Fe_2O_3	LC	C	Y	DY

R=rose Br=brown T=turquoise B=blue G=green C=cream Y=yellow

Results for the experiments with coloured glazes.

In Table 5 is given the image of the coloured glazes after firing. By coloured metal oxides a rich palette of different colour tones were obtained. Tin oxide (SnO_2) gave an opaque coating and matt surface. Iron oxide (Fe_2O_3) gives a brown to red colour and cobalt oxide (CoO) gives a blue colour. Copper oxide changes to blue-green in a leadless glaze-mixture. The colour reactions of chromium oxide are strong and already an amount of 2 % gives a covering and deep green colour. The colour of manganese oxide is from red to brown.

The coloured engobes and their reactions with coloured glazes.

The combination of engobes and coloured metal oxides gives a lot of beautiful blue and green tones. An iron oxide glaze on an engobe coloured with copper oxide and cobalt oxide gave coloured tones, which replace beautiful tones obtained by lead glazes. The use of soapstone in pink engobes softened the tones into a more brown tone.

Conclusion

The leadless glaze named L2 fulfils the requirements of the glaze. There are no cracks when applied as a thin layer on the iron containing red ware. The glaze is transparent when melting, without white or bluish side color effects, which is often called the milky effect. The milky effect is easily developed with different boron silicate frits on the red ware due to the high iron concentration of the clay and due to the content of sodium borate in the frits. The sodium borate containing frits increase the white milky image, which apparently is due to the formation of small crystals [4, 5]. Calcium oxide (CaO) as the calcium borate frit seems to be the best fluxing raw material, which has a good eutectic relation to other chosen materials in glaze compositions. The firing temperature for the testing glaze L2, which contained a red clay with high iron content, were as low as 1020°C and some of the tested glazes gave good results at temperature close to 1100°C. The empirical formula of glazes L2.1 and L2.2 indicate possibilities for good results on other types of the red clay surfaces. If it possible to fire red clay at higher temperatures, when even strontium carbonate with a high viscosity will be suitable as a raw material for leadless glazes.

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