LEAD RELEASE BY EARTHENWARE GLAZES CONTAINING COLORING ENGOBES

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Lead glazes, which melt at 1020-50^{o}C, have been investigated together with different engobes. Two different kind lead frits have been used as starting materials for lead oxides in the glazes. The glazes have been tested according to ISO 64886/1-1981 test methods. The results indicate that these lead glazes have a low lead release according to EEC directive 84/500.
The low lead release glazes are tested over the different engobe compositions melted with borax frits or lead frits or when 5 % copper oxide has been added.
Tests show an increasing amount of lead release. From the results can be concluded that lead solubility is not stable if you use glazes to cover the engobe decoration. The different engobe compositions with lead or borax frits cause the lead release on the surface of lead glazes.

1. INTRODUCTION

From the point of view of the Finnish ceramic-culture the natural clay which turns red at 1000^{o}C is of importance. It is the only natural clay found in Finland, which can be used as such in the brick and ceramic industry. The color of the clay, which is used in the present investigation, has the strongest red tone in the sintering point fired at 1020-1050^{o}C. Finnish Earthenware clay: Kultela Brick factory, chemical analyze SiO_2 50 %, Al_2O_3 17.1 %, Fe_2O_3 9.0 %, CaO 1.5 %, MgO 3.3 %, K_2O 4.2 %, Na_2O 2.0 %, C3.7 %, L.O.I.9.2%.
The color of the terra-cotta clay changes according to the application of alkali or lead glazes. The low fired temperature and the red-brown clay, rich in iron (9%), reduces the choices of glaze raw-materials. It has been tested that the most suitable coloring effect from iron oxide is giving by lead bearing glazes fired at 1000-1040^{o}C. The low soluble lead bearing glazes have been selected to research instead of alkali glazes or combinations of these two. One important reason of the investigation of lead bearing glazes is that they are known to pick up the strong color with different metal oxides as an application over terra-cotta clay. The lead glazes have been favored by the Chinese masters during Tang-dynasty, the ceramic artists of majolica in Italy and the Scandinavian masters during the 17.th and18.th centuries, in order to obtain the yellow of iron(III)oxide, the blue of cobalt oxide and the green of copper oxide, which was copper(II)oxide.

1.1. Aims of the present work

The investigation is concerned with the changes in the solubility of the lead glazes and as an application with the colored engobes.
- Is there the increasing effect of the solubility between two different lead frits?
- How the application of the engobe will change the release of low lead glazes?
- What kind of changes will occur to the application of colored engobes and commercial transparent glazes with the low solubility?
- The technical effects during the firing time and the control of glaze layer increasing release of lead are kept constant in this research.

2. EXPERIMENTAL

2.1. Materials

It will be used as a starting material the lead borosilicate glaze (AB30) developed during an earlier work (Hortling 1992). The glaze AB30 is tested by method of International Standard (ISO 6486/1-1981 (E). The release of lead is 0.83mg/l in firing temperature 960^{o}C and in temperature1000^{o}C release lowers to 0.65mg/l. The permissible limit of release of lead is 4mg/l used test pieces as small hollow ware according to directive 84/500/EEC (European Economical Community).

Empiric Formula of Lead glaze AB30 (Ref 1)
Firing temperature Sc.07a-05a (960-1000^{o}C)

0.148 K_2O		
0.080 Na_2O		
0.255 CaO	0.321 Al_2O_3	2.522 SiO_2
0.473 PbO		0.185 B_2O_3
0.041 ZnO		

2.1.1 Frits

In the AB30-glaze lead monosilicate was used as a frit. The lead release from the glaze also affects the selection of the frit. PbO is released from the lead compounds in proportion to its own amount and the amount of other oxides in the compound.

Table I: Solubility of Lead oxide from Lead Frits (Ref.2)

Lead Frit Formula	PbO (Wt%)	Solubility of PbO (Wt%)
1,00 PbO. 1,00 SiO_2	78,8	22,8
1,00 PbO. 2,00 SiO_2	65,01	4,59
1,00 PbO. 0,254 Al_2O_3.1,91 SiO_2	61,35	0,7

According to the English law all commercial lead frits are low solubility frits having a lead solubility of less than 5 %.conformed to the requirements of the Ministry of Education Memorandum 517. The commercial lead frit compositions shown in table II are used in lead bearing glazes in table III. In the lead bisilicate P2950 is the amount 64.9 (Wt%) PbO.

Table II: Compositions of Commercial Lead Frits by Pottery crafts Ltd (Ref3)

Lead Frit	Formula	Firing range ^{o}C
Lead Bisilicate P2950	1,00 PbO.0,086 Al_2O_3.1,86SiO_2	900-1100
Lead Sesquisilicate P2951	1,00 PbO.0,125 TiO_2.1,54 SiO_2	880-1080

Table III: Lead bearing Glaze Series A33 A34, A35, and Series A331, A341, A351

Raw material	A33	A34	A35	A331	A341	A351
Lead bisilicate P2950	67	70	74	-	-	-
Lead sesquisilicate P2951	-	-	-	67	70	74
Feldspar FFF[1)]	17	20	20	17	20	20
Lime	5	4	4	5	4	4
Zinc oxide	1	2	2	1	2	2
China Clay[2)]	3	2	-	3	2	-
Quartz[1)]	7	2	-	7	2	-

1) Finnish Raw materials: Flotation Feldspar and Quartz
2) ECC (English China Clay): Standard Porcelain Clay

2.1.2. Lead Glazes

The low release lead glazes in table III were developed after borosilicate lead glaze AB30 taking into consideration the ratio of aluminum oxide and silica oxide (0,321Al_2O_3-2,522 SiO_2).The aluminum-silica ratio is important for the melting of PbO in a glaze. Because the alkalis and boron oxide increase the release of lead even when small amounts are used. The lead frits, P2950 and P2951, were chosen to melt lead glazes in new research for two reasons: Lead release and to avoid the lilac coloring effect with iron oxide and alkalis together on terra-cotta clay. Two series of test glazes were planned. The lead bisilicate P2950 was used in the glazes A33-35 and the sesquisilicate P2951 was used in the glazes A331, A341 and A351.
To the test glazes Stellmittel-liquid (Schimmer & Schwarz product) 0,5 - 1,0 % was added in order to hinder the sedimentation and to get an even glaze layer.

2.1.3. Commercial lead glazes from Pottery crafts Ltd England

It was decided to empirically test lead glazes with low lead releases P2001 and P2002, the formulas are not available. The small hollow test wares were glazed as above and were also tested with application of engobes in the table. The tested commercial glazes were:

Transparent Glaze P2001 with low solubility temperature range 850 - 960^{o}C
Super gloss suitable for Raku (Ref. 3)

Transparent Glaze P2002 wit low solubility temperature range 960 - 1020^{o}C.
A high-gloss glaze is suitable for application over white and red firing earthenware (Ref 3).

2.1.4. Engobes

To the engobe was added, in addition to the clay material, the soft borax frit P2964 and the lead bisilicate P2950, table IV. The function of the frit is to help the clay particles in the engobe to adhere to the mass and also to adhere to the glaze above. To our knowledge there was no information about how the composition of the engobe affects the changes of the solubility of the lead glaze placed above the engobe.

The corresponding behaviour of the commercial glazes is also investigated in order to find out how the solubility of a low release lead glaze is changed if an artist decorates her product with an engobe and chooses a glaze which behaves according to the English legislation.

Table IV: Engobe Compositions A, B, C, D and E

Raw material	A	B	C	D	E
Finnish earthenware	50	50	15	50	50
Ball clay[1)]	40	40	80	40	40
Soft borax frit P2964[2)]	10	-	-	10	-
Lead frit P2950[2)]	-	10	-	-	10
Copper oxide	-	-	5	5	5
Cobalt oxide	-	-	1	-	-

1) ECC: Hyplas 64
2) Pottery crafts Ltd

2.2. Test pieces and method

Test bowls jiggered from Finnish natural clay have a volume of 2dl. Two as identical test pieces as possible have been prepared from each glaze. The test bowl is burned in an oxidizing atmosphere in a 110l electrical furnace in three layers at an end temperature of 1020^{o}C at which the bowl is kept for 15 minutes. The accuracy of the temperature is 20 – 40^{o}C.

The lead release is determined according to the method of ISO Standard 6486/1(E) 1981 and to EEC directive 84/500 with permissible limit of release of lead 4.0 mg/l the small hollow wares. Two determinations were performed for each sample and the average values are given in the table VI. The permissible limits of values are after.

3. RESULTS AND DISCUSSION

For low lead release glazes the effect of the composition of two different frits is investigated. For the special interest was the effect of the content of lead- or boron frits in the engobe in relation to the measured lead release. When the lead frit is replaced by a lead sesquisilicate frit the amount of lead oxide is changed in the glaze.

From the empirical formula it is possible to decide, what it is the fraction of PbO in the RO-group. The ratio of Al_2O_3- SiO_2 decides the bonding and release of PbO, table V. For the commercial glazes empiric formula are not used.

Table V: Empiric formulas of the Lead Glazes

Glaze	PbO	K_2O	Na_2O	CaO	ZnO	Al_2O_3	SiO_2	TiO_2
A33	0.679	0.051	0.045	0.181	0.043	0.201	2.426	-
A331	0.636	0.045	0.040	0.160	0.038	0.126	2.011	0.079
A34	0.672	0.056	0.050	0.140	0.081	0.198	2.164	-
A341	0.630	0.50	0.045	0.124	0.072	0.125	1.781	0.079
A35	0.685	0.053	0.049	0.135	0.078	0.171	1.999	-
A351	0.631	0.49	0.045	0.124	0.072	0.104	1.639	0.07

Table VI: The Release of Lead in the Lead Glazes with Coloring Engobes

Engobe[1)]	Lead release of different glazes[2)]			
	A33	A331	A34	A341
Lead glaze	(0.27)[3)]	(0.32)	(0.39)	(0.58)
A. Borax frit P2964 10%	0.39	0.36	0.68	0.93
B Lead frit P295 0 10%	0.30	0.47	0.65	0.77
C CuO 5%	6.6	9.1	11	8.80
D CuO 5% +Borax frit P2964 10%	0.41	0.51	0.58	0.97

1) The engobes are described in table IV
2) The lead solubility is determined according standard ISO 6486/2-1981 (E)
3) In the parentheses are given the lead solubility of the pure glazes.

Table VII: The Release of Lead in the Lead Glazes A35 and A351 and in the Commercial Glazes with Coloring Engobes.

Engobe[1]	Lead solubility of different glazes[2]			
	A35	A351	P2001	P2002
Lead glaze	(0.59)[3]	(0.70)	(0.36)	(0.26)
A Soft Borax fr.P2964 10%	0.79	1.00	-	-
B Lead frit P2950 10%	0.62	0.64	-	-
C CuO 5%	12	12	5.0	22
D CuO 5% +Borax frit P2964 10%	0.98	1.10	3.9	23
E CuO 5% +Lead frit P2950 10%	-	-	5.3	38

1) The engobes are described in table IV
2) The lead solubility is determined according standard ISO 6486/2-1981 (E)
3) In the parentheses are given the lead solubility of the pure glazes.

According to an earlier investigation the lead release of a lead glaze decreases if PbO is bonded and reacts with SiO_2.

Differences in the parallel determinations are rather low (relative deviation 0.6 - 20 %) and this deviation depends mostly on the inaccuracy (20 - 40^{o}C) of the exact firing temperature.

4. CONCLUSION

According to an earlier investigation the lead release from a lead glaze decreases if PbO is bonded to and reacts with SiO_2. The process occurred better if aluminum oxide or calcium oxide were not used to a large extent. Calcium oxide affects distinctly the increase in viscosity and weakens the formation of lead silicate, which is a prerequisite for a low lead release.

The lead release is changed as a function of the composition of the under laying engobe

The release is considerably increased with the addition of CuO alone

The release is increased by using the boron frit in the engobe to a greater extent than the lead frit

The sesquisilicate increases the lead release more than the bisilicate when they are used in the same amount.

In the engobe to which CuO has been added the boron frit affects the lead release less than the lead frit.

The increase of the lead release of the lower temperature commercial glazes is considerably lower than the higher temperature commercial glazes.

During the testing conditions with the engobes the commercial glazes do not fulfill the release values of the ISO standard.

The engobe D has the lowest lead release, compared to the engobes A, B, C and E, when used together with the investigated lead glazes. The commercial lead glazes are not accounted for.

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