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SOME LEADLESS BOROSILICATE GLAZES
MATURING AT ABOUT 1100° C

BY

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I. OBJECT OF THE INVESTIGATION

The glazes used on white-ware are composed of borosilicates of the alkalies, lime, lead, and alumina, which are applied to a body previously fired to the desired maturing point approaching vitrification more or less closely. The same type of glaze is also employed with American porcelain and the English bone china as distinguished from the Austrian, French, and German products where, because of the low biscuit and high glost firing temperatures, it is possible to use leadless glazes. The use of the latter type is feasible only when temperatures above cone 8 (approximately 1170° C) are involved. In the production of American and English tableware it is essential, therefore, that the maturing point of the glazes be considerably below the vitrification temperature of the body (about cone 3, approximately 1100° C) in

order to avoid undue softening of the body and consequent deformation and loss. To accomplish this purpose such low-fusing glasses as borosilicates containing lead oxide are necessarily employed. At the same time the long temperature range, brilliancy, and low viscosity of the lead glazes are desirable qualifications.

The use of lead oxide, commonly introduced as the carbonate, has given rise to a wide-spread agitation concerning the poisonous nature of the compound and its deleterious influence upon the health of the workmen under conditions permitting careless operation and neglect of ordinary sanitary precautions. A study of American white-ware potteries shows, however, that such conditions as have been described as existing in European works do not prevail and that in reality the ill effects due to plumbism are very slight in extent. It can not be denied that there is a potential danger, but the enforcement of rules concerning ordinary cleanliness and ventilation suffices to prevent lead poisoning.

Two alternatives which have been suggested in regard to the employment of lead glazes are, the preliminary fusion of the lead oxide with silica, borax, boric acid, feldspar and whiting to form a practically insoluble plumbiferous borosilicate glass (frit) which when ground together with kaolin and additional flint forms the desired glaze, and secondly the complete elimination of the objectionable lead.

The first offers a fairly satisfactory solution of the problem, but introduces difficulties in the application of the glaze on the ware. With our present knowledge of flocculating and deflocculating reagents this plan should offer no insurmountable obstacle. The second alternative is not sufficiently justified at the present time.

Chiefly on account of the poisonous nature of the lead compounds used in making the usual type of white-ware glaze, the subject of leadless glazes has aroused the interest and has received the serious attention of both technical ceramists and manufacturers for many years. As has been set forth, white-ware and china glazes, made with lead compounds, either fritted in or added raw, may be used under proper conditions and by observing

suitable precautions, without any danger to the health of the operatives.

On the other hand, wherever leadless glazes can be developed and used, such precautions, which in themselves increase the cost of manufacture, do not have to be taken and every element of risk is thus eliminated to the mutual advantage of both employer and employee. Also while lacking some of the valuable characteristics and qualities of lead glazes, it can be shown that leadless glazes have a few distinct advantages of their own.

The question, therefore, of lead glazes vs. leadless glazes for china or white-ware becomes one of purely technical and practical interest involving the factors of working properties, quality of finished product, and cost. It becomes then the purpose of the present work to investigate the merits of the various types of leadless glaze thus far reported, to study their properties and possibilities, to improve them if possible, and to make a general comparison from a technical standpoint, between lead and leadless glazes for white-ware and china at a glaze heat of Seger cone 3 (about 1100° C to 1120° C in a 24-hour burn).

II. DESCRIPTION OF THE WORK

1. REQUIREMENTS TO BE MET

A leadless glaze that can be considered at all practical must meet the following requirements:

(a) When suitably prepared and handled it must work equally as well as a lead glaze in the dipping room.

(b) It must have a sufficiently long heat range for all practical purposes in firing and flow over minor defects well enough so that the per cent of "seconds" does not run appreciably higher than in the case of lead glazes.

(c) It must permit the use of as wide a range of both under-glazes and on-glaze colors as do lead glazes.

(d) It must produce a finished piece of ware of at least equally pleasing appearance and equally as durable as that produced by the use of lead.

(e) The cost of the glazing operation as a whole, including all losses chargeable to the glaze, must not exceed that for lead glazes.

2. OUTLINE OF THE INVESTIGATION

There have been practically no further contributions of importance to our knowledge of leadless glazes from a technical standpoint since Seger¹ published his valuable researches on the subject.

Seeger's work and the general rules for leadless glazes which he deduced were, therefore, closely followed in outlining the work. This information, together with a general knowledge of what this type of glaze should be, made only a short series of glazes necessary, as it was not the writer's purpose to try to lay down the limits of composition of these glazes, but to develop the best leadless glazes possible. The first series outlined was for the purpose of determining the best type formula and the suitability of the RO fluxes selected. The second series was designed to further improve the best glaze developed in the first series. All glazes were tested over six standard underglaze colors of known composition, and all properties were studied in comparison with a standard lead white-ware or china glaze used over a half of each trial piece, the other half being dipped in the leadless test glaze.

Series No. I².35 Al₂O₃ GROUP

Glaze B1		Frit	
.25 K ₂ O	$\left. \begin{array}{l} .05 \text{ Na}_2\text{O} \\ .50 \text{ CaO} \\ .10 \text{ BaO} \\ .05 \text{ MgO} \\ .05 \text{ SrO} \end{array} \right\} .35 \text{ Al}_2\text{O}_3 \left\{ \begin{array}{l} 3.1 \text{ SiO}_2 \\ 0.125 \text{ B}_2\text{O}_3 \end{array} \right.$	.1875 K ₂ O	$\left. \begin{array}{l} .0625 \text{ Na}_2\text{O} \\ .5000 \text{ CaO} \\ .1250 \text{ BaO} \\ .0625 \text{ MgO} \\ .0625 \text{ SrO} \end{array} \right\} .1875 \text{ Al}_2\text{O}_3 \left\{ \begin{array}{l} 2.535 \text{ SiO}_2 \\ .1565 \text{ B}_2\text{O}_3 \end{array} \right.$
.05 Na ₂ O		.0625 Na ₂ O	
.50 CaO		.5000 CaO	
.10 BaO		.1250 BaO	
.05 MgO		.0625 MgO	
.05 SrO		.0625 SrO	
		.8 equiv. of frit used. Comb. wt. 259.7	

¹ Leadless Glazes, H. A. Seger, Collected Works, vol. i, p. 453.

² The chemical formulæ are of an empirical nature and are used for the systematic presentation of the glaze compositions. It would be difficult to compare glazes or glasses if only their percentage composition were known. The computation of the formula has for its object the arrangement of the oxides into three groups. These are: Bases of the R₂O and RO type which always add up to unity; the sesqui oxides, R₂O₃; and the acids RO₂. This artifice makes possible the comparison of glazes with reference to acidity, fusibility, translucency, brilliancy, resistance to reagents, crazing, etc.

The formula is calculated from the composition, expressed in parts by weight, by dividing the molecular weight of each substance into its quantity and adding the quotients representing the R₂O and RO oxides. Each quotient is then divided by this sum. By arranging the values obtained in the three groups, the desired empirical formula results.

As an aid in the classification of glazes the acidity or oxygen ratio (O. R.) is frequently used. By this is meant the ratio of the atomic oxygen equivalent in the silica to that of the bases. Thus the oxygen ratio of the formula RO.₂Al₂O₃.₃SiO₂ is $6 \div 1.6 = 3.75$.

.35 Al₂O₃ GROUP—Continued

Glaze B2		Frit
.25 K ₂ O	.35 Al ₂ O ₃ { 3.1 SiO ₂ 0.35 B ₂ O ₃	.1875 K ₂ O
.05 Na ₂ O		.0625 Na ₂ O
.50 CaO		.5000 CaO
.10 BaO		.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO
		.8 equiv. of frit used. Comb. wt. 299.8

Glaze B3		Frit
.25 K ₂ O	.35 Al ₂ O ₃ { 3.1 SiO ₂ 0.5 B ₂ O ₃	.1875 K ₂ O
.05 Na ₂ O		.0625 Na ₂ O
.50 CaO		.5000 CaO
.10 BaO		.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO
		.8 equiv. of frit used. Comb. wt. 312.9

.40 Al₂O₃ GROUP

Glaze C1		Frit
.30 K ₂ O	.40 Al ₂ O ₃ { 3.25 SiO ₂ 0.35 B ₂ O ₃	.2500 K ₂ O
.50 CaO		.5000 CaO
.10 BaO		.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO
		.8 equiv. of frit used. Comb. wt. 319.4

Glaze C2		Frit
.30 K ₂ O	.40 Al ₂ O ₃ { 3.7 SiO ₂ 0.5 B ₂ O ₃	.2500 K ₂ O
.50 CaO		.5000 CaO
.10 BaO		.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO
		.8 equiv. of frit used. Comb. wt. 366.3

.50 Al₂O₃ GROUP

Glaze D1		Frit
.40 K ₂ O	.50 Al ₂ O ₃ { 4.0 SiO ₂ 0.5 B ₂ O ₃	.3750 K ₂ O
.40 CaO		.3750 CaO
.10 BaO		.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO
		.8 equiv. of frit used. Comb. wt. 406.3

Glaze D2		Frit
.40 K ₂ O	.50 Al ₂ O ₃ { 4.0 SiO ₂ 1.0 B ₂ O ₃	.3750 K ₂ O
.40 CaO		.3750 CaO
.10 BaO		.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO
		.8 equiv. of frit used. Comb. wt. 450.1

Glaze D3		Frit
.40 K ₂ O	.50 Al ₂ O ₃ { 3.5 SiO ₂ 1.0 B ₂ O ₃	.3750 K ₂ O
.40 CaO		.3750 CaO
.10 BaO		.1250 BaO
.05 MgO		.0625 MgO
.05 SrO		.0625 SrO
		.8 equiv. of frit used. Comb. wt. 412.6

.60 Al_2O_3 GROUP

Glaze E1		Frit	
.40 K_2O	.60 Al_2O_3 {	.3750 K_2O	.50 Al_2O_3 {
.40 CaO		.3750 CaO	
.10 BaO		.1250 BaO	
.05 MgO		.0625 MgO	
.05 SrO		.0625 SrO	
		.8 equiv. of frit used. Comb. wt. 419.1	
Glaze E2		Frit	
.40 K_2O	.60 Al_2O_3 {	.3750 K_2O	.50 Al_2O_3 {
.40 CaO		.3750 CaO	
.10 BaO		.1250 BaO	
.05 MgO		.0625 MgO	
.05 SrO		.0625 SrO	
		.8 equiv. of frit used. Comb. wt. 462.8	
Glaze E3		Frit	
.40 K_2O	.60 Al_2O_3 {	.3750 K_2O	.50 Al_2O_3 {
.40 CaO		.3750 CaO	
.10 BaO		.1250 BaO	
.05 MgO		.0625 MgO	
.05 SrO		.0625 SrO	
		.8 equiv. of frit used. Comb. wt. 425.30	

A careful study of Seger's results³ on leadless glazes, of Stull's work⁴ on whiteware glazes low in lead, and of many successful whiteware and china glazes shows clearly that the best glazes of this type, lead or leadless, occur at or very near to an oxygen ratio of 1 : 2 when B_2O_3 is figured as a sesquioxide base. Before discussing the above glaze and frit formulae in detail the location of these glazes with reference to the 1 : 2 oxygen ratio line is shown in the following diagram, Fig. 1.

Fig. 1.—Diagram showing location of glazes produced in field of compositions

The glazes of series No. I are divided into four groups with increasing Al_2O_3 contents as follows: Group B, with .35 Al_2O_3 ; group C, with .40 Al_2O_3 ; group D, with .50 Al_2O_3 ; and group E, with .60

³ Loc. cit.

⁴ Trans. Am. Cer. Society, vol. 12, p. 129.

Al_2O_3 . In each group, with the RO and the SiO_2 constant except in one or two special cases, the B_2O_3 content is varied within the group. The frits, except in a few instances where it was impossible to do so, have the same oxygen ratio as the glazes. It must also be said in explanation that in this series the theoretical formula and combining weight of orthoclase feldspar was used instead of the actual one, as the analysis of the feldspar used was not available when the work was started, but was made later and used in calculating the glazes for series No. II.

In group B glaze B1 was suggested to the writer by Mr. Ernest Mayer, of the Mayer China Co. Glaze B2 is the same glaze with the B_2O_3 increased to .35 B_2O_3 , which places this glaze on the 1 : 2 oxygen ratio line when B_2O_3 is figured as basic. Glaze B3 was taken from Mellor's report on leadless glazes and is one which he terms the old type of the leadless glaze. In this glaze the frit does not possess exactly the same oxygen ratio as the glaze, it being necessary to reduce the SiO_2 in the frit somewhat in order to leave sufficient SiO_2 to satisfy the raw constituents.

In group C both glazes C1 and C2 possess the oxygen ratio of 1 : 2, and both frits have the same ratio as the glazes.

In group D the formula for glaze D1, with the exception of the RO fluxes, was taken direct from Seger's work. Both the glaze and frit have a 1 : 2 oxygen ratio. Glaze D2 is one of Seger's with 1.0 B_2O_3 . The frit has not the same oxygen ratio as the glaze, the SiO_2 being reduced a little for the same reason as in B3. Glaze D3 was designed from a glaze reported by Mellor⁵ as the best type of leadless glaze thus far developed in England. The glaze reported is as follows:

Glaze D3 varies somewhat from this formula in order to make it conform to the rest of the group. It shows the effect of reducing the SiO_2 slightly from that used in glaze D2. The same remark on the SiO_2 in the frit applies here as in D2.

In group E we have group D duplicated except for the increase of Al_2O_3 from .50 Al_2O_3 to .60 Al_2O_3 in order to show the effect of further increasing this constituent in glazes high in B_2O_3 .

⁵ Trans. Eng. Cer. Society, 12, p. 7.

Series No. II

As glaze D_I proved to be the best glaze of series No. I, the second series was designed to further improve this glaze if possible by making changes in its RO fluxes. In this series the true formula and combining weight of the feldspar was used as determined by analysis. The other raw materials were so near to the theoretical in composition that no allowance was made for any of the materials excepting the feldspar.

Glaze D1a

Frit

.8 equiv. of frit used. Comb. wt. 394.75

Glaze D1b

Frit

.8 equiv. of frit used. Comb. wt. 399.9

Glaze D1c

Frit

.8 equiv. of frit used. Comb. wt. 392.0

Glaze D1d

Frit

.8 equiv. of frit used. Comb. wt. 397.0

In these glazes the molecular coefficients of the SiO_2 in the frits are a little less than in the frit of D_I for the reason that in using the true formula of the feldspar in series No. II, more SiO_2 is required to satisfy the feldspar in the raw portion of the glaze batch and, as no flint is added raw, the additional SiO_2 must necessarily come out of the frit.

Along with this series the glaze before mentioned as being reported by Dr. Mellor as the best type of leadless glaze thus far developed was made up as given in the Transactions, English Ceramic Society, vol. 12, page 7, using Cornwall stone in place of feldspar in its composition. The formula is as follows:

The mixtures of the various glazes, expressed in parts by weight, are compiled in the following table, No. 1:

3. MATERIALS USED

The materials used in these glazes were Ohio silica flint; potash feldspar from the Maine Feldspar Co., Auburn, Me.; M. G. R. No. 2 English china clay and Great Beam English ball clay from Moore and Munger, New York; Cornwall stone from the Mayer China Co., Beaver Falls, Pa., together with the other standard glaze materials.

The ultimate chemical analyses of some of these materials are as follows:

TABLE 2
Ultimate Analyses of Some of the Materials Used.

	Ohio silica flint	Maine feldspar	M. G. R. No. 2 English china clay	Great beam English ball clay	Whiting	Cornwall stone
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
SiO ₂	99.23	70.79	46.63	46.55	0.74	72.21
Al ₂ O ₃	.32	16.75	37.13	38.38	.46	15.32
Fe ₂ O ₃	.10	.22	.62	.93	.15	.00
TiO ₂	.00	.00	.81	.05	.00	.00
CaO.....	.08	.24	.72	.25	55.16	2.02
MgO.....	.13	.18	.19	.23	.20	.20
K ₂ O.....	.00	8.26	.33	.70	.00	4.39
Na ₂ O.....	.00	3.29	.12	.25	.00	2.86
Loss on ignition.....	.22	.46	13.35	12.80	43.38	1.97
Total.....	100.08	100.19	99.89	100.14	100.09	99.97

The formula of the feldspar is:

Comb. weight 658.4.

The formula of the Cornwall stone:

Comb. weight 745.2.

4. UNDERGLAZE COLORS USED

The six standard underglaze colors used in the work have the following compositions:

Pink:	Per cent	Victoria green:	Per cent
Tin oxide.....	50.0	Chromium oxide.....	50.0
Whiting.....	25.0	Flux.....	50.0
Flint.....	18.0		100.0
Potassium bichromate.....	3.0	Flux:	
Borax.....	4.0	Flint.....	30.0
	100.0	Potassium bichromate.....	6.0
Yellow:		White lead.....	3.0
Alumina.....	8.0	Whiting.....	3.0
Tin oxide.....	16.0	Potassium nitrate.....	1.0
Black oxide of antimony.....	32.0	Blue green:	
Red lead.....	44.0	Chromium oxide.....	20.0
	100.0	Cobalt oxide.....	5.0
Brown:		China clay.....	27.5
Ferric oxide.....	18.0	Spar.....	27.5
Chromium oxide.....	17.0	Zinc oxide.....	20.0
Alumina.....	11.5		100.0
Zinc oxide.....	53.5	Blue:	
	100.0	Cobalt oxide.....	44.5
		Alumina.....	55.5
			100.0

5. METHOD OF PREPARING THE GLAZES

All frits were weighed out, thoroughly mixed in the dry state, and fritted in a small crucible drop frit furnace, the frit being caught and chilled in water. Wherever clay was called for in any of the frits, English china clay was used. After the frits were prepared, dried and pulverized fine enough for the ball mill, the whole glaze batch was weighed out, sufficient water added, and the glaze ground in a porcelain ball mill until it would pass a 200-mesh lawn. In the glazes of series No. I English ball clay was used for the raw clay of the glaze batch, and in series No. II English china clay was used for the purpose of comparing the effect of the two clays on the settling and on the dipping behavior of the glazes.

After lawning, the glazes were placed in glass jars, allowed to settle, and all excess water was siphoned off. A few drops of a saturated solution of magnesium sulphate were used in all cases to bring the glazes to just the right dipping weight or thickness.

6. PREPARATION OF THE TRIALS

The trial pieces were small butter dishes of a hard nonabsorbent porcelain body supplied through the kindness of Mr. Ernest Mayer, of the Mayer China Co. The six underglaze colors were applied upon these dishes in narrow bands as used in decorating. The trials were then appropriately marked and dipped half in the leadless trial glaze and half in a standard lead glaze.

The lead glaze used was a very brilliant one and one that has been used commercially with perfect satisfaction. Its formula is as follows:

Glaze		Frit	
.0640 K ₂ O	.2811 Al ₂ O ₃ { 2.8070 SiO ₂ .3845 B ₂ O ₃	.0311 K ₂ O	.2713 Al ₂ O ₃ { 2.5471 SiO ₂ .5459 B ₂ O ₃
.1920 Na ₂ O		.2727 Na ₂ O	
.4903 CaO		.6962 CaO	
.2534 PbO			
		.704 equiv. of frit used.	
		Comb. wt. 277.52.	

The glaze and frit mixtures in parts by weight are as follows:

Frit mixture:		Glaze mixture:	
Feldspar.....	17.3	Frit.....	195.37
Borax.....	104.2	Feldspar.....	23.39
Whiting.....	69.6	White lead.....	65.38
Clay.....	61.9	Clay.....	12.38
Flint.....	112.8	Flint.....	39.91
	365.8		336.43

7. FIRING THE TRIALS

The glazes of series No. I were fired at both Seger cones 1 and 3. Those of series No. II were carried to cone 3 only. The trials were fired in saggers washed with a very thin coat of the standard lead glaze, in a large test kiln, with natural gas as fuel. The duration of each burn was approximately 24 hours. The kiln was cooled rapidly in all cases.

III. RESULTS

In the following paragraphs the appearance and condition of the glazes themselves and their effect on the underglaze colors at cone 1 (1070° C) and at cone 3 (1100° C) are reported.

Series No. 1

.35 Al_2O_3 GROUP

Glaze B₁ at cone 1.—Glaze smooth but slightly immature. No opalescence noted. All colors good.

Glaze B₁ at cone 3.—Glaze bright and smooth, but surface slightly wavy and eggshell-like in appearance. Possibly not quite mature. No opalescence noted. All colors good.

Glaze B₂ at cone 1.—Glaze slightly immature. Quite strong opalescence. All colors good.

Glaze B₂ at cone 3.—Glaze mature, bright, and smooth. A very slight eggshell surface. No opalescence. All colors good.

Glaze B₃ at cone 1.—Glaze immature. Quite strong opalescence. All colors good.

Glaze B₃ at cone 3.—Glaze bright and smooth, apparently mature, but slightly eggshell-like. Opalescence quite marked where glaze is thick and noticeable throughout the glaze, giving it a dull, milky appearance.

All glazes of the .35 Al_2O_3 group are immature at cone 1 and mature or nearly so at cone 3. Glaze B₂ at cone 3 is the best glaze of the group. It is a very good glaze, being nearly equal in appearance to glaze D₁, which proved to be the best developed in the whole series. It is slightly less brilliant and, being slightly eggshelled, has not so fine a surface texture. A little higher heat or a longer firing would probably overcome the slight eggshell appearance.

This group illustrates the increase of opalescence with increase of B_2O_3 , the rest of the formula being constant.

.40 Al_2O_3 GROUP

Glaze C₁ at cone 1.—Not tested.

Glaze C₁ at cone 3.—A fine, bright, smooth glaze, fully matured. No opalescence. A better glaze than C₂ at cone 3, and very nearly equal to glaze D₁ at cone 3. All colors good.

Glaze C₂ at cone 1.—Glaze slightly immature. Quite strongly opalescent. All colors good.

Glaze C₂ at cone 3.—Glaze fine, bright, smooth, and mature. Shows slight opalescence where glaze is thick. This glaze is equal

to B2 at cone 3, except for the slight opalescence which it shows. The surface texture is good, but not quite equal to glaze D1 at cone 3.

.50 Al_2O_3 GROUP

Glaze D1 at cone 1.—Glaze very slightly immature, best gloss and transparency not quite developed. No trace of opalescence. All colors good.

Glaze D1 at cone 3.—The best glaze developed in the series. Mature, fine, bright, and smooth. Though not quite so brilliant as the standard lead glaze it is whiter in color. No trace of opalescence. All colors fine.

Glaze D2 at cone 1.—Glaze immature. Strong, milky opalescence. Pink destroyed. Other colors good.

Glaze D2 at cone 3.—Glaze still has the appearance of immaturity. Strong, milky opalescence. Pink color destroyed. Other colors good.

Glaze D3 at cone 1.—Glaze slightly immature and slightly opalescent. Bubbled especially where thick. Pink color destroyed, but others good.

Glaze D3 at cone 3.—Glaze mature and bright. A very slight tendency toward opalescence, but a strong inclination to bubble, especially where the glaze is a little thick. Pink color is destroyed. Other colors good.

All of the glazes of the .50 Al_2O_3 group are slightly immature and opalescent at cone 1 except D1, which shows no opalescence. Glaze D1 at cone 3 is the best glaze developed in the series. The higher alkali and lower lime content, as well as the rather high B_2O_3 , all help to make this glaze brilliant. The underglaze colors are all excellent. It has a brilliancy, transparency, and surface texture nearly, if not quite equal, to the standard lead glaze and a whiteness that is superior.

The glazes of this, as well as those of the .60 Al_2O_3 group, show that all compositions containing 1.0 B_2O_3 will spoil the chrome-tin pink color. Glazes D2 and D3, also E2 and E3, show that with the formula otherwise the same and where the B_2O_3 is already high an increase in the SiO_2 increases the opalescence, as Seger has pointed out.

.60 Al_2O_3 GROUP

Glaze E₁ at cone 1.—Glaze slightly immature and milky from immaturity. No opalescence. All colors good.

Glaze E₁ at cone 3.—Glaze bright and smooth, but appears to be still slightly immature. No opalescence. All colors good. It gives promise of being equal to glaze D₁ at a little higher temperature.

Glaze E₂ at cone 1.—The glaze appears to be mature, but the surface is eggshelled. Strong tendency to bubble where glaze is thick. Practically no opalescence. Pink destroyed, but other colors good.

Glaze E₂ at cone 3.—Glaze mature, but surface eggshelled. Strong tendency to bubble. Practically no opalescence.

Glaze E₃ at cone 1.—Glaze appears to be mature, but bubbles badly and destroys the pink color. No opalescence.

Glaze E₃ at cone 3.—Glaze mature, bubbles badly where at all thick and destroys pink color. No opalescence.

The glazes of the .60 Al_2O_3 group containing 1.0 B_2O_3 show less opalescence than those of the .50 Al_2O_3 group, due to their higher Al_2O_3 content, but as a whole are not as good glazes at the temperatures used. The .60 Al_2O_3 content seems to have raised their maturing temperature somewhat.

Series No. II

This series, designed to improve glaze D₁ if possible by varying the RO fluxes, failed to give any glaze quite equal to D₁ in all respects.

Glaze D_{1a} at cone 3.—A fine, bright, mature glaze, about equal in surface texture and brilliancy to D₁. Shows no opalescence. It, however, destroys the pink color, probably due to too low a lime content in the glaze.⁶ All other colors good.

Glaze D_{1b} at cone 3.—A bright, smooth glaze, but with quite a marked tendency to develop many minute bubbles. It destroys the pink color and alters the shade of the greens. The change in the greens from green to an olive or brown is due to the ZnO in the glaze.

⁶ Trans. Am., Cer. Soc. 14, pp. 176-7.

Glaze D1c at cone 3.—A bright, smooth glaze with the same faults as glaze D1b.

Glaze D1d at cone 3.—A fine, bright, smooth glaze, but with a tendency to bubble where thick. It destroys the pink colors, probably for the same reason as given under D1a above.

The Mellor glaze at cone 3.—A bright, smooth glaze, but has a very bad effect on colors. It destroys the pink and yellow, flows the blue, and in general has a strong tendency at this heat, at least, to flow or drain on sloping surfaces and to bubble where at all thick.

IV. DISCUSSION OF RESULTS

The results of this investigation confirm Seger's findings in regard to leadless glazes in every particular. In the first place we observe that in general an increase in B_2O_3 in a given glaze increases opalescence. This point is brought out very nicely in the .35 Al_2O_3 group of series No. .I We also note that in order to avoid opalescence in this type of glaze, we must have a high content of alumina, and at the same time a comparatively low content of SiO_2 . In a glaze high in B_2O_3 any increase in SiO_2 over that necessary for a stable and bright glaze will aid the B_2O_3 in increasing opalescence.

In glazes with .5 B_2O_3 or less it is quite noticeable that we get opalescence as soon as the molecular coefficient of the B_2O_3 in the formula becomes greater than that of the Al_2O_3 , the SiO_2 remaining the same. In glazes with 1.0 B_2O_3 opalescence can be avoided with .5 Al_2O_3 to .6 Al_2O_3 if the SiO_2 is kept as low as possible.

In many of the trials it is also noticed that in a glaze which shows opalescence slightly this defect is often entirely removed by a longer or a somewhat higher heat treatment. This has been noted by others.⁷

Let us now see in what measure the leadless glazes developed in this work are able to fulfill the requirements set forth earlier.

1. *Dipping.*—Both English ball clay and English china clay were used as the raw clay added in the glaze batch and both were found to work well. None of the glazes settled. Those made up with ball clay seemed to dip a little better than the others in that

⁷ Trans. Eng. Cer. Soc., Vol. 20, p. 129.

they appeared to adhere somewhat better and more evenly to the ware. There is the danger, however, of getting a bad color from the use of ball clay. Florida kaolin would obviate this difficulty and at the same time give sufficient plasticity. No difficulty in dipping has been reported by other investigators so far as known, and the writer believes that a leadless glaze can be made to dip equally as well as a lead glaze if prepared with care and intelligence.

2. In regard to heat range we can say that leadless glazes in general do not possess so long a range of fusion, but that the maturing limits, though a little higher in the temperature scale, are sufficiently wide to take care of the variations met with in very uniform firing. Leadless glazes do not flow as readily as those made with lead and therefore do not cover bare spots as well. Neither do they for the same reason flow colors.

There are many interesting opinions and facts on this subject in the report of the English "Lead Commission," published in London in 1910. In the investigation which the commission made of the use of lead in the potteries equally reliable firms testified that the number of "seconds" was and was not greater from the use of leadless glazes. The majority, however, state that the number of "seconds" is larger and that from this cause the cost of manufacture is at least 10 per cent greater.

3. *Underglaze colors.*—The best leadless glazes developed in this study have a beneficial rather than a detrimental effect on the colors tested. It is also possible that a number of colors not now in use under lead glazes can be developed for use under leadless glazes. As has already been stated, all glazes containing 1.0 B_2O_3 destroy the pink color; in fact this tendency is noticed in a very slight degree with glazes containing as low as 0.5 B_2O_3 , though the pink still remains a strong and pleasing color. It is noted also that such glazes as D1 do not flow blues, for example, as much as lead glazes under such accidental conditions as too thick a dip, where the color has been used on a sloping or vertical surface. It must also be said, however, that if leadless glazes are dipped too thick they have a tendency to dull the colors.

4. *Appearance and durability.*—The consensus of opinion among English manufacturers who are using leadless glazes seems to be

that for the grades of ware for which they at present employ leadless glazes, they produce ware of an equally pleasing, though not identical, appearance, the leadless glaze being whiter and a little less brilliant.

Mr. Ernest Mayer, of the Mayer China Co., in the course of the work produced a few small pieces of ware of very creditable appearance compared with a standard lead glaze. The differences mentioned above were noted and seem to be inherent characteristics of this type of glaze. These glazes are harder by test than the lead glazes, and their durability has been pretty thoroughly established by actual use.

5. *Cost.*—The cost of the raw materials for leadless glazes is about equal to or a little less than that for lead glazes. The cost of the glazing operation is no more, but the loss from "seconds" is and probably will continue to be greater, especially in the better grades of ware. This is partially offset, however, by the saving in the expense necessary to provide the special safeguards for employees where lead glazes are used, or incurred in complying with the laws regulating the use of lead in potteries where such laws are in force.

V. CONCLUSIONS

The most authoritative report that we have at the present time on the subject of the practical use of leadless glazes is the above-mentioned report of the investigation in England by the "Lead Commission." This gives the actual experience and opinion of many English manufacturers who have been using or attempting to develop leadless glazes for many years past, due largely to the stringent English laws regulating the use of lead in the potteries. In the United States, as far as known, there are no leadless glazes used for white ware, china, or porcelain tableware.

As is to be expected during the period of its development, we find in this English report almost exactly opposite opinions expressed on almost every point discussed in regard to leadless glazes. From a technical standpoint this diversity of opinion is interesting, and shows that we are progressing, but that there is still much more to be learned regarding leadless glazes. We can afford to make mistakes in experimentation, as it is only by these mistakes

that we progress in our knowledge of the subject. However, when we come to consider the matter from a practical and commercial standpoint we must be more conservative, for here we can not afford to make mistakes. In the writer's opinion it would be very premature at the present time to say that we can make a leadless glaze for white-ware, china, or porcelain that could be substituted for the present lead glazes. Both have special faults and special virtues, but for use under general factory conditions, make them as perfect as we can, we are not likely to find any element, compound, or combination of compounds which will exactly duplicate the many excellent properties of lead as a glaze ingredient.

I desire to acknowledge my indebtedness to Prof. A. V. Bleining, of the Bureau, and to Mr. Ernest Mayer, of the Mayer China Co., for many helpful suggestions and for assistance in making some of the tests during the course of this investigation.

WASHINGTON, December 15, 1913.

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