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Red glazes

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RED GLAZES

BY

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THESIS

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Approved by .....
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INTRODUCTION

Ceramists for many years have had a demand for a cone 4 commercial red glaze. To produce this, requires much time and research work with different coloring oxides, different temperatures, and different kiln conditions. To approach a commercial glaze of any color does not constitute merely the addition of a coloring oxide to a good transparent base glaze but means the changing of the whole composition of the glaze to get the desired results.

In the preparation of colored glazes there are three definite steps of procedure:[2]

The first is the Glaze Compounding. This includes the selection of a good base glaze and the correct coloring ingredient to give the desired results. The selection of the raw materials, and their grinding is also important to the ultimate success of the glaze. Care must also be exercised in the weighing of the glaze as slight variations will cause a wide variation in the color range of the glaze.

The second is the glaze application. In this it is necessary to discover the correct specific gravity at which the glaze will apply well to the tile. Also important in glaze application is the selection of the proper bisque ware. Care must be taken to have all bisque ware so fired that there will be equal absorption on glaze application.

The third is firing treatment. This is very important since glaze colors change very much with temperature change. It is sometimes necessary to have controlled cooling rates as well as controlled heating rates since glaze colors often change with different rates of cooling. The atmospheric condition of the kiln must also be taken into consideration. Many colored glazes depend on oxidizing conditions and many on reducing conditions of the kiln.

SCOPE OF INVESTIGATION

The object of this study was to produce a commercial red glaze at cone 3 from a base glaze of colemanite and steatite.

METHOD OF INVESTIGATION

Since colemanite and steatite were not available for use, the oxides were added in such proportions as to give the same oxide ingredients as colemanite and steatite would give.

To produce a clear, transparent glaze, to which coloring oxides could be added, end members were made up for five, 36 member rectangular systems. In each system the RO content was held constant for that system, and the AL_2O3, SiO_2, and B_2O_3 contents varied. The RO content was changed with the change of the system, but similar members of all five systems had the same AL_2O_3, SiO_2 and B_2O_3 content.

The following tables show the position of each of the 36 members in each series and the percentages used for blending of the intermediate members.

Table 1

Glaze I

$$IRO \cdot 22AL_2O_3 \quad \overset{4.oSiO_2}{\cdot 3B_2O_3}$$

Glaze 6

$$IRO \cdot 44AL_2O_3 \quad \overset{2.oSiO_2}{\cdot 45B_2O_3}$$

100% of 1 1	83% of 1 17% of 6 2	67% of 1 33% of 6 3	33% of 1 67% of 6 4	17% of 1 83% of 6 5	100% of 6 6
83% of 1 17% of 31 7	83% of 2 17% of 32 8	83% of 3 17% of 33 9	83% of 4 17% of 34 10	83% of 5 17% of 35 11	83% of 6 17% of 36 12
67% of 1 33% of 31 13	67% of 2 33% of 32 14	67% of 3 33% of 33 15	67% of 4 33% of 34 16	67% of 5 33% of 35 17	67% of 6 33% of 36 18
33% of 1 67% of 31 19	33% of 2 67% of 32 20	33% of 3 67% of 33 21	33% of 4 67% of 34 22	33% of 5 67% of 35 23	33% of 6 67% of 36 24
17% of 1 83% of 31 25	17% of 2 83% of 32 26	17% of 3 83% of 33 27	17% of 4 83% of 34 28	17% of 5 83% of 35 29	17% of 6 83% of 36 30
100% of 31 31	83% of 31 17% of 36 32	67% of 31 33% of 36 33	33% of 31 67% of 36 34	17% of 31 83% of 36 35	100% of 36 36

Glaze 31

$$IRO \cdot 44AL_2O_3 \quad \overset{4.oSiO_2}{\cdot 45B_2O_3}$$

Glaze 36

$$IRO \cdot 22AL_2O_3 \quad \overset{2.oSiO_2}{\cdot 38_2O_3}$$

Following is the RO content for the five different series:

Table I

	ZnO	K_2O	CaO	BaO	MgO
Series 1 - Glaze A	.40	.20	.20	.10	.10
Series 2 - Glaze B	.25	.40	.20	.10	.05
Series 3 - Glaze C	.25	.20	.40	.05	.10
Series 4 - Glaze D	.30	.20	.20	.30	.00
Series 5 - Glaze E	.30	.20	.25	.00	.25

MATERIALS USED

The materials used were Pennsylvania flint, English china clay, Buckingham feldspar, zinc oxide, calcium carbonate, borax glass, magnesium carbonate, and potassium carbonate.

METHOD OF PREPARING GLAZE

The zinc oxide for all end members was calcined to cone 8. This was done to reduce to a minimum the amount of crazing. The other oxides were calculated and added as raw batch.

The composition of the raw batches are given in table II below:

Table II

Batch weights of corner members in percentages

Series 1 - Glaze A.

Ingredient	Member 1	Member 6	Member 31	Member 36
ZnO	7.86	7.58	7.26	11.50
Buck.Feld.	27.70	25.90	24.80	39.20
$CaCO_3$	4.99	4.66	4.45	7.07
$B_2O_3 3H_2O$	9.74	13.33	12.80	13.46
$BaCO_3$	4.92	4.60	4.41	6.97
$Mg\ CO_3$	2.10	1.96	1.88	2.97
Flint	41.40	28.07	31.09	17.01
Clay	1.29	13.90	13.31	1.82

Series 2 - Glaze B.

Ingredient	Member 1	Member 6	Member 31	Member 36
ZnO	4.76	5.78	6.04	6.57
Buck.Feld.			33.16	
K_2CO_3	12.91	15.41		17.86
$CaCO_3$	4.68	5.58	6.00	6.51
$B_2O_3 3H_2O$	8.92	16.00	17.07	12.64
$BaCO_3$	4.63	5.51	5.86	6.36
$Mg\ CO_3$	.97	1.17	1.21	1.32
Flint	49.83	18.81	27.61	30.37
Clay	13.30	31.74	3.05	18.37

Table II (continued)

Series 3 - Glaze C.

Ingredient	Member 1	Member 6	Member 31	Member 36
ZnO	4.89	5.87	4.20	7.59
K_2CO_3	6.66			
Buck.Feld.		33.51	23.12	41.16
$CaCO_3$	9.65	11.67	8.35	14.93
$B_2O_3 3H_2O$	9.18	16.74	12.11	14.22
$BaCO_3$	2.38	2.80	2.72	3.70
$MgCO_3$	2.04	2.38	1.70	3.16
Flint	51.60	9.71	35.42	13.32
Clay	13.60	17.32	12.48	1.92

Series 4 - Glaze D.

Ingredient	Member 1	Member 6	Member 31	Member 36
ZnO	6.56	8.21	5.57	9.74
Buck.Feld.	29.90	37.35	25.35	44.40
$CaCO_3$	5.37	6.68	4.57	7.99
$B_2O_3 3H_2O$	10.23	19.29	13.09	15.20
$BaCO_3$	1.58	1.99	1.35	2.36
Clay	1.38	20.02	13.60	2.06
Flint	44.98	6.46	36.47	18.25

Series 5 - Glaze E.

Ingredient	Member 1	Member 6	Member 31	Member 36
ZnO	9.00	7.24	5.53	8.47
Buck.Feld.	40.90		25.12	
K_2CO_3		8.19		9.60
$CaCO_3$	9.23	7.42	5.65	8.70
$B_2O_3 3H_2O$	14.05	17.00	12.95	13.25
$Mg\ CO_3$	8.08	6.50	5.72	7.60
Flint	16.84	19.95	31.55	32.62
Clay	1.90	33.70	13.48	19.76

The glaze was ground in a porcelain lined pebble mill for two hours and then passed thru a 100 mesh screen.

The specific gravity of the glaze was adjusted to 1.40, and the intermediate members of the rectangular system were made by volume blending of the corner members.

MAKING OF THE TILE

Tile trials were made with a mixture of Empire Fire clay and Number 9 Tennessee Ball clay, using fifty per cent of each. The clay was mixed and molded into $1\frac{1}{2}$" by $1\frac{1}{2}$" by $\frac{1}{2}$" glaze trials and dried. The tile was bisqued at cone 3.

APPLICATION OF THE GLAZE

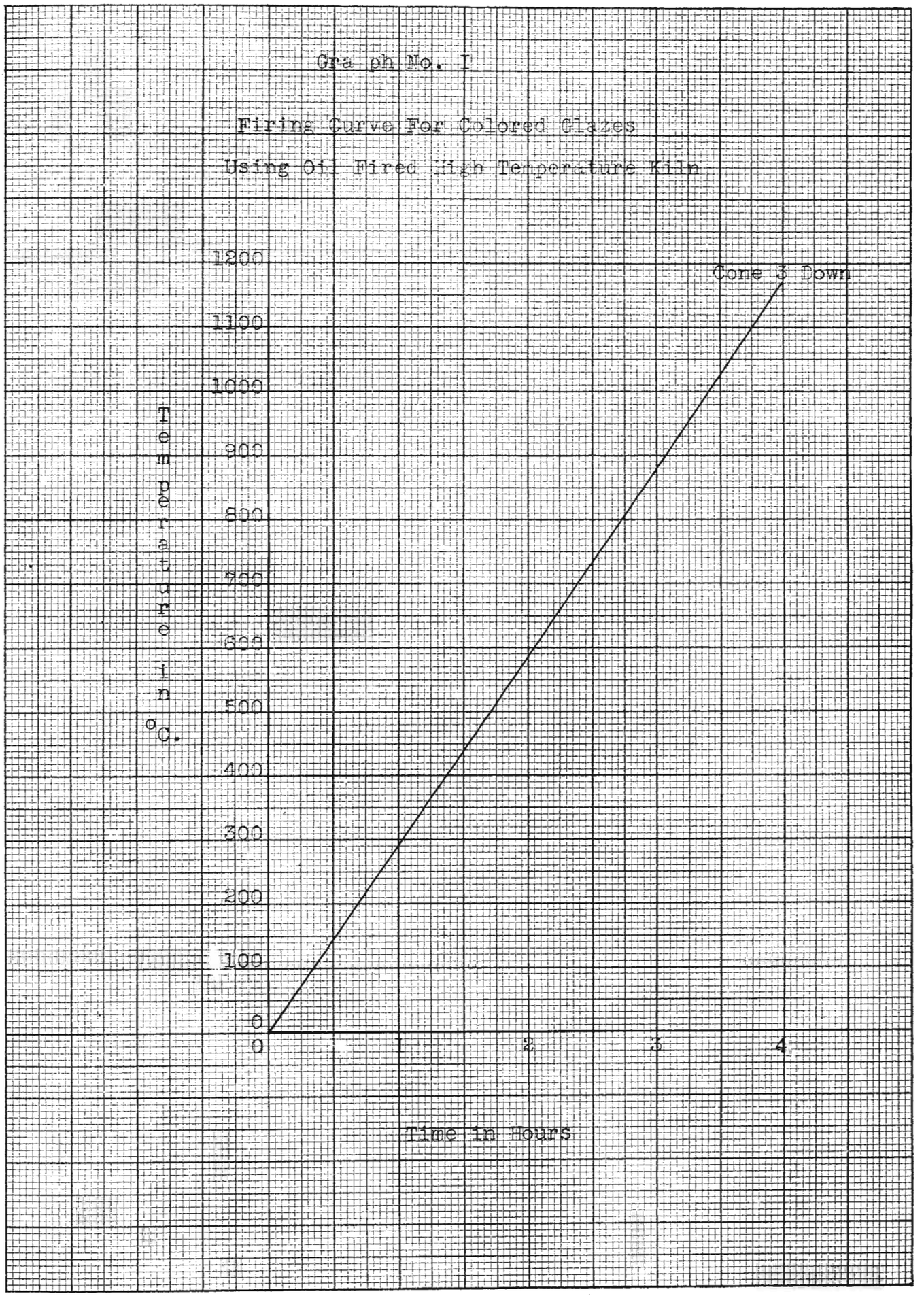
The glaze was applied by dipping two trials in each glaze and when dry, fettling the edges with a spatula.

The glazed trials were fired in saggers in an oil fired high temperature kiln to cone 3. The temperature of the kiln was raised to cone 3 in four hours at a rate of approximately 290° centigrade per hour.

Graph No. I

Firing Curve For Colored Glazes

Using Oil Fired High Temperature Kiln



RESULTS OF FIRST FIRING

Upon removal from the kiln, most of the glaze trials were badly crazed. There were approximately fifty trials that showed no signs of crazing. These trials were placed in an autoclave at 75 pounds steam pressure for two hours. With autoclave treatment all of these trials crazed, except number 20 of the first series or glaze A. The composition of this member was calculated and this glaze used in experimenting with the coloring oxides. The composition of this glaze is given as follows:

Series 1 - Glaze A.

Material	Member 20
ZnO	32.58
Buck.Feld.	111.10
$CaCO_3$	20.02
$B_2O_3 3H_2O$	48.43
$BaCO_3$	19.74
$MgCO_3$	8.42
Flint	129.23
Clay	40.00

ADDITION OF COLORING OXIDES

The coloring oxides were added, in the amounts shown below, to the base glaze as percentages of the raw batch. Uranium, chromium, bismouth, tatanium, iron, manganese, copper, tin and selenium were the oxides used in an effort to get a red color.

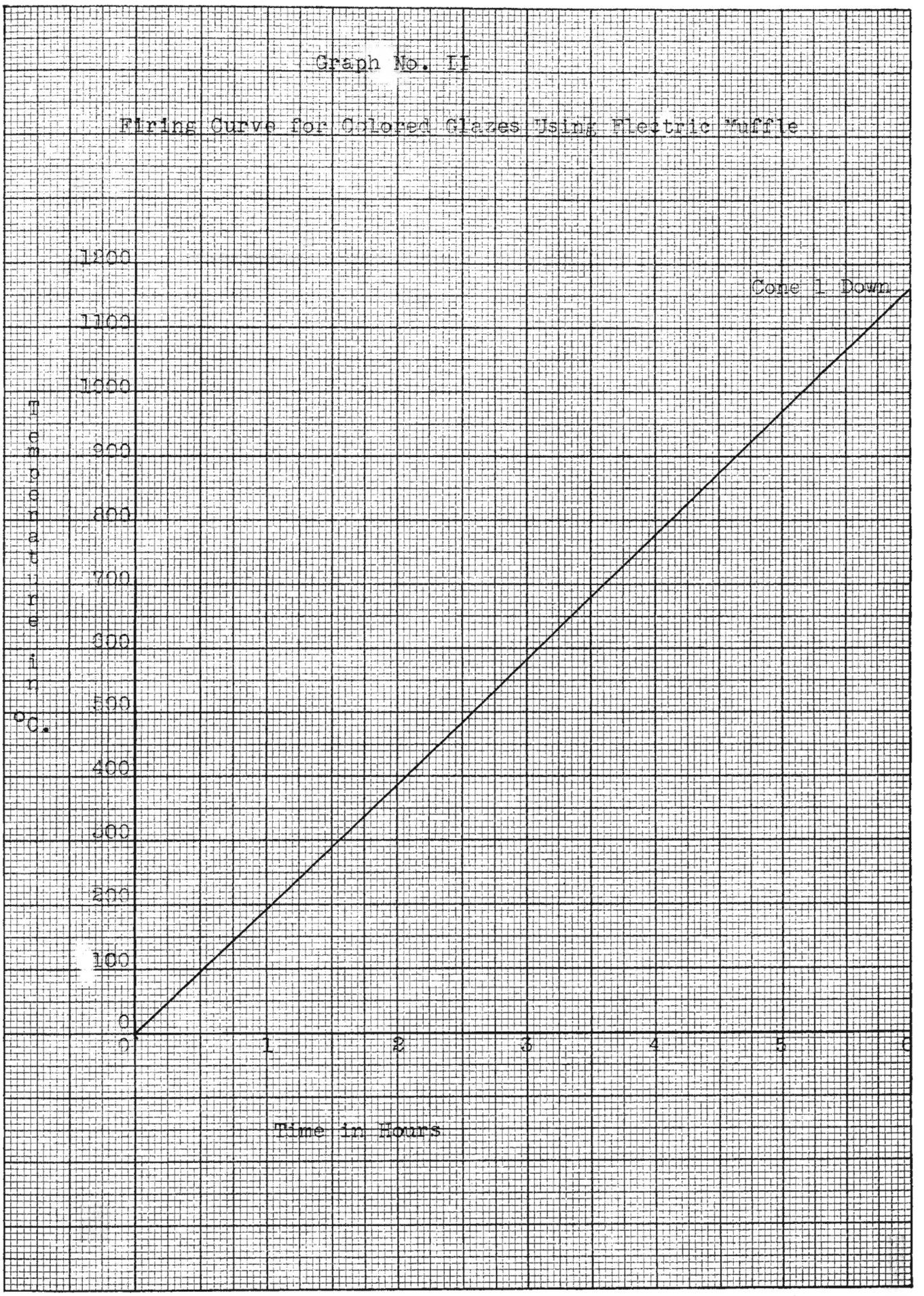
Oxide	Percent
Uranium	30%
Chromium	5%
Bismouth	1.5%
Uranium	6.8%
Titanium	3.8%
Bismouth	1.8%
Uranium	7.2%
Iron	.71%
Manganese	1.20%
Copper	.54%
Copper	.3%
Tin	.3%
Carborundum	.5%
Selenium	2%

FIRING

The test trials were fired in closed saggers in the oil fired high temperature kiln to cone 3. An electric muffle was also used in testing for color, cone 1 being reached in six hours.

Graph No. II

Firing Curve for Colored Glazes Using Electric Muffle



DISCUSSION OF RESULTS

The glazes in which the uranium was added produced a dark greenish color when fired in the oil fired kiln to cone 3. The same glazes were fired in the electric muffle to cone 1 and showed an orange yellow to brown matt color the glaze having not completely matured. No crazing took place in the glazes.

The glazes in which the chromium was added produced a light green color with no signs of red. A good green glaze at cone 3.

The next glaze trials contained bismouth, uranium and titanim. When fired to cone 3 in the oil fired kiln these glazes gave a yellowish brown color but the glaze was badly crazed. This was probably due to one of the three coloring oxides. When fired in the electric muffle to cone 1 the glaze did not mature and gave a light brown matt color.

The glazes containing both bismouth and uranium gave a light green color when fired to cone 3 in the oil fired kiln. When fired to cone 1 in the electric muffle a yellow color was produced.

The glazes containing iron, manganese, and copper oxides were fired in the electric muffle to cone 1. The color produced was a light green color. The glaze was badly crazed, again being due to the coloring oxides added.

Uranium was again tried, this time with a lower alumina and silica content. The color produced was an orange matt color which did not hold well to the body. This was fired to cone 1 in the electric muffle.

Next a glaze combining copper, tin, and corborundum was fired in the electric muffle to cone 1 in a highly reducing atmosphere. A steady gas stream was kept going thru the muffle during the firing to give the reducing atmosphere. The corborundum was used to help give a reducing condition to the glaze. The glaze did not mature but the color produced was a matt red.

An addition of selenium was tried as a last effort. The color produced was a clear white with a few dark spots showing thru. Only 10 grams of selenium was used in a 500 gram batch.

CONCLUSIONS

It is concluded that:

1. Uranium cannot be used to produce a red color in a glaze containing colemanite and steatite. It would be highly probable to get a red glaze at a lower temperature but this would necessitate a lower alumina and silica content which would be impossible in a colemanite, steatite glaze. Zimmerman[4] produced a red glaze using uranium but his glaze contained less than .2 alumina and less than 1 equivalent of silica. His glaze matured at cone 07a.

2. Chromium alone, in a colemanite, steatite glaze will not give red at cone 3.

3. Any combination of bismouth, uranium and titanium will not give a red glaze when using a colemanite, steatite glaze.

4. A combination of iron, manganese and copper will not give a red color at cone 3.

5. A copper glaze containing tin and carborundum and fired in a reducing atmosphere is most likely to give a good red color if further work is done.

6. Selenium will not give a red color when added in small additions. A red might be obtained if enough selenium were added but selenium is rather expensive.

7. A good red glaze with a colemanite, steatite base glase is very difficult to obtain due to the high alumina and silica content.

8. A low silica, alumina, content must be used in a glaze before a red can be produced satisfactorily.

RECOMMENDATIONS

For further work on this subject, it would be advisable to try for a red glaze with different base glazes varying the alumina, silica content and varying the firing temperatures.

ACKNOWLEDGMENT

I wish to acknowledge the kind assistance and practical advice rendered by Professor Dodd of the Ceramic Department, and for the always willing assistance of Mr. Terrell Evans.

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J. A. C. S. Vol. 3, P. 913, 1920

(4) Dr. Zimmerman - Uranium - Red Glazes.

Keramos Vol. 7, T4-1, 1928

(5) H. Eska - Weather - Proof Uranium Red Glazes

Sprechsaal - Vol. 66, P. 59, 1933.

ABSTRACTS

Uranium - Red Glazes.

Zimmerman - Keramos Vol. 7, T4-1, 1928

The results of the authors work is as follows: The glaze must be basic. The most favorable silica content is .5 mol.; it must not exceed 1.0 mol. and must not be less than .4 mol. The alumina content may be between .1 and .2 mol. The bases must be mainly lead oxide, but potassium oxide up to .1 mol. is also favorable. Small amounts of zinc oxide (.1 to .2 mol.) and boric acid (.05 mol.) are not harmful. Calcium oxide is quite useless.

Weather Proof Uranium Red Glazes.

H. Eska Sprechsaal, Vol. 66, Page 59, 1928.

The author states that Na_2O destroys or greatly weakens the red color; a low quartz content is necessary to obtain the red colors, which, however, soon fades on exposure to an acid atmosphere. In more resistant uranium glazes can be obtained with a high quartz content and no Na_2O. The kaolin content should not exceed .1 mol. The addition of uranium oxide may vary from .15 to .20 mol. according to the composition of the glaze. The best firing temperature is between 940° 960° C; at cone 05 a discoloration occurs.