1939

Effects of zirconium compounds on a bright glaze

Stuart Dods

EFFECTS OF ZIRCONIUM COMPOUNDS ON A BRIGHT GLAZE

BY

STUART DODS

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

BACHELOR OF SCIENCE IN CERAMIC ENGINEERING

Rolla, Mo.

1939

Approved by Paul G. Herold
Assistant Professor of Ceramic Engineering.

TABLE OF CONTENTS

INTRODUCTION 1

SCOPE OF INVESTIGATION 2

METHOD OF INVESTIGATION 2-3

MATERIALS USED 3-4

METHOD OF PREPARING THE GLAZE 4-5

MAKING OF THE TILE 5

APPLICATION OF THE GLAZE 6

FIRING.....7-8

RESULTS (Data) 9-16

DISCUSSION OF RESULTS 17

CONCLUSION 17

ACKNOWLEDGEMENT 18

ABSTRACTS 18-19

THE EFFECTS OF ZIRCONIUM COMPOUNDS ON A BRIGHT GLAZE

INTRODUCTION

The standard method for producing opacity and to some extend mattness in a glaze has always been the use of small amounts of tin oxide. This oxide, however, is very expensive and tends to fluccuate in price over a wide range due to world market conditions. The ceramic industry, therefore, has been searching for some substitutes for the tin oxide with some success. At the present time zinc oxide, antimony oxide, and zirconium oxide are used with varying degrees of success as opacifiers.

Zirconium oxide and compounds are less soluble than the other oxides previously used. There fore, it is greatly possible that zirconium compounds should produce crystalline structure in lower percentages than the other oxides.

With this knowledge it is the object of this experiment to determine the possibilities of the uses of zirconium compounds at percentages capable for commercial use in producing the same effects as tin oxide.

SCOPE OF INVESTIGATION

The object of this study was to determine the effects of zirconium compounds on a bright glaze, with the main regard to ability to produce a matt, opacity, and body fitness, at cone 07 down.

METHOD OF INVESTIGATION

A glaze known to be a bright clear fritted glaze when fired at cone 07 down, was used as a base for the addition of the zirconium compounds at different percentages. Because of the price of some of the compounds, and all the compounds are rather high priced to be used in large percentages on the commercial scale the maximum amount of zirconium compounds used was 10%. Three other trials were run at 2.5, 5, and 7.5% by dry weight.

The zirconium compounds were added dry to the base glaze, screened thru a 100 mesh sieve three times to insure thorough mixing. Normally the compounds would be ground in with the charge but in this case would require too large a batch, and time did not permit.

The glazes were fired on biscuit tile (cone 03) in an electric muffle furnace at cone 07 down.

MATERIALS USED

The materials used were Pennsylvania flint, English China Clay, zinc oxide, tin oxide, borax, litharge, talc, calcium chloride, and #9 Tennessee Ball clay.

The zirconium compounds were:-

1. Tam zircon milled
2. potassium zirconium silicate
3. Sodium " "
4. Magnesium " "
5. Barium " "
6. Calcium " "
7. Lead " "
8. Zinc " "
9. Tam C.P. " "
10. Lead zirconate
11. Zinc "
12. Zirconium spinel
13. Meltopax X grade
14. Opax

Chemical analysis of some of the zirconium compounds used are given below. Code number on previous page.

Analysis	#1	#4	#6	# 14
ZrO_2	64.82	53.78	51.12	87.40
SiO_2	0.04	0.03	0.02	0.29
Na_2O	34.78	26.92	25.41	7.50
CaO	0.003	0.01	0.01	1.30
MgO	0.05	0.005	0.005	0.25
Al_2O_3	0.005	0.20	22.23	0.05
FeO	0.03	18.54	0.70	1.50
Fe_2O_3	0.004	0.005	0.005	0.07
P_2O_5	0.08			0.02
MnO_2	0.001	0.06	0.10	trace
B_2O_3	0.005	0.02	0.05	1.00
Cr_2O_3	0.05	0.05	0.06	trace
CuO	0.001	0.001	0.001	0.10
V_2O_5		0.005	0.005	
CO_2	0.005			
Sulphur				
Moisture		0.05	0.03	0.08
Ign.Loss		0.17	0.14	0.28
Total	99.91	99.85	99.90	99.5
Color	white	white	cr.wht.	white
Sp.gr.	4.55	4.35	4.30	5.22
M.P.	3900°F	3260°F	2880°F	4537°F

METHOD OF PREPARING THE GLAZE

The frit portion of the glaze given on the next page in the emperical formula, was prepared in a pot furnace. The other oxides were added to the frit as a raw batch.

The glaze was ground in a one gallon porcelain pebble mill for eight hours and then passed thru a 100 mesh sieve.

The specific gravity of the glaze was adjusted to 1.60.

R O	R_2O_3	RO_2
.239 Na_2O		
.351 PbO	.159 Al_2O_3	1.528 SiO_2
.410 ZnO	.151 SnO_2	.478 B_2O_3
1.000		

All materials fritted except ZnO, SnO_2 and $\frac{1}{2}$ of E.C.C.*

MAKING OF THE TILE

The tile were dry pressed into shapes $2\frac{1}{2}$" x 1" x 1/4" from number nine Tennessee Ball clay, and talc with eight (8) per cent moisture. Using 75% talc, and 25% Ball Clay. A small amount of iron oxide in the talc gave the body, when fired, a reddish brown color which helped to show the effect of opacity. The tile was bisqued at cone 03.

* E.C.C. denotes English china clay.

APPLICATION OF THE GLAZE

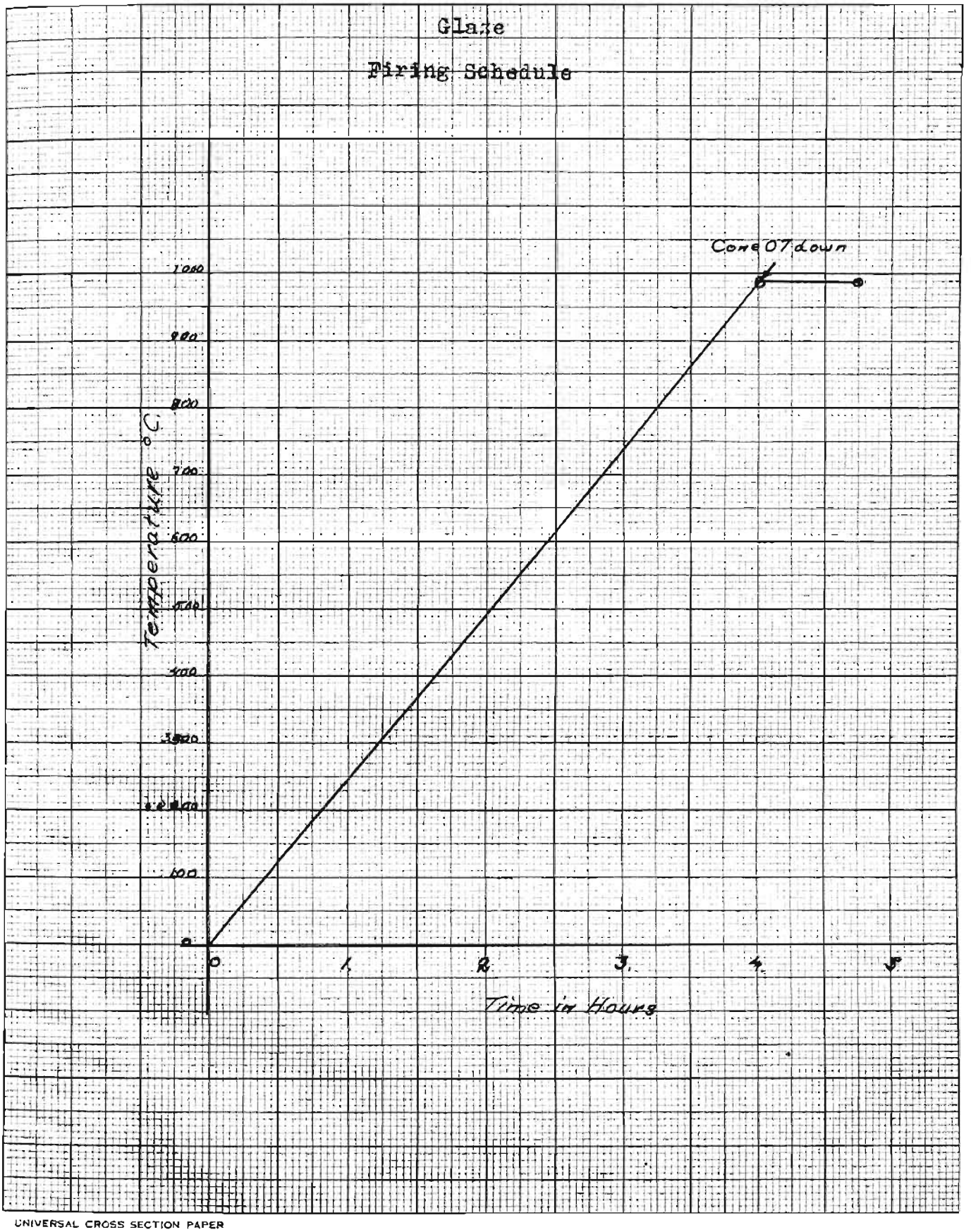
The glaze was applied by dipping two trials thin and two heavy, and when dry, fetting the edges with a spatula.

The glazed pieces were fired in the electric muffle furnace to cone 07 down. Cone 07 down was reached in four hours and allowed to soak for three fourths of an hour.

The firing schedule for the biscuit fire and the glaze fire are on the following pages.

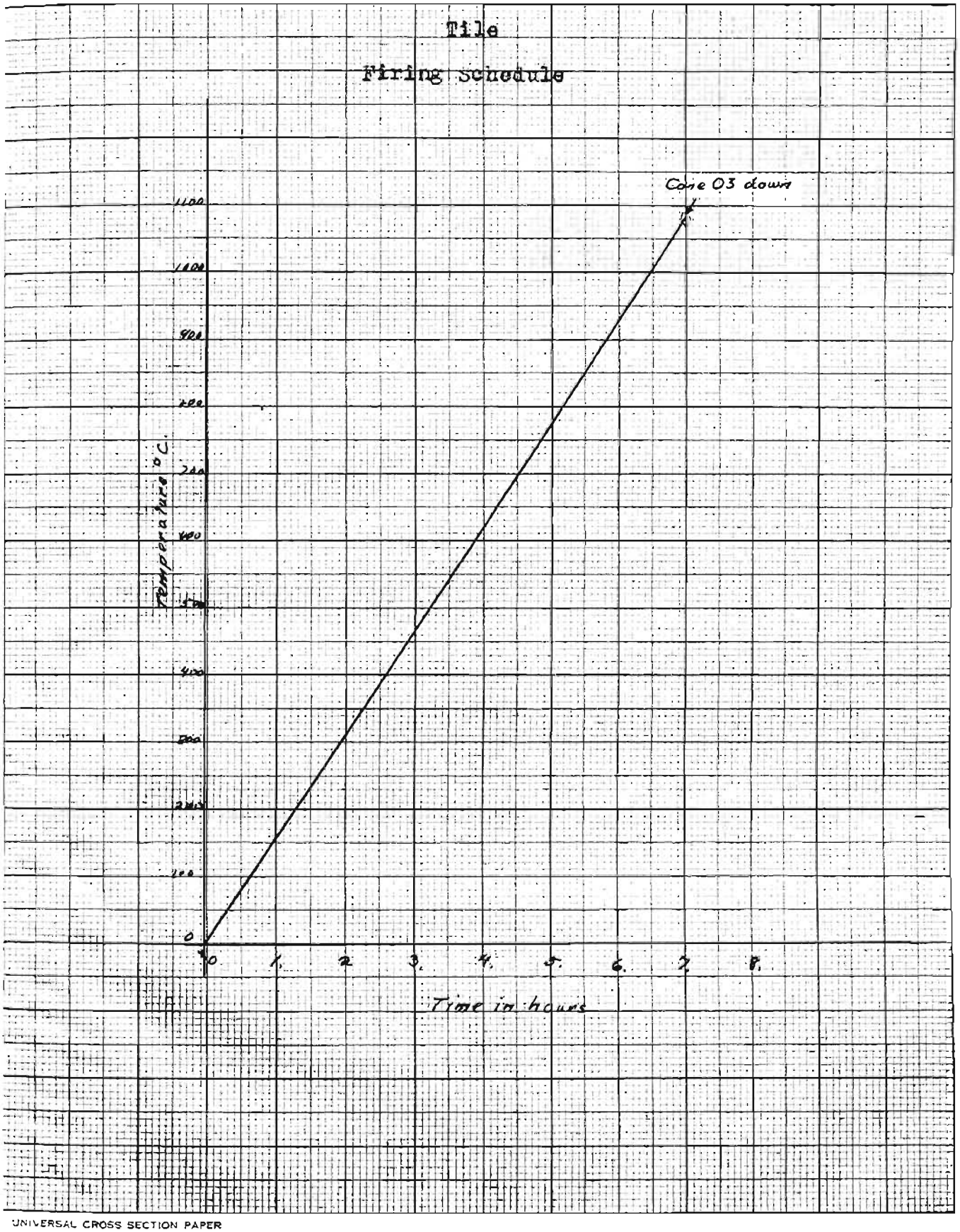
Glaze

Firing Schedule



Tile

Firing schedule



UNIVERSAL CROSS SECTION PAPER

RESULTS
(Data)

Glaze # A100 (Base Glaze)

This glaze fired very clear, body showing thru, when under fired tended to become opaque, no pinholing, one trial had a very slight craze.

Glaze # B-100

This glaze contained 2.5% of Tam zircon milled.
Had no distinct difference than glaze # A-100.

Glaze # B-101

This glaze contained 5% of Tam zircon milled.
Had a little more opacity than B-100

Glaze # B-102

This glaze contained 7.5% Tam zircon milled.
Had a little more opacity than B-100, a large per cent of its area was under fired.

Glaze # B-103

This glaze contained 10% of Tam zircon milled.
Had a little more opacity than B-100, but no noticable change.

Glaze # C-100

This glaze contained 2.5% of potassium zirconium silicate.
This glaze was the same as A-100

Glaze # C-101

This glaze contained 5% of potassium zirconium silicate.

This glaze had a slight tendency towards opacity, no tendency to matt.

Glaze # C-102

This glaze contained 7.5% of potassium zirconium silicate.

More opacity than C-101, pin holes small, crazed slightly.

Glaze # C-103

This glaze contained 10% of potassium zirconium silicate.

Opacity increasing, started to matte, no pin holing.

Glaze # D - 100

This glaze contained 2.5% of Sodium zirconium silicate.

The same as A-100.

Glaze # D-101

This glaze contained 5% of Sodium zirconium silicate.

Was under fired, opacity increased, slight pin hole.

Glaze # D-102

This glaze contained 7.5% of Sodium zirconium silicate.

Opacity increased over D-101, no pin hole.

Glaze # D-103

This glaze contained 10% of Sodium zirconium silicate.

Opacity increased, semi-matte, higher fusion, slight craze, seemed to overcome crazing at higher fire.

Glaze # E-100

This glaze contained 2.5% of Magnesium zirconium silicate.

Same as A-100 except crazed badly.

Glaze # E-101

Contained 5% of Magnesium zirconium silicate.

Opacity increased, still bright, no crazing.

Glaze # E-102

Contained 7.5% of Magnesium zirconium silicate.

Still bright, opacity same as E-101, very slight crazing.

Glaze # E-103

Contained 10% of Magnesium zirconium silicate.

More opacity, slight matte, very slight crazing.

Opacity still very slight.

Glaze # F-100

Contained 2.5% of Barium zirconium silicate.

Same as A-100

Glaze # F-101

Contained 5% of Barium zirconium silicate.

Same as A-100

Glaze # F-102

Contained 7½% of Barium zirconium silicate.

Same as A-100

Glaze # F-103

Contained 10% of Barium zirconium silicate.

Slightly opaque and matte, no crazing.

Glaze # G-100

Contained 2.5% of Calcium zirconium silicate.

Same as A-100.

Glaze # G-101

Contained 5% of Calcium zirconium silicate.

Slightly opaque, going to matte.

Glaze # G102

Contained 7.5% of Calcium zirconium silicate.

More opaque than G-101, slight matte.

Glaze # G103

Contained 10% of Calcium zirconium silicate.

Slightly more matte, and opaque, however is still a poor matte, and not strong in opacity.

Glaze # H-100

Contained 2.5% of Lead zirconium silicate.

Same as A-100, little more fusible.

Glaze # H-101

Contained 5% of Lead zirconium silicate.

Same as A-100.

Glaze # H-102

Contained 7.5% of Lead zirconium silicate.

Same as A-100.

Glaze # H-103

Contained 10% of Lead zirconium silicate.

Goes to matte, tends to opacity.

Glaze # J-100

Contained 2.5% of Zinc zirconium silicate.

Same as A-100.

Glaze # J-101

Contained 5% of zinc zirconium silicate.

Slight tendency to be opaque and matte.

Glaze # J-102

Contained 7.5% of zinc zirconium silicate.

Slightly more opaque and matte.

Glaze # J-103

Contained 10% of zinc zirconium silicate.

Has a tendency to become opaque and matte, however, not at the percentages used.

Glaze # K-100

Contained 2.5% of (C.P.) Zirconium silicate.

Same as A-100.

Glaze # K-101

Contained 5% of (C.P.) Zirconium silicate.

Same as A-100 with slightly more matte.

Glaze # K-102

Contained 7.5% of (C.P.) Zirconium silicate.

Same as K-101.

Glaze # K-103

Contained 10% of (C.P.) Zirconium silicate.

Slight matte, at the percentages used.

Glaze # L-100

Contained 2.5% of Lead zirconate.

Slightly more matte, and opaque than A-100.

Glaze # L-101

Contained 5% of Lead zirconate.

Slightly more matte, and opaque than A-100.

Glaze # L-102

Contained 7.5% of Lead zirconate.

Slightly more matte, and opaque than A-100.

Glaze # L-103

Contained 10% of Lead zirconate.

Slightly more matte, and opaque than A-100.

Glaze # M-100

Contained 2.5% of zinc zirconate.

Same as A-100.

Glaze # M-101

Contained 5% of zinc zirconate.

Tendency to become matte, and opaque.

Glaze # M-102

Contained 7.5% of zinc zirconate.

Tendency to become matte, and opaque.

Glaze # M-103

Contained 10% of zinc zirconate.

Under fired, tendency to be matte, and opaque.

Glaze # N-100

Contained 2.5% of Zirconium Spinel.

Slightly matte, few pin hole,

Glaze # N-101

Contained 5% of Zirconium Spinel.

Under fired, slight opacity.

Glaze # N-102

Contained 7.5% of Zirconium Spinel.

If fired properly a good opacity and tendency to matte.

Glaze # N-103

Contained 10% of Zirconium Spinel.

More matte and more opaque than N-102. Fairly good for matting and opacity.

Glaze # P-100

Contained 2.5% of Meltopax X Grade.

Same as A-100

Glaze # P-101

Contained 5% of Meltopax X Grade.

Slight tendency to be matte and opaque.

Glaze # P-102

Contained 7.5% of Meltopax X Grade.

Tendency to be a matte and opaque.

Glaze # P-103

Contained 10% of Meltopax X Grade.

Tendency to be matte, and opaque.

Glaze # R-100

Contained 2.5% of Opax.

Same as A-100.

Glaze # R-101

Contained 5% of Opax.

Very opaque and matte.

Glaze # R-102

Contained 7.5% of Opax.

This glaze should give the desired effect for use in opacity and mattness. Both of which is very good.

Glaze # R-103

Contained 10% of Opax.

Overfired, Opacity and mattness the same as R-102.

DISCUSSION OF RESULTS

In most cases the glazed trials were underfired, due to a short soaking period.

It was found that in the majority of the cases that it was very hard, by observation, to determine crazing. In most cases the crazing showed up by the application of ink on the glazed portion. It would, however, be much more desirable to have run the trials in an autoclave.

When the pieces were underfired it was noticed that a matting effect was produced, which showed a narrow range of vitrification for the glaze. All of the trials were fired at the same time. The underfiring was due to location in the kiln.

CONCLUSION

It was found that the Opax gave the most desirable opacity, and mattness. This can be applied to commercial use in the ceramic industry.

"A zirconium oxide opacifier for cast iron enamels both wet and dry process and sheet steel enamels. This has also found large usage in the glaze field." **

The zirconium spinel was found to produce opacity, and if slightly underfired would produce a matte. This compound can be used commercially in the ceramic industry.

"This compound finds use as an opacifier for glazes or as an auxiliary opacifier for enamels. Where the rest of the glaze composition favors its use, it produces more opacity per unit than even opax and with an improved surface and texture. Has an advantageous effect on certain colors.** Improves gloss of certain super-opaque enamels."

**From private communication.

ACKNOWLEDGMENT

I wish to acknowledgment the practical advise and assistance rendered by Doctor P.G.Heorld of the Ceramic Department, and The titanium Alloy Manufacturing Company for samples donated.

ABSTRACTS

C.H.Commons,Jr.; Recent Developments in zirconium Glazes and the effect of Various Materials on the Results; The Bulletin of the American Ceramic Society; Volume 17; Number 11; Pages 433 - 434; 1938.

C.J.Kinzie and C.H.Commons,Jr.: The effect of Various Zirconium and Titanium Compounds on a Glaze; The Bulletin of the American Ceramic Society; Volume 16; Number 1; pages 1-4; 1937.