A STUDY OF VANADIUM IN GLAZES

By

CHESTER WILMONT BROWN

A THESIS

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CHAPTER I

PURPOSE

The purpose of this investigation was to study some of the effects of vanadium pentoxide in glazes under oxidizing and reducing conditions and to develop a green and a blue glaze containing vanadium pentoxide.

CHAPTER II

INTRODUCTION

Vanadium, although in the elemental form does not occur in nature, is one of the more abundant of the minor constituents of the earth's crust, for it is more abundantly distributed than nickel, copper, zinc, or lead. According to Clarke and Washington[1], it constitutes 0.038 per cent of the ten mile crust. The vanadium minerals include: Patronite - a vanadium sulphide, Bravoite - an iron nickel sulphide containing vanadium, Alaite - $V_2O_5 \cdot H_2O$, Roscoelite - vanadium mica, Eosite - a lead vanadate, Chileite - a lead copper vanadate, Vanadialite - a siliceous lead vanadate, and Carnotite - a potassium uranium complex.

The vanadium minerals occur in Europe, Asia, Africa, Australia, South America, and the United States. In the United States, vanadium occurs principally in Colorado and Utah and in the Rocky Mountain region of Arizona and New Mexico. Some carnotite occurs in Pennsylvania and vanadium ores have been reported in Michigan, California, Oregon and Nevada. The asphaltites of Oklahoma and Arkansas are vanadiferous[2].

Vanadium commonly occurs in clays, especially in titaniferous clays, and produces in damp weather a yellow - greenish scum of

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[1] F. W. Clarke and H. S. Washington, "The Composition of the Earth's Crust," Washington, 1924.

[2] J. W. Mellor, "A Comprehensive Treastise on Inorganic and Theoretical Chemistry," Volume IX.

alkali vanadates. The addition of some lead compounds has been used to advantage in removing the scum.

Vanadium occurs as a replacement for other elements in mica, spinels, magnetite, and other mineral species. It has not been completely understood nor determined in what form vanadium occurs in asphalt and petroleum deposits. The vanadium minerals, with the exception of the lead vanadates and a few other species, are collodial or cryptocrystalline.[3]

Vanadium furnishes four well defined oxides:

1) Vanadium dioxide, or hypovanadous oxide, V_2O_2, vanado - oxide.
2) Vanadium trioxide, or vanadous oxide, V_2O_3, vanadi - oxide.
3) Vanadium tetoxide, or hypovanadic oxide, V_2O_4, vanade - oxide.
4) Vanadium pentoxide, or vanadic oxide, V_2O_5, vanadan - oxide.

A fifth oxide, vanadium hemioxide, V_2O, vanada - oxide was suggested by Roscoe[4]. The four oxides of vanadium give distinct colors to salts derived from them, as lavender or violet from the dioxide; green from the trioxide; blue from the tetroxide; and yellow from the pentoxide.

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[3] F. F. Franklin, "The Vanadium Minerals," Vancoram Review, 6 (2) 11 (1950).

[4] J. W. Mellor, loc. cit.

The end product of the oxidation of the element vanadium, the lower oxides, the nitride, or the sulfides, by roasting in air is vanadic anhydride, V_2O_5, or as it is commonly called, vanadium pentoxide. Werner's nomemclature for the pentoxide is vanadan - oxide. Throughout this investigation, the term vanadium pentoxide is used.

The position of vanadium in the periodic table of the elements shows it to be a member of the transition group. Vanadium has a variable valence from one to five and is like its neighbors, chromium and iron in that they have a variety of valences and a different color ion for each valence. Like chromium and iron, which show a variety of colored ions, vanadium, to even a greater extent follows the same pattern. The coloration which is given by the various ions of the elements probably is due to the electrons in the outer shells shifting from one orbit to another.

K. Fuwa[5] published the first systematic investigation of the use of vanadium as a glass colorant. He stated that the color given to glass by vanadium pentoxide resembles chromic oxide, though the latter has a stronger tint in yellow than the former. Reducing agents, such as potassium tartrate and arsenious acid, decrease the yellow color while oxidizing agents, such as potassium nitrate,

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5. K. Fuwa, "Color Given to Glass by Vanadium," Jour. Japanese Cer. Assoc., 369 236-240 (1923); Cer. Abs., 2 (11) 243 (1923).

tend to act the other way. Weyl[6] disagrees with Fuwa[7], who states that the color imparted by vanadium pentoxide was independent of the composition of the glass involved. Weyl further states that the grey colors of vanadium glasses probably arise from a cause similar to that which induces grey colors in iron and copper glasses, namely the simultaneous presence of an element in two states of valency.

A behavior of colors in vanadium glasses and the reasons for such colors have been reported by Weyl, Pincus, and Badger[8]. They reported that the yellow color which is attributable to the V^5 ion is due to an absorption starting in the ultraviolet and extending into the violet, while an excess of V^5 ion extends the absorption band to include some blue, and the yellow deepens to amber. The gray color obtained with glasses high in boric oxide is caused by the insolubility of vanadium pentoxide in this solvent. Further experiments with vanadium showed that the acid glasses favored lower valences and, finally, the colorless vanadate ion. Also an excess of alkali, as with sodium metasilicate, favored the formation of the colorless vanadate ion.[9]

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[6] W. A. Weyl, "The Colours Produced by Vanadium," J. Soc. Glass Tech., 28 185-9 (1944).

[7] K. Fuwa, loc. cit.

[8] W. A. Weyl, A. G. Pincus, and A. E. Badger, "Vanadium as a Glass Colorant," J. Amer. Cer. Soc., 22 (11) 374-77 (1939).

[9] W. A. Weyl, A. G. Pincus, and A. E. Badger, loc. cit.

Many investigators have resorted to the use of stains in furthering their studies of vanadium as a ceramic colorant. A yellow stain of 96.0 parts stannic oxide and 4.0 parts by weight of ammonium vanadate, using a feldspathic glaze, showed a variation in hue ranging from a light yellow for the specimens fired in a neutral atmosphere to a mottled orange-yellow for specimens fired in pure oxygen. This change was explained as due to the colloidal deposition of vanadium pentoxide on the inert stannic oxide particles analogous to chrome - tin pinks[10]. Andrews and Zwermann[11], using a yellow vanadium stain in an enamel, found that the yellow enamel lost its color at extreme heat treatments, possibly due to solution. The stain made a nice color, but a change in its composition is indicated.

L. Jackson, in an article written for the Vancoram Review, indicates that blue, green, yellow, shadings of turquoise, apple - green, and peach can be produced with vanadium.[12] Also, she believes that some of the colors involve trade secrets. Remington[13] states that a blue and a green can be obtained using vanadium and zirconia,

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[10] W. F. McDevit, "Effect of Firing Atmosphere on Development of Colors in Ceramic Glazes," J. Amer. Cer. Soc., 27 (6) 165-75 (1944).

[11] A. I. Andrews and C. H. Zwermann, "Fundamentals of Colors in Porcelain Enamels," J. Amer. Cer. Soc., 22 65-72 (1939).

[12] L. Jackson, "Vanadium as a Ceramic Colorant," Vancoram Review, 5 (4) 9 (1950).

[13] V. H. Remington, "Pigments During and After the War," Bull. Am. Cer. Soc., 27 57-59 (1948).

but he does not give the composition of the glaze that he used. However, he does state that the vanadium was added as either ammonium vanadate or vanadium pentoxide. The beauty and brilliance of crystal separations in flowing, running, marbled, streaked, and shaded glazes are enhanced by the addition of small quantities of the oxides of tungsten, molybdenum, and especially from 0.2 to 2 per cent vanadium.[14]

The reported use of vanadium in ceramic glazes is very limited. Therefore, the study of the colors produced in high lead, fritted, and leadless glazes under oxidizing and reducing conditions should prove very interesting.

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[14] C. W. Parmelee, Ceramic Glazes, pp. 185-6.

CHAPTER III

PROCEDURE

The following is the procedure used throughout for the preparation of all glazes:

For raw glazes the ingredients were weighed, mixed by screening through a 20 mesh screen, and ground for three hours in a pebble mill with 40 per cent water. The glaze was then removed and screened through 100 mesh.

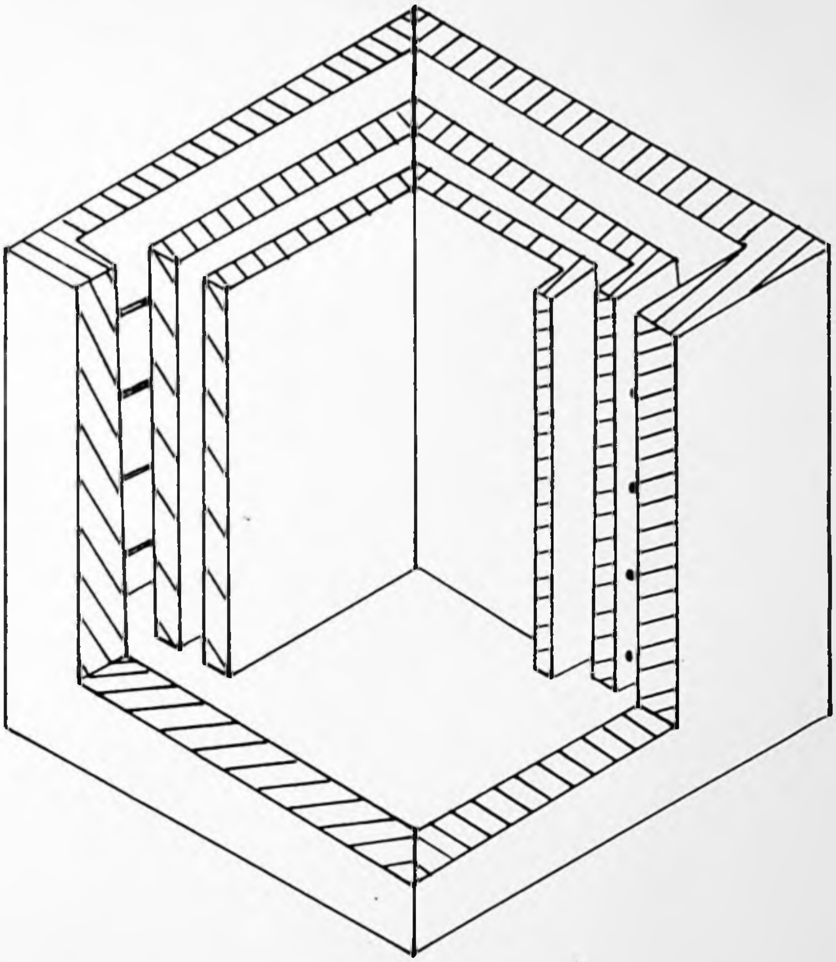
Three raw glazes, containing a high lead oxide content and maturing at cone 05 were formulated. The glazes were then sprayed on tile test pieces and fired to cone 05. Glaze C, which gave the best gloss and texture, was used as the base glaze for initial experimental work on raw lead glazes. (See Tables I, II, and III).

A 1500 gram batch of glaze C was prepared, using 40 per cent water. Two glazes designated as C-1 and C-2 were prepared, using 40 per cent water and substituting 15 per cent vanadium pentoxide and 15 per cent stannic oxide, respectively, for the "Zircopax" (ground zircon) in the base glaze C.

Glazes C, C-1, and C-2 formed the corners of a triaxial diagram and were blended on a dry basis to study the effect of "Zircopax" and the stannic oxide with vanadium pentoxide in a glaze. (See Figure I). The glazes were blended on increments of 20 per cent as shown in Figure I. Four test plaques of each composition were sprayed, placed in the electric laboratory kiln and the temperature of the kiln allowed to reach 1500° F overnight. Then the rate of fire was at 50° F per hour up to cone 04 where the glazes were allowed to soak for two hours and then the firing continued to cone 05 at the rate of 50° F per hour. Two plaques were then refired to 1575° F and reduced with natural gas for one hour and allowed to cool slowly to room temperature.

In order to have a satisfactory reducing atmosphere, it was necessary to build a muffle inside a laboratory electric kiln. This muffle consisted of two fire-brick partitions. Partition 1, which is the partition next to the globars, was constructed of insulating brick well plastered with Cordova fire clay on one side to prevent the natural gas, which was used for a reducing atmosphere, from leaking and to prevent the needless destruction of the globars. Partition 2, which is the inside partition, was constructed of insulating brick but no fire clay was used on the walls. The natural gas was run from the outside into the opening between the two partitions and allowed to seep through the porous walls of the inside partition. (See Sketch I). The reducing temperature was maintained at 1575° F for one hour, the power shut off and the kiln cooled to 1400° F under reducing conditions.

Another triaxial diagram of glazes was developed using glaze C as the base glaze. (See Figure II). In this diagram, glaze C with 10 per cent "Zircopax", glaze C without any "Zircopax", and glaze C with 5 per cent vanadium pentoxide, were used instead of



Sketch I

Reduction Muffle

the 15 per cent as in Figure I. These glazes were blended dry in increments of 20 per cent as shown in Figure II. Four test plaques of each composition were sprayed, placed in the laboratory electric kiln and the temperature of the kiln allowed to reach 1500° F overnight. Then the rate of fire was at 50° F per hour up to cone 04, where the glazes were allowed to soak for two hours, and then the firing continued to cone 05 at the rate of 50° F per hour. Two plaques were then refired to 1575° F and reduced with natural gas for one hour, the power shut off and the kiln cooled to 1400 ° F under reducing conditions. The reduction in this field differed from the previous reduction. The gas was allowed to seep into the electric laboratory kiln without the assistance of a muffle.

For fritted glazes the ingredients were weighed, mixed by screening through a 20 mesh sieve, placed in a clay pot with a hole in the bottom and fritted at a temperature of 1800° F. The frit was then ground in a pebble mill, screened through an 80 mesh screen, added to the mill addition with 40 per cent water as in Tables 5, 6, and 7, and then reground in a pebble mill, screened through 100 mesh and aged for 24 hours.

Two fritted glazes, designated D and E, were made, sprayed on tile, and fired at cones varying from 05 to 5 to determine the best glaze to be used for experiments with vanadium pentoxide in fritted glazes. Glaze D at cone 01 was found to have the best gloss and was used as the base glaze. (See Tables 5 and 6). Fritted glaze

D-1 was prepared, using an addition of 0.1 molecular equivalent of vanadium pentoxide, as shown in Table 7.

Glaze D-2 was formed by adding 15 per cent "Zircopax" to glaze D and glaze D-3 by adding 15 per cent stannic oxide to glaze D. These glazes and D-1 formed the corners of a triaxial diagram and were blended as shown in Figure III in increments of 20 per cent, and all blends were made on a dry weight basis. Four test plaques of each composition were sprayed, placed in the laboratory electric kiln and the temperature of the kiln allowed to reach 1500° F overnight. Then the rate of fire was at 50° F per hour up to cone 02 where the glazes were allowed to soak for two hours and then the firing continued to cone 01 at the rate of 50° F per hour. Two plaques were then refired to 1575° F and reduced with natural gas for one hour, the power shut off and the kiln cooled to 1400° F under reducing conditions. These glazes were reduced in the muffle to see what colors could be produced with glazes containing vanadium pentoxide, "Zircopax", and stannic oxide.

Three stains, designated as S-1, S-2, and S-3, as shown in Table 8, were developed. These stains were calcined in a small electric laboratory furnace at 2300° F and ground in a pebble mill for 48 hours. The stains were added to the base glaze D in increments of 2.5, 5, and 10.0 parts of stain per hundred parts of glaze D on a dry weight basis. "Zircopax" and stannic oxide were varied with the stains in increments of 2.5, 5, and 10.0 parts of stain and oxide per hundred parts of glaze D. These compositions are shown in Tables 9, 10, 11, 12, and 13. Four test plaques of each composition were sprayed, placed in the laboratory electric kiln and the temperature of the kiln allowed to reach 1500° F overnight. Then the rate of fire was at 50° F per hour up to cone 02 where the glazes were allowed to soak for two hours and then the firing continued to cone 01 at the rate of 50° F per hour. Two plaques were then refired to 1575° F and reduced with natural gas for one hour, the power shut off and the kiln cooled to 1400° F under reducing conditions. These stains were reduced in the muffle to determine the various colors that might be produced when vanadium pentoxide, stannic oxide, "Zircopax", or when all three of the above were fired under reducing conditions.

TABLE I

GLAZE "A"

	Per Cent
White Lead	41
Whiting	4
Feldspar	15
Flint	20
Zinc Oxide	5
Florida Kaolin	5
Zircopax	15
	100
Gum Arabic	4
Water	40

TABLE II

GLAZE "B"

	Per Cent
Red Lead	41
Whiting	4
Feldspar	15
Flint	20
Florida Kaolin	5
Zircopax	15
Zinc Oxide	5
	100
Gum Arabic	4
Water	40

TABLE III

GLAZE "C"

	Per Cent
White lead	45.6
Whiting	4.4
Feldspar	16.6
Flint	22.2
Strontium Carbonate	5.6
C & C Ball Clay	5.6
	100.00
Gum Arabic	3.0
Water	40.0

TABLE IV

COMPOSITION OF LAKELAND NEPHELINE SYENITE*

Empirical Composition	
SiO_2	.988
Al_2O_3	.242
CaO	.0052
Na_2O	.160
K_2O	.054

Percent Composition	
SiO_2	59.3
Al_2O_3	24.7
Fe_2O_3	0.06
CaO	0.27
MgO	0.02
Na_2O	9.9
K_2O	5.1
TiO_2	0.002
Ignition Loss	0.44

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*Produced by the Great Lakes Foundry Sand Company, Detroit, Michigan.

FIGURE I

VARIATIONS OF "ZIRCOPAX", STANNIC OXIDE,
VANADIUM PENTOXIDE IN RAW LEAD GLAZES

GLAZE "C"

	%
White Lead	45.6
Whiting	4.4
Feldspar	16.6
Flint	22.2
$SrCO_3$	5.6
C & C Ball Clay	5.6
	100.0
Gum Arabic	3.0
Water	40.0

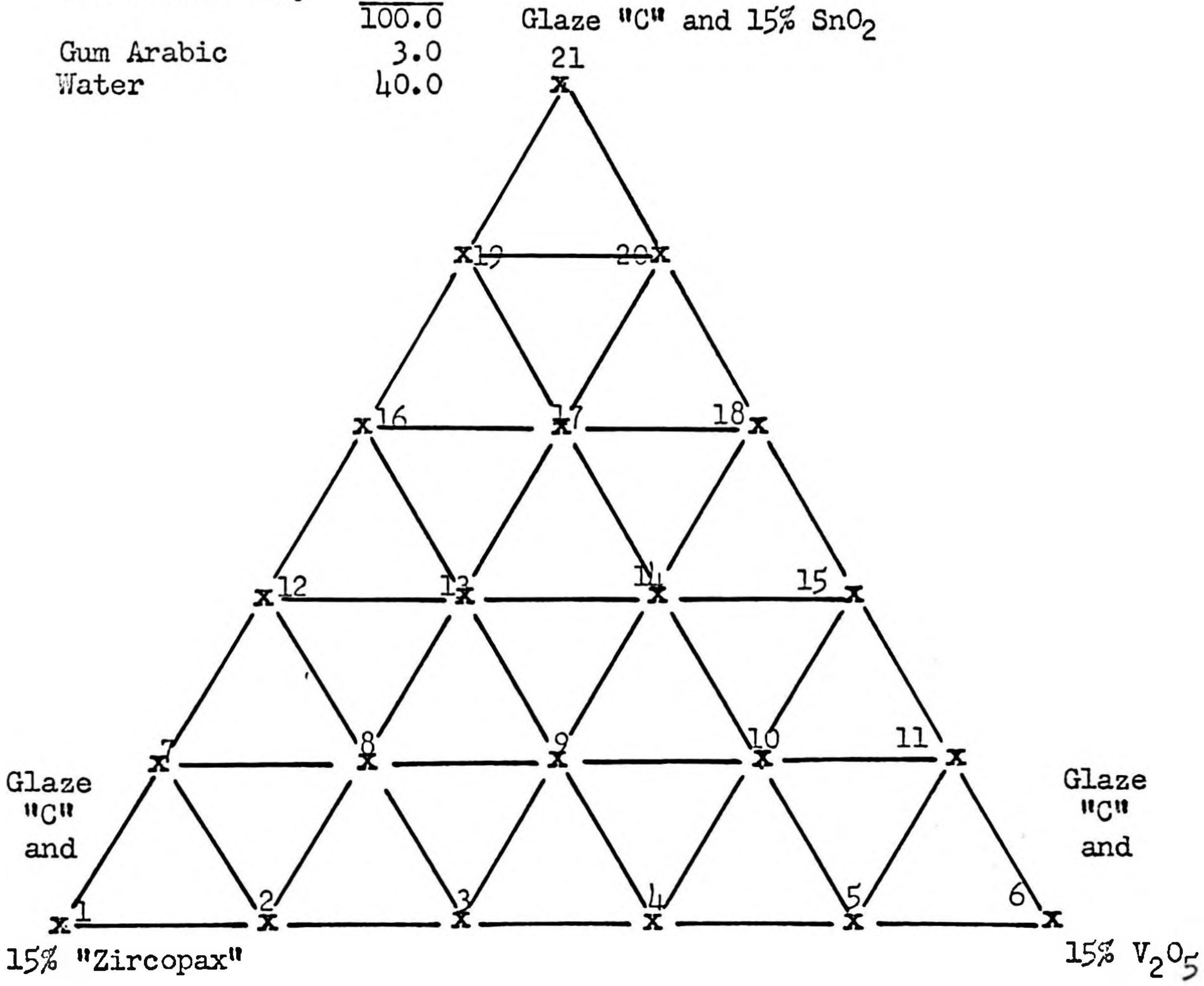

FIGURE II

VARIATIONS OF "ZIRCOPAX" AND VANADIUM PENTOXIDE

IN RAW LEAD GLAZES

GLAZE "C"

	%
White Lead	45.6
Whiting	4.4
Feldspar	16.6
Flint	22.2
$SrCO_3$	5.6
C & C Ball Clay	5.6
	100.0
Gum Arabic	3.0
Water	40.0

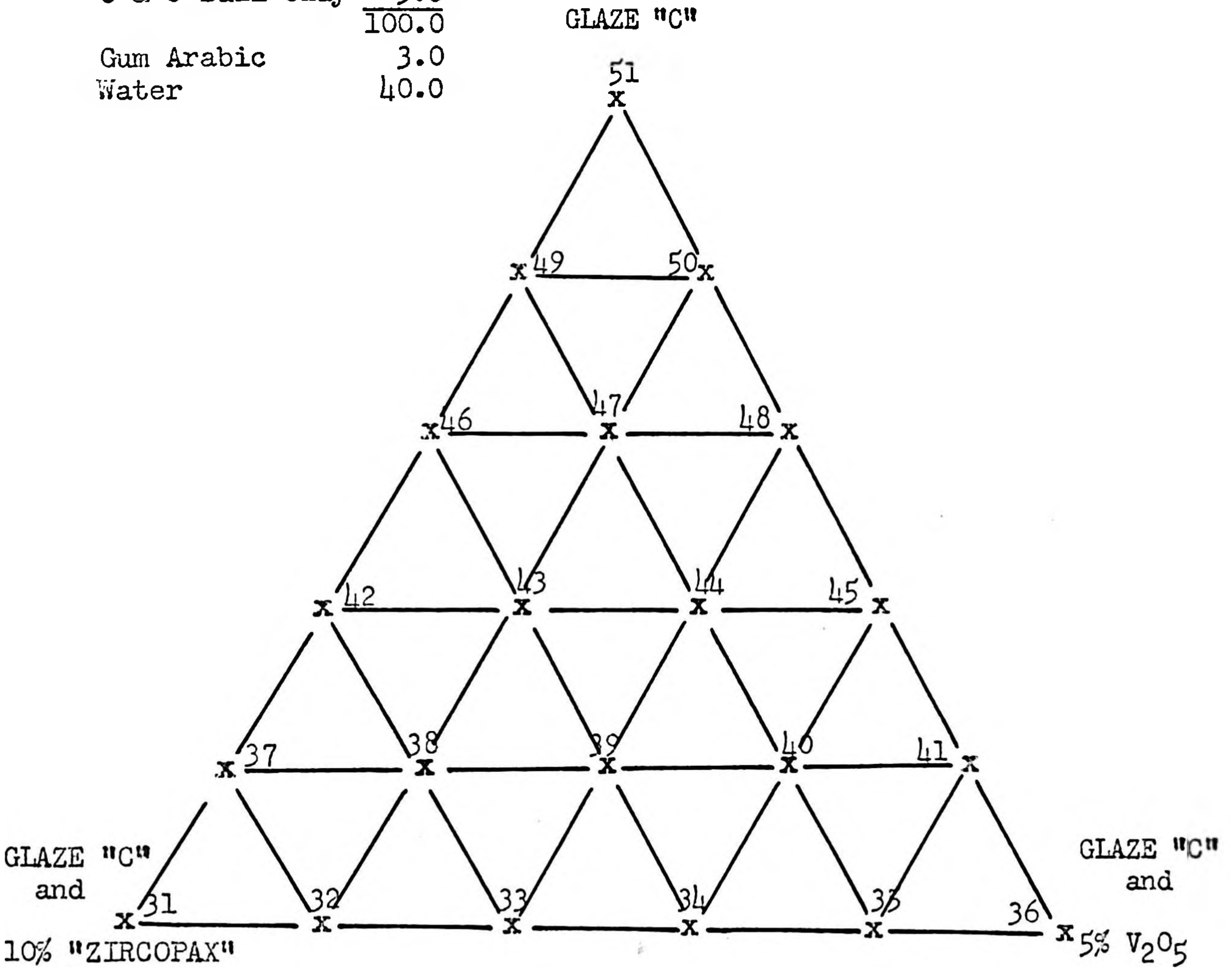

FIGURE III

VARIATIONS OF "ZIRCOPAX", STANNIC OXIDE, AND VANADIUM PENTOXIDE IN FRITTED GLAZES

GLAZE "D"

	%
Frit	48.5
Nepheline Syenite	20.6
C & C Ball Clay	3.9
Flint	16.5
Barium Carbonate	6.0
Whiting	4.5
	100.0
Gum Arabic	3.0
Water	40.0

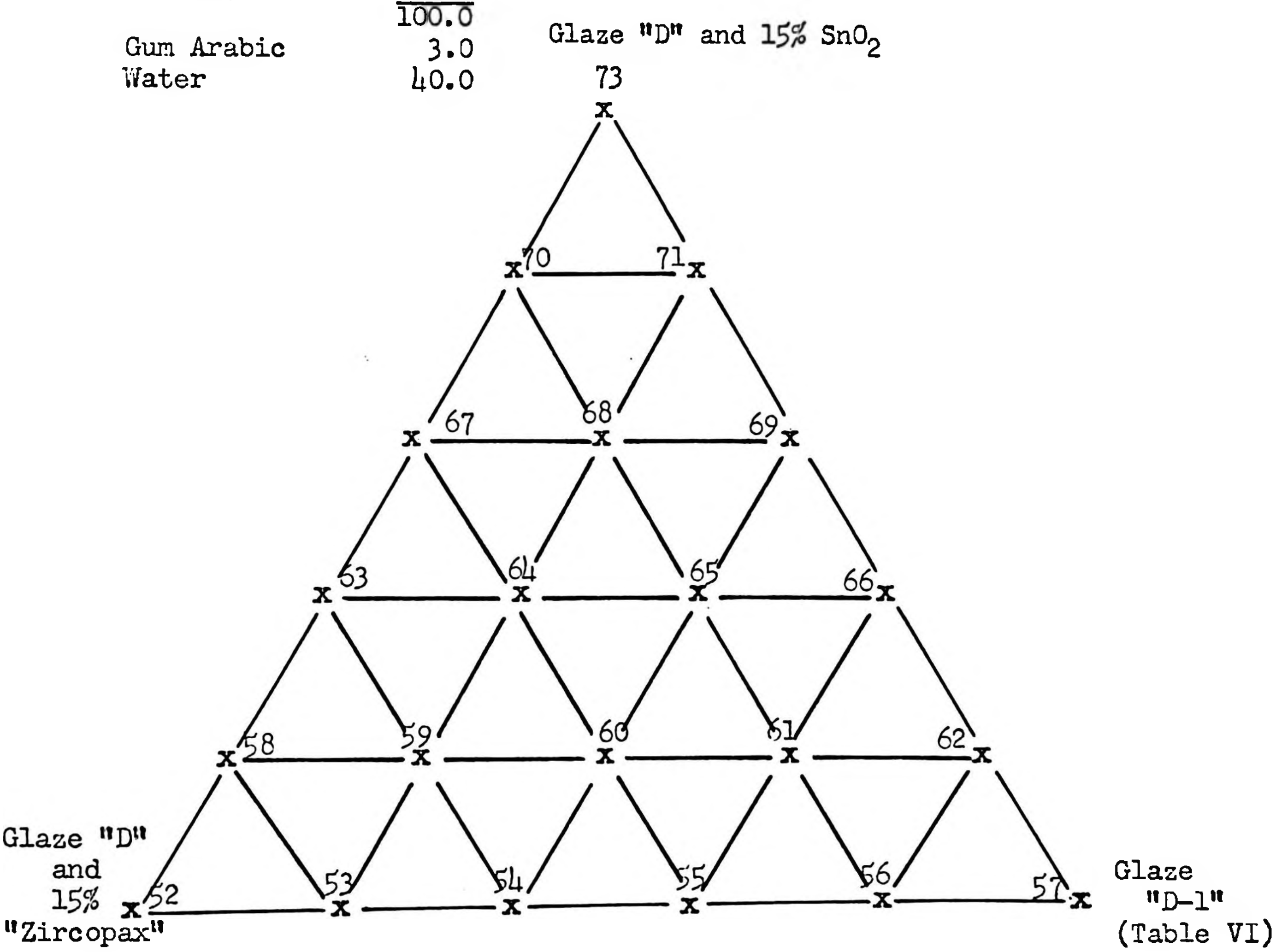

TABLE 5

GLAZE "D"

Empirical Formula

NaKO	.4				
SrO	.1	B_2O_3	.3		
BaO	.1			SiO_2	2.7
CaO	.4	Al_2O_3	.333		

Frit Empirical Formula

NaKO	.5	B_2O_3	.6		
SrO	.2			SiO_2	2.0
CaO	.3	Al_2O_3	.226		

Frit Batch

	Eq. Wt.	%
.3 Borax x 380	114	35.8
.2 Nepheline Syenite x 452.25	90.5	28.4
.295 Whiting x 68	20.1	6.3
.2 Strontium Carbonate x 147.64	29.5	9.3
1.077 Flint x 60	64.6	20.2
	318.7	100.0

Glaze Batch

Moles	Material	Molecular Weight	Equivalent Weight	%
.5	Frit	318.7	159.4	48.5
.15	Nepheline Syenite	452.25	67.8	20.6
.05	C & C Ball Clay	256.0	12.8	3.9
.907	Flint	60.1	54.4	16.5
.1	Barium Carbonate	197.37	19.7	6.0
.215	Whiting	68.0	14.6	4.5
			328.7	100.0

TABLE 6

GLAZE "E"

Empirical Formula

SrO	.2				
BaO	.4	Al_2O_3	.2	SiO_2	2.0
CaO	.3				
NaKO	.1				

Frit Formula

NaKO	.1				
SrO	.2	Al_2O_3	.1	SiO_2	1.0
BaO	.3				

Batch Formula

	%
Frit	47.2
Barium Carbonate	13.4
Calcium Carbonate	10.2
C & C Ball Clay	8.8
Flint	20.4
	100.0
Gum Arabic	3.0
Water	40.0

TABLE 7

GLAZE "D-1"

Empirical Formula

NaKO	.4				
SrO	.1	B_2O_3	.3	SiO_2	2.7
CaO	.4	Al_2O_3	.333	V_2O_5	.1
BaO	.1				

Frit Empirical Formula

NaKO	.5	B_2O_3	.6	SiO_2	2.0
SrO	.2				
CaO	.3	Al_2O_3	.226	V_2O_5	.2

Frit Batch

Moles	Material	Molecular Weight	Equivalent Weight	%
.3	Borax	380.00	114	32.2
.2	Nepheline Syenite	452.25	90.5	25.5
.295	Whiting	68.00	20.1	5.7
.2	Strontium Carbonate	147.64	29.5	8.3
.2	Vanadium Pentoxide	181.9	36.4	10.1
1.077	Flint	60.1	64.6	18.2
			355.1	100.0

Glaze Batch

Moles	Materials	Molecular Weight	Equivalent Weight	%
.5	Frit	355.1	177.6	51.2
.15	Nepheline Syenite	452.25	67.8	19.5
.05	C & C Ball Clay	256.00	12.8	3.7
.907	Flint	60.1	54.4	15.7
.1	Barium Carbonate	197.37	19.7	5.7
.215	Whiting	68.0	14.6	4.2
			346.9	100.0

TABLE 8

STAINS "S-1", "S-2", and "S-3"

Stain No.	% V_2O_5	% SnO_2	% "Zircopax"	% $Al(OH)_3$
S-1	37.5	37.5	----	25.0
S-2	37.5	----	37.5	25.0
S-3	15.0	----	----	85.0

TABLE 9

BLENDING OF STAINS WITH GLAZE "D"

Glaze No.	Parts S-1	Parts S-2	Parts S-3	Parts "Zircopax"	Parts SnO_2	Parts Glaze "D"
73	2.5					100.0
74	5.0					100.0
75	10.0					100.0
76		2.5				100.0
77		5.0				100.0
78		10.0				100.0
79			2.5			100.0
80			5.0			100.0
81			10.0			100.0

TABLE 10

BLENDING OF S-1, "ZIRCOPAX", AND GLAZE "D"

Glaze No.	Parts S-1	Parts "Zircopax"	Parts Glaze "D"
82	2.5	2.5	100.0
83	2.5	5.0	100.0
84	2.5	10.0	100.0
85	5.0	2.5	100.0
86	5.0	5.0	100.0
87	5.0	10.0	100.0
88	10.0	2.5	100.0
89	10.0	5.0	100.0
90	10.0	10.0	100.0

TABLE 11

BLENDING OF S-2, SnO_2, AND GLAZE "D"

Glaze No.	Parts S-2	Parts SnO_2	Parts Glaze "D"
91	2.5	2.5	100.0
92	2.5	5.0	100.0
93	2.5	10.0	100.0
94	5.0	2.5	100.0
95	5.0	5.0	100.0
96	5.0	10.0	100.0
97	10.0	2.5	100.0
98	10.0	5.0	100.0
99	10.0	10.0	100.0

TABLE 12

BLENDING OF S-3, "ZIRCOPAX", AND GLAZE "D"

Glaze No.	Parts S-3	Parts "Zircopax"	Parts Glaze "D"
100	2.5	2.5	100.0
101	2.5	5.0	100.0
102	2.5	10.0	100.0
103	5.0	2.5	100.0
104	5.0	5.0	100.0
105	5.0	10.0	100.0
106	10.0	2.5	100.0
107	10.0	5.0	100.0
108	10.0	10.0	100.0

TABLE 13

BLENDING OF S-3, SnO_2, AND GLAZE "D"

Glaze No.	Parts S-3	Parts SnO_2	Parts Glaze "D"
109	2.5	2.5	100.0
110	2.5	5.0	100.0
111	2.5	10.0	100.0
112	5.0	2.5	100.0
113	5.0	5.0	100.0
114	5.0	10.0	100.0
115	10.0	2.5	100.0
116	10.0	5.0	100.0
117	10.0	10.0	100.0

CHAPTER IV

DISCUSSION OF RESULTS

In the raw glazes shown in Figure 1, the opacity of the glazes containing "Zircopax" was identical in appearance to the glazes opacified with stannic oxide. As the vanadium pentoxide increased from 0 to 15 per cent, a range of yellows varying from a light cream to a medium yellow was obtained. These colors were slightly darker than the colors of the glazes in Figure II where the vanadium pentoxide content was 5 per cent. All glazes in Figure 1, with the exception of glaze 6 which contained 15 per cent vanadium pentoxide, were good bright glazes. Glaze 6 had a rough, immature surface. When this glaze was fired at temperatures as high as 2400° F, no change in texture or maturity was noticed. It was, therefore, concluded that in this glaze some reaction involving vanadium had taken place. Concentrations of vanadium pentoxide above 9 per cent in this field showed no increase in color when compared to glazes in Figure II, which were below 9 per cent vanadium pentoxide concentration. Extreme blistering of the glazes with the lead oxide being reduced to metallic lead was encountered.

Glazes shown in Figure II fired under oxidizing conditions resulted in a field of glazes varying from a light tan to a medium yellow. Due to the white tile body to which the glazes were applied, the opacity normally expected from the "Zircopax" was not noticed.

Glaze 31, containing 10 per cent "Zircopax", was a light tan color, this same color prevailed as the "Zircopax" was decreased to glaze 51 (a clear glaze containing no opacifiers). The light tan color probably was due to the high lead oxide content of the glaze. The yellow color was caused by the slight reduction of the lead oxide. Glaze 51 when fired on a white body exhibits a yellow color. As the percentage of vanadium pentoxide increased, the glazes containing a larger percent of vanadium became a deeper yellow. No effect of the variations of the "Zircopax" with the vanadium pentoxide could be noticed.

All glazes were reduced to determine the colors that could be produced by vanadium if reduced from the pentoxide to the other valences of vanadium. The glazes in Figure II, when reduced without a muffle, produced results that were not uniform. They showed that glazes high in lead oxide content can be reduced but it is not advisable to do so. Rough, discolored surfaces were prominent throughout the field except for the glazes high in "Zircopax", which showed no reduction. Glazes high in vanadium pentoxide were brownish yellow but the real color was obstructed by the reduction of the lead oxide. In the center of the field where the "Zircopax" and vanadium pentoxide were present in nearly equal amounts, a light blue color was present, which was probably due to the reduction of the vanadium pentoxide to vanadium tetroxide.

No difficulties were encountered in the grinding of the glaze batches in which the vanadium pentoxide content in the raw glaze was low. As the vanadium pentoxide content increased above 5 per cent, swelling or fluffing of the batch was noticed and this swelling made the glaze batch difficult to grind. To avoid this swelling, the vanadium pentoxide was calcined at 2000° F and in later experiments where a fritted glaze was used, the vanadium pentoxide was incorporated in the frit.

Boric oxide is known to give a grey color when incorporated in a glaze containing vanadium pentoxide. In the fritted glazes with boric oxide present in large concentrations, the color, as compared with the raw lead glazes, changed from a medium yellow to a light cream and with the concentration of vanadium greater than 3 per cent, the color was a light tan. In this field (Figure III), the opacity of the stannic oxide is much greater than the "Zircopax". It is apparent that a high percentage of lead oxide gives a yellow cast to the glazes, regardless of the opacifying agent present. In the leadless fritted glaze, the opacity imparted by stannic oxide was greater than the opacity imparted by an equal weight of "Zircopax".

The fritted glazes high in "Zircopax" and stannic oxide when reduced showed a dark grey color for "Zircopax" and a light grey for stannic oxide. As the vanadium pentoxide increased in concentration, the grey turned to a brownish green. Glaze 62 gave the best color, a dark green which was so green that it appeared to be black. The glaze containing the highest concentration of vanadium pentoxide when reduced gave a rough, immature glaze.

Spectrographic work conducted on glaze D-1, before and after fritting, gave an indication that the vanadium did not volatilize when fritted or fired as a glaze. The film showed that the spectrographic lines were of the same intensity for both samples.

Stains incorporated in glazes have been widely used for the glazing of ware. A review of literature revealed that little has been written on stains containing vanadium pentoxide.[1] Since "Zircopax" and stannic oxide have been used with vanadium pentoxide throughout this investigation to determine the colors that could be produced under oxidizing and reducing conditions, they were incorporated with vanadium pentoxide in the stains developed. Quantitative spectrography could have been used to determine the concentrations of materials used to make the stains that were on hand, but only qualitative spectrography was available.

The stannic oxide-vanadium pentoxide bearing stain gave a yellow as expected, yet the color was lighter than expected for the amount of colorant used. With "Zircopax" blended in a vanadium stain, a light greenish-blue was apparent as the concentration of the stain increased. Vanadium pentoxide plus aluminum hydrate, which was used to avoid adding any more alkali substances and silica to the glaze, gave a dull grey color and the color increased as the amount of stain increased in the glazes. Glazes containing only vanadium approached a true matt glaze whereas the other glazes

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[1] L. Jackson, loc. cit.

were bright.

The color of the glazes resulting from the blending of "Zircopax" with the stannic oxide-vanadium stain varied from a yellowish-tan to a greenish-yellow as the concentration of the "Zircopax" and the stain increased. On the other hand, when stannic oxide was blended with the "Zircopax"-vanadium stain the colors varied from a light cream white to a white with a yellowish cast.

The vanadium-aluminum hydrate stain when blended with "Zircopax" gave a color similar to those from the "Zircopax"-vanadium stain and stannic oxide blends. The colors ranged from a light cream to a grey cream with a slight green cast. Also, there was a similarity between the all-vanadium stain when blended with stannic oxide. In this blending, the colors were a cream to a yellowish grey as the concentration of the stannic oxide and the stannic increased. The last three glazes in this field approached a true matt glaze.

The stains, after being prepared and calcined, were ground to pass 200 mesh. These stains, when incorporated in the glazes, resulted in glazes which had a speckled appearance, indicating that the stains had not been gound to the correct fineness. These stains when ground for a period of 48 hours in water and then introduced into the glaze resulted in glazes with a uniform color.

A grey color resulted from the reduction in the muffle of all the glazes containing stains. The color varied from a brownish grey for the clear stains to a very dark grey for the vanadium stain with stannic oxide added. Again there was a marked similarity in the colors resulting from the blending of the vanadium stain with "Zircopax" and the "Zircopax"-vanadium stain blended with stannic oxide.

CHAPTER V

CONCLUSIONS

Glazes containing a large amount of lead oxide are not applicable as base glazes for colorants which must be reduced.

Vanadium pentoxide when introduced in a glaze batch, raw or uncalcined, fluffs or swells and makes the glaze unsuitable due to the high water content necessary to make the glaze fluid.

Raw or uncalcined vanadium pentoxide incorporated into a glaze lacks the strong coloring properties it exhibits when added as a stain.

The reduction of glazes containing vanadium pentoxide and zircon ("Zircopax") indicated that a grey-blue color could be produced, however, a good true color was not produced.

Vanadium pentoxide in concentrations of approximately 15 per cent seemed to react with the ingredients in a high lead glaze. This is an indication that the vanadium pentoxide did not volatilize from the glaze. The spectrographic analyses showed that there was no apparent loss in the intensity of the vanadium lines.

The use of stains containing vanadium pentoxide stabilized the color properties of vanadium. Good yellows were obtained under oxidizing conditions in stains containing high stannic oxide and vanadium pentoxide.

A blue-green color was produced using a stain consisting of "Zircopax" and vanadium pentoxide under oxidizing conditions.

The reduction of glazes containing stannic oxide-vanadium pentoxide, "Zircopax"-vanadium pentoxide, and vanadium pentoxide-aluminum hydrate resulted in a grey color. These colors, which ranged from a brownish grey to a dark grey probably were caused by the reduction of the vanadium pentoxide to a lower valence form.

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