The development of spinels in two component coloring oxide systems and their applications as underglaze and overglaze colors

Michael Edward Green
THE DEVELOPMENT OF SPINELS IN TWO COMPONENT COLORING OXIDE SYSTEMS AND THEIR APPLICATIONS AS UNDERGLAZE AND OVERGLAZE COLORS

BY

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A
THESIS
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THE DEVELOPMENT OF SPINELS IN
TWO COMPONENT COLORING OXIDE SYSTEMS AND THEIR
APPLICATIONS AS UNDERGLAZE AND OVERGLAZE COLORS

INTRODUCTION

For many years the fact has been known that when two or more of the coloring oxides are intimately mixed together and fired, there is a reaction between the components of the mixture. Little is known of these reactions - whether they are chemical, physical or mineralogical changes in the nature of the substances.

The purpose of this investigation has been to ascertain the true nature of these reactions and the effect of the changes in the two components making up the system, upon their uses as underglaze and overglaze colors as applied in the ceramic industry.

In the color field very little is known about the nature of the reactions and little effort has been made to study these changes with the tools of modern investigation now at hand. In this field the procedure has been almost entirely, up to the last few years, a trial and error method of compounding. It is almost impossible to duplicate the exact shade of a
certain color mixture since all, with a few rare exceptions, have been done without the aid of the instruments for precision work.

REVIEW OF THE LITERATURE

There is little in the literature that gives much light upon the development of spinels and solid solutions and the properties of the resulting mixture as colors.

Certain of the two component systems have been studied in the trend of the phase rule from the pure scientific points of view; that is with reference to the nature of the melt and the crystalline portion at various temperatures and per cent compositions.

Some investigation has been carried on from the more practical viewpoint but nearly all is with reference to the changes within the ceramic body when it is subjected to firing. Much of this, as far as it goes, is applicable to the changes in the coloring oxides but is all insufficient for the purpose of this investigation.

1 Findlay, Alexander; "The Phase Rule and Its Applications"; New York: Longmans, Green and Company; 1931; pages 68-204.
There is reported the formation of synthetic spinels with certain select materials\textsuperscript{3,4}, but like other investigations they have reference to ideal conditions and high temperature firing which is impossible with many of the commonly used coloring oxides which are easily vaporized. These investigations merely have ascertained that it is possible to form artificial spinels and very little further is stated as to the properties of the melt and the crystalline phases.

\textsuperscript{2} Hall, F.P. and Insley, Herbert; "A compilation of Phase Rule Diagrams of Interest to the Ceramist and Silicate Technologist.; Jour.Amer.Ceram.Soc.; Vol. 169, Oct. 1933; Pages 455-568.

\textsuperscript{3} Parmelee, Cullen W., Badger, Alfred E., and Ballam, George A. "A Study of a Group of Typical Spinels" University of Illinois Bulletin; Vol. XXIX, No. 84; 1932.

The cobalt and corundum mixture has been studied in some detail for its optical properties and other characteristics, but the application as a coloring oxide mixture has been neglected. 5

**METHOD OF PROCEDURE**

**PROPOSED LABORATORY PROCEDURE**

The proposed method of procedure was to prepare mixtures, 20 grams in all, of available oxides in the following percent compositions: 25% - 75%, 50% - 50%, 75% - 25%, and molecular percent. These mixtures were to be made into cylindrical pellets approximately one-half inch in diameter and three-fourths to one inch in height. These pellets were to be made under pressure. The plan was to fire these pellets of the mixtures to 1335°C. (Cone 12) with a special firing rate in a three-phase, Globar electrical furnace. This rate was to be as follows: Bring the furnace to the temperature of 1335°C, in five

---

hours and then hold this temperature for three hours to encourage the growth of crystalline spinels.

After firing, the pellets were to be ground in an agate mortar and applied to test tiles as under-glaze colors with and without a body, and to glazed test tile as overglaze colors, applied wet with approximately 50% low temperature fritted flux. The under-glaze color test tiles were to be fired in an oil-fired furnace to cone 4; and the overglaze test tiles, to the fusing temperature of the flux (between 900°C. and 1000°C.).

Petrographic studies were also to be made of the fired members of each series to learn the character of the changes, if any, brought about by the heat treatment of the initial firing.

**ACTUAL LABORATORY PROCEDURE**

The two oxides used in each member of the thirty series were compounded in the proportions as described in the proposed procedure. Each of the mixtures were intimately ground together in an agate mortar and then slightly moistened with a solution of gum arabic, which was added as a bond. The pellets were formed under pressure in a steel mould with a round plunger (just the size of the mould). This
forced the grains close together and encouraged more rapid growth of new compounds.

After thoroughly drying in air, the pellets were fired in the Globar furnace at the special firing rate of 1335°C.

When cooled after the firing, the pellets were ground dry in an agate mortar and placed in specimen bottles, which were carefully labeled to preserve the identity of each mixture. The color of the fired mixture was observed to be compared with the color of the mixture when used as underglaze and overglaze color.

When used as underglaze colors, the fired mixtures were carefully reground to pass a 200 mesh Tyler screen. The color mixtures were applied wet in a thin stripe on test tile with a camel hair brush. To two test tiles the color was applied with no additions while to two other tiles the fired mixture was intimately ground with approximately 50% of the following body and applied:

<table>
<thead>
<tr>
<th>Buckingham Feldspar</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 4 Kentucky Ball Clay</td>
<td>15%</td>
</tr>
<tr>
<td>English China Clay</td>
<td>30%</td>
</tr>
<tr>
<td>Flint</td>
<td>35%</td>
</tr>
</tbody>
</table>
One of each of the test tiles were glazed with the following fritted glaze applied at 1.4 specific gravity:

\[0.25 \text{ PbO} \]
\[0.15 \text{ K}_2\text{O} \]
\[0.20 \text{ Na}_2\text{O} \]
\[0.30 \text{ CaO} \]
\[0.05 \text{ BaO} \]
\[0.05 \text{ MgO} \]

The frit:

\[0.10 \text{ PbO} \]
\[0.20 \text{ CaO} \]
\[0.20 \text{ Na}_2\text{O} \]
\[0.05 \text{ BaO} \]
\[0.05 \text{ MgO} \]

Both the unglazed and the glazed trials were fired to cone 4 in a high temperature oil-fired furnace. All properties of each member of each series as an underglaze color were noted and are reported elsewhere in this paper.

To ascertain the properties of each series member as an overglaze decoration color, the fired mixtures were put through the 200 mesh Tyler screen and then mixed with approximately 50% of the following fritted flux:
The series member and the flux mixture were moistened with a liquid composed of equal parts of glycerine and water and applied to tile, glazed with the same glaze as used in obtaining the underglaze properties of the oxide mixtures. The wet mixtures were applied in thin uniform stripes across the test tile with a camel hair brush. The trials were fired in an electrically fired muffle furnace to the fusion temperature of the flux which is 1000°C.

Each member of all thirty of the test series were carefully examined with a petrographic microscope to observe the formation of spinels, solid solution and other facts that are obtainable with such an instrument.

THE MATERIALS USED

The materials used in this study were various common oxides of metals which were available in the Missouri School of Mines ceramic engineering
department laboratory. These oxides are the same oxides that are commonly employed in the commercial plants in which stains of the various types are prepared for the general market.

A greater portion of this study is devoted to series in which aluminum oxide ($\text{Al}_2\text{O}_3$) is one of the two components since a spinel is formed by combination of $\text{RO}$ and $\text{R}_2\text{O}_3$ (such as $\text{MgO}$ and $\text{Al}_2\text{O}_3$). Aluminum oxide is very refractory in nature and has a high softening point. The crystalline form of $\text{Al}_2\text{O}_3$ is known as corundum. A component of one or more of the remaining series was either ferric oxide ($\text{Fe}_3\text{O}_4$), chromium oxide ($\text{Cr}_2\text{O}_3$), or cobaltous oxide ($\text{CoO}$), which was assumed to react as cobaltic oxide ($\text{Co}_3\text{O}_4$) as well as cobaltous oxide.

The other oxides employed as a component in one or more of the series was titanium oxide ($\text{TiO}_2$), nickel oxide ($\text{NiO}$), manganese dioxide ($\text{MnO}_2$), ferrous oxide ($\text{FeO}$), uranium trioxide ($\text{UO}_3$), stannic oxide ($\text{SnO}_2$), antimony oxide ($\text{Sb}_2\text{O}_3$), magnesium oxide ($\text{MgO}$), zinc oxide ($\text{ZnO}$), and silica ($\text{SiO}_2$). The following carbonates were used as sources of calcium oxide ($\text{CaO}$), barium oxide ($\text{BaO}$), sodium oxide ($\text{Na}_2\text{O}$), potassium oxide ($\text{K}_2\text{O}$), cadmium oxide ($\text{CdO}$), and strontium oxide ($\text{SrO}$); calcium carbonate ($\text{CaCO}_3$),
barium carbonate (BaCO₃), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), cadmium carbonate (CdCO₃), and strontium carbonate (SrCO₃).

DATA

On the following pages each series is reported in detail with all the ascertained data arranged in the same manner for each series.

The Al₂O₃ - CoO Series:

PERCENT Al₂O₃

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Fired Color</th>
<th>As an Underglaze Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%</td>
<td>Navy blue</td>
<td>Deep blue, rubs off easily</td>
</tr>
<tr>
<td>50%</td>
<td>Dark blue</td>
<td>Medium blue, blue, rubs off</td>
</tr>
<tr>
<td>75%</td>
<td>Royal blue</td>
<td>Bright blue, blue, rubs off</td>
</tr>
<tr>
<td>57.6%</td>
<td>Rich medium</td>
<td>Medium light blue, rubs off</td>
</tr>
</tbody>
</table>

Trials Unglazed

Without Body

Deep blue, Medium blue, rubs off easily

Bright blue, rubs off easily

Medium light blue, rubs off easily
The Al₂O₃ - CoO Series continued:

With Body

Deep blue, rubs Medium blue, rubs Light blue, rubs Medium
off slightly off slightly off slightly light
blue, rubs off easily

Trials Glazed

Without Body

Deep blue, no Dark blue, no Medium blue, Dark
solution, good solution, good no solution, blue,
good no solution, good

With Body

Deep blue, no Deep blue, no Medium blue, Dark
solution, good solution, good no solution, blue,
good no solution, good
good
The Al₂O₃ – CoO Series continued:

**AS AN OVERGLAZE COLOR**

Deep blue, Dirty blue, Medium blue, Medium deep blue, poor fusion poor fusion poor fusion fair fusion

**PETROGRAPHIC ANALYSIS**

There is spinel present but the blue color of the cobalt oxide obscures the presence of it somewhat. The spinel content seems to increase as the percent of Al₂O₃ increases. Unaltered corundum is very evident in all members but decreases as the percent of Al₂O₃ decreases. There is some solution and the index is reduced by an increase in the CoO content.
The $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ Series:

PERCENT $\text{Al}_2\text{O}_3$

<table>
<thead>
<tr>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep nile green</td>
<td>Dull dark green</td>
<td>Dull medium green</td>
<td>Moderately dark green</td>
</tr>
</tbody>
</table>

AS AN UNDERGLAZE COLOR

**Trials Unglazed**

Without Body

- Dark green,
- Rubs off: badly

With Body

- Dark green,
- Rubs off: slightly

**Trials Glazed**

Without Body

- Dark green,
- No solution: good

With Body

- Dark green,
- No solution: excellent
The $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ Series continued:

**AS AN OVERGLAZE COLOR**

Deep green, Dirty medium Light brown, Medium
good fusion green, good good fusion green, good fusion

**PETROGRAPHIC ANALYSIS**

A solid solution in all members, with a decrease in the index as the percent of $\text{Cr}_2\text{O}_3$ is increased.

**The $\text{Al}_2\text{O}_3 - \text{CuO}$ Series:**

<table>
<thead>
<tr>
<th>PERCENT $\text{Al}_2\text{O}_3$</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>55.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td>Dull dark</td>
<td>Dirty brown</td>
<td>Brown with</td>
<td>Dirty brown</td>
</tr>
<tr>
<td></td>
<td>green, appears crystalline</td>
<td>specks of lighter brown</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**AS AN UNDERGLAZE COLOR**

**Trials Unglazed**

Without Body
The Al₂O₃ - CuO Series continued:

Dark yellow - Dirty yellow - Dirty yellow - Dirty yellow -

ish green, ish green, ish green, ish green,
no rub off, slight rub slight rub slight rub
off, off, off.

With Body

Dirty yellow - Dirty yellow - Dirty yellow - Dirty yellow -

ish green, ish green, ish green, ish green,
no rub off, no rub off, no rub off, no rub off.

Trials Glazed

Without Body

Medium Medium Medium Medium

bright green, bright green, bright green, bright green,
slight solu- slight solu- slight solu- slight solu-
tion. tion. solution. solution.

With Body

Medium Light bright Light bright Light bright

bright green, green, no green, no green, no
solution solution solution.

AS AN OVERGLAZE COLOR

Medium green, Full green, Deep grass, Grass green,
Poor color poor color green, metal - very metal -
and fusion. and fusion. lic in spots, lic in spots
poor color poor color
and fusion, and fusion.
PETROGRAPHIC ANALYSIS

There is solid solution with no evidence of spinel formation. Increase in purest CuO increases the indices of corundum.

The Al₂O₃ – Fe₂O₃ Series:

PER CENT \( \text{Al}_2\text{O}_3 \)

<table>
<thead>
<tr>
<th>FIRED COLOR</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>37.55%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chocolate brown</td>
<td>Dark brown</td>
<td>Light brown</td>
<td>Very dark brown</td>
<td></td>
</tr>
</tbody>
</table>

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

Dark brown, Dark brown, Light brown, Dark brown,  
rubs off badly, rubs off badly,  

With Body

Medium brown, slight brown, slight brown  
rub off, slight rub off,  

Trials Glazed

Without Body
The $\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3$ Series Continued:

Brownish green, Glaze tended to pull off over stripe, Glaze tended to pull off over stripe.

Brown, Glaze Medium Dark brown,

Brown, Glaze Glaze tended to pull off, Glaze tended to pull off over stripe.

Very dark Brown, Medium Dark brown, brown, no solution, brown, no solution, good.

Dark brown, Medium Dark brown, no solution, brown, no solution, good.

AS AN OVERGLAZE COLOR

Deep brown, Rich brown, Medium Medium dark

Brown, poor fusion, Brown, poor fusion, Brown, poor fusion.

PETROGRAPHIC ANALYSIS

A solid solution formed with an increase in the indices of the corundum as the percent of $\text{Fe}_2\text{O}_3$ increased. There appears to be a slight bit of hercynite ($\text{FeO. Al}_2\text{O}_3$). Magnetite formed in decreasing amounts as $\text{Fe}_2\text{O}_3$ content decreased.
The $\text{Al}_2\text{O}_3 - \text{MnO}_2$ Series:

<table>
<thead>
<tr>
<th>PERCENT $\text{Al}_2\text{O}_3$</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>54.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rich dark</td>
<td>Rich dark</td>
<td>Dark brown</td>
<td>Chocolate brown</td>
<td></td>
</tr>
<tr>
<td>brown</td>
<td>brown</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

AS AN UNDERGLAZE COLOR

Trials Unglazed

<table>
<thead>
<tr>
<th>Without Body</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very dark</td>
</tr>
<tr>
<td>brown, rubs</td>
</tr>
<tr>
<td>off slightly</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>With Body</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very dark</td>
</tr>
<tr>
<td>brown, no</td>
</tr>
<tr>
<td>rub off</td>
</tr>
</tbody>
</table>

Trials Glazed

<table>
<thead>
<tr>
<th>Without Body</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brown, glaze</td>
</tr>
<tr>
<td>tended to</td>
</tr>
<tr>
<td>pull away</td>
</tr>
<tr>
<td>from stripe,</td>
</tr>
<tr>
<td>slight solu-</td>
</tr>
<tr>
<td>tion.</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
The $\text{Al}_2\text{O}_3 - \text{MnO}_2$ Series Continued:

With Body

Dark rich Dark brown, Dark brown, Dark brown,
brown, no no solution, no solution, no solution,
solution, solution, good. fair. fair.
good.

AS AN OVERGLAZE COLOR

Dirty brown, Metallic Metallic Metallic brown,
poor color brown, poor brown, poor poor color
and fusion, color and color and and fusion.
fusion, fusion.

PETROGRAPHIC ANALYSIS

There is solid solution with no evidence of
spinel. Index decreases with increase in percent of
$\text{MnO}_2$. Corundum seems to have unlimited solubility for
$\text{MnO}_2$.

The $\text{Al}_2\text{O}_3 - \text{NiO}$ Series:

<table>
<thead>
<tr>
<th>PERCENT $\text{Al}_2\text{O}_3$</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>57.7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td>Powder blue. Medium green- Robin-egg Greenish blue. ish blue.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The Al₂O₃ - NiO Series Continued:

AS AN UNDERGLAZED COLOR

**Trials Unglazed**

**Without Body**

Olive green, Bluish green, Light blue, Bluish green,
rubs off easily. slightly.
rubs off easily. slightly.

**With Body**

Olive green, Bluish green, Light blue, Bluish green,
rubs off no rub off. slightly.
rubs off slightly.

**Trials Glazed**

**Without Body**

Drab green, Dirty green, Olive green, Dull dark
no solution. no solution. good.

**With Body**

Dirty green, Dark green, Olive green, Dull dark
no solution. no solution. green, no fair.

AS AN OVERGLAZE COLOR
The $\text{Al}_2\text{O}_3 - \text{NiO}$ Series Continued:

Light green, Grass green, Medium Leaf green, fair fusion, fair fusion, green, fair fair fusion.

PETROGRAPHIC ANALYSIS

There is solid solution present with no evidence of spinel. The index of the solution decreases as the percent of NiO increases. Corundum appears to have unlimited ability for NiO.

The $\text{Al}_2\text{O}_3 - \text{UO}_2$ Series:

<table>
<thead>
<tr>
<th>PERCENT $\text{Al}_2\text{O}_3$</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>26.4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Earthy color. Non-descript Dirty tan Dull brown. color, earthy gray.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

Very dark Grayish Light gray  Dirty yellowish yellowish yellow, ish yellow, yellow, rubs green, rubs rubs off rubs off off badly.

deadly. badly. badly.
The Al₂O₃ - UO₃ Series Continued:

With Body

Very dirty yellow, no rub off. Light gray – Dirty Yellow, no rub off. no rub off.

Trials Glazed

Without Body

Dirty yellow, Dirty yellow, Dirty yellow, Dirty yellow, Dirty yellow, no solution, no solution, no solution, no solution.

With Body

Dirty yellow, Dirty yellow, Dirty yellow, Dirty yellow, Dirty yellow, no solution, no solution, no solution, no solution.

AS AN OVERGLAZE COLOR

Poor deep yellow, poor yellow, poor color and fusion, and fusion, and fusion.

PETROGRAPHIC ANALYSIS

The UO₃ was reduced to a lower oxide. There is solid solution with the corundum being lowered in respect to index as the percent of UO₃ increased. These are clusters of the lower oxides of UO₃ evident with the microscope.
The CoO - MnO₂ Series:

PERCENT CoO

<table>
<thead>
<tr>
<th></th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>46.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Good black.</td>
<td>Good black.</td>
<td>Good black.</td>
<td>Good black.</td>
<td></td>
</tr>
<tr>
<td>AS AN UNDERGLAZE COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trials Unglazed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black, slight</td>
<td>Black, slight</td>
<td>Black, slight</td>
<td>Black, slight</td>
<td></td>
</tr>
<tr>
<td>rub off.</td>
<td>rub off.</td>
<td>rub off.</td>
<td>slight</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>rub off.</td>
<td></td>
</tr>
<tr>
<td>With Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black, no</td>
<td>Black, no</td>
<td>Black, no</td>
<td>Black, No</td>
<td></td>
</tr>
<tr>
<td>rub off.</td>
<td>rub off.</td>
<td>rub off.</td>
<td>rub off.</td>
<td></td>
</tr>
<tr>
<td>Trials Glazed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Very dark</td>
<td>Very dark</td>
<td>Dark blue,</td>
<td>Dark blue,</td>
<td></td>
</tr>
<tr>
<td>blue, slight</td>
<td>blue, slight</td>
<td>slight</td>
<td>slight</td>
<td></td>
</tr>
<tr>
<td>solution.</td>
<td>solution.</td>
<td>solution.</td>
<td>solution.</td>
<td></td>
</tr>
<tr>
<td>With Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Very dark</td>
<td>Very dark</td>
<td>Dark blue,</td>
<td>Very dark</td>
<td></td>
</tr>
<tr>
<td>blue, no</td>
<td>blue, no</td>
<td>no solution.</td>
<td>blue, no</td>
<td></td>
</tr>
<tr>
<td>solution.</td>
<td>solution.</td>
<td>solution.</td>
<td>solution.</td>
<td></td>
</tr>
<tr>
<td>AS AN OVERGLAZE COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Black, poor Very deep Deep blue, Brownish fusion. brown, poor poor fusion. black, poor fusion.

Petrographic Analysis

Powder was too dark to observe much but there is evidence of solid solution. Color is too dark for microscopic study.

The CoO - TiO₂ Series:

<table>
<thead>
<tr>
<th>PER CENT COO</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>48.4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium dull</td>
<td>Very dark</td>
<td>Appears</td>
<td>Dark green.</td>
<td></td>
</tr>
<tr>
<td>green.</td>
<td>green.</td>
<td>black.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As An Underglaze Color

Trials Unglazed

Without Body

Dark greenish blue, Very dark Black, bad Dark greenish blue, bad rub off. Dark greenish blue, bad rub off.

bad rub off. blue, bad rub off.

rub off.

With Body

Medium blue, Medium blue, Dark blue, Medium blue, Medium blue,

very slight very slight no rub off. very slight rub off.

rub off. rub off.
The CoO - TiO₂ Series Continued:

Trials Glazed

Without Body

Medium dark | Dark blue, | Very dark | Medium dark
blue, no solu- | no solu- | blue, no | blue, no
tion, good. | glaze | solution, | solution,
tended to | good. | good.
pull off.

With Body

Dark blue, | Dark blue, | Very dark | Dark blue,
no solution, | no solution, | blue, no | no solution,
good. | good. | solution, | good.
good.

AS AN OVERGLAZE COLOR

Greenish | Good blue, | Deep blue, | Medium bluish
blue, poor | good fusion. | blue, no | good fusion, green, good
fusion.

PETROGRAPHIC ANALYSIS

There is solid solution. There is much solution in all members except 75% CaO - 25% TiO₂. This series is too dark in color for complete microscopic analysis.
The CoO – ZnO Series:

PERCENT CoO

<table>
<thead>
<tr>
<th></th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>47.8%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium</td>
<td>Dull dark</td>
<td>Appears Dark green.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>green.</td>
<td>green.</td>
<td>black.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS AN UNDERGLAZE COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trials Unglazed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark blue,</td>
<td>Dark blue,</td>
<td>Black, bad</td>
<td>Dark blue,</td>
<td>bad rub off.</td>
</tr>
<tr>
<td>bad rub off.</td>
<td>bad rub off.</td>
<td>rub off.</td>
<td>bad rub off.</td>
<td></td>
</tr>
<tr>
<td>With Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium dark</td>
<td>Medium dark</td>
<td>Dark blue,</td>
<td>Medium blue,</td>
<td></td>
</tr>
<tr>
<td>blue, slight</td>
<td>blue, slight</td>
<td>slight rub</td>
<td>slight rub</td>
<td></td>
</tr>
<tr>
<td>rub off.</td>
<td>rub off.</td>
<td>off.</td>
<td>off.</td>
<td></td>
</tr>
<tr>
<td>Trials Glazed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Very dark</td>
<td>Very dark</td>
<td>Very dark</td>
<td>Very dark</td>
<td></td>
</tr>
<tr>
<td>blue, glaze</td>
<td>blue, glaze</td>
<td>blue, glaze</td>
<td>blue, glaze</td>
<td></td>
</tr>
<tr>
<td>tended to</td>
<td>tended to</td>
<td>tended to</td>
<td>tended to</td>
<td></td>
</tr>
<tr>
<td>pull off,</td>
<td>pull off,</td>
<td>pull off,</td>
<td>pull off,</td>
<td></td>
</tr>
<tr>
<td>solution.</td>
<td>solution.</td>
<td>solution</td>
<td>solution</td>
<td></td>
</tr>
<tr>
<td>With Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium dark</td>
<td>Dark blue,</td>
<td>Very dark</td>
<td>Dark blue,</td>
<td></td>
</tr>
<tr>
<td>blue, slight</td>
<td>slight solu-</td>
<td>blue, slight</td>
<td>slight solu-</td>
<td></td>
</tr>
<tr>
<td>solution.</td>
<td>tion.</td>
<td>solution.</td>
<td>solution.</td>
<td></td>
</tr>
</tbody>
</table>
The CoO - ZnO Series Continued:

AS AN OVERGLAZE COLOR

Deep blue, Deep green, Medium green, Deep greenish
fair fusion, ish blue, good fusion, blue, good
but pinholed, good fusion, fusion.

PETROGRAPHIC ANALYSIS

There is some solid solution. There is free
CoO in all members except 75% ZnO - 25% CoO. This series
is too dark in color for complete microscopic analysis.

The Al₂O₃ - FeO Series:

<table>
<thead>
<tr>
<th>PERCENT Al₂O₃</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>59.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metallic</td>
<td>Dull brown, Medium brown, black.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS AN UNDERGLAZE COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trials Unglazed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Body</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Very dirty Dark brown, Light brown, Medium brown, bad</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bad rub off, bad rub off, brown, bad rub off.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With Body
The $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ Series Continued:

Dirty brown, Medium brown, Light brown, Dull light
no rub off, no rub off, no rub off, brown, no
rub off.

Trials Glazed
Without Body
Almost black, Dark brown, Medium Medium
with yellow with yellow light brown, brown.
specks, no specks, no no solution.
solution. solution.

With Body
Almost black, Dirty yellow- Medium Dark brown,
with yellow ish brown, brown, no no solution.
specks, no no solution. solution.
solution.

As an overglaze color
Poor black Poor brown, Fair brown, Fair brown,
with yellow fair fusion, fair fusion, fair fusion.
specks, fair fusion,

Petrographic Analysis

There is some solid solution. Decreasing
amounts of magnetite present as $\text{Fe}_2\text{O}_3$ percent decreased.
The index of corundum changed only slightly.
The Cr₂O₃ - Co₂O₃ Series:

PERCENT Cr₂O₃

<table>
<thead>
<tr>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>87%</th>
</tr>
</thead>
</table>

FIRED COLOR

Very dark  Very dark  Very dark

green, almost green.  green.  green.

black.

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

Bluish black, Bluish black, Dark green, Dark green,

bad rub  bad rub  bad rub  bad rub off.

off.  off.  off.

with Body

Bluish black, Bluish black, Dark green, Bluish green.

slight rub  slight rub  slight rub  slight rub

off.  off.  off.

Trials Glazed

Without Body

Black, no  Black, no  Greenish  Greenish black,

solution.  solution.  black, no  no solution.

good.  good.  solution.

With Body
The Cr₂O₃ - CoO Series Continued:

Black, no solution, good. Black, no solution, good. Dark green, Dark green, bluish cast, bluish cast, no solution.

AS AN OVERGLAZE COLOR

Metallic blue, poor color and fusion. Metallic blue, poor color and fusion. Medium blue green, green, good color and fusion. Deep bluish green, green, good color and fusion.

PETROGRAPHIC ANALYSIS

There is spinel formed. Its presence is more noticeable in molecular percent member but present in the entire series.

The Cr₂O₃ - SiO₂ Series:

PERCENT Cr₂O₃

25% 50% 75% 88.4%

Fired Color


AS AN UNDERGLAZED COLOR

Trials Unglazed

Without Body
The Cr₂O₃ - SiO₂ Series Continued:

Dark green, Dark green, Dark green, Medium green, Medium green, Medium green.
rubs off rubs off rubs off rubs off rubs off.
badly, badly, badly, badly, badly.

With Body

Dark green, Dull dark Medium green, Light green, Medium green.
rubs off, green, rubs rubs off, rubs off.

Trials Glazed

Without Body

Dark green, Dark green, Dark green, Green, slight
slight solution, slight solution, solution, glaze
slight solution, glaze solution, glaze pull-
tended to tended to tended to pulled off
entirely. entirely. entire.
pull off, pull off, entirely.

With Body

Dark green, Dark green, Dark green, Dark green, Dark green,
solution, solution, slight solution, no solution,
slight solution, glaze tended glaze tended
ed to pull off, to pull off, tended to
pinhole.

AS AN OVERGLAZE COLOR

Deep green, Deep green, Deep green, Deep green,
good fusion, good fusion, good fusion, good fusion.
The Cr₂O₃ - SiO₂ Series Continued:

PETROGRAPHIC ANALYSIS

There was spinel formed in small amounts with quartz evident in all members. There was solid solutions formed also. Spinel was more evident in lower percent SiO₂ members with more spinel in molecular percent member than in the other three.

The Cr₂O₃ - SnO₂ Series:

<table>
<thead>
<tr>
<th>PERCENT Cr₂O₃</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>50.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td>Dull dark</td>
<td>Dark green,</td>
<td>Dark green,</td>
<td>Not used as too near 50-50 member to show any additional data.</td>
</tr>
<tr>
<td></td>
<td>green.</td>
<td>Dark green,</td>
<td>dark green,</td>
<td></td>
</tr>
</tbody>
</table>

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

Dark green, Dark green, Dark green, bad rub off, bad rub off, bad rub off.

With Body

Dark green, Dark Green, Dark green, slight slight slight rub off, rub off, rub off.
The $\text{Cr}_2\text{O}_3 - \text{SnO}_2$ Series Continued:

Trials Glazed

Without Body

<table>
<thead>
<tr>
<th>Very dark</th>
<th>Very dark</th>
<th>Very dark</th>
<th>Not used as too</th>
</tr>
</thead>
<tbody>
<tr>
<td>green, no</td>
<td>green, no</td>
<td>green, no</td>
<td>near 50-50 member</td>
</tr>
<tr>
<td>solution,</td>
<td>solution,</td>
<td>solution</td>
<td>to show any adding</td>
</tr>
<tr>
<td>glaze tended</td>
<td>glaze tended</td>
<td>glaze tended</td>
<td>to show any additive data.</td>
</tr>
<tr>
<td>to pull off</td>
<td>to pull off</td>
<td>to pull off</td>
<td></td>
</tr>
<tr>
<td>slightly</td>
<td>slightly</td>
<td>slightly</td>
<td></td>
</tr>
</tbody>
</table>

With Body

| Dark green, | Dark green, | Dark green, |
| no solution, | no solution, | no solution, |
| good. | good. | good. |

AS AN OVERGLAZE COLOR


{Excellent colors; amount of $\text{Cr}_2\text{O}_3$ does not alter color materially.}

PETROGRAPHIC ANALYSIS

There is solid solution with no visible spinel formation. The crystal structure of SnO$_2$ is retained. There is some free Cr$_2$O$_3$ increasing as percent Cr$_2$O$_3$ increases. The index of SnO$_2$ increased with increase of the percent of Cr$_2$O$_3$. 

The Cr₂O₃ - TiO₂ Series:

<table>
<thead>
<tr>
<th>PERCENT Cr₂O₃</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>65.6%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td>Black</td>
<td>Black</td>
<td>Black</td>
<td>Black</td>
</tr>
</tbody>
</table>

**AS AN UNDERGLAZE COLOR**

**TRIAL UNGLAZED**

**Without Body**

<table>
<thead>
<tr>
<th></th>
<th>Black, bad</th>
<th>Black, bad</th>
<th>Black, bad</th>
<th>Black, bad</th>
</tr>
</thead>
<tbody>
<tr>
<td>rub off</td>
<td>rub off</td>
<td>rub off</td>
<td>rub off</td>
<td></td>
</tr>
</tbody>
</table>

**With Body**

<table>
<thead>
<tr>
<th></th>
<th>Gray, slight</th>
<th>Medium gray, slight</th>
<th>Dark gray, slight</th>
<th>Medium gray, slight</th>
</tr>
</thead>
<tbody>
<tr>
<td>rub off</td>
<td>rub off</td>
<td>rub off</td>
<td>rub off</td>
<td>rub off</td>
</tr>
</tbody>
</table>

**Trial Glazed**

**Without Body**

<table>
<thead>
<tr>
<th></th>
<th>Very dark green, no solution,</th>
<th>Very dark green, no solution,</th>
<th>Very dark green, no solution,</th>
<th>Very dark green, no solution,</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>glaze tended to pull off.</td>
<td>glaze tended to pull off.</td>
<td>glaze tended to pull off.</td>
<td>glaze tended to pull off.</td>
</tr>
</tbody>
</table>

**With Body**

<table>
<thead>
<tr>
<th></th>
<th>Very dark green, no solution,</th>
<th>Very dark green, no solution,</th>
<th>Very dark green, no solution,</th>
<th>Very dark green, no solution,</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>good.</td>
<td>good.</td>
<td>good.</td>
<td>good.</td>
</tr>
</tbody>
</table>
The Cr₂O₃ - TiO₂ Series Continued:

AS AN OVERGLAZE COLOR

Poor black, Poor black, Medium Brownish

good fusion, good fusion, black, poor black, fair fusion, fusion.

PETROGRAPHIC ANALYSIS

There is some solid solution. The lower percent TiO₂ members give better evidences of solution.

With the lower percent Cr₂O₃ members the brown color of rutile (TiO₂) blots out any evidences of solution or spinel formation.

The Cr₂O₃ - ZnO Series:

PERCENT Cr₂O₃

<table>
<thead>
<tr>
<th></th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>65.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dull dark.</td>
<td>Dark brown,</td>
<td>Olive green,</td>
<td>Dark brown.</td>
<td></td>
</tr>
</tbody>
</table>

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

Medium brown, Dark brown, Medium green, Dark brown

bad rub off, bad rub off, bad rub off, bad rub off.

With Body

Light gray, Gray, no Grayish green, Gray, bad

slight rub off, rub off, bad rub off, rub off.
The Cr₂O₃ - ZnO Series Continued:

Trials Glazed

Without Body

Dark brown, Dark brown, Dull dark Brown, no
no solution, no solution, green, no solution,
glaze tended glaze tended solution, glaze tended
to pull off, to pull off, good, to pull off.

With Body

Medium brown, Dull dark Olive green, Dull greenish
no solution, brown, no no solution, brown, no

Olive green, Dull greenish green, good solution,
good. good. solution,
good. good.

AS AN OVERGLAZE COLOR

Earthy brown, Earthy brown, Medium Poor brown,
good fusion. good fusion. green, good color not even,
good fusion. good fusion. good fusion.

color and
good fusion.

Petrographic Analysis

The free ZnO is evident in all members. The
index of the ZnO is increased by solution of Cr₂O₃.
Spinel is formed but in small quantities only. With the
25% ZnO - 75% Cr₂O₃ member free Cr₂O₃ is present.
The $Fe_2O_3 - CoO$ Series:

<table>
<thead>
<tr>
<th>PERCENT $Fe_2O_3$</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>68.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRED COLOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td>Black</td>
<td>Medium black</td>
<td>Medium black</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Medium black</td>
<td>Medium black</td>
<td>Medium black</td>
<td></td>
</tr>
</tbody>
</table>

**AS AN UNDERGLAZE COLOR**

**Trials Unglazed**

**Without Body**

<table>
<thead>
<tr>
<th></th>
<th>Black, bad</th>
<th>Black, bad</th>
<th>Black, bad</th>
<th>Black, bad</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rub off.</td>
<td>rub off.</td>
<td>rub off.</td>
<td>rub off.</td>
</tr>
</tbody>
</table>

**With Body**

<table>
<thead>
<tr>
<th></th>
<th>Very dark</th>
<th>Dark blue, Bluish gray, Dirty gray</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>blue, slight</td>
<td>slight</td>
</tr>
<tr>
<td></td>
<td>rub off.</td>
<td>rub off.</td>
</tr>
</tbody>
</table>

**Trials Glazed**

**Without Body**

<table>
<thead>
<tr>
<th></th>
<th>Bluish black, Very dark</th>
<th>Very dark</th>
<th>Very dark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>very slight blue, very</td>
<td>blue, slight blue, no</td>
<td></td>
</tr>
<tr>
<td></td>
<td>solution.</td>
<td>solution.</td>
<td>evidence of solution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>yellow, no</td>
<td>solution</td>
</tr>
</tbody>
</table>

**With Body**

<table>
<thead>
<tr>
<th></th>
<th>Bluish black, Very dark</th>
<th>Very dark</th>
<th>Very dark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no, solution, blue, no</td>
<td>blue, slight blue, no</td>
<td></td>
</tr>
<tr>
<td></td>
<td>good.</td>
<td>solution.</td>
<td>evidence of solution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>yellow, no</td>
<td>good.</td>
</tr>
</tbody>
</table>
The \( \text{Fe}_2\text{O}_3 \) - CoO Series Continued:

**AS AN OVERGLAZE COLOR**

Deep blue, Blue, uniform Poor black, Yellowish
Metallic in color, good blue, good
specks, fair fusion, fusion.
poor fusion.

**PETROGRAPHIC ANALYSIS**

This series appears metallic in nature and nothing can be observed with the microscope.

The following series were not used as possibilities as underglaze and overglaze for reasons that are very self evident:

**The \( \text{Al}_2\text{O}_3\)-BaO series:**

The molecular percent of this series is 39.8% \( \text{Al}_2\text{O}_3 \)-60.2% BaO. The entire series is white.

The microscope shows there is no isotropic mineral formed in this series but there is a series of \( x\text{BaO}-y\text{Al}_2\text{O}_3 \) minerals which are anisotropic in nature with an index of refraction about 1.65 and up. In this series there is solid solution with the indices slightly below 1.70.
The \( \text{Al}_2\text{O}_3-\text{CaO} \) series:

The molecular percent of this series is 64.6\% \( \text{Al}_2\text{O}_3-35.4\% \text{CaO} \). This entire series is white.

There has been reaction in all four members of this series. The optical properties of the corundum have been destroyed. Apparently a series of compounds of the formula \( x\text{CaO}-y\text{Al}_2\text{O}_3 \) which are both isotropic and anisotropic in nature have been formed. The index of all the material in the members is below 1.70. There appears to be some solid solution with the index below 1.70 also.

The \( \text{Al}_2\text{O}_3-\text{CdO} \) series:

The molecular percent of this series is 45\% \( \text{Al}_2\text{O}_3-55\% \text{CdO} \). This entire series is white.

The microscope reveals that there is solid solution. There is no corundum evident in any member but the 75\% CdO - 25\% \( \text{Al}_2\text{O}_3 \) member. The solid solution formed has an index below 1.70 and this increases with a decrease in the CdO content. A part of the CdO was probably volatilized in the firing.

The \( \text{Al}_2\text{O}_3-\text{K}_2\text{O} \) series:

This series has a molecular percent member of 52\% \( \text{Al}_2\text{O}_3 - 48\% \text{K}_2\text{O} \). The entire series is white.

There is solid solution. The index is lowered with the addition of the \( \text{K}_2\text{O} \).
The Al₂O₃-MgO series:

The molecular percent of this series is 71.7%
Al₂O₃ - 28.3% MgO. The entire series is white.

There appears to be a ring of spinel about each
grain of corundum ranging to pure corundum in the center
of the grain. The index of refraction is much lower on the
outside than on the interior. The ring is broader with
the 75% MgO - 25% Al₂O₃ member in which member both corun-
dum and periclase exist unaltered.

The Al₂O₃ - Na₂O series:

The molecular percent of this series is 62.2%
Al₂O₃ - 37.8% Na₂O. The entire series is white.

There is solid solution in this series. The
index of refraction in all cases is lower than 1.70. As
the Na₂O percent is increased the index is lowered more,
but not greatly. The grains are blue in polarized
light. The index is lowered more with K₂O than with
Na₂O.

The Al₂O₃ - Sb₂O₃ series:

The molecular percent of this series is 25%
Al₂O₃ - 75% Sb₂O₃. The entire series is white.

There is solid solution in the members of
this series. As the percent of Sb₂O₃ is increased the
index of the solution increases.
The $\text{Al}_2\text{O}_3 - \text{SrO}$ series:

The molecular percent of this series is 49.6% $\text{Al}_2\text{O}_3 - 50.4\% \text{SrO}$. The entire series is white.

There is definitely solid solution present in this series with the probability of a compound of varying composition as well. The indices of refraction are not as they might first be believed: the 25% and 75% SrO members have indices above 1.70 while the other two members have indices below 1.70. There is a small amount of unaltered corundum present indicating that a part of the SrO must have been volatilized.

The $\text{Al}_2\text{O}_3 - \text{SnO}_2$ series:

The molecular percent of this series is 40.5% $\text{Al}_2\text{O}_3 - 59.5\% \text{SnO}_2$. The series is not white as might be expected but each has a faint tint of blue but this blue color comes from contamination with CoO.

There is solid solution in the various members but the crystal structure of the SnO$_2$ has been retained. There is a very slight increase in the index of refraction with the increase in the SnO$_2$ content.

The CoO - CuO series:

The molecular percent ratio of this series is 48.4% CoO - 51.6% CuO. All members of this series were badly fused to the $\text{Al}_2\text{O}_3$ plaque. All the members were black in color.
There is evidence of some solution but the members are too dark in color to be examined with a microscope.

**The Fe$_2$O$_3$ - FeO series:**

The molecular percent ratio of the series is 68.9% Fe$_2$O$_3$ - 31.1% FeO. The entire series is very metallic in nature and for that reason was not tested as underglaze or overglaze colors. The oxides of iron have been reduced in some parts to metallic iron. The entire series is black in color.

Magnetite formed in varying amounts in the series members. There is more magnetite evident in the molecular percent member than in any other member.

**The Fe$_2$O$_3$ - SiO$_2$ series:**

The molecular percent ratio of the series is 72.7% Fe$_2$O$_3$ - 27.3% SiO$_2$. There is a variation in the color from brown to black, but all the members are metallic in nature.

Under the microscope all the members appear metallic to some extent but there is a small quantity of spinel evident. There is the most spinel present in the molecular percent member. Much solid solution has been formed in the entire series.
DISCUSSIONS

The $\text{Al}_2\text{O}_3 - \text{CoO}$ series:

The members of this series, when employed as stains, both underglaze and overglaze, are good blues in color. As underglaze colors they are excellent. The color is apparently due to the spinel and solid solution, which are very blue. Had the heat soaking period been longer than three hours there would have undoubtedly been much more spinel developed. This two component series has excellent possibilities for commercial use.

The $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ series:

This series, generally speaking, are green in color. The $75\% \text{Al}_2\text{O}_3 - 25\% \text{Cr}_2\text{O}_3$ member, however, is a brown in color when exposed directly to the heat of the furnace; this is probably due to a transformation in the molecular state of the chromium atom. There are the green, brown and red oxides of chromium. There was no spinel developed, as might be expected, as spinel is a $\text{R}_2\text{O}_3 - \text{RO}$ compound and the $\text{Cr}_2\text{O}_3$ was not converted to $\text{CrO}$ sufficiently to permit any reaction between the oxide molecules.

The $\text{Al}_2\text{O}_3 - \text{CuO}$ series:

This series, as stains, is green in color. This series tended to fuse somewhat in the initial
firing. The colors after the initial firing would indicate the CuO has been changed somewhat to Cu₂O in all members except the 25% Al₂O₃ - 75% CuO, which is green. In this member there is a large excess of CuO which has probably been altered to Cu₄O, an olive green compound. When this series is used as stains, the conversion to Cu₄O is continued as all members give green colored underglaze and overglaze stains. There was no spinel developed for the fact that the CuO is essential for spinel growth and it has all been altered to lower oxides of copper by the reducing conditions of the furnace atmosphere.

The Al₂O₃ - Fe₃O₄ series:

The colors of this series and the microscopic study shows the Fe₃O₄ has been reduced to lower oxide forms of iron. The formation of hercynite (Al₂O₃·FeO) and magnetite indicate these facts. Had the atmosphere been less reducing, more hercynite would have formed but the tendency appears to be for the FeO formed to associate itself with the unaltered Fe₃O₄ and form Fe₃O₄ which is a spinel.

The Al₂O₃ - FeO series:

The presence of yellow specks in some members shows ferrous oxide remained unaltered. The formation of magnetite shows there was alteration in the state of
the iron atom. The absence of hercymite is odd since it is essential for its formation that FeO be present. The Fe$_2$O$_3$ molecules produced by the heat treatment have more affinity for the FeO than the Al$_2$O$_3$, if the results of this series are conclusive.

**The Al$_2$O$_3$ - MnO$_2$ series:**

This series, being brown in color, indicates the MnO$_2$ has been converted to the red Mn$_2$O$_4$ to some extent. This would prevent the formation of spinel.

**The Al$_2$O$_3$ - NiO series:**

The colors of this series are as they might be expected, but there was nothing present to encourage the formation of spinel. The NiO is changed to Ni$_2$O$_3$ at about 400°C and reverts back to NiO at 600°C. Had there been a mineralizer present, spinel would probably have been formed.

**The Al$_2$O$_3$ - UO$_2$ series:**

Within this series during the heat treatment the UO$_2$ has been decomposed and lowered oxides of uranium have resulted. These lower oxides have formed in spots within the mixture. The yellow color of the members as stains comes from unchanged UO$_2$ and the dirty appearance is from the lower oxides.

**The CoO - MnO$_2$ series:**

In this series it was hoped the CoO would be
changed to $\text{Co}_2\text{O}_3$ and it would react as such. However
the $\text{Mn}_2\text{O}_3$ was altered also by the heat treatment. The
color of the resulting stains would indicate the $\text{CoO}$
is in the same condition as in the $\text{Al}_2\text{O}_3$ -- $\text{CoO}$ series.
In some members, however, the $\text{Mn}_2\text{O}_3$ is too strong and
the resulting color is brown.

The $\text{CoO} - \text{TiO}_2$ series:

This series behaved very odd in regard to
color. The source of the green color in the initially
fired members and the members as unglazed colors
without added body is difficult to explain. This
color may have resulted from a combination of the blue
color of the cobalt oxide and the yellow color of
$\text{TiO}_2$, which may have been produced from $\text{TiO}_2$.

The $\text{CoO} - \text{ZnO}$ series:

This series is very similar in behaviour to
the $\text{CoO} - \text{TiO}_2$ series in that a green color resulted
in the initially fired members. There is a yellow
oxide of zinc ($\text{ZnO}_2$), which with the resulting blue of
the cobalt oxide may account for this green color.
There is limited solubility of the zinc oxide for the
cobalt oxide.

The $\text{Cr}_2\text{O}_3 - \text{CoO}$ series:

The CoO oxide in this series has deepened
the color of the $\text{Cr}_2\text{O}_3$ somewhat but still the re-
sulting colors are predominately green. The forma-
tion of spinel in all members indicates the activity of these two oxides toward each other. There appears to be no tendency for the $\text{Cr}_2\text{O}_3$ to have been converted to a lower oxide form.

**The $\text{Cr}_2\text{O}_3 - \text{SiO}_2$ series:**

The formation of spinel might be expected but the small quantities and the existence of unaltered quartz in all members is surprising. More spinel growth in the molecular percent member is in accord with the ratio necessary for spinel formation (one molecule of $\text{R}_2\text{O}_3$ to a molecule of $\text{RO}$). The peculiar thing of this series is the intensity of all colors of the members as stains; to the naked eye there seemed to be very little difference in the color of any of the members except the molecular percent member, which is much lighter in color when applied to test tile and biscuit fired tile, than any other member. This fact may result from the greater spinel formation in this particular member.

**The $\text{Cr}_2\text{O}_3 - \text{SnO}_2$ series:**

This series is like the $\text{Cr}_2\text{O}_3 - \text{SiO}_2$ series in that the color of its members as stains is very similar. There appears to be no difference in the shade of the green color with the change of the percent of $\text{Cr}_2\text{O}_3$. The fact that the $\text{SnO}_2$ retains its
crystal structure when its melting point is slightly over 1100°C is unexplainable, except that the presence of the Cr₂O₃ may have raised the melting point of the SnO₂ as the solid solution was produced.

The Cr₂O₃ - TiO₂ series:

In this series there is rutile (TiO₂) in abundance in all members. The lack of spinel and the black in some places may be explained by the formation of CrO to some extent. CrO is black and this would give rise to the black stains.

The Cr₂O₃ - ZnO series:

This series gives good evidence that the Cr₂O₃ has been altered to a brown modification. The one green member is due to free Cr₂O₃ which was in excess in the unfired member (75% Cr₂O₃ - 25% ZnO). The presence of unaltered ZnO in all members and unaltered Cr₂O₃ in one member as well is very strange. Apparently there is a catalyst necessary for spinel formation in this series.

The Fe₃O₄ - CoO series:

This series was extremely metallic in nature and was only tested as a stain to ascertain if there was any possibilities for such combinations. The Fe₃O₄ was undoubtedly reduced to free iron, FeO, and magnetite
The remaining series:

The discussion that might be given for the remaining series is self evident and nothing further will be said concerning these than is given with the data.

CONCLUSIONS

In the following list there are conclusions of a general nature which need no elaboration:

1. The heat treatment was not sufficient (that is for a long enough period of time) or the temperature of the initial firing was too low to promote the formation of much spinel in oxide mixtures which previous research has found to form spinels.

2. The atmosphere of the electric furnace used in initial fire was not controlled and this may have had serious consequences upon the final results.

3. In many cases solid solution took place instead of compound formation as was expected due to previous research.

4. There was some volatilization as was expected.

5. The fact is very evident that two compound stains have possibilities in the ceramic industry as underglaze stains.
CONCLUSIONS (Continued)

6. Most of the stains produced in this research were too refractory to be employed as over-glaze colors.

SUGGESTIONS FOR FURTHER RESEARCH

There are many parts of this research that lend themselves to further work to ascertain the complete reason for the unexpected behavior.

Much further information could be obtained from x-ray analysis of each of the members of the thirty series. X-ray would give the answer to the strange behavior in some of the series in which Cr₂O₃ is one component.

The same members of this series should be studied after heat treating at various temperatures and in different atmospheres. The atmosphere of the furnace in this study was somewhat reducing.

This research has only begun a study of ceramic stains in a true scientific manner and should be extended to include more two-component, three-component, and even four-component systems.

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