1937

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

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

BY

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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, Missouri.

1937.

Approved by Paul G. Herold.

Instructor of Ceramic Engineering

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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[1] 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 view point but nearly all is with reference to the changes within the ceramic body when it is subjected to firing[2]. 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[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.

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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.

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.

4 Bayilavich, A.; "Synthesis of Spinels"; Mineral Suire; Vol. 9, No. 9, page 25, 1934; Chemical Abstracts, Vol. 29, 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

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5 "Chemical and Physical Studies of Synthetic Spinels Colored with Cobalt", Nenes phrb. Mineral Geology, Vol. 68A, page 349, 1934; Chemical Abstracts, Vol.29, 1911.

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 underglaze colors with and without a body, and to glazed test tile as overglaze colors, applied wet with approximately 50% low temperature fritted flux. The underglaze 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:

Buckingham Feldspar	20%
No. 4 Kentucky Ball Clay	15%
English China Clay	30%
Flint	35%

One of each of the test tiles were glazed with the following fritted glaze applied at 1.4 specific gravity:

.25 PbO		
.15 K_2O		
.20 Na_2O	.35 Al_2O_3	3.25 SiO_2
.30 CaO	.40 B_2O_3	
.05 BaO		
.05 MgO		

The frit:

.10 PbO		
.20 CaO		
.20 Na_2O	.40 B_2O_3	1.00 SiO_2
.05 BaO		
.05 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:

.10 K_2O		
.40 Na_2O		
.35 CaO	.10 Al_2O_3	2.00 SiO_2
.05 MgO	.60 B_2O_3	
.05 BaO		
.05 ZnO		

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 (Al_2O_3) is one of the two components since a spinel is formed by combination of RO and R_2O_3 (such as MgO and Al_2O_3). Aluminum oxide is very refractory in nature and has a high softening point. The crystalline form of Al_2O_3 is known as corundum. A component of one or more of the remaining series was either ferric oxide (Fe_2O_3), chromium oxide (Cr_2O_3), or cobaltous oxide (CoO), which was assumed to react as cobaltic oxide (Co_2O_3) as well as cobaltous oxide.

The other oxides employed as a component in one or more of the series was titanium oxide (TiO_2), nickel oxide (NiO), manganese dioxide (MnO_2), ferrous oxide (FeO), uranium trioxide (UO_3), stannic oxide (SnO_2), antimony oxide (Sb_2O_3), magnesium oxide (MgO), zinc oxide (ZnO), and silica (SiO_2). The following carbonates were used as sources of calcium oxide (CaO), barium oxide (BaO), sodium oxide(Na_2O), potassium oxide (K_2O), cadmium oxide (CdO), and strontium oxide (SrO); calcium carbonate ($CaCO_3$), barium carbonate ($BaCO_3$), sodium carbonate (Na_2O_3), potassium carbonate (K_2CO_3), cadmium carbonate ($CdCO_3$), and strontium carbonate ($SrCO_3$).

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 Al_2O_3 - CoO Series:

PERCENT Al_2O_3

25%	50%	75%	57.6%

FIRED COLOR

Navy blue	Dark blue	Royal blue	Rich medium

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

Deep blue, rubs off easily	Medium blue rubs off easily	Bright blue rubs off easily	Medium light blue, rubs off easily

The Al_2O_3 - CoO Series continued:

With Body

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

Trials Glazed

Without Body

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

With Body

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

<u>The Al_2O_3 - CoO Series continued:</u>

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 Al_2O_3 increases. Unaltered corundum is very evident in all members but decreases as the percent of Al_2O_3 decreases. There is some solution and the index is reduced by an increase in the CoO content.

The Al_2O_3 - Cr_2O_3 Series:

PERCENT Al_2O_3	25%	50%	75%	40%
FIRED COLOR	Deep nile green	Dull dark green	Dull medium green	Moderately dark green
AS AN UNDERGLAZE COLOR				
Trials Unglazed				
Without Body	Dark green, Rubs off badly	Dark green, Rubs off badly	Light brown, Rubs off badly	Medium green, Rubs off badly
With Body	Dark green, Rubs off slightly	Dark green, Rubs off slighlty	Light brown, Rubs off slightly	
Trials Glazed				
Without Body	Dark green, no solution, good	Dark green, no, solution	Medium green, no solution	Dark green, no solution
With Body	Dark green, no solution, good	Dull dark green, no solution	Olive green, no solutiom	Medium green, no solution excellent

The Al_2O_3 - Cr_2O_3 Series continued:

AS AN OVERGLAZE COLOR

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

PETROGRAPHIC ANALYSIS

A solid solution in all members, with a decrease in the index as the percent of Cr_2O_3 is increased.

The Al_2O_3 - CuO Series:

PERCENT Al_2O_3

25%	50%	75%	56.2%
FIRED COLOR			
Dull dark green, appears crystalline	Dirty brown	Brown with specks of lighter brown	Dirty brown

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

The Al_2O_3 - CuO Series continued:

Dark yellowish green, no rub off.	Dirty yellowish green, slight rub off.	Dirty yellowish green, slight rub off.	Dirty yellowish green, slight rub off.

With Body

Dirty yellowish green, no rub off.	Dirty yellowish green, no rub off.	Dirty yellowish green, no rub off.	Dirty yellowish green, no rub off.

Trials Glazed

Without Body

Medium bright green, slight solution.	Medium bright green, slight solution.	Medium bright green, slight solution.	Medium bright green, slight solution.

With Body

Medium bright green,	Light bright green, no solution	Light bright green, no solution.	Light bright green, no solution.

AS AN OVERGLAZE COLOR

Medium green, Poor color and fusion.	Full green, poor color and fusion.	Deep grass, green, metallic in spots, poor color and fusion.	Grass green, very metallic in spots poor color and fusion.

PETROGRAPHIC ANALYSIS

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

The Al_2O_3 - Fe_2O_3 Series:

PER CENT Al_2O_3

FIRED COLOR

25%	50%	75%	37.55%
Chocolate brown.	Dark brown.	Light brown.	Very dark brown.

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

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

With Body

Medium brown, slight rub off.	Medium brown, slight rub off.	Light brown slight rub off.	Medium brown, slight rub off.

Trials Glazed

Without Body

The Al_2O_3 - Fe_2O_3 Series Continued:

Brownish green, Glaze tended to pull off over stripe.	Brown, Glaze tended to pull off over stripe.	Medium brown, Glaze tended to pull off over stripe.	Dark brown, Glaze tended to pull off over stripe.
With Body			
Very dark brown, no solution, good.	Dark brown, no solution, good.	Medium brown, no solution, good.	Dark brown, no solution, good.
AS AN OVERGLAZE COLOR			
Deep brown, poor fusion.	Rich brown, poor fusion.	Medium brown, poor fusion.	Medium dark brown, poor fusion.

PETROGRAPHIC ANALYSIS

A solid solution formed with an increase in the indices of the corundum as the percent of Fe_2O_3 increased. There appears to be a slight bit of hercymite ($FeO.Al_2O_3$). Magnetite formed in decreasing amounts as Fe_2O_3 content decreased

The Al_2O_3 - MnO_2 Series:

PERCENT Al_2O_3			
25%	50%	75%	54.0%
FIRED COLOR			
Rich dark brown.	Rich dark brown.	Dark brown.	Chocolate brown.
AS AN UNDERGLAZE COLOR			
Trials Unglazed			
Without Body			
Very dark brown, rubs off slightly.	Dark brown, rubs off badly.	Dark brown, rubs off badly.	Dark brown, rubs off slightly.
With Body			
Very dark brown, no rub off.	Dark brown, no rub off.	Dark brown, no rub off.	Dark brown, no rub off.
Trials Glazed			
Without Body			
Brown, glaze tended to pull away from stripe, slight solution.	Brown, glaze tended to pull away from stripe, slight solution.	Dark brown, no solution, glaze tended to pull off.	Dark brown, no solution, glaze tended to pull off.

The Al_2O_3 - MnO_2 Series Continued:

With Body

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

AS AN OVERGLAZE COLOR

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

PETROGRAPHIC ANALYSIS

There is solid solution with no evidence of spinel. Index decreases with increase in percent of MnO_2. Corundum seems to have unlimited solubility for MnO_2.

The Al_2O_3 - NiO Series:

PERCENT Al_2O_3

25%	50%	75%	57.7%

FIRED COLOR

Powder blue.	Medium greenish blue.	Robin-egg blue.	Greenish blue.

The Al_2O_3 - NiO Series Continued:

AS AN UNDERGLAZED COLOR

Trials Unglazed

Without Body

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

With Body

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

Trials Glazed

Without Body

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

With Body

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

AS AN OVERGLAZE COLOR

The Al_2O_3 - NiO Series Continued:

Light green, fair fusion.	Grass green, fair fusion.	Medium green, fair fusion.	Leaf green, 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 Al_2O_3 - UO_3 Series:

PERCENT Al_2O_3

25%	50%	75%	26.4%

FIRED COLOR

Earthy color.	Non-descript color, earthy gray.	Dirty tan	Dull brown.

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

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

The Al_2O_3 - UO_3 Series Continued:

With Body

Very dirty yellow, no rub off.	Grayish yellow, no rub off.	Light grayish yellow, no rub off.	Dirty Yellow, no rub off.

Trials Glazed

Without Body

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

With Body

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

AS AN OVERGLAZE COLOR

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

PETROGRAPHIC ANALYSIS

The UO_3 was reduced to a lower oxide. There is solid solution with the corundum being lowered in respect to index as the percent of UO_3 increased. These are clusters of the lower oxides of UO_3 evident with the microscope.

The CoO - MnO_2 Series:

PERCENT CoO

25%	50%	75%	46.3%
FIRED COLOR			
Good black.	Good black.	Good black.	Good black.
AS AN UNDERGLAZE COLOR			
Trials Unglazed			
Without Body			
Black, slight rub off.	Black, slight rub off.	Black, slight, rub off.	Black, slight rub off.
With Body			
Black, no rub off.	Black, no rub off.	Black, no rub off.	Black, No rub off.
Trials Glazed			
Without Body			
Very dark blue, slight solution.	Very dark blue, slight solution.	Dark blue, slight solution.	Dark blue, slight solution.
With Body			
Very dark blue, no solution.	Very dark blue, no solution.	Dark blue, no solution.	Very dark blue, no solution.

AS AN OVERGLAZE COLOR

Black, poor fusion.	Very deep brown, poor fusion.	Deep blue, poor fusion.	Brownish 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 $CoO - TiO_2$ Series:

PER CENT CoO			
25%	50%	75%	48.4%
FIRED COLOR			
Medium dull green.	Very dark green.	Appears black.	Dark green.
AS AN UNDERGLAZE COLOR			
Trials Unglazed			
Without Body			
Dark greenish blue, bad rub off.	Very dark greenish blue, bad rub off.	Black, bad rub off.	Dark greenish blue, bad rub off.
With Body			
Medium blue, very slight rub off.	Medium blue, very slight rub off.	Dark blue, no rub off.	Medium blue, very slight rub off.

The CoO - TiO_2 Series Continued:

Trials Glazed

Without Body

Medium dark blue, no solution, good.	Dark blue, no solution, glaze tended to pull off.	Very dark blue, no solution, good.	Medium dark blue, no solution, good.

With Body

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

AS AN OVERGLAZE COLOR

Greenish blue, poor fusion.	Good blue, good fusion.	Deep blue, good fusion.	Medium bluish green, good fusion.

PETROGRAPHIC ANALYSIS

There is solid solution. There is much solution in all members except 75% CaO - 25% TiO_2. This series is too dark in color for complete microscopic analysis.

The $CoO - ZnO$ Series:

PERCENT CoO			
25%	50%	75%	47.8%
FIRED COLOR			
Medium green.	Dull dark green.	Appears black.	Dark green.
AS AN UNDERGLAZE COLOR			
Trials Unglazed			
Without Body			
Dark blue, bad rub off.	Dark blue, bad rub off.	Black, bad rub off.	Dark blue, bad rub off.
With Body			
Medium dark blue, slight rub off.	Medium dark blue, slight rub off.	Dark blue, slight rub off.	Medium blue, slight rub off.
Trials Glazed			
Without Body			
Very dark blue, glaze tended to pull off, solution.	Very dark blue, glaze tended to pull off, solution.	Very dark blue, glaze tended to pull off, solution	Very dark blue, glaze tended to pull off, solution.
With Body			
Medium dark blue, slight solution.	Dark blue, slight solution.	Very dark blue, slight solution.	Dark blue, slight solution.

The CoO - ZnO Series Continued:

AS AN OVERGLAZE COLOR

Deep blue, fair fusion but pinholed.	Deep greenish blue, good fusion.	Medium green, good fusion.	Deep greenish blue, good 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 Al_2O_3 - FeO Series:

PERCENT Al_2O_3			
25%	50%	75%	59.0%
FIRED COLOR			
Metallic black.	Dull brown.	Medium brown.	Brown.
AS AN UNDERGLAZE COLOR			
Trials Unglazed			
Without Body			
Very dirty brown, bad rub off.	Dark brown, bad rub off.	Light brown, bad rub off.	Medium brown, bad rub off.

With Body

The Al_2O_3 - FeO Series Continued:

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

Trials Glazed

Without Body

Almost black, with yellow specks, no solution.	Dark brown, with yellow specks, no solution.	Medium light brown, no solution.	Medium brown.

With Body

Almost black, with yellow specks, no solution.	Dirty yellowish brown, no solution.	Medium brown, no solution.	Dark brown, no solution.

AS AN OVERGLAZE COLOR

Poor black with yellow specks, fair fusion.	Poor brown, fair fusion.	Fair brown, fair fusion.	Fair brown, fair fusion.

PETROGRAPHIC ANALYSIS

There is some solid solution. Decreasing amounts of magnetite present as FeO percent decreased. The index of corundum changed only slightly.

The Cr_2O_3 - CoO Series:

PERCENT Cr_2O_3

25%	50%	75%	67%
	FIRED COLOR		
Very dark green, almost black.	Very dark green.	green.	Very dark green.
	AS AN UNDERGLAZE COLOR		
	Trials Unglazed		
	Without Body		
Bluish black, bad rub off.	Bluish black, bad rub off.	Dark green, bad rub off.	Dark green, bad rub off.
	With Body		
Bluish black, slight rub off.	Bluish black, slight rub off.	Dark green, slight rub off.	Bluish green, slight rub off.
	Trials Glazed		
	Without Body		
Black, no solution, good.	Black, no solution, good.	Greenish black, no solution.	Greenish black, no solution.
	With Body		

The Cr_2O_3 - CoO Series Continued:

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

AS AN OVERGLAZE COLOR

Metallic blue, poor color and fusion.	Metallic blue, poor color and fusion.	Medium bluish green, good color and fusion.	Deep bluish 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 Cr_2O_3 - SiO_2 Series:

PERCENT Cr_2O_3

25%	50%	75%	68.4%

FIRED COLOR

Dark green.	Dark green.	Very dark green.	Dark green.

AS AN UNDERGLAZED COLOR

Trials Unglazed

Without Body

The Cr_2O_3 - SiO_2 Series Continued:

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

With Body

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

Trials Glazed

Without Body

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

With Body

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

AS AN OVERGLAZE COLOR

Deep green, good fusion.	Deep green, good fusion.	Deep green, good fusion.	Deep green, good fusion.

The Cr_2O_3 - SiO_2 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 SiO_2 members with more spinel in moleuclar percent member than in the other three.

The Cr_2O_3 - SnO_2 Series:

PERCENT Cr_2O_3

25%	50%	75%	50.5%
FIRED COLOR			
Dull dark green.	Dark green,	Dark green,	Not used as too near 50-50 member to show any additional data.

AS AN UNDERGLAZE COLOR

Trials Unglazed

Without Body

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

With Body

Dark green, slight rub off.	Dark Green, slight rub off.	Dark green, slight rub off.

<u>The Cr_2O_3 - SnO_2 Series Continued:</u>

Trials Glazed

Without Body

Very dark green, no solution, glaze tended to pull off slightly	Very dark green, no solution, glaze tended to pull off slightly.	Very dark green, no solution glaze tended to pull off slightly.	Not used as too near 50-50 member to show any additional data.

With Body

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

AS AN OVERGLAZE COLOR

Deep green, good fusion.	Deep green, good fusion.	Deep green, good fusion.

(Excellent colors; amount of Cr_2O_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_2O_3 increasing as percent Cr_2O_3 increases. The index of SnO_2 increased with increase of the percent of Cr_2O_3.

The Cr_2O_3 - TiO_2 Series:

PERCENT Cr_2O_3			
25%	50%	75%	65.6%
FIRED COLOR			
Black	Black	Black	Black
AS AN UNDERGLAZE COLOR			
TRIAL UNGLAZED			
Without Body			
Black, bad rub off.	Black, bad rub off.	Black, bad rub off.	Black, bad rub off.
With Body			
Gray, slight rub off.	Medium gray, slight rub off.	Dark gray, slight rub off.	Medium gray, slight rub off.
Trial Glazed			
Without Body			
Very dark green, no solution, glaze tended to pull off.	Very dark green, no solution, glaze tended to pull off.	Very dark green, no solution, glaze tended to pull off.	Very dark green, no solution, glaze tended to pull off.
With Body.			
Very dark green, no soltuion, good.	Very dark green, no solution, good.	Very dark green, no solution, good.	Very dark green, no solution, good.

The Cr_2O_3 - TiO_2 Series Continued:

AS AN OVERGLAZE COLOR

Poor black, good fusion.	Poor black, good fusion.	Medium black, poor fusion.	Brownish black, fair fusion.

PETROGRAPHIC ANALYSIS

There is some solid solution. The lower percent TiO_2 members give better evidences of solution. With the lower percent Cr_2O_3 members the brown color of rutile (TiO_2) blots out any evidences of solution or spinel formation.

The Cr_2O_3 - ZnO Series:

PERCENT Cr_2O_3

25%	50%	75%	65.3%
FIRED COLOR			
Dull dark.	Dark brown,	Olive green,	Dark brown.
AS AN UNDERGLAZE COLOR			
Trials Unglazed			
Without Body			
Medium brown, bad rub off.	Dark brown, bad rub off.	Medium green, bad rub off.	Dark brown bad rub off.
With Body			
Light gray, slight rub off.	Gray, no rub off.	Grayish green bad rub off.	Gray, bad rub off.

The Cr_2O_3 - ZnO Series Continued:

Trials Glazed

Without Body

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

With Body

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

AS AN OVERGLAZE COLOR

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

PETROGRAPHIC ANALYSIS

The free ZnO is evident in all members. The index of the ZnO is increased by solution of Cr_2O_3. Spinel is formed but in small quantities only. With the 25% ZnO - 75% Cr_2O_3 member free Cr_2O_3 is present.

The Fe_2O_3 - CoO Series:

PERCENT Fe_2O_3

25%	50%	75%	68.1%
FIRED COLOR			
Black	Black	Medium black.	Medium black.
AS AN UNDERGLAZE COLOR			
Trials Unglazed			
Without Body			
Black, bad rub off.	Black, bad rub off.	Black, bad rub off.	Black, bad rub off.
With Body			
Very dark blue, slight rub off.	Dark blue, slight rub off.	Bluish gray, no rub off.	Dirty gray no rub off.
Trials Glazed			
Without Body			
Bluish black, very slight solution.	Very dark blue, very slight solution.	Very dark blue, slight evidence of yellow, no solution.	Very dark blue, no solution.
With Body			
Bluish black, no, solution, good.	Very dark blue, no solution, good.	Very dark blue, slight evidence of yellow, no solution.	Very dark blue, no solution, good.

<u>The Fe_2O_3 - CoO Series Continued</u>:

AS AN OVERGLAZE COLOR

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

PETROGRAPHIC ANALYSIS

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

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

<u>The Al_2O_3-BaO series</u>:

The molecular percent of this series is 39.8% Al_2O_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 xBaO-yAl_2O_3 minerals which are anistropic 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.

<u>The Al_2O_3-CaO series</u>:

The molecular percent of this series is 64.6% Al_2O_3-35.4% 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 xCaO-yAl_2O_3 which are both isotropic and anis-tropic 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.

<u>The Al_2O_3-CdO series</u>:

The molecular percent of this series is 45% Al_2O_3-55% 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% Al_2O_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.

<u>The Al_2O_3-K_2O series</u>:

This series has a molecular percent member of 52% Al_2O_3 - 48% K_2O. The entire series is white.

There is solid solution. The index is lowered with the addition of the K_2O.

The Al_2O_3-MgO series:

The molecular percent of this series is 71.7% Al_2O_3 - 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% Al_2O_3 member in which member both corundum and periclase exist unaltered.

The Al_2O_3 - Na_2O series:

The molecular percent of this series is 62.2% Al_2O_3 - 37.8% Na_2O. 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 Na_2O percent is increased the index is lowered more, but not greatly. The grains are blue in polarized light. The index is lowered more with K_2O than with Na_2O.

The Al_2O_3 - Sb_2O_3 series:

The molecular percent of this series is 25% Al_2O_3 - 75% Sb_2O_3. The entire series is white.

There is solid solution in the members of this serids. As the percent of Sb_2O_3 is increased the index of the solution increases.

The Al_2O_3 - SrO series:

The molecular percent of this series is 49.6% Al_2O_3 - 50.4% SrO. The entire series iswhite.

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 indicies below 1.70. There is a small amount of unaltered corundum present indicating that a part of the SrO must have been volatilized.

The Al_2O_3 - SnO_2 series:

The molecular percent of this series is 40.5% Al_2O_3 - 59.5% 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 Al_2O_3 plague. 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_2O_3 - FeO series:

The molecular percent ratio of the series is 68|9% Fe_2O_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_2O_3 - SiO_2 series:

The molecular percent ratio of the series is 72.7% Fe_2O_3 - 27.3% SiO_2. There is a variation in the color from brown to black, but allthe 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 Al_2O_3 - 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 Al_2O_3 - Cr_2O_3 series:

This series, generally speaking, are green in color. The 75% Al_2O_3 - 25% Cr_2O_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 R_2O_3 - RO compound and the Cr_2O_3 was not converted to CrO sufficiently to permit any reaction between the oxide molecules.

The Al_2O_3 - 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 Cu_2O in all members except the 25% Al_2O_3 - 75% CuO, which is green. In this member there is a large excess of CuO which has probably been altered to Cu_4O, an olive green compound. When this series is used as stains, the conversion to Cu_4O 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 Al_2O_3 - Fe_2O_3 series:

The colors of this series and the microscopic study shows the Fe_2O_3 has been reduced to lower oxide forms of iron. The formation of hercymite (Al_2O_3.FeO) and magnetite indicate these facts. Had the atmosphere been less reducing, more hercymite would have formed but the tendency appears to be for the FeO formed to associate itself with the unaltered Fe_2O_3 and form Fe_3O_4 which is a spinel.

The Al_2O_3 - 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_2O_3 molecules produced by the heat treatment have more affinity for the FeO than the Al_2O_3, if the results of this series are conclusive.

The Al_2O_3 - MnO_2 series:

This series, being brown in color, indicates the MnO_2 has been converted to the red Mn_3O_4 to some extent. This would prevent the formation of spinel.

The Al_2O_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_2O_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_2O_3 - UO_3 series:

Within this series during the heat treatment the UO_3 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_3 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 Co_2O_3 and it would react as such. However the MnO_2 was altered also by the heat treatment. The color of the resulting stains would indicate the CoO is in the same condition as in the Al_2O_3 - CoO series. In some members, however, the Mn_3O_2 is too strong and the resulting color is brown.

The CoO - 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 TiO_3, which may have been produced from TiO_2.

The CoO - ZnO series:

This series is very similar in behaviour to the CoO - TiO_2 series in that a green color resulted in the initially fired members. There is a yellow oxide of zinc (ZnO_3), 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 Cr_2O_3 - CoO series:

The CoO oxide in this series has deepened the color of the Cr_2O_3 somewhat but still the resulting colors are predominately green. The formation of spinel in all members indicates the activity of these two oxides toward each other. There appears to be no tendency for the Cr_2O_3 to have been converted to a lower oxide form.

The Cr_2O_3 - 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 R_2O_3 to a molecule of 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 Cr_2O_3 - SnO_2 series:

This series is like the Cr_2O_3 - 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 Cr_2O_3. The fact that the SnO_2 retains its crystal structure when its melting point is slightly over 1100°C is unexplainable, except that the presence of the Cr_2O_3 may have raised the melting point of the SnO_2 as the solid solution was produced.

<u>The Cr_2O_3 - TiO_2 series</u>:

In this series there is rutile (TiO_2) 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.

<u>The Cr_2O_3 - ZnO series</u>:

This series gives good evidence that the Cr_2O_3 has been altered to a brown modification. The one green member is due to free Cr_2O_3 which was in excess in the unfired member (75% Cr_2O_3 - 25% ZnO). The presence of unaltered ZnO in all members and unaltered Cr_2O_3 in one member as well is very strange. Apparently there is a catalyst necessary for spinel formation in this series.

<u>The Fe_2O_3 - CoO series</u>:

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 Fe_2O_3 was undoubtedly reduced to free iron, FeO, and magnetite

<u>The remaining series</u>:

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 overglaze 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 Cr_2O_3 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.

ACKNOWLEDGEMENT

The writer of this report is very grateful to Dr. Paul G. Herold for all the assistance and helpful suggestions which he rendered in its preparation.

He is also grateful to Professor C. M. Dodd for his encouragement.

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