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## An Experiment With Mineral Pigments in a Prepared Frit

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**AN EXPERIMENT WITH MINERAL PIGMENTS IN A  
PREPARED FRIT**

by

Cecelia Long

A thesis submitted in partial fulfillment of the  
requirements for the degree of Master of  
Education, in the Graduate School of  
the Central Washington College  
of Education

August 1951

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Education in the Graduate School of the Central Washington College of Education.

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## Chapter I

### INTRODUCTION

The making of pottery ware has a history as long as time itself. Although the origin of the art is lost in obscurity, its story can be traced back to ancient peoples in various parts of the world. It has a double identity, since it is not only a fine art, but also has a very practical and utilitarian aspect as an applied art. This dual personality makes ceramics appealing to the amateur in search of a hobby, to the student of industrial arts; in fact, to anyone who desires to create with his own hands an object of usefulness or beauty.

The necessary supplies are inexpensive and easily obtained, and much of the equipment can be fashioned in the amateur workshop. During recent years the making of pottery has become part of the curriculum in schools offering instruction in the industrial arts. The subject owes part of its appeal to the fact that in only one semester the student can become acquainted with the basic principles of the work and begin to turn out pieces of his own. Once he knows the fundamentals, the ceramist can experiment endlessly with all phases of the art.



This paper concerns itself with one such experiment.

### Statement of the Problem

It was the purpose of the writer to conduct a series of line blend experiments with mineral pigments in a prepared fritted glaze with the intention of finding: (1) the effects of the different mineral pigments, and (2) the desired quantities of these coloring agents in a given glaze. It was expected that the experiment would result in a set of sample tiles which could then be used in teaching.

The writer undertook to make the present experiment primarily because the Art Department of Central Washington College of Education had never used a prepared frit in pottery classes, and was interested in cataloging the resulting colors when such a frit was used in a line blend. The set of color samples produced by the experiment were expected to be useful as a teaching aid, and possibly as the basis for further experiments. The literature of the field offered no descriptions of such an experiment, although there were many related problems covered in the periodicals devoted to ceramics. To be most useful, it was determined that the experiment should be conducted under conditions most nearly like those generally found

in school laboratories.

For this reason no elaborate equipment was used, and the procedures were kept as simple as possible, using a low-temperature prepared frit. The nine coloring oxides employed were chosen because of the ease with which they may be obtained and used, and the ease with which they may be fired. The kiln used in the firing was one constructed by the writer, who likewise prepared the test tiles.

Making the experiment, however, required a knowledge of the whole art and its history. For clarification it seemed advisable to scan briefly the history of pottery-making and glazing, to supply a philosophy of glazing, and to define terms and review related experiments, before presenting the experiment and its results.

### History of Glazing

During the past half century there has been great advance in the study of ancient history. Archeologists continue to unearth civilizations and disclose much detailed information on the lives of the peoples. In countries like Mesopotamia, which lacks stone and metal, the art of the potter was well developed, and relics reveal much of how the people lived. They ate from clay vessels,

lived in clay houses, wrote on clay tablets, and were buried in clay coffins furnished with clay images. Pottery relics provide one of the best chronological scales, despite the fact that these relics seldom bear a date. The archeologist depends upon associated material, or catalogs prepared from previously excavated sites, to assign them to the proper period.<sup>1</sup>

The art of glazing, according to the brief history given in Parmelee,<sup>2</sup> is attributed to the Egyptians at least as early as 5000 B. C. It may be supposed that, as in many arts, the first clay wares were made because of necessity, and that the glazing was eventually added to make the jars more waterproof and easier to clean.

The earliest objects were steatite, made of a pure clay (see p. 12) coated with a vitreous layer. Relics dating back to the third millenium included scarabs, amulets, and statuettes, with larger vases appearing about 2000 B. C. The earliest glazed fragment bearing a date, 330 B. C., was inscribed in the name of King Mena,

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1. Debevoise, Neilson C., "The History of Glaze and Its Place in the Ceramic Technique of Ancient Seleucia on the Tigris," American Ceramic Bulletin, 12, No. 7-13, 1933-34, pp. 293-300.
  2. Parmelee, Cullen Warner, Ceramic Glazes, Chicago: Industrial Publications, 1948, p. 2.

and was done in polychrome in a complicated technique.

In India and Mesopotamia the development of bodies and glazes can be traced back to about 3000 B. C. and the relics are similar in composition and technique to those made by the Egyptians. Obviously following the trade routes of the time, glazed objects appear to have been introduced from Egypt into Crete during the third millennium B. C. and then to have spread to Greece. The Greeks and other peoples of the eastern Mediterranean eventually achieved a more interesting and varied glaze technique as used on clay bodies.

The technical skill in the use of glazes in the ancient times is clearly seen in the fine craftsmanship of the elaborate monumental embellishments of great buildings erected by the Assyrians and Babylonians. The palace of Sargon near Mosul, Iraq, built 722-705 B. C., was decorated on a heroic scale with numerous figures of animal life. These figures were constructed of molded paste and later, claybrick coated with colored glaze. Fortunately, the library of Ashur-bani-pal, King of Assyria 668-626 B. C., was found, and clay tablets inscribed with cuneiform characters describing details of the compositions and procedures for glazing, preparing

pastes, and possibly glass, are being translated.<sup>3</sup>

The pure clay used in these early times was highly siliceous and required a highly alkaline and siliceous glaze which produced a high gloss. This body had only slight plasticity, and when other clay bodies were developed it was necessary to coat the body with a siliceous "under-slip" to act as a foundation for the alkaline glaze.

Thus, step by step, as the art was introduced through Asia Minor, and by the Moors to North Africa and thence to Europe, where variations in the craft were added.

When and where the use of lead in glazes was discovered is not known. It may have been used by the Egyptians, and the Greeks and Romans apparently had some knowledge of its value and are generally credited with having introduced it into Gaul. The Moors in Europe used it, and by the twelfth century it was an important procedure in France. It is believed that the use of lead compounds in glazes did not originate in any one country, since the principles of the metallurgy were known long before the Christian era and the ores distributed over a wide geographical area.

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3. Parmelee, loc. cit.

The development of tin-enamel was another important advance in the progress of the potter. While the properties of the metal were known in the Middle East in the time of the Phoenicians and the ore may have been used in Assyria, the earliest recorded reference to tin-enameled ware was in Italy about 1330 A. D. From Italy the secret of the preparation was carried both to Germany and France. A Frenchman is frequently credited with "discovering" the process in the middle of the sixteenth century.

The use of frits in glazes can likewise be traced as far back as the Egyptians, but it was not until firing at high temperatures, with the development of kilns, that porcelain glazes were perfected, early in the eighteenth century.

The use of a mixture (of clays, fluxes and non-plastics) known as "slip" or "engobe" is added to clay bodies, both before and after the glaze, to form a homogeneous coating to cover surface defects and coarse particles, and also to provide a base for delicately colored glazes. This application has been traced to remote ages and all stages of culture in many parts of the world.<sup>4</sup> Pottery which has been found in eastern Asia,

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4. Parmelee, op. cit., p. 240.

dating from about 3000 B. C., shows decorations of red, black, and white slips, not glazed. Egyptian potters of the Twelfth Dynasty (2160-1788 B. C.) used engobes in various colors, in a technique so skillfully perfected that the color was selected to enhance or modify the color produced with the glaze itself. In one example of this early work, two shades of blue were had under different areas of the same blue glaze by using a white engobe under those portions where a lighter shade was desired, furnishing a contrasting light-colored pattern on a darker blue background. The history of this technique follows the pattern of transfer across areas of the world, appearing in relics from Corinth earlier than the sixth century B. C.; in Britain during the Roman occupancy; and in Gaul and Germany at an early period, in a technique in which the engobe was applied thickly and molded to form a pattern in relief.

#### Philosophy of Glazing

Ceramic products are the result of the action of fire on earthy materials. They are usually molded; but in principle it does not matter whether the article is molded from cold plastic clay only, or with the addition of viscous glass at high temperatures. It is also of no

consequence whether fire is applied early or late in the creative cycle or at some intermediate point. The ceramist begins with this basic fact, but beyond that the craft offers endless possibilities for variation.

It has been stated that many schools include ceramics in art programs. The craft is part of the educative process beyond the mere creation of wares. Such a course develops clearness of thought and expression by demanding accurate work in the laboratory and accuracy of planning and performance. Constructive imagination is fostered by a craft that has few principles, many variations, and frequently-changing theories. The results of working in this art include open-mindedness and tolerance. Growth in esthetic appreciation follows from working in design that is three-dimensional. The student learns to appreciate not only the beauty but the composition when he is mixing his own glaze and shaping the clay body. An appreciation of utility as well as appearance is also encouraged.

An example of the many avenues open to the ceramist may be shown in the following instance. Crackle has always been regarded as one of the special and popular features of Chinese porcelain. It furnishes an illustration of the clever way in which the Chinese potter used



an annoying defect as a means of adding an artistic feature. crazing of pottery ware is a source of trouble to the potter, and he does not do it intentionally. Many Chinese potters made a habit of it, and deliberately placed a glaze with a different rate of contraction from that of the body, so that crazing would take place. This crazing was controlled so that there was a fine mesh or a wide mesh as the potter desired, and the crazings were colored to make the fault a distinctive part of the ware.<sup>5</sup>

The art of pottery making, then, grew from a utilitarian craft to a fine art, and today both kinds are highly developed. Many of the techniques came from accidental discoveries; others were the result of much patient experimentation. The primary requisites of the ceramist are a knowledge of the basic techniques, an interest in experimentation, and an unhampered imagination.

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5. Hetherington, A. L., Chinese Ceramic Glazes, Cambridge University Press, 1937, p. 59.

## Chapter II

### DELINEATION OF MATERIALS AND REVIEW OF RELATED EXPERIMENTS

#### Clay and Clay Bodies

The pattern used here in the presentation of the kinds and composition of clays follows the delineation as given in Kenny,<sup>1</sup> although the information is so general that it may be found in many of the books given in the bibliography.

#### Natural Clays

There is no single answer to the question "What is clay?" Chemically it is a mixture of several substances, the chief of which is aluminum silicate. Impurities which effect the working properties are not only present but are present in varying amounts in clay coming from the same piece of ground. Two essential properties are always present, plasticity when the clay is moist and hardness when it is heated. Familiarity with a few clay bodies and a few chemical elements, their symbols and their behavior, is desirable for the potter. Certainly he should know the

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1. Kenny, John, The Complete Book of Pottery Making, New York: Greenberg Publisher 1949, 152 ff.

chemical composition of the various minerals which he commonly uses.

It has already been stated that aluminum silicate is the chief ingredient of clay. It is also the element which makes up 58% of the earth's surface. This silicon, the symbol for which is written (Si), is followed in order by aluminum (Al), which constitutes 15% of the earth's surface. When these elements are combined with oxygen, as they usually are, they become silica ( $\text{SiO}_2$ ), and alumina ( $\text{Al}_2\text{O}_3$ ). "Pure clay" is composed of one part alumina and two parts silica, plus chemically combined water, and the formula becomes  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and the chemical name becomes hydrous alumina silicate. It should be noted that this chemically combined water is an integral part of the clay and is not the water which gives the clay its plasticity.

Clay, however, is a product of change rather than an original substance, in that the original material was feldspathic rock decomposed by weathering into the material feldspar. All the several kinds of feldspar contain alumina and silica plus some other elements. These other elements were dissolved out of the feldspar during the weathering process, leaving the alumina and silica to form clay.

The varying atmospheric and erosive conditions of weathering left unwanted elements in the resulting clay, so that there is very little "pure" clay, where only the three elements are present. Clay most nearly pure is that which has remained in the same place where it was formed. This residual clay, one type of which is Kaolin, is coarse in texture, non-plastic, and highly resistant to heat. It is used in making fine china and porcelain.

As was stated, most clay did not stay where it was formed, but was moved great distances by streams, winds, or glaciers. The results of this transportation are that it was ground finer, but contains many impurities. It is more plastic and less resistant to heat (less refractory) which makes it easier to work with, but the impurities present make it less reliable in resulting color, since its natural color may be anything, and its color when fired somewhat unpredictable.

Some of these sedimentary clays commonly used by the potter include:

Plastic kaolin. Because it was relatively uncontaminated during transportation this clay retains the whiteness of a residual clay but has a fine-grained texture that makes it more workable than pure kaolin.

Ball clay. The transporting agent in this clay was

water, with the result that it is highly plastic and usually contains some carbonaceous material. It fires almost white and is sometimes used in china and porcelain ware bodies to provide workability.

Fire clay. This clay is rough-textured, usually dark in color, and able to stand high temperature because it is not plastic. It is not generally used for making ware but rather it is used as an ingredient in making stoneware bodies. Fire clays are used commercially in the making of refractory brick.

Stoneware clay. Stoneware clays are like fire clays in their capacity for standing high temperatures, but they are smoother and more plastic and fire to a light buff color. Dark grey or brown may be achieved in a reducing fire.

Common clay. This most abundant type of clay is used to make bricks. One common characteristic is that it hardens at low temperature, but widely varying differences in compositions offer unlimited possibilities to the potter wishing to experiment.

#### Preparing Common Clay

The studio potter generally relies on commercially prepared products, but much can be learned from digging

common clay and preparing it for use. Because of its great abundance finding the clay is not usually a problem. However, since clays differ so greatly in composition, color, reaction to fire, and the method by which it can be worked, discovering this method involves several steps.

Preparation. It is seldom possible to use the clay just as it comes from the ground, because it contains extraneous material such as sticks, rocks, or lumps, which must be removed. The potter must dry the clay, break up lumps by hand or in a mixer, and then put the clay into a pail of water. After the clay has soaked, it must be stirred and forced through as fine a sieve as can be conveniently used. The clay is now quite fluid (called "slip") and must be left in plaster drying bats to harden to the proper consistency for working.

Testing the physical properties. Since the various characteristics of the clay are unknown to the potter it is necessary to test the physical properties of the clay.

1. Plasticity and working quality can be judged by handling it when the clay is moist. The degree of plasticity desired is more or less a matter of personal choice. In general, clay that is plastic enough to be pulled into a thin cylinder about the size and shape of a pencil is desirable. This is referred to

as "long"; "short" being clay that is less plastic, breaking and crumbling when handled this way.

Fineness of grain and the presence of organic matter have something to do with the degree of plasticity. Aging seems to make the clay work more easily, but there is no way for the potter to determine why these things are so. All he can do is to increase the plasticity by adding aged clay, adding acid, or one or two percent bentonite. Sometimes the clay is not plastic enough simply because there is not enough water in it. Generally the higher the percentage of water the more plastic the clay, but a general percentage gram for gram is between thirty and forty-five grams of water per one hundred grams of dry clay powder. The resulting consistency is workable without being too soft.

2. It has been stated that the second essential property of clay is that it becomes hard (dense) when fired, and reference to the kinds of clay above will show that clays require different degrees of temperature to achieve this hardness. To find the ideal temperature to which to fire any given clay so that the clay achieves the maximum hardness without slumping or changing shape it is necessary to run a series

of test firings. An easy and quick way is to make a test tile 6" long,  $1\frac{1}{2}$ " wide, and  $\frac{1}{4}$ " thick, and put it into the kiln on props for firing. A cone pat (see p. 55) with four or five cones is also put into the kiln near the test bar. When the test tile bends in the middle one of the cones in the pat will also bend. The temperature of the cone is known; therefore the maximum temperature of the clay is likewise known.

It may be that the maturing point of the clay being used is higher than the kiln will fire. In this case the maturing point of the clay can be lowered by the addition of a flux. A prepared frit is a commonly used flux. The potter makes a number of test bars of the clay, each bar containing a different amount of flux, and fires them as described above. The ideal percentage to be used is the one present in the bar which does not slump. The potter should remember that while common clay usually matures at a relatively low temperature, it also has an inflexible firing range; that is, a clay which matures at cone 04 will be seriously over-fired by the time it reaches cone 02. The higher-fire clays such as stoneware and fire clay are usually more flexible, one like Monmouth clay having a firing range between cone 1 and cone 10.



If or when the clay is not properly matured it will show faults which are described below.

3. When the ceramist has determined the best firing temperature for the clay he should test the density at that point. One simple test is to tap the ware and listen to the ring; the denser the ware the clearer the tone. Density is tested more accurately, however, by the absorption test, in which a piece of fired clay is weighed, soaked in water overnight and weighed again. The formula giving the percentage of absorption is:

$$\frac{\text{weight wet minus weight dry}}{\text{weight dry}} \times 100 = \% \text{ absorption}$$

An absorption of 5 to 10% is considered satisfactory, but anything above 10% will make the ware useless.

Glazes may craze (see Faults p. 29) and the ware may leak. Density can be increased by adding fluxes, or by adding flint in various amounts and running a series of test firings as described above.

4. Porosity is the property which allows water to leave the ware during firing. When the clay is not porous enough the ware may become distorted. Something must be added to "open up" the clay, while at the same time the potter must be careful not to

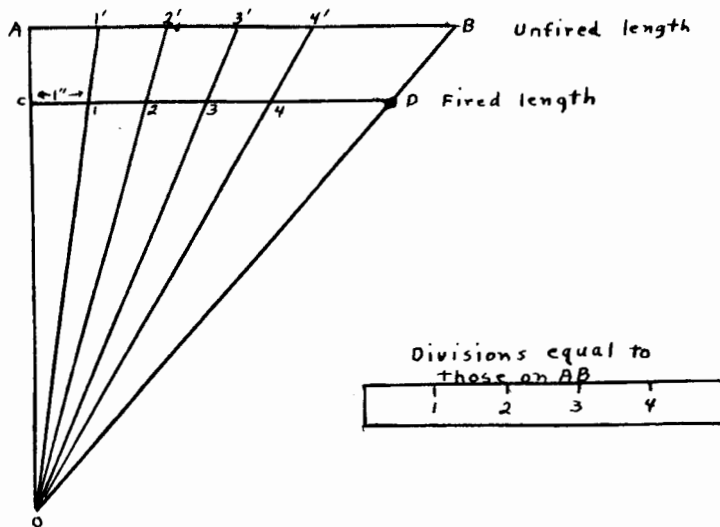
destroy the plasticity. Adding flints in various proportions may solve the problem. If it does not, it may be that too fine a sieve was used in preparing the clay and that the materials which give the natural clay its porosity were screened out. The obvious remedy is to use a coarser sieve (40 - 60) and add "grog." Grog is clay which has been fired, ground up, and screened. These particles provide openings through which moisture can escape. Some experimentation may be necessary to determine the amount of grog to be added, although 10 to 20% is most common.

5. Clay shrinks as it dries and when it is fired; and different clays shrink in different amounts. To measure shrinkage make a test bar of clay and score lines on the top surface ten centimeters apart, dry the tile and measure between the points to get the dry shrinkage. Fire the tile to the maturing point and remeasure between the lines to get the firing shrinkage. The percentages of shrinking may be expressed in the formula:

$$\frac{\text{original length minus fired length}}{\text{original length}} \times 100 = \% \text{ shrinkage}$$

When the potter knows the shrinkage that will take place in the clay he is using he can make a

shrinkage rule for future use. This rule has the following form:<sup>2</sup>



Horizontal line AB is equal to the unfired length. Line CD is equal to the fired length. Vertical lines touching AC and BD are drawn out to a point where they meet on O. On CD lay off points one inch apart and draw lines from point O through the one inch points on CD extending the lines to cut the line AB. The distances between the points on AB will give the needed length of a piece of clay when wet in order that it will be one inch long when fired. A shrinkage rule showing the length of spaces equal

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2. Kenny, op. cit., p. 160.

to those on line AB can then be used to measure unfired clay so that the fired clay will be the correct length.

### Clay Bodies

Clay as it comes from the ground is used in heavy clay products such as bricks and earthenware. In making finer wares the potter must blend various combinations of materials into what is called a "clay body." This clay body, as has been pointed out above, must be plastic enough to work, must be porous enough so that shrinkage can be controlled and the danger of warping eliminated, and must result in a ware that reaches density at a practicable temperature.

Clay bodies can be prepared with the simple equipment available to the amateur potter. The steps to be followed in blending the ingredients include preparing the natural clay (see above) and adding whatever is necessary in the way of other clays, of flux, and of completing processes such as aging, until the resulting clay body contains the qualities needed to make a ware that matures within the temperature range possible in the kiln being used.

The potter may work out his own body formula or may use clay body recipes to be found in books on ceramics and

in commercial catalogues, or he may make further experiments by varying the amounts of ingredients given in the prepared recipes. He is limited only by the heat capacity of his kiln. Generally speaking, high temperature firing results in finer ware with fewer technical problems. Obviously, wares fired at high temperatures will call for ingredients different from those used in low temperature ware.

The ceramist may also experiment with color, using the colors both in the clay body and in the glazes. In this paper the use of color in glazes is treated in the section on glazes. Coloring the clay body may be done by adding grog, using prepared body stains or adding coloring oxides. Several tests may have to be run before the ceramist is satisfied with the resulting color.

### Glazes

Glazes are silicate mixtures fused on clay wares. Usually the resulting surface is highly reflecting or glossy, except on matt glazes when the surface has the appearance of glaze kid; however, all gradations of glossiness or mattness may be observed.

Glaze surfaces may be colored or colorless, transparent, translucent, or opaque. Whatever the appearance

the glaze may give, this coating is used on claywares to make the ware waterproof and to improve its appearance.<sup>3</sup> The glaze always contains three essential ingredients: silica; flux to lower the melting point of the silica; and alumina to give viscosity. It is always produced on the ware by the action of heat.

### Kinds

Glazes are classified first according to the kind of flux used, whether raw (material in raw state) or fritted (prepared) materials. In frits the ingredients are fired into a glass and pulverized before using. There are special types of glazes, such as slip glazes or engobes, salt glazes, and lustres, which make a third classification.<sup>4</sup>

Lead glazes. Lead is the most widely used flux in low temperature glazes. Either red lead or white lead is commonly used, the former being harder to handle.

Raw lead glazes are unfritted and may be fired from cone 015 and lower to cone 6 or even cone 8. However, the usual range for a lead glaze is cone 05 to 02. By the introduction of the proper coloring oxides an extensive

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3. Parmelee, op. cit., p. 1.

4. Kenny, op. cit., p. 179 ff.

variety of color may be produced.

The advantages of lead as a glaze constituent are:

The wide range in the amount of lead which may be used.

The ready fusibility of its silicates and alumina-silicates.

The relative insolubility in water of the available lead compounds.

The low viscosity and low surface tension of its fused compounds.

The unique color effects it produces.

The relative economy of its use. (Considering its fusing powers, it is the cheapest flux.)

The disadvantages of lead as a glaze constituent are:

Raw leads are poisonous. Continued contact with the raw material or with raw glazes is harmful to the operator unless care is exercised.

Lead compounds have relatively high vapor pressures, consequently volatilize freely so that wares, thus coated, must be enclosed in a suitable container during firing to prevent impoverishment of the glaze and loss of gloss.

Crazing is a common defect but fully avoidable.

The glazes are easily scratched and frequently harmfully affected by atmospheric gases which cause a filmy coating to form on the surface after prolonged exposure at room temperature.

Incorrectly proportioned glazes may be susceptible to chemical attack by fruit and vegetable juices, and foods stored in such containers may in time become unsafe to use.<sup>5</sup>

Alkaline glazes. The alkalies used by the ceramist are compounds of sodium, potassium, and lithium. The alkalies are strong fluxes and increase the fluidity of

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5. Parmelee, op. cit., p. 222.

the glaze and have important influences upon the development of color. They increase the brilliancy of the glaze and, within certain limits, lessen the resistance to weathering.

Sodium decreases the tensile strength and the elasticity as compared to other bases commonly used. Sodium closely resembles potassium in many chemical characteristics but it is not advisable to substitute one for the other except in small amounts. The compounds used by the ceramist are sodium carbonate, which is known in the trade as soda ash and is, with the exception of borax, the chief source of sodium used by the potter.

Fritted glazes. A frit is a glaze which may either be purchased ready made from commercial concerns or made from raw material by the ceramist. Preparing the raw materials requires a special kiln and a long tedious process. There are many advantages to using prepared frits. Soluble materials become insoluble, and the raw materials which have to burn out during the firing process are eliminated.

Ground glass glazes. Ground glass is sometimes used as a glaze by adding clay to keep it from running. This glaze is not recommended however, because of the lack of



knowledge concerning its chemical structure which makes its use a matter of trial and error.

Leadless glazes. In these glazes the lead flux has been substituted generally by calcium and zinc. Leadless glazes are generally fired at cone 4 and above. Porcelain, bristal, salt, loam or earth, aventurine, iridescent, and crystalline glazes are all of the leadless type glazes.

Salt glazes. Salt glazing is an extremely hard glaze achieved by throwing salt into a special made kiln when the temperature has reached its highest point. It is considered a high-temperature glaze because it works best from cone 4 to cone 9. Salt glazes are good for carved or decorated surfaces, but are used mainly to coat pipe lines which carry water under the streets.

Lustre glaze. A lustre glaze is obtained by putting a thin film of metal on top of the glaze so that it reflects light. To obtain a lustre, reduction is necessary. In electric kilns this is obtained by the introduction of organic matter after the glaze has been fired to its maturing heat.

Slip glazes. Slip glaze is one made of liquid clay and clay. It must be fired at a lower temperature than that needed by the green ware. Slip glazes may be put on unfired or fired ware.

### Preparation of Glazes

Weighing the ingredients is the first step in preparing a glaze. The most practical equipment includes a beam balance showing a graduated scale in one-tenth gram intervals, since the metric weight eliminates the calculations involved in the use of pounds and ounces.

The weighed materials must then be mixed thoroughly. Usually sufficient water (between 50 to 70% of the dry ingredients) is added to facilitate mixing, whether the mixing is done by hand or mill. Pebble mill mixing is preferable where coarse materials are present, after which the glaze is strained through a fine meshed sieve (100 to 120).

When the glaze has settled and the clear water siphoned off the working consistency of the glaze may be improved by the addition of such effective materials as gum tragacanth, gum arabic, sodium alginate, magnesium sulphate, and others, including certain commercial conditioners, all in very small amount. In the case of gums, it is usual to add a tablespoonful of the prepared gum to a batch of 300 grams of glaze. If dry salts are used about 1% of the dry batch by weight is added.

When a glaze is to be applied by dipping, the specific

gravity of the glaze will be varied depending upon the porosity of the ware. When very porous ware is to be glazed it is desirable to saturate it in water before dipping thus preventing the accumulation of too heavy a coat and eliminating the necessity of using a glaze of very low specific gravity.

The thickness of the application varies according to the type of glaze used and the effect desired. For ordinary work the glaze is applied to a thickness .025 inch while for matt glazes and textural glazes it may be two or three times the normal thickness.

When spraying is the method of application the porosity of the ware is not the determining factor, since the thickness of the coat can be more readily controlled. In this method it is desirable to finish off with a slightly wet application to consolidate the glaze, removing the danger of damage during handling and producing a smooth finish.

It happens rarely that body and glaze and fire are so adjusted that the finished ware is without faults. The cure for these faults is not necessarily specific. Since there may be an occasional trouble or a complication of troubles, the remedy indicates the line along which relief may be found.

## Faults

According to Divine and Blackford<sup>6</sup> a lack of harmony between clay and the glaze may result in the following faults.

### Crazing

This common fault is caused by unequal coefficients of expansion of the glaze and the body, with the result that the glaze is covered with minute cracks. If prepared glazes are used adding flint to the body will remedy the defect. It should be noted, however, that prepared glazes must not be confused with prepared frits, the latter being merely a constituent of the glaze. Another method of curing crazing is the addition of flint and feldspar to the glaze.

When the cause of crazing is under-firing the cracks may not appear for days and these cracks will grow long and irregular as the ware stands. The obvious remedy is to refire the pot. In the case of over-firing the cracks will be evident immediately when the pot is withdrawn from the kiln, although they will not as a rule become any worse with standing. Refiring, with or without rubbing fresh glaze into the cracks, is a remedy sometimes used.

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6. Divine, J. A. F., and Blackford, G., Pottery Craft, New York: Frederick Warne and Company, Ltd., 1939.

### Shivering or Peeling

Shivering is due to the glaze's being too large for the body. The remedy is to reduce the percentage of flint in either the body or the glaze.

### Crawling

In this case the glaze settles in little blobs and lumps, caused by underfiring the body, grinding the glaze too much, or having too much clay in the glaze. A glaze that cracks before firing will usually result in crawling.

### Running or Flowing

In this fault the glaze may run and expose bare patches. Add clay or flint to the glaze as a remedy.

### Blistering

Both bright and matt glazes may develop blisters, which may either have melted down to small craters in the kiln or remained unbroken when the kiln is open. The cause of this fault is generally due to the sulphur content in the clay, especially aged clay, which tends to produce a scum on the ware. The glaze attacks this sulphate gum, generating a gas which boils out and causes the blisters. A little barium carbonate added to the old clay will help to effect a cure. Occasionally the glaze

contains impurities in the form of sulphates and these will cause the blisters.

### Matt Glazes Resulting in Bright Surfaces

Matt glazes must be used in a very thick coat if they are not to fire bright. Other causes are that the fire may be too high or that the fire may be "reducing," that is, with insufficient oxygen.

### Pinholes

The appearance of pinholes in the glaze when cool is the result of too rapid cooling.

### Colored Lead Glazes

"The production of color in glazes is controlled by the choice of coloring oxides, the amounts and kinds of RO members, the amounts of the alumina and silica, and temperature of firing."<sup>7</sup>

Lead glazes may be produced in a great variety of colors, because of the many oxides available in silicate melts. There are exceptions, as in the case of refractory oxides and those requiring extremely low temperatures; for example, chrome oxide is not suitable for use in

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7. Parmelee, op. cit., p. 233.

producing glaze below cone 05, because the oxide has slight solubility and the glaze must be relatively high in bases and low in silica, which conditions are unfavorable for the development of a good green color. In the case of a highly refractory color base such as the chrome-alumina, pink is obviously impracticable.

A few of the most commonly used oxides, given in terms of the resulting color, may be discussed here for purposes of illustration. Parmelee's review of various studies was used as a basis for this section. It was not possible to trace the source of his citations when he did not indicate them. Since the purpose of this section was not essentially historic, the author did not attempt the necessary research of minor points.

### Green

Copper oxide. This oxide is readily soluble in lead glazes producing a transparent green color which is susceptible to the kind and amount of other bases present and to the temperature. Apparently it voltitizes more readily from lead-containing glazes than other types. Walker<sup>8</sup>

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8. Parmelee, op. cit., p. 233; citing Walker, F. W., Notes on the Development of Greens From Cupric Oxide in Glazes, Trans. American Ceramic Society, IV: 278 (1903).

reports that the effects of various oxides upon the development of greens using copper as follows: calcium in any quantity (at cones 02 to 2) had no effect upon the color; zinc oxide made the color more brilliant and produced more variations of shades; potassium and sodium produced various shades of green; barium and magnesium had specific effects. If potassium is used with zinc oxide, the color will deepen as the former is replaced by zinc oxide. Other investigators have reported that calcium aids the magnesium and magnesium diminishes the intensity of the green color. Ramsden<sup>9</sup> found that the solubility of the oxide in glazes melting below 1100°C varies from 3 to 8%. This may be increased by raising the silica content, decreasing the alumina (avoiding divitrification) and increasing the alkali content at the expense of the lead. If the lead oxide exceeds 0.7 molecular equivalent, a small portion may be replaced with zinc or magnesia. An excess of clay or copper oxide in the composition and firing above 1100°C gives a browner shade. The author is of the opinion that calcium and barium oxides have little influence on the green color.

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9. Parmelee, op. cit., p. 234; citing Ramsden, C. E., Solubilities of Metallic Oxides in Glazes, Trans. Engineering Ceramic Society, 7:21 (1907-8).



Chromium oxide. Whereas the relatively easy solubility of the copper oxide in lead silicate fusion gives transparent greens, the less soluble chromium oxide - seldom greater<sup>10</sup> than 1% below 1100°C, yields opaque glazes. When the amount of the oxide is so low as to be dissolved, the color will be yellowish green. The color is made browner by alumina, zinc, and barium oxides, also by tin which later, under favorable conditions, gives pink to red. Calcium may be expected to give yellowish or orange tones but the evidence seems to be contradictory.

Nickle oxide. The solubility of nickel oxide in silicate fusion is not greater than 1 to 3% at temperatures below 1100°C. The lead oxide should be less than 0.7 molecular equivalents, and may be replaced in part by zinc oxide. A green may be had by the use of nickel with magnesium as RO members in a lead glaze.<sup>11</sup>

Cobalt-uranium. A green may be had by blending the oxides of cobalt and uranium in a stain. In order to insure the absence of specks, the nitrates may be mixed in the approximate proportions of four or five parts of

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10. Loc. cit., p. 234.

11. Parmelee, op. cit., p. 235; citing Holscher, H. H., Some Lead Borosilicate Glazes Containing Nickel Oxide, Journal of American Ceramic Society, 12:111 (1929).

the uranium nitrate to one part of the cobalt nitrate. These are added to a frit.

### Yellow, Orange, Cream, Tan, and Buff

Ferric oxide. Ferric oxide may be used in lead silicate glazes to produce a weak yellow, tans, and buff. It was much used by the Chinese, during the seventh century of the present era and subsequently, to give yellows.

Uranium oxide. Colors ranging from light yellow to a deep orange may be had with uranium oxide according to the amount used and the bases present. About 10% of sodium ironate is needed for the deepest color. The alkaline earths do not affect the color; the alkalis, including lithia, lighten the color. Ivory colored shades may be produced by the addition of 6% tin oxide and 1 to 2% of sodium ironate to a lead glaze containing zinc oxide.<sup>12</sup>

Molybdenum oxide. This oxide will give a yellow which varies in intensity according to the amount used, 2 to 10%. Barrett<sup>13</sup> considers it a strong coloring agent.

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12. Parmelee, op. cit., p. 235; citing Kautz, K., The Effect of Glaze Composition Upon Colors Produced by Sodium Uranate, Journal of American Ceramic Society, 17:8 (1931).

13. Parmelee, op. cit., p. 235; citing Barrett, W. E., Glazes Colored by Molybdenum, Journal of American Ceramic Society, 8:306 (1925).

The composition reported as giving satisfactory yellows was a typical raw lead glaze having  $PbO$ ,  $CaO$ , and  $K_2O$  fired at cone 02 to 2. Cream colors may be had by the addition of rutile, with or without tin oxide, to a lead glaze.<sup>14</sup>

### Brown

Manganese oxide. The solubility of manganese oxide varies from about 1 to 4% in lead containing glazes fired at 1100°C or lower. An increased temperature is accompanied by a greater solubility with some loss of quality of the color which will be a claret brown. Alumina favors the development of the color but should be kept low. Zinc oxide, lime, and silica promote the formation of the pinker shades. Manganese shows a tendency to volatilize and is quite sensitive to the presence of sulfur oxides in the kiln gases which form a thin film dulling the gloss.

Iron oxide. The solubility of ferric oxide in glazes varies from 3 to 14% at temperatures up to 1100°C.<sup>15</sup> Lowering the lime, zinc oxide, and alumina and raising the

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14. Parmelee, op. cit., p. 235; citing anon., Unusual Pink and Maroon Glazes by the Use of Colemanite, Ceramic Industry, 31:42 (1938).

15. Ibid., p. 236; citing Ramsden, loc. cit.

amount of lead oxide increases the solubility. Raising the temperature has the same effect but impoverishes the color. The color is improved by the presence of alumina, clay, and barium oxide. Magnesia diminishes the color.

Nickel oxide. The color obtained by using nickel oxide in lead-containing glazes is strongly influenced by the other bases present. It is most commonly some shade of brown varying from straw to purplish. The colors are likely to be variable. Holscher,<sup>16</sup> using a simple lead glaze and successively substituting zinc oxide, lime, barium oxide, and magnesia, obtained amber, blue, browns, and green.

Chromium oxide. Magnesia,<sup>17</sup> zinc oxide, and alumina tend to produce fawns, tans, and brownish shades when chromium oxide is used with them in lead glazes.

## Blue

Cobalt oxide. Cobalt oxide is relatively easily soluble in lead containing glazes. It has very high tinc-torial power and is somewhat susceptible to the influence

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16. Parmelee, op. cit., p. 236; citing Holscher, loc. cit.

17. Parmelee, op. cit., p. 236; citing Minton, R. H., The Effect of Variation of RO Elements Upon Chromium Oxide in a Matt Glaze, Trans. American Society XVI: 248 (1914).

of the choice of the alkalies and alkaline earths present, but not to the extent that is true in the leadless types.

Nickel oxide. A slate blue and a "good" blue have been reported by experimenters, who used lead oxide and zinc oxide, or lead oxide, zinc oxides, and alkalies in simple glaze compositions maturing at cones 1 to 3.

### Red

Iron oxide. Red colors may be had in highly silicious, lead-containing glazes when the alkalines are high and lime (and the other alkaline earths) is not present.

Uranium oxide. Uranium oxide is a reliable reagent for producing reds at temperatures up to cone 04 and above, but occasionally higher. Cordt<sup>18</sup> states that the lead and silica content should be high; zinc oxide is not harmful to the color and may be useful in producing a matt texture if not more than 1% which is introduced in the mill batch; little kaolin may be added, but no whiting, if it can be avoided, and no boric oxide.

Chrome-tin oxide. Chromium and tin oxides in the proportion of 1.17 to 20 give pink.<sup>19</sup> The tin oxide is

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18. Parmelee, op. cit., p. 236; citing Cordt, F. W., Production of Red Glazes, Ceramic Industry, 21:172 (1933).
  19. Parmelee, op. cit., p. 237; citing Mellor, J. W., Chemistry of the Chrome-tin Colors, Trans. Engineering Ceramic Society, 36:16 (1937).

supposed to be inert and serves as a mordant on the glaze upon which the aerosol, or highly dispersed chromium oxide, is deposited. These extremely fine particles of chromium oxide are red whereas the massive form is green. Rieke says that as little chromium oxide as 0.0025% gives a definite coloration. Similar red products may be had by precipitating a little chromic oxide with hydrated alumina, magnesia, or zinc oxide and calcining the mixture. If the glaze dissolves the mordant, i.e. the tin oxide, magnesia, etc, the red color disappears, to be replaced by green; hence tin oxide is used because of its inertness.

The presence of silica and of lime limit their production to the cone temperature range of about 013 to 05, rarely higher.

#### Colored Fritted Glazes

The production of colored fritted glazes has a much wider scope than is possible in any other type, because of (1) the greater choice of kinds and amounts of the bases, (2) the wider heat range, (3) the significant effect of the boric oxide, (4) the omission of the lead if necessary, and (5) the use of greater amounts of the alkalies, if desired.<sup>20</sup> In all cases the results obtained will be

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20. Parmelee, op. cit., p. 215 ff.

dependent upon the manipulation of these factors. If lead oxide is an important member of the bases, the colors obtained with the various oxides will be similar to those had with the raw lead glazes subject, in some cases, to the modifying effects of the boric oxide. In leadless glazes, notable variations from the above colors may be had.

### Brown

Manganese oxide will produce claret browns in leadless and lead-containing glazes in the presence of alumina and boric oxide. Ferric oxide in quantities of 3, 5, and 6% produces browns which are compositions. The color is strengthened by presence of barium oxide. More color is needed in the leadless glazes. Zinc oxide is said to give a better color tone with a range from brownish-yellow to chocolate. Nickel oxide will yield a straw-brown color in all glazes containing lead. The alkaline glazes will give grey colors with low concentration of the nickel, but the larger amounts and increases in the content of alumina on boric oxides produce browns. The color may be intensified by substituting strontium for calcium, barium for strontium, potassium for lithium. The maximum amount of nickel oxide used is about 2%. The brown and buff shades are

sensitive to various temperatures.

### Tan

Tan colors were produced by Holscher<sup>21</sup> using nickel oxide in some leadless borosilicate glazes containing 0.35 equivalents or more, (preferably 0.45 equivalents) of calcium oxide, while the barium oxide should not be over 0.2 equivalents and the sum of the barium magnesium oxides not over 0.3 equivalents.

### Blue

Cobalt compounds are the usual source of blue colors in all variations of glaze compositions and throughout the entire firing range. The shades of blue may be altered by the choice of the bases, the amounts of the cobalt compounds employed and the presence of certain other elements which may be used accidentally or intentionally. It is known that the colors of some modern glazes and glosses are not identical with antique products, in some cases, for this reason. This has been noted in the results obtained with the use of old recipes for preparation of

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21. Parmelee, op. cit., p. 216; Holscher, W. H., Some Lead Borosilicate Glazing Containing Nickel Oxide, Journal of American Ceramic Society, 12:69 (1929).



colors employing the more highly purified materials available today. Thus Mellor suggests that the Chinese cobalt blues may contain very small quantities of nickel oxides in addition to the known content of manganese oxide.

Minute traces of elements are not always sought nor identified in routine analysis. The presence of lead produces the warmer tones approaching the ultra-marine as the concentration increases. The leadless glazes are colder in tone and lighter in shade. Appreciable differences are affected by the presence of magnesia and zinc. The influence of the latter is said to be variable. Plusch reports that a high zinc content produces a violet shade, and lesser quantities give a cold blue.

### Blue-Green

Blue-green (turquoise color) is obtained in leadless glazes in the absence of alumina. The amount of copper oxide required varies between 5 and 10%. The color is destroyed by temperatures above  $1100^{\circ}\text{C}$ , sometimes at  $1000^{\circ}\text{C}$ .

### Yellow

Sodium uranate, the commercial uranium oxide, will produce yellow colors in glazes containing a high content of sodium and barium, a medium content of lime and zinc

oxides. The presence of lead and boric oxide impairs the color somewhat, the former more than the latter. Boric oxide as such or as borax gives a greenish tinge. The amount of the  $U_2O_3$  used will be from 0.003 molecular equivalents upwards.

### Orange

Orange colored glazes may be had with the use of sufficiently high content of "uranium oxide" (up to 10%) added to glaze compositions containing high lead and zinc, low alkalies and alkaline earths. Bismuth and cadmium intensify or darken the color in cone 07 glazes. Five per cent of titanium oxide in the presence of 6 to 8% of the uranate is said to give a brownish-orange. The molecular equivalents of the  $U_2O_3$  used for the maximum color will be of the order 0.05.

### Red

Bright red glazes may be obtained by using compositions of the iron aventurine type, i.e., containing little else but alkalies, lead oxide, boric oxide, silica, and, of course, the iron oxide. The temperature must be low and the firing done under oxidizing conditions.

Chromium oxide in company with tin oxide calcined together with non-coloring compounds, or chromium and

chromium and tin oxides in a glaze composition will form various shades of red. Some leadless glazes, high in lime and boric oxide, destroy the color. Relatively high lime and low alumina in the color stain with a high proportion of lime in the glaze may develop milkiness in the glaze or scumming.<sup>22</sup> Increasing the lime in the glaze makes the color more crimson and stable at the temperatures of cone 6 and above. Increasing silica tends to make the glaze more violet or blood red, and, in the presence of boric oxide, it maintains the color. An excess of alumina tends to alter the pink to a green. Zinc oxide may replace lead oxide up to 0.15 equivalent without detriment; barium oxide may be satisfactorily used in a limited amount (0.2 to 0.3 equivalents) if lead is present. In either case a scummy surface may form. Strontium produces a brighter and more fusible glaze than barium with a stronger action on the color. Magnesium, even in quantities as small as 0.05 equivalents, is harmful to the color, i.e., destructive.<sup>23</sup>

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22. Parmelee, op. cit., p. 218; citing Mellor, J. W., Chemistry of the Chrome-tin Colors, Trans. Ceramic Engineering Society, 36:16 (1936-37).

23. Ibid., p. 218; citing Ramsden, C. E., A Study of Chromium Red Glazes, Trans. Ceramic Engineering Society, 12:239 (1912-13).

## Green

Copper oxide used in alkaline glazes produces the greenish blue, or turquoise color. If lead is present, the color is definitely a green which varies greatly in intensity as the concentration is increased. In a borosilicate glaze containing also zinc, lime, and the alkalis, the color is lightened by increasing the boric oxide content. Chromium oxide differs strikingly from copper oxide in being little soluble in glaze fusion; consequently, the glazes in which it is present are opaque, lacking the characteristic transparency accompanying the use of copper oxide. Moreover, chromium oxide is very refractory.

### Colored Porcelain Glazes<sup>24</sup>

The color palette of porcelain glazes is limited as compared with those maturing at the lower temperatures. There is a considerable difference between "hard" and "soft" porcelains, and cone 10 may be designated, arbitrarily, as the limit of usefulness of the more sensitive colors; for example, those prepared with iron, and with copper. At the higher temperatures those colors either volatilize to such a degree that the color is impaired, or

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<sup>24</sup>. Parmelee, op. cit., p. 163 ff.

bubbling and blistering injure the surface finish; or chemical changes occur in the colorant to its detriment. The choice of the kind and the amounts of the bases used is of very great importance and in general potassa has a more satisfactory effect upon color development than soda. Magnesia performs some special services, in this respect, otherwise it is undesirable. Pleasing effects are had most frequently by blending the stronger colorants thus avoiding the hard effects otherwise accompanying the sole use of primary colors. The oxide of iron and the oxide of nickel are sometimes employed as "shading" or "toning" colors for the same reasons. Oxidizing conditions during the firing is the normal practice since some colorants are injured by reduction, e.g., manganese may be made to yield a dirty grey under such conditions. On the other hand, the typical green or greenish blue is furnished by copper oxide, if oxidized, but it gives interesting and even beautiful shades of red under the influence of the reduction.

The color oxides suitable for the extreme temperatures and which have low volatility and high tinctorial power, thus limiting the amount required to small replacements of the more active bases, are: cobalt, manganese, chromium, nickel, iron, titanium, and uranium. Seger recommends that oxides of the RO and R<sub>2</sub>O types be introduced in place

of molecular equivalents of the alumina. Hegeman<sup>25</sup> recommends:

8 molecular equivalent uranium nitrate for  
4 of calcia  
5 molecular equivalent cobalt oxide for  
5 of calcia  
8 molecular equivalent ferric oxide for  
4 of calcia  
8 molecular equivalent manganese for  
4 of calcia  
4 molecular equivalent copper oxide for  
4 of calcia

However, the substitution should be governed by the nature of the other RO members and the color desired.

### Blue

Three to five per cent of cobalt oxide, or 0.025 to 0.10 molecular equivalents of the cobalt oxide, introduced in the RO group, are the customary limits to produce the range of concentration of color from the light to the deep blue. Calcium has a beneficial effect. Barium promotes the formation of the Turkish blue; the presence of phosphoric acid yields a violet shade of color and a more luminous quality. The pleasing effect of some of the best Chinese blues is attributed to the presence of very small amounts of the oxides of iron or nickel.

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25. Parmelee, op. cit., p. 164; citing Hegeman, H., Die Herstellung des Porzellans, 2nd. edition, p. 137 (1938).

## Greens

Only one or two per cent of chrome oxide may be used because it is very refractory but, fortunately, a strong colorant. The maximum and the minimum molecular equivalents are 0.15 and 0.015 respectively. Between these limits are found the variations from light to dark green. The addition of a small amount of cobalt is good practice, and a reducing atmosphere for the firing is beneficial providing that the lime content of the glaze is low. The presence of a small amount of calcium fluoride enlivens the color. An addition of barium with calcium intensifies the color. Baria with potassa yields a yellowish or hedge apple-green. Baria with magnesia and potassa gives greyish colors. Calcia and magnesia and potassa give brownish shades, but if the calcium is absent, the result is a fawn color. Small amounts of zinc oxide are said to be unobjectionable with chromium, although giving a greyish shade, but larger quantities give tans and browns. Alumina with chromium has the latter effect and tin oxide will produce useful pinks and maroons. Copper oxide may be used alone to produce bluish greens at temperatures below about cone 9. A high lime content is desirable in the glaze. The minimum and the maximum quantities used are 0.125 to 0.20 molecular equivalents. Uranium yellow and cobalt blue,

properly proportioned, will give greens, and praesodymium phosphate give light and moss green colors.

### Browns

Faintly violet to strong browns may be had by the use of manganese oxide if added within the minimum amount of 0.10 molecular equivalents and the maximum of 0.25 molecular equivalents. Iron oxide will give light tan with the use of 0.025 molecular equivalents, and a brown if the amount is increased to 0.10 equivalents. Nickel oxide will produce light to dark browns if used between the limits 0.05 and 0.15 molecular equivalents. Chromium is reported to furnish brownish shades if used with the bases: potassa, calcia, and magnesia in the same RO. Very strong browns may be had by using a mixture of equal proportions, in molecular equivalents, of the oxides of manganese, chromium and iron.

### Yellow and Cream

Uranium oxide will produce yellow glaze if they are fired under oxidizing conditions, otherwise they become greyish to black. The addition of a small amount of calcium fluoride (fluorspar) will improve the yellow color. The minimum amount of the uranium oxide necessary for a faint yellow will be about 0.01 molecular equivalents.



This must be considerably increased in order to intensify the color. Titanium oxide or rutile with only a slight amount of iron oxide will yield a cream color if used in quantities ranging from 1 to 3%. Oxidizing conditions must prevail in the kiln if rutile is used.

### Black

This color may be had by the addition of 1 to 2% of cobalt oxide to a brown glaze or 2 to 4% manganese oxide to a blue glaze. In with chromium general, the principle is used of mixing two or more oxides of high tinctorial power in such a proportion as to produce an optical effect in which the action of any single component does not dominate. Iridium will produce a black but it is very expensive. Platinum produces grey. Uranium, as already stated, produces a black when fired under reducing conditions.

### Red and Pink

The chrome-tin pinks calcine may be used for the low and medium fire porcelain glazes. Its preparation and use was described earlier. Some shade of red may be had without the use of a calcine providing the essential constituent oxides, tin and chromium, are introduced in a glaze of a suitable chemical character.

The practical limit of the chrome-tin pink color is about cone 9. Iron oxide is unstable at high temperatures giving greys and blackish colors, but fiery reds may be had, within the proper temperature limits, if alkalies are used as the bases to the exclusion of lime and probably the other alkaline earths.

### Colored Bristol Glazes

The colorants used and the effects produced in Bristol glazes are the same as those discussed under the topic Porcelain Glazes, with a few notable exceptions. The most important of these is the zinc oxide, which is the most characteristic component of this variety of glaze. It lightens the shade of blue obtained with cobalt oxide.

With the use of the following compositions maturing at cone 5, Pence<sup>26</sup> obtained light browns with 0.005 equivalents of nickel oxide, purplish blues with intermediate amounts, and a light blue with the maximum, 0.02 equivalent.

Glaze composition-- cone 5

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26. Parmelee, op. cit., p. 174; citing Pence, F. P., Colors Produced by Nickel Oxide in Ceramic Mixtures Containing Zinc, Trans. American Ceramic Society, XIV:143 (1912).

	0.25	K <sub>2</sub> O		
0.14 to	0.28	CaO		
0.21 to	0.42	BaO	0.30	Al <sub>2</sub> O <sub>3</sub>
0.05 to	0.40	ZnO	2.00	SiO <sub>2</sub>

As previously stated, a small amount of zinc oxide is permissible with the chromium oxide in compositions prepared to give greens, but larger amounts produce brownish yellows, and further increases give red browns. The presence of magnesia with the zinc and chromium oxide gives pinkish shades in the lower concentration of the colorant. Bright yellow buffs to brilliant yellows may be had by the proper selection of the amounts of color oxide, the lime, and the zinc oxide. Six per cent of the commercial "uranium oxide" (sodium uranate) was used by Squires<sup>27</sup> for this purpose in the following composition:

Potash feldspar.....	53.0%
Flint.....	18.5%
English ball clay.....	4.5%
Whiting.....	6.5%
English China clay.....	4.5
Barium carbonate.....	13.0%

Cones 5 to 6 in a muffle kiln.

The production of pinks or reds by the use of chromium and tin oxides or the chrome-tin stain cannot be done successfully in the presence of zinc.

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27. Parmelee, op. cit., p. 175; citing Squires, L. R., Raw Yellow Glazes for Terra Cotta and Development Phenomena, Journal of American Ceramic Society, 11: 584 (1928).

### Salt Glazes

The color obtained from salt glazing depends upon the character of the kiln atmosphere and the nature of the body. With an oxidizing fire the colors are lighter than with a reducing fire. If flashing is done it will darken the color. It is the practice in some factories to mix crude oil with the salt in order to intensify the color and even to produce a dull black. In this case the color is probably due in part to particles of carbon becoming entrapped in the glaze. A stoneware clay fired under oxidizing conditions will have a greyish color. Buff bodies give light yellow to dark brown, red bodies give dark brown to reddish brown, increasing in intensity with the repetition of the flashing treatment. In general, reduction is used in developing commercial color, especially on light-burning or buff color bodies used for sewer pipes. Green colors are sometimes obtained due to the presence of lime in such a form and of such a quality as to produce that effect.

The addition of sand to clays which are deficient has been found to be of value in the development of a good salt glaze.

Schurecht has reported on the relation between the content of iron oxides, alumina, and silica in clays and

their effect on the formation of color in a good salt glaze. Schurecht<sup>28</sup> summarizes the relationship as follows:

White to tan, if the ferric oxide content is not above 1% and the silica is low; or up to 2.19% ferric oxide if the silica is high. (The ferric oxide content is calculated on the basis of calcined clay).

Light brown, if the silica is low and the ferric oxide does not exceed 3½%; or with ferric oxide 2.19 to 3.5% if the silica is high.

Brown, if the iron oxide lies between 3.5 to 4.75%.

Mahogany, if the iron oxide exceeds 4.75% but is less than 8.2%.

Black, if the content of iron oxide is greater than 8.2%.

Clays containing high ferric oxide should be salt glazed at a lower temperature than those low in the oxide. With the same content of ferric oxide, darker glazes are had with high alumina than with high silica.

The same investigator<sup>29</sup> discussed the effects of the presence of lime upon the color and brightness of the glaze and concluded: that even as little as 1% lime in the clay will prevent the formation of a bright glaze at low temperatures. They can best be glazed at low temperatures above cone 5, providing that the content of ferric oxide

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28. Parmelee, op. cit., p. 179; citing Schurecht, H. G., Clay Sewer-pipe Manufacture, Journal of American Ceramic Society, 6:717 (1923).

29. Parmelee, op. cit., citing Schurecht, H. G., Influence of Varying Lime Content in Clays, Journal of American Ceramic Society, 7:539 (1924).

is low. Clays containing much lime can be glazed at higher temperatures if the iron is not too high (above 3.5%).

### Firing

The method of firing is as important as the clay and the glazes, since it is the agent which causes the change of a soft plastic material to a hard and brittle ware and also creates changes in color and waterproofs the vase. To bring about this change the heat must be applied properly and controlled until the clay is matured. Controlling the heat implies not only regulating the degree of temperature but confining it within a small space.

The high degree of heat required to fire the ware cannot be measured by ordinary thermometers and other pyrometric devices must be used, the most popular of which is the pyrometric cone. In this device three cones of clay, each with a different melting point were inserted into a pat of clay containing a comparatively large amount of grog. When the first cone, which contains the lower melting flux, melts this acts as a warning to the potter that the temperature of the kiln is approaching the point needed to mature the ware. The second cone contains the same amount of flux as the ware; therefore when it melts, the kiln has reached the required temperature. The third cone,

which contains flux needing a higher melting point, serves as a warning that the kiln is too hot for the ware. Each cone of clay plus a given flux was assigned a number beginning with 022 requiring a Fahrenheit temperature of 1121 degrees, ascending to cone 15 requiring a temperature of 2615 degrees F. (See Table I) The potter may gauge the temperature by watching the color of the fire, but by this method he may only approximate the heat.

Some electric kilns are equipped with a pyrometer. In this device for measuring the temperature there is a metal bead made of two different elements, usually platinum and rhodium, soldered together. Heating this bead generates a tiny electric current which can be measured by an ammeter. These measurements are then translated into degrees.

For large commercial furnaces a more complicated pyrometer, embodying the same principles, is used, except that the reading is made from the amount of current passing through the wire itself, rather than making the translation into degrees.

TABLE I  
TABLE OF CONE TEMPERATURES<sup>30</sup>

Cone	Centi- grade	Fahren- heit	Color of Fire	What Happens to Clay	Type of Ware and Glazes
15	1435	2615			
14	1400	2552			
13	1350	2462		Porcelain	Porcelain
12	1335	2435		matures	
11	1325	2417			China
10	1305	2381	White		bodies
9	1285	2345		Stoneware	Stoneware
8	1260	2300		clays mature	Salt glazes
7	1250	2282			
6	1230	2246			
5	1205	2201			
4	1190	2174		Red clays	China glazes
3	1170	2138		melt	
2	1165	2129			Semi-vitreous ware
1	1160	2120			
01	1145	2093	Yellow		
02	1125	2057		Buff clays	Earthenware
03	1115	2039		mature	
04	1060	1940			
05	1040	1904			
06	1015	1859		Red clays	
07	990	1814		mature	Low fire earthenware
08	950	1742			
09	930	1706	Orange		Low fire lead glazes
010	905	1661			
011	895	1643			
012	875	1607	Cherry red		Lustre glazes
013	860	1580			
014	830	1526			
015	805	1481		Organic matter in clay	Chrome red glazes
016	795	1463		burns out	
017	770	1418			
018	720	1328	Dull red		Overglaze colors
019	660	1220			Enamels
020	650	1202			
021	615	1139			
022	605	1121		Dehydration begins	

30. Kenny, *op. cit.*, p. 167.



### Review of Related Experiments

For a knowledge of what has been done with various metallic oxides in different kinds of glazes, the author reviewed a number of experiments in an effort to reach some general conclusions about the function of these oxides. Though there are variations in many important points, such as the temperature of firing, the kind of kiln used, and the fact that the glazes used were not always of the same type as the one used in the present problem, the writer felt that these experiments were well worth investigation because the basic principles were the same and the majority of the oxides vary comparatively little. It was felt that reviewing the related experiments might serve to establish the maximum and minimum amount of the oxides and to provide a pattern for interpreting the results of the present study.

The experiments cited below were taken from a reference work by Koenig and Earhart,<sup>31</sup> since the writer did not have access to the ceramic magazines containing the original dissertations.

Following the abstracted experiments the author attempted to summarize any general conclusions. These

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31. Koenig, J. H., and W. H. Earhart, Literature Abstracts of Ceramic Glazes, Chicago: Industrial Publications, Inc., 1942.

conclusions must necessarily be regarded as inconclusive, because of the fact that most of the experiments were made under widely varying conditions. Since the present study was primarily concerned with color in glazes, the conclusions drawn from the following experiments are grouped under the various oxides.

### Colors in a Zinc Silicate Glaze<sup>32</sup>

A study was made of the effects of common coloring oxides when introduced in a typical zinc silicate or willemite crystalline glaze.

The preferential color absorption by the crystals seem to be in the following order:

- (a) Cobalt is absorbed in large amount and the color of crystal deepens to almost a blue-black before the glaze is affected.
- (b) Copper is retained by the glaze with no noticeable amount of volatilization. The green color is totally absorbed by the crystal.
- (c) Manganese is not absorbed as much as the cobalt and copper oxides and the color of the background darkens with increase in color.

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32. Kramer, H. M., "Colors in a Zinc Silicate Glaze," Journal of American Ceramic Society, 7(12):868-877 (1924).

- (d) Nickel and iron act very much alike as regards to their being absorbed by the crystal except that nickel begins to prevent crystallization at about 0.05 molecular equivalents, FeO may be added up to 0.2 molecular equivalents, the background darkening in color faster than the crystals, the crystallization not being affected.

A Glaze Study Involving Some Interesting Colors Produced by Nickel Oxide<sup>33</sup>

A study was undertaken with the object of determining the influence of various RO combinations on productions of greys.

Replacing BaO by ZnO varies the colors from a purplish brown in the low ZnO members to a bluish purple in the higher ZnO members. These glazes higher in MgO become successively more grey until a neutral grey is reached. Where PbO was employed the greys are of decided yellowish tone, due no doubt to influence of the PbO in producing browns.

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33. Whitmer, J. D., "A Glaze Study Involving Some Interesting Colors Produced by Nickel Oxide," Journal of American Ceramic Society, 3(8):663-670 (1920).

### Cobalt-Uranium Green Glaze for Terra Cotta<sup>34</sup>

The characteristics and methods of promoting green colors in glazes were outlined.

Copper greens are used extensively. At cones 6 or 7 the greater part of the copper is volatilized and the resultant shades of green are light and uneven.

Chromium and chromium stains when used in most glazes of the Bristol type give greens which appear yellow when compared with the deep greens. The chromium can only be used in glazes in which the zinc content is very low. With even small amounts of chromium, glazes containing zinc oxide fade to brown and glazes containing tin are apt to be streaked with pink. The nickel green colors are variable. Iron compounds, if used alone, produce variable yellow-green colors. Greens may be produced by the blending of blue and yellow colors.

Wilson tried first a dull mat glaze as a base, adding uranium oxide and a cobalt stain in varying amounts. A bright glaze was then tried as a base. The colors obtained with these uranium-cobalt greens are deeper than those afforded by the majority of chromium greens burned under

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34. Wilson, H., "Cobalt-Uranium Green Glaze for Terra-Cotta," Journal of American Ceramic Society, 1(14): 238-246 (1918).

similar conditions.

### Colored Porcelain Glazes at Cone 10<sup>35</sup>

In developing a cone 10 glaze, which matured giving a bleb free film, the investigators arrived at the following conclusions:

Colors from CoO: 0.025 CoO give a fine strong light blue and increasing depth of color is obtained up to 0.10 CoO which in a good thick dip gives a very deep, rich, cobalt blue.

Colors from CuO: 0.125 CuO gives a very pale, delicate copper green. 0.150 CuO gives greens of a little deeper shade, but the color is rather feeble and uneven through volatilization.

Colors from MnO<sub>2</sub>: 0.1 MnO<sub>2</sub> will practically all burn out. 0.25 MnO<sub>2</sub> gives a fairly deep manganese violet brown.

Colors from Cr<sub>2</sub>O<sub>3</sub>: In the glaze containing no zinc, 0.15 Cr<sub>2</sub>O<sub>3</sub> produced a light chrome green and 0.15 Cr<sub>2</sub>O<sub>3</sub> a very dark chrome green.

Colors from Fe<sub>2</sub>O<sub>3</sub>: 0.025 Fe<sub>2</sub>O<sub>3</sub> produces practically no color in the glaze, 0.05 Fe<sub>2</sub>O<sub>3</sub> gives a pleasing light tan and 0.10 Fe<sub>2</sub>O<sub>3</sub> gives dark olive tan or brown.

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35. Montgomery, E. T., and I. A. Kruson, "Colored Porcelain Glazes at Cone 10," Trans. American Ceramic Society, XVI:347-363 (1914).

Colors from yellow oxide or uranium: 0.10  $U_2O_3$  gives a very pleasing light lemon yellow, and 0.02  $U_2O_3$  gives a slightly darker yellow. An increase to 0.06  $U_2O_3$ , which is equivalent to about 10% of oxide in the glaze batch, gives only a slight increase in the depth of color.

Colors from NiO: 0.05 NiO gives a light, pleasing nickel brown; 0.10 NiO gives a darker medium brown; and 0.15 NiO gives a very dark nickel brown.

### Cobalt and Nickel Colors<sup>36</sup>

The simple cobalt blue colors can be arranged in two classes: (1) calcining cobalt oxide and flint or spar at high temperatures gives the characteristic ultramarine blue or cobalt silicate. Glazes rich in MgO may develop deep pink or purple colors: (2) calcining cobalt oxide and alumina at a high temperature gives the commonly called mat blue or "Thenard's blue." In the ceramic industries, it is made from alumina and cobalt oxide, with or without ZnO. In some cases, the phosphate blue is employed.

### Further Experiments in the Problem of the Turquoise Alkaline Glaze<sup>37</sup>

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36. Mellor, J. W., "Cobalt and Nickel Colors," Trans. Engineering Ceramic Society, Vol. 36, p. 1 (1936-37).
37. French, M. M., "Further Experiments in the Problem of the Turquoise Alkaline Glaze," Journal of American Ceramic Society, 8 (3):143-144 (1925).

The blueness of the glaze was found to be influenced by the maturity of the body, the amount of copper used and the fire of the glaze.

The addition of 6 to 12 parts of copper gave the bluest color at cone 04.

### My Experience with Crystal Glazes<sup>38</sup>

In several cases, very acceptable results were obtained with zinc-containing glazes using fritted rutile.

The most beautiful development of the glaze was obtained at temperatures between cones 4 and 7. From an olive colored ground there are developed numerous fine greenish-brown starshaped crystals.

1. It is not desirable to frit  $TiO_2$  or rutile. This is also true of the metal oxides and other admixtures.
2. Glazes containing Cu and  $MnO_2$  or mixtures of both give the best results.
3. Crystals are developed to the best advantage at temperatures between cones 4 and 7.
4. Small additions of vanadic, molybdic, and tungstic acid prompt the development of crystals, but

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38. Pukall, W., "My Experience with Crystal Glazes," Trans. American Ceramic Society, X:183-215 (1908).

their effect is not the same in all cases. In each individual case, it must be determined which one of the three acids have their influence.

5. The influence of the batch grinding upon the development of the crystal glaze is trifling.
6. It is advantageous to use a very easily fusible frit and to charge it rather heavily with raw metallic oxides, rutile, etc., as well as those raw substances that are required in proper glaze formulation.
7. Fine stoneware is especially well adapted as a basis for the production of rutile crystal glazes.
8. For the production of pretty titanium crystal glazes, a rapid rise of temperature prevailing during the reduction.
9. The effects of reduction are variously manifested according to the temperature prevailing during the reduction.
10. By the process of infiltration or vapor treatment, color schemes and effects may be obtained that are hard to duplicate.

### Crystalline Glazes<sup>39</sup>

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39. Purdy, R. C., and J. F. Krehbiel, "Crystalline Glazes," Trans. American Ceramic Society, IX:319-407 (1907).



Crystals have been produced in glazes having a wide variety of compositions, and at nearly all temperatures.

General conclusions of the investigation were:

1. Of the two alkalies, potash and soda, the latter in every case was the most conducive to the development of crystals. The crystals formed in the soda matrices were not only the largest, but had the most pleasing habits of growth and grouping.
2. The proportion of zinc and alkali most conducive to the development of crystallization in every case, save that of the glazes high in titanitic acid was:

0.3 ZnO	to	0.6 ZnO
0.7 KNaO		0.4 KNaO

3. Manganese oxide had by far the greatest crystallizing tendency, producing not only large crystals but also crystals of surprisingly varied habits of growth. Zinc oxide had a tendency to produce large crystals in local areas as though the crystallizing substances had segregated. Titanitic acid, on the other hand, produced crystals that were small but evenly distributed throughout the mass.

4. The character and shape of crystals induced by manganese can not be adequately described. The globular growths, that under a magnifying glass were handsome, produced en masse in lighter tints, were superb, and the latter crystals producing variegated fawn-colored effects were very beautiful.
5. The limits of oxygen ratio permissible in the crystalline glazes were not established. The results, however, do seem to warrant the statement that an oxygen ratio of 1:28 is better suited to the development of crystals than that of 1:4 as used in practice today.

Uranium Oxide Colors and Crystals in Low Temperature Glaze Combinations<sup>40</sup>

A study is made of the color and crystallization of some uranium, lead, sodium, and boron glazes fired in a pure oxidizing atmosphere, both alone and with the addition of certain inorganic compounds. The colors obtainable are yellow, orange, red, green, brown, and black. By using only uranium oxide and red lead it is possible to produce

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40. Lorah, J. L., "Uranium Oxide Colors and Crystals in Low Temperature Glaze Combinations," Journal of American Ceramic Society, 10 (10):813-820 (1927).

any shade from light yellow to dark orange or red. About 10% of yellow uranium oxide is required to produce the deepest shade of orange.

Using only uranium oxide in a lead glaze, a shade from light yellow to deep orange or almost a red may be obtained by simply varying the quantity. Five per cent will produce a bright orange and 10% a dark orange, with a higher percentage seeming to darken the color very little. If the percentage is sufficiently increased it also acts as a refractor. Black spots noted in some glazes were undoubtedly due to the reduction of large masses of yellow uranium oxide to the black oxide ( $UO_2$ ) by some of the gases produced in the furnace. It cannot be due to high temperature alone, since all oxides of uranium are changed to the yellow from ( $U_3O_8$ ) upon being heated to high temperatures in the presence of air.

Glazes containing either borax or boric acid with silica give yellow glazes with a greenish tinge and show no tendency toward the formation of any orange colors.

A Study of Color and Its Application to Ceramic Art<sup>41</sup>

Color is recognized as having three dimensions, (1)

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41. Lenchner, T., "A Study of Color and Its Application to Ceramic Art," Journal of American Ceramic Society, 10 (7):538-542 (1927).

warmth or coolness, known as hue, (2) lightness or darkness, known as value, and (3) brightness or dullness, known as intensity or chroma. Two existing color theories were outlined and the proper application of colors discussed.

Notes on the Development of Greens from Cupric Oxide in Glazes<sup>42</sup>

Green glazes produced with copper are subject to so many changes when under fire, that it becomes very necessary to use every care, both in making and burning of the glaze. The least variation of the temperature or the method of firing the kiln, will change the color, varying from a bright green to a brown or yellow shade. Experiments were made for the purpose of ascertaining the action of basic oxides, the change of color and the fluxing produced in combination with oxide of copper, and correction of these troubles. In the experiments, 0.1 equivalent of cupric oxide was used in all the glazes, this being thought sufficient copper strength to show the changes; this left 0.9 equivalents to be made up by the other RO elements. One-hundred-thirty-seven glazes were prepared.  $K_2O$ ,

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42. Walker, F. W., "Notes on the Development of Greens from Cupric Oxide in Glazes," Trans. American Ceramic Society, IV:278-301 (1902).

Na<sub>2</sub>O, PbO, BaO, ZnO, and MgO were varied from 0.45 equivalents to 0; CaO from 0.45 equivalents to 0.15; Al<sub>2</sub>O<sub>3</sub> from 0.5 equivalents to 0.2; SiO<sub>2</sub> from 3.5 equivalents to 1.0; and B<sub>2</sub>O<sub>3</sub> from 0.5 to 0. These glazes were fired at cone 02 and cone 2.

In summing up the facts demonstrated from these experiments, SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> can be used in any desired content, while Al<sub>2</sub>O<sub>3</sub> should not exceed 0.25 equivalents, unless the shade of green is desired to be yellow tint; while in the RO elements, not over 0.30 equivalents should be used of any one base for best effects.

### Zirconium Compounds<sup>43</sup>

Some zirconium glazes were tested on typical semi-vitreous bodies. Zirconium oxide, when added in amounts of 4% or more, showed a tendency to increase the resistance to crazing, regardless of whether it was added as "opax" or as "milled zircon." ZrO<sub>2</sub> showed about the same crazing resistance as TiO<sub>2</sub> at low percentages, but considerably more at higher percentages. The opacity began to develop when the ZrO<sub>2</sub> content approached 3% and it increased with increasing percentages of the oxide.

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43. Anon., "Zirconium Compounds," Ceramic Industry 32 (2): 41-42 (1939).

Additions of zirconium oxide up to 4 or 5% showed no apparent change in texture, either with "opax" or "milled zircon." Percentages above that amount showed a trend toward a mat texture when "opax" was used, but the glazes remained bright up to 8%  $ZrO_2$  when it was added in the "milled zircon" form. An advantage of zirconium, especially for glaze works, is the fact that the presence of chrome vapors will not produce a pink discoloration, as has been known to happen with tin. Glazes for pottery, tile and whiteware opacified with zirconium compounds, covering the range to superopaque, brilliants to full mat, are in commercial use at the present time.

#### Turquoise Glazes<sup>44</sup>

Copper oxide will color lead glasses green and alkali glasses blue. If the latter coloring turns out pure, it will contain no trace of green and yet the blue is of so peculiar a character that it can never be mistaken for cobalt blue. Glass particles thus obtained will show probably the most beautiful and glowing copper blue that can be obtained. Naturally a sharply oxidizing fire is necessary and for this reason the oxidizing red lead is

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44. Berdel, E., "Turquoise Glazes," Ceramic Industry, 17 (3):195-198 (1931).

better than litharge, especially since the latter may contain particles of free lead.

It is peculiar that, in so many turquoise glaze formulas, lead oxide is wholly avoided while lime and boric acid are taken in. The reason for this probably is that one man is satisfied with a green-blue mixture and does not work towards obtaining a pure copper blue.

One great difficulty which all glazes rich in alkali and of relatively low temperature show are the hairlines which manifest themselves. The alkali glazes have so high a coefficient of expansion and contract so violently in cooling, that turquoise glazes rarely are obtained without crazing. For the most part, one makes a virtue of necessity and colors the cracks black to produce a crackle ware piece. However, these cracks can be prevented by firing the glaze to a high temperature in combination with an increase in silicic acid from one and one-half to two times the normal amount. An addition of steatite is permissible and frequently counteracts the formation of cracks. Enrichment of the ware with finely ground quartz sand will also function against the tendency to form cracks. Above all, the body of the ware must be absolutely free from lime.

Solubilities of Metallic Oxide in Glazes, (a) NiO and MnO<sub>2</sub> in Glazes<sup>45</sup>

The extent to which a glaze will continue to take up a metallic oxide and yet remain clear varies considerably and is governed by the following factors:

- (1) Chemical composition of glaze
- (2) Physical properties of glaze (viscosity, fluidity, etc.)
- (3) Physical condition of coloring oxide
- (4) Temperature of firing
- (5) Cooling rate

The object of this investigation was to throw some light on these points and incidentally to note:

- (1) Color effects produced by variations in glaze formula
- (2) Influence of temperature on color
- (3) Whether and under what conditions any reduction of content of coloring oxide could be made while maintaining the finished color
- (4) What volatilization of oxide (if any) take place
- (5) Effects produced by large excess of oxide

It was decided to make up a series of glazes maturing at about 1050°C. and introduce definite percentages of

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45. Ramsden, C. E., "Solubilities of Metallic Oxide in Glazes, (a) NiO and MnO<sub>2</sub> in Glazes," Vol. 5, p. 1 (1905-6): "(b) Cr<sub>2</sub>O<sub>3</sub> and CuO in Glazes," Vol. 7, p. 21 (1907-8).



oxides. Whenever possible, glazes were compounded raw, only those containing alkalies and boric acid being fritted. The carbonates of the coloring oxides were ground raw with the colorless glazes in a mortar and pestle.

### Part I - NiO Glazes

With these glazes, Ramsden concludes that a very small amount of  $\text{SnO}_2$  not exceeding 2%, makes a glaze capable of dissolving more NiO, resulting color being slightly greener.

#### Conclusions:

- (1) Solubility of NiO in glazes maturing below  $1100^\circ\text{C}$ . is never greater than 1%.
- (2) Solubility varies with glaze composition and can be increased as follows:
  - (a) Raise acidity ( $\text{SiO}_2$ ) to at least 1.5 in lead glazes.
  - (b) In lead and leadless glazes maintain a high acidity and replace  $\text{SiO}_2$  by  $\text{B}_2\text{O}_3$ . Molecular ratio of  $\text{SiO}_2$  to  $\text{B}_2\text{O}_3$  must never be less than 2:1 or opalescence will result even with moderately quick cooling.
  - (c) Add a small quantity, say .5%, of  $\text{SnO}_2$  to the glaze.
  - (d) Lower  $\text{Al}_2\text{O}_3$  as much as is consistent with prevention of devitrification in both lead and leadless glazes.
  - (e) In absence of R2O bases, the PbO must not be lower than .7 molecular parts.
  - (f) If PbO exceeds .7, replace some by other RO bases.

- (g) ZnO is a very valuable base and may replace PbO up to .2 molecular.
- (h) Replace PbO and other RO bases with alkalies.
- (3) A temperature of 1050°C. gave best results, although in some cases the temperature might be raised up to 1100°.
- (4) The quicker the cooling rate the freer the glaze from color separations.
- (5) The color of all the lead glazes is straw brown, except those containing MgO, which is green. The alkali glazes are grey, though converted to brown by increase of either NiO, Al<sub>2</sub>O<sub>3</sub>, or B<sub>2</sub>O<sub>3</sub>.

## Part II - MnO Glazes

MnO added as the dioxide or pyrolusite

### Conclusions:

- (1) The solubility of MnO in glazes maturing at a temperature not higher than 1100°C. varies from about 1% to 4% MnO.
- (2) Solubility can be increased by altering the glaze composition in the same way as for NiO, with following exceptions:
  - (a) Lower the Al<sub>2</sub>O<sub>3</sub> as much as possible in a lead glaze, but in an alkali glaze; this doesn't seem to be necessary.
  - (b) In an alkali glaze the replacement of SiO<sub>2</sub> by B<sub>2</sub>O<sub>3</sub> has no marked effect on solubility.
- (3) Increasing firing temperature to 1050°C. raises the solubility, but the color is generally better the lower the temperature.
- (4) The quicker the cooling rate the better.
- (5) The color is claret brown in lead and alkaline glazes, but this can be considerably modified

both by altering the composition and firing temperature. Pinker shades are obtained by the presence of  $PbO$ ,  $ZnO$  and  $CaO$ . Increase in  $SiO_2$  has the same result. Brown tints are produced by alumina and boric acid in both lead and leadless glazes.

- (6) Some evidences of volatilization of  $MnO$  were observed.

A glaze is a mutual solution of its chemical constituents, either as oxides or as silicates. The glazes used here are the same as given previously, with the addition of a  $PbO$  plus  $BaO$  plus  $SiO_2$  glaze.

### Part III - Chromium Oxide

Introduced in glazes as .25 to .50 to .75 and 1.00%  $Cr_2O_3$  obtained by gentle ignition of ammonium bichromate.

#### Conclusions:

- (1) Solubility in glazes maturing below  $1100^{\circ}C$ . is seldom greater than 1%  $Cr_2O_3$ .
- (2) Solubility increased by same methods as given in  $NiO$  glazes with the following exception:
  - (a) In both lead and leadless glazes the ratio should never be less than 1  $B_2O_3$ :5  $SiO_2$ .
- (3) Best results obtained if the firing temperature of the glaze is less than  $1050^{\circ}C$ .
- (4) Quick cooling gives best results.
- (5) When clear, the color of lead glazes is yellowish-green, but if super-saturated with oxide, the usual green tint predominates. Color made browner by alumina, clay, tin oxide,  $BaO$  and  $CaO$  which produce an orange tint. The finest greens with this oxide were obtained in a slightly reducing atmosphere. A bright green quite distinct from the lead glazes was obtained with the leadless

glazes, and this is made more yellow by alumina.

- (6) Volatilization from a transparent chrome glaze appears to be quite small, but this is not so when the glaze is saturated.

#### Part IV - Iron Oxide

Pure  $\text{Fe}_2\text{O}_3$  was added to the glazes in amounts equivalent to 3, 5 and 6%  $\text{Fe}_2\text{O}_3$ .

#### Conclusions:

- (1) Solubility in glazes maturing at less than  $1100^\circ\text{C}$ . varies from 3% to upwards of 14%  $\text{Fe}_2\text{O}_3$ .
- (2) Solubility may be increased by same methods as given for NiO glazes, with the following exceptions:
  - (a) Lower the alumina as much as possible, though this will impoverish the colors in both lead and leadless glazes.
  - (b) In a lead glaze replace the silica by boric acid up to 0.5  $\text{B}_2\text{O}_3$  and in leadless glazes up to 1.5  $\text{B}_2\text{O}_3$ .
  - (c) Replace CaO by PbO in a lead glaze. This is contrary to results with other coloring oxides considered thus far.
  - (d) As in the chrome glazes, additions of ZnO to a lead glaze reduces the solubility of  $\text{Fe}_2\text{O}_3$ .
- (3) In both lead and leadless glazes the colors are impoverished at  $1100^\circ$  or higher.
- (4) The quicker the cooling after complete fusion, the clearer the glazes.
- (5) The color of all the glazes containing  $\text{Fe}_2\text{O}_3$  is the well known brown. In a lead glaze the color is improved by alumina, clay or boric acid, and

is greatly augmented by the presence of BaO. Far more oxide is required to give the same tint in a soda-lime glaze as compared with a lead glaze. The color is strengthened by silica, alumina and B<sub>2</sub>O<sub>3</sub>.

#### Part V - Copper Oxide Glazes

Copper was added to the glazes in the form of pure malachite (2 CuO. CO<sub>2</sub>. H<sub>2</sub>O) and in amounts equivalent to 5, 6 and 7% CuO. In some cases as much as 10% was necessary to saturate the glaze, and in other cases 5% was more than enough.

#### Conclusions:

- (1) Solubility in glazes melting below 1100° varies from about 3% to 8% CuO.
- (2) Solubility can be increased by same methods as described in NiO glazes with the following exceptions:
  - (a) Reduce the amount of kaolin in both the lead and leadless glazes.
  - (b) If the lead exceeds 0.7 PbO, a small portion may be replaced with ZnO or MgO. CaO and BaO appear to have little influence. This is contrary to the other coloring oxides, except Fe<sub>2</sub>O<sub>3</sub>.
- (3) Quick cooling gives best results and brightest glaze.
- (4) Firing temperature seems not to influence the solubility of CuO in lead glazes, although the leadless glazes are clearer at the higher temperature. The colors are generally spoiled at 1100°C. and the turquoise tint of the leadless glaze is destroyed above 1000°C.

- (5) The color of the lead glazes is green. This is made browner by increase of kaolin, CuO and higher firing temperature. The leadless glazes are blue-green and the beautiful turquoise color is obtained at a low temperature in the absence of alumina and by increasing the silica.
- (6) Volatilization of copper occurs from most of the glazes, and is generally greater from a lead glaze.

In conclusion, "the finest brown possible to obtain in ceramics," can be made by introducing nickel oxide into the body in rather large amounts and firing "under peculiar conditions" between 1200° and 1400°C.

#### Some Lead Borosilicate Glazes Containing Nickel Oxide<sup>46</sup>

A study of the effect of the various glaze constituents on the color and other properties of some leadless borosilicate glazes containing nickel oxide as a colorant is given. Nickel oxide has not proved useful in glossy non-opaque glazes. It is not recommended for use where a deep (dark) color is desired but can be made to produce very pretty opaque glazes, light tan in color and of a semi-matt character. The CaO content for the latter must be high (0.35 or above, preferably 0.45 or over) while the BaO should be not over 0.2 equivalent and the sum of BaO

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<sup>46</sup>. Holscher, H. H., "Some Lead Borosilicate Glazes Containing Nickel Oxide," Journal of American Ceramic Society, 12 (2):111-117 (1929).

and MgO not over 0.3 equivalent. When these limits are exceeded the glazes may have undesirable color or poor opacity, which is not satisfactory with nickel oxide as a colorant. These glazes are easily reproducible in firing.

### General Conclusions Drawn From Findings

#### Cobalt

Cobalt is absorbed in large amount and the color of the crystal deepens to almost a blue-black before the glaze is affected.

Greens may be produced by blending of blue and yellow colors.

Colors obtained with uranium-cobalt greens are deeper than those offered by the majority of chromium greens.

0.025 cobalt give a fine strong light blue an increasing depth of color is obtained up to 0.10 cobalt which in a thick dip gives a very deep, rich, cobalt blue.

Calcining cobalt oxide and flint or spar at high temperatures gives the characteristic ultramarine blue.

Calcining cobalt oxide and alumina at high temperature gives the commonly called "mat blue."

#### Copper

Copper is retained by the glaze with no noticeable volatilization. The green color is totally absorbed by

the crystal.

Copper greens are used extensively. At cones 6 or 7 the greater part of the copper is volatilized and the resultant shades of green are light and uneven. Greens may be produced by the blending of blue and yellow colors.

0.125 copper gives a very pale, delicate copper green. 0.15 copper gives greens of a little deeper shade, but the color is rather feeble and uneven through volatilization.

Green glazes produced with copper are subject to many changes when under fire. The least variation of the temperature or the method of firing the kiln will change the color, varying from a bright green to a brown or yellow shade.

Copper will color lead glazes green and alkali glasses blue.

Solubility in glazes melting below  $1100^{\circ}$  varies from about 3% to 8% copper.

Solubility can be increased by same methods as described below in NiO glazes with the following exceptions:

- (1) Reduce the amount of kaolin in both the lead and leadless glazes.
- (2) If the lead exceeds 0.7 PbO, a small portion may be replaced with ZnO or MgO. CaO and BaO appear to have little influence. This is contrary to the other coloring oxides, except  $Fe_2O_3$ .



## Nickel

Nickel and iron act very much alike as regards their being absorbed by the crystal, except that nickel begins to prevent crystallization at about 0.05 molecular equivalents, FeO may be added up to 0.2 molecular equivalents, the background darkening in color faster than the crystals, the crystallization not being affected.

Replacing BaO by ZnO varies the colors from a purplish brown in the low ZnO members to a bluish purple in the higher ZnO members. Where PbO was employed the greys are of decided yellowish tone, due no doubt to influence of the PbO in producing browns.

0.05 NiO gives a light, pleasing nickel brown; NiO gives a darker medium brown; and 0.15 NiO gives a very dark nickel brown.

Solubility of NiO in glazes maturing below 1100°C is never greater than 1%.

Solubility varies with glaze composition and can be increased as follows:

- (1) Raise acidity ( $\text{SiO}_2$ ) to at least 1.5 in lead glazes.
- (2) In lead and leadless glazes maintain a high acidity and replace  $\text{SiO}_2$  by  $\text{B}_2\text{O}_3$ . Molecular ratio of  $\text{SiO}_2$  to  $\text{B}_2\text{O}_3$  must never be less than 2:1 or opalescence will result even with moderately quick cooling.

- (3) Add a small quantity, say .5% of  $\text{SnO}_2$  to the glaze.
- (4) Lower  $\text{Al}_2\text{O}_3$  as much as is consistent with prevention of devitrification in both lead and leadless glazes.
- (5) In absence of  $\text{R}_2\text{O}$  bases, the  $\text{PbO}$  must not be lower than .7 molecular parts.
- (6) If  $\text{PbO}$  exceeds .7, replace some by other  $\text{RO}$  bases.
- (7)  $\text{ZnO}$  is a very valuable base and may replace  $\text{PbO}$  up to .2 molecular.
- (8) Replace  $\text{PbO}$  and other  $\text{RO}$  bases with alkalies.

A temperature of  $1050^\circ\text{C}$ . gave best results, although in some cases the temperature might be raised up to  $1100^\circ$ .

The quicker the cooling rate the freer the glaze from color separations.

The color of all the lead glazes is straw brown, except those containing  $\text{MgO}$ , which is green. The alkali glazes are grey, though converted to brown by increase of either  $\text{NiO}$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{B}_2\text{O}_3$ .

### Manganese

Manganese is not absorbed as much as the cobalt and copper oxides and the color of the background darkens with increase in color.

At cone 10 0.1  $\text{MnO}_2$  will practically all burn out and 0.25  $\text{MnO}_2$  gives a fairly deep manganese violet brown.

In crystalline glazes manganese oxide had by far the greatest crystallizing tendency.

The solubility of MnO in glazes maturing at a temperature not higher than 1100°C. varies from about 1% to 4% MnO.

Solubility can be increased by altering the glaze composition in the same way as for MnO, with the following exceptions:

- (1) Lower the  $Al_2O_3$  as much as possible in a lead glaze, but in an alkali glaze, this doesn't seem to be necessary.
- (2) In an alkali glaze the replacement of  $SiO_2$  by  $B_2O_3$  has no marked effect on solubility.

Increasing firing temperature to 1050°C. raises the solubility, but the color is generally better the lower the temperature.

The quicker the cooling rate the better.

The color is claret brown in lead and alkaline glazes, the composition and firing temperature. Pinker shades are obtained by the presence of PbO, ZnO and CaO. Increase in  $SiO_2$  has the same result. Brown tints are produced by alumina and boric acid in both lead and leadless glazes.

Some evidences of volatilization of MnO were observed.

### Iron

Iron acts very much like nickel as regards its

absorption by the crystals. Iron may be added up to 0.2 molecular equivalents, the background darkening in color faster than the crystals, the crystallization not being affected.

At cone 10, 0.025  $\text{Fe}_2\text{O}_3$  produces practically no color in the glaze, 0.05  $\text{Fe}_2\text{O}_3$  gives a pleasing light tan and 0.10  $\text{Fe}_2\text{O}_3$  gives dark olive tan or brown.

Solubility in glazes maturing at less than  $1100^\circ\text{C}$ . varies from 3% to upwards of 14%  $\text{Fe}_2\text{O}_3$ .

Solubility may be increased by same methods as given for NiO glazes, with the following exceptions:

- (1) Lower the alumina as much as possible, though this will impoverish the colors in both lead and leadless glazes.
- (2) In a lead glaze replace the silica by boric acid up to 0.5  $\text{B}_2\text{O}_3$  and in leadless glazes up to 1.5  $\text{B}_2\text{O}_3$ .
- (3) Replace CaO by PbO in a lead glaze. This is contrary to results with other coloring oxides considered thus far.
- (4) As in the chrome glazes, additions of ZnO to a lead glaze reduces the solubility of  $\text{Fe}_2\text{O}_3$ .

In both lead and leadless glazes the colors are impoverished at  $1100^\circ$  or higher.

The quicker the cooling after complete fusion, the clearer the glazes.

The color of all the glazes containing  $\text{Fe}_2\text{O}_3$  is the

well known brown. In a lead glaze the color is improved by alumina, clay or boric acid, and is greatly augmented by the presence of BaO. Far more oxide is required to give the same tint in a soda-lime glaze as compared with a lead glaze. The color is strengthened by silica, alumina and  $B_2O_3$ .

### Chromium

The chromium can only be used in glazes in which the zinc content is very low. With even small amounts of chromium, glazes containing zinc oxide fade to brown and glazes containing tin are apt to be streaked with pink. Chromium and chromium stains when used in most glazes of the Bristol type give greens which appear yellow when compared with the deep greens.

At cone 10, in glazes containing no zinc, 0.15  $Cr_2O_3$  produced a light chrome green and 0.15  $Cr_2O_3$  a very dark chrome green.

Solubility in glazes maturing below  $1100^{\circ}C$ . is seldom greater than 1%  $Cr_2O_3$ .

Solubility increased by same methods as given in NiO glazes with the following exception:

- (1) In both lead and leadless glazes the ratio should never be less than 1  $B_2O_3$ : 5  $SiO_2$ .

Best results obtained if the firing temperature of

the glaze is less than 1050°C.

Quick cooling gives best results.

When clear, the color of lead glazes is yellowish-green, but if super-saturated with oxide, the usual green tint predominates. Color made browner by alumina, clay, tin oxide, BaO and CaO which produce an orange tint. The finest greens with this oxide were obtained in a slightly reducing atmosphere. A bright green quite distinct from the lead glazes was obtained with the leadless glazes, and this is made more yellow by alumina.

Volatilization from a transparent chrome glaze appears to be quite small, but this is not so when the glaze is saturated.

### Zirconium

Zirconium oxide, when added in amounts of 4% or more, showed a tendency to increase the resistance to crazing, and showed no apparent change in texture.

An advantage of zirconium, especially for glaze works, is the fact that the presence of chrome vapors will not produce a pink discoloration, as has been known to happen with tin.

### Uranium

Colors from yellow oxide or uranium: 0.10 U<sub>2</sub>O<sub>3</sub> gives

a very pleasing light lemon yellow, and 0.02  $U_2O_3$  gives a slightly darker yellow. An increase to 0.06  $U_2O_3$  which is equivalent to about 10% of oxide in the glaze batch, gives only a slight increase in the depth of color.

By using only uranium oxide and red lead it is possible to produce any shade from light yellow to dark orange or red. About 10% of yellow uranium oxide is required to produce the deepest shade of orange.

Using only uranium oxide in a lead glaze, a shade from light yellow to deep orange or almost a red may be obtained by simply varying the quantity. Five per cent will produce a bright orange and 10% a dark orange, with a higher percentage seeming to darken the color very little.

### Chapter III

#### PRESENTATION OF THE PROBLEM

In the present problem the author was concerned with finding all possible blends of nine different coloring oxides. Each basic glaze contained the same frit and the same kind of clay. The glazes differed in the coloring oxides only. The kiln temperature remained the same throughout the experiment; at cone 04.

In a series of test firings on 2" by 1½" by ¼" test tiles the proportions of mixtures were systematically varied until all possible combinations had been tried. The nine different glazes were lettered A through I and referral to Table III below will show the combination in each case.

In the first experiment all of one glaze was used; in the second, 0.8 of one and 0.2 of another; in the third, a proportion of 0.6 to 0.4; in the fourth, 0.4 to 0.6; in the fifth, 0.2 to 0.8; and in the sixth, all of the second glaze.

All of one glaze, (i.e. A) was used in all possible combinations with B. Proceeding in the same pattern through each of the nine glazes resulted in the line blend



shown in Table II. Obviously, by the time the ninth glaze was reached there was only one experiment to make.

The compositions of the nine glazes used are given in Table II, following. Table III shows in graphic form the line blend upon which the experiment is based, and upon which the results can be interpreted.

#### Method of Procedure

The present experiment called for the use of a prepared frit, ball clay, and nine coloring oxides, fired at a constant temperature of cone 04, in a series of nine line blends. The only variant in each line was in the amounts of the colorants. It was desired that the experiment should result in medium colors, and that, as nearly as possible, one colorant should not black out the other.

Since a survey of the literature of the field did not reveal any similar studies, determining the amounts of the coloring oxides was the first step in the preliminary preparation. From a review of the experiments reviewed in Chapter II of the present study, an approximate maximum and minimum of absorption by the crystals was obtained.

#### Test One

In the first test experiments small batches of glaze were mixed using 5 grams of Ferro 3496 frit, .5 gram of

ball clay, and .5 gram tin oxide, and water to which a few drops of gum arabic had been added. The coloring oxides were used in the following amounts:

A. Cobalt.....1%	E. Green chromium oxide..2%
B. Black copper oxide..2%	F. Ferro yellow base.....3%
C. Red iron oxide.....3%	G. Ferro pink oxide.....3%
D. Manganese carbonate.3%	H. Rutile.....2%
	I. Nickel.....2%

The test tiles used were made from mineral products clay which had been formed in a wooden jig 12" by 1½" by ¼" and the resulting strips cut into tiles 2" long by 1½" by ¼". The test glazes were applied to the tiles and fired at cone 04. Using the above proportions it was found that (1) the glazes were too opaque, which seemed to indicate that the tin oxide should be left out; (2) the green oxide of chromium was too strong; and (3) the rutile apparently had too much water with it, so another test was made using the same amount of the colorant and less water.

### Test Two

The second test was made using, in each case, 5.5 grams of frit and .5 gram of ball clay, with no tin oxide, and the coloring oxides in the same amounts as in Test One. The results showed the colors to be brighter and more

transparent when the tin oxide was left out. It was found, however, that some of the oxides were too strong, and that another test was necessary.

### Test Three

In this test, 5.5 grams of frit and .5 gram of ball clay were again used with the proportions of colorants, reduced where necessary, as follows:

- A. Cobalt reduced to  $\frac{1}{2}$  of 1%
- B. Black copper oxide reduced to  $\frac{1}{2}$  of 1%
- D. Manganese carbonate reduced to 1%
- E. Green chromium oxide reduced to 1%

When it became evident that 1% of manganese carbonate was still too strong, a re-test was made using  $\frac{1}{2}$  of 1% of that oxide, a proportion which tested satisfactorily. It was found, too, in the third trial, that the cobalt and green chromium oxide were too strong, and a proportion of 1/6 of 1% was chosen for the fourth test.

### Test Four

At this point in the preparation the action of the colorants was clear enough so that it was practical to make a trial line blend without re-testing each oxide in every case. Accordingly, larger batches of the frit and

clay were mixed, using 250 grams of frit, and 25 grams of ball clay. In the line blend charted below, the author took 30 grams of the glaze, adding  $\frac{1}{6}$  of 1% of cobalt (A),  $\frac{1}{2}$  of 1% of black copper oxide (B) and  $\frac{1}{6}$  of 1% green chromium oxide (E). The selection of the black copper oxide (B) was made simply because it was to be the first blend used in the experiment as originally planned, (see Table III).

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A	A -.8	A -.6	A -.4	A -.2	B -10
	B -.2	B -.4	B -.6	B -.8	

---

	A -.8	A -.6	A -.4	A -.2	E -10
	E -.2	E -.4	E -.6	E -.8	

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This test showed that both the cobalt and green chromium oxide were still dominant and must be further reduced before the experiment could proceed.

#### Test Five

Cutting the proportions of the cobalt and green chromium oxide each to  $\frac{1}{18}$  of 1%, test five was made using small amounts of glaze - 5.5 grams of frit and .5 of ball clay. These resulted in satisfactory colors, and it was decided to make the experiment without further testing. For convenience the final proportions of the colorants are

repeated here:

A. Cobalt -	1/18 of 1%
B. Black copper oxide -	1/2 of 1%
C. Red iron oxide -	3%
D. Manganese carbonate -	1/2 of 1%
E. Green chromium oxide -	1/18 of 1%
F. Ferro yellow base -	3%
G. Ferro pink oxide -	2%
H. Rutile -	2%
I. Nickel -	2%

The glaze was mixed in batches of 250 grams of Ferro frit (#3496) and 25 grams of ball clay. Beginning with all possible blends of the first coloring oxide, the experiment proceeded as outlined in Table III. In each case the letter on the chart designates the colorant, since the frit and clay in the glaze remained the same.

During the course of this preliminary experimenting, a large batch of glaze was mixed and left overnight. The glaze settled and hardened so that it was impossible to mix the ingredients by shaking. One tablespoon of epsom salts was added, and in a few minutes the solution was mixable. This information was not necessary to this experiment, but is inserted here as an aid in any future experiment.

Table II

## Basic Glazes

Glaze A.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	Co <sub>3</sub> O <sub>4</sub> .....	1/18 of 1%
Glaze B.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	CUO.....	1/2 of 1%
Glaze C.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	Fe <sub>2</sub> O <sub>3</sub> .....	3%
Glaze D.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	MnCo <sub>3</sub> .....	1/2 of 1%
Glaze E.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	Gr Cr <sub>2</sub> O <sub>3</sub> .....	1/18 of 1%
Glaze F.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	F2486.....	3%
Glaze G.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	F875.....	3%
Glaze H.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	Rutile.....	2%
Glaze I.	Frit No. 3496.....	250 grams
	Ball Clay.....	25 grams
	NiO.....	2%

Table III

## Line Blend

A and B	A and C	A and D	A and E	A and F	A and G	A and H	A and I
B and C	B and D	B and E	B and F	B and G	B and H	B and I	
C and D	C and E	C and F	C and G	C and H	C and I		
D and E	D and F	D and G	D and H	D and I			
E and F	E and G	E and H	E and I				
F and G	F and H	F and I					
G and H	G and I						
I							

Table IV  
Experiment Number 1

All possible blends of Glaze A  
Glaze A and B

A-1.0	A-0.8	A-0.6	A-0.4	A-0.2	
Blue	B-0.2	B-0.4	B-0.6	B-0.8	B-1.0
Glaze A	Green Blue	Blue Green	Aqua	Green	Aqua
	Glaze A and C				

A-0.8	A-0.6	A-0.4	A-0.2		
C-0.2	C-0.4	C-0.6	C-0.8	C-1.0	
Gray	Yellow Tan	Tan Yellow	Lt. Mustard	Mustard	
	Glaze A and D				

A-0.8	A-0.6	A-0.4	A-0.2		
D-0.2	D-0.4	D-0.6	D-0.8	D-1.0	
Lavendar	Gray	Lavendar	Lavendar	Tan	
Blue	Lavendar	Gray	Tan	Lavendar	
	Glaze A and E				

A-0.8	A-0.6	A-0.4	A-0.2		
E-0.2	E-0.4	E-0.6	E-0.8	E-1.0	
Gray Blue	Blue Gray	Green Gray	Gray Green	Pastel Green	
	Glaze A and F				

A-0.8	A-0.6	A-0.4	A-0.2		
F-0.2	F-0.4	F-0.6	F-0.8	F-1.0	
Blue Gray	Green Gray	Gray Green	Green Yellow	Pastel Yellow	
	Glaze A and G				

A-0.8	A-0.6	A-0.4	A-0.2		
G-0.2	G-0.4	G-0.6	G-0.8	G-1.0	
Lavendar	Red Lavendar	Lavendar	Red Mulberry	Mulberry	
	Glaze A and H				

A-0.8	A-0.6	A-0.4	A-0.2		
H-0.2	H-0.4	H-0.6	H-0.8	H-1.0	
Gray Blue	Lt. Blue	Gray	Gray	Gray	
	Glaze A and I				

A-0.8	A-0.6	A-0.4	A-0.2		
I-0.2	I-0.4	I-0.6	I-0.8	I-1.0	
Olive Green	Gray Olive	Blue Olive	Olive	Olive	
	Green	Green	Green	Green	



Table V  
Experiment Number 2

All possible blends of Glaze B  
Glaze B and C

B-1.0	B-0.8	B-0.6	B-0.4	B-0.2	
Aqua	C-0.2 Medium Green	C-0.4 Yellow Green	C-0.6 Green Tan	C-0.8 Yellow Tan	C-1.0 Mustard
Glaze B and D					

B-0.8	B-0.6	B-0.4	B-0.2		
D-0.2	D-0.4	D-0.6	D-0.8	D-1.0	
Lt. Aqua	Gray Aqua	Gray	Lavendar Tan	Tan Lavendar	
Glaze B and E					

B-0.8	B-0.6	B-0.4	B-0.2		
E-0.2	E-0.4	E-0.6	E-0.8	E-1.0	
Aqua	Aqua Blue	Lt. Blue Green	Gray Green	Pastel Green	
Glaze B and F					

B-0.8	B-0.6	B-0.4	B-0.2		
F-0.2	F-0.4	F-0.6	F-0.8	F-1.0	
Med. Green	Yellow Green	Green Yellow	Lt. Green Yellow	Pastel Yellow	
Glaze B and G					

B-0.8	B-0.6	B-0.4	B-0.2		
G-0.2	G-0.4	G-0.6	G-0.8	G-1.0	
Gray Lavendar	Red Lavendar	Lavendar Red	Red Mulberry	Mulberry Red	
Glaze B and H					

B-0.8	B-0.6	B-0.4	B-0.2		
H-0.2	H-0.4	H-0.6	H-0.8	H-1.0	
Blue Green	Gray Blue Green	Gray Green	Green Gray	Gray	
Glaze B and I					

B-0.8	B-0.6	B-0.4	B-0.2		
I-0.2	I-0.4	I-0.6	I-0.8	I-1.0	
Green	Gray Green	Green Gray	Gray Olive Green	Olive Green	

Table VI  
Experiment Number 3

All possible blends with Glaze C  
Glaze C and D

C-1.0	C-0.8	C-0.6	C-0.4	C-0.2	
Mustard	D-0.2 Yellow Tan	D-0.4 Tan Yellow	Tan	D-0.8 Lavendar Tan	D-1.0 Tan Lavendar

Glaze C and E

C-0.8	C-0.6	C-0.4	C-0.2	
E-0.2 Mustard	E-0.4 Gray Mus- tard	E-0.6 Mustard Gray	E-0.8 Gray Green	E-1.0 Pastel Green

Glaze C and F

C-0.8	C-0.6	C-0.4	C-0.2	
F-0.2 Yellow Mustard	F-0.4 Mustard Yellow	F-0.6 Yellow Tan	F-0.8 Gray Yel- low	F-1.0 Pastel Yellow

Glaze C and G

C-0.8	C-0.6	C-0.4	C-0.2	
G-0.2 Coral Brown	G-0.4 Brown Coral	G-0.6 Mulberry Brown	G-0.8 Red Mulberry	G-1.0 Mulberry Red

Glaze C and H

C-0.8	C-0.6	C-0.4	C-0.2	
H-0.2 Yellow Mustard	H-0.4 Mustard Yellow	H-0.6 Gray Mustard	H-0.8 Mustard Gray	H-1.0 Gray

Glaze C and I

C-0.8	C-0.6	C-0.4	C-0.2	
I-0.2 Brown Mustard	I-0.4 Mustard Brown	I-0.6 Green Brown	I-0.8 Brown Green	I-1.0 Olive Green

Table VII  
Experiment Number 4

All possible blends with Glaze D  
Glaze D and E

D-1.0	D-0.8	D-0.6	D-0.4	D-0.2	
Tan	E-0.2	E-0.4	E-0.6	E-0.8	E-1.0
Lavendar	Tan	Lavendar	Green Tan	Tan Green	Pastel
	Lavendar	Tan			Green
Glaze D and F					
D-0.8	D-0.6	D-0.4	D-0.2		
F-0.2	F-0.4	F-0.6	F-0.8	F-1.0	
Lavendar	Tan	Yellow Tan	Tan Yellow	Pastel	
Tan				Yellow	
Glaze D and G					
D-0.8	D-0.6	D-0.4	D-0.2		
G-0.2	G-0.4	G-0.6	G-0.8	G-1.0	
Red Lilac	Lilac Red	Gray	Red	Mulberry	
		Mulberry	Mulberry	Red	
Glaze D and H					
D-0.8	D-0.6	D-0.4	D-0.2		
H-0.2	H-0.4	H-0.6	H-0.8	H-1.0	
Tan	Lavendar	Gray	Lilac Gray	Gray	
Lavendar	Tan	Lavendar			
Glaze D and I					
D-0.8	D-0.6	D-0.4	D-0.2		
I-0.2	I-0.4	I-0.6	I-0.8	I-1.0	
Lavendar	Olive Green	Tan Olive	Gray Olive	Olive Green	
Tan	Tan	Green			

Table VIII  
Experiment Number 5

All possible blends with Glaze E  
Glaze E and F

E-1.0	E-0.8	E-0.6	E-0.4	E-0.2	
Pastel Green	F-0.2 Pastel Green	F-0.4 Yellow Green	F-0.6 Gray Yel- low Green	F-0.8 Green Yellow	F-1.0 Pastel Yellow
Glaze E and G					

E-0.8	E-0.6	E-0.4	E-0.2		
G-0.2 Red Lilac	G-0.4 Lilac Red	G-0.6 Gray Lilac	G-0.8 Mulberry	G-1.0 Mulberry Red	
Glaze E and H					

E-0.8	E-0.6	E-0.4	E-0.2		
H-0.2 Gray	H-0.4 Gray Green	H-0.6 Green Gray	H-0.8 Green Gray	H-1.0 Gray	
Glaze E and I					

E-0.8	E-0.6	E-0.4	E-0.2		
I-0.2 Green Brown	I-0.4 Tan Green	I-0.6 Green Tan	I-0.8 Green Tan	I-1.0 Olive Green	

Table IX  
Experiment Number 6

All possible blends with Glaze F  
Glaze F and G

F-1.0	F-0.8	F-0.6	F-0.4	F-0.2	
Pastel Yellow	G-0.2 Coral Tan	G-0.4 Tan Coral	G-0.6 Gray Mulberry	G-0.8 Red Mulberry	G-1.0 Mulberry Red
Glaze F and H					
F-0.8	F-0.6	F-0.4	F-0.2		
H-0.2 Tan Yellow	H-0.4 Yellow Tan	H-0.6 Yellow Gray	H-0.8 Tan Gray	H-1.0 Gray	
Glaze F and I					
F-0.8	F-0.6	F-0.4	F-0.2		
I-0.2 Green Tan	I-0.4 Darker Green Tan	I-0.6 Brown Green	I-0.8 Green Brown	I-1.0 Olive Green	

Table X  
Experiment Number 7

All possible blends with Glaze G  
Glaze G and H

<u>G-1.0</u>	<u>G-0.8</u>	<u>G-0.6</u>	<u>G-0.4</u>	<u>G-0.2</u>	
Mulberry	H-0.2	H-0.4	H-0.6	H-0.8	H-1.0
Red	Gray Mul-	Gray Coral	Coral Gray	Pink Gray	Gray
	berry Red				
	Glaze G and I				
<u>G-0.8</u>	<u>G-0.6</u>	<u>G-0.4</u>	<u>G-0.2</u>		
I-0.2	I-0.4	I-0.6	I-0.8	I-1.0	
Gray	Redish	Medium	Green	Olive	
Mulberry	Brown	Brown	Brown	Green	

Table XI  
Experiment Number 8

All possible blends with Glaze H  
Glaze H and I

H-1.0	H-0.8	H-0.6	H-0.4	H-0.2	
	I-0.2	I-0.4	I-0.6	I-0.8	I-1.0
Gray	Green Gray	Green Tan	Olive Green	Olive Green	Olive Green

Table XII  
Experiment Number 9

All possible blends with Glaze I

I-1.0

Olive Green



## Presentation of Results and Conclusions

### The Experiment with Mineral Pigments

The experiment was conducted over a period of twenty weeks, since the kiln could take only fifteen tiles at one firing. The glaze was mixed in batches of 250 grams of prepared frit and 25 grams of ball clay, with coloring oxides added as needed. The total number of tiles in one set was 189, and each tile took approximately 5 grams of glaze, brushed on thick enough to cover, but not to bubble. The writer made two tiles of each color, however, to avoid a break in the set should one tile become chipped or broken, or show faults. A tally was kept of each part of the experiment as it was completed.

When the tiles were all fired, a chart was made on heavy showcard paper, showing the colorant in each line and the proportions throughout. The tiles were then placed on the card and a colored photograph was taken. (Plate 1) Since the lighting was difficult the colors do not show true in all cases. For this reason an attempt was made (on Table IV through XII) to name the colors across the line to show the variance as the coloring oxides were lessened or increased.

To interpret the results in color, it is necessary to



refer to both the plate and Tables IV through XII.

Of the first experiment, all possible blends of glaze A, the cobalt maintained its superiority (reading across) to the third tile, after which the copper (B) was dominant. This was true except in the final line, where even .2 of the nickle obscured the blue. The line containing the rutile was flecked throughout; while in the other lines the fleck, fairly pronounced where the cobalt was predominant, became progressively less noticeable. These flecks do not show up at all in the photograph.

In the experiment using all possible blends of B, the variation in color was consistent, in that the color which predominated in proportion also predominated in the shade obtained. The line containing the rutile was flecked throughout; in all other lines the fleck was negligible.

The third and fourth experiments also resulted in colors that were consistently true depending upon the percentage of colorant predominating, with flecks appearing in the line containing rutile.

In experiment five, however, the line using rutile showed this oxide to be dominant even in small percentages; i.e., the rutile blacked out the green chromium.

The lines in experiments six and seven show consistent variation across in all cases. In the eighth experiment,

however, the nickle outweighed the rutile in all but the first tile. The line in experiment nine showed consistent change in color.

With regard to the total experiment, the solid colors, in general, were consistent in the fact that the shade reflected the larger percentage of coloring oxide. All the lines containing rutile were flecked, but flecking was negligible in the rest of the tiles. In all cases where the manganese was used in larger proportion there was bubbling. It can be assumed, also, that probably the nickle should have been reduced further, since in many cases it blacked out the other colorant.

## Chapter IV

### CONCLUSIONS AND RECOMMENDATIONS

An experiment using basic materials and a simple procedure was undertaken primarily to produce a set of color tiles to be used as a teaching aid in classes in ceramics, and to find the effects of nine coloring oxides when used in a given glaze. Making such an experiment presupposed a knowledge of the history and techniques of glazing, and required a survey of pertinent literature to insure that such an experiment had not already been made and to discover if possible, suggestions regarding a procedure.

The history of glazing reveals that the art is an ancient one, begun at first, probably as a useful one but later developing as a fine art form as well. The many techniques, some discovered by chance, come from many countries, and from all eras. The unlimited possibilities for experiment is one of the greatest appeals of the art, and the fact that the tools and materials are simple and relatively inexpensive make the craft one that can be enjoyed by many people.

The information regarding the materials used by the

ceramist is available in widely scattered sources. It seemed advisable, therefore, to review briefly the kinds and compositions of the various clays, and a method of making clay workable both by itself and in mixtures.

Glazes were likewise reviewed in the same manner. As the ceramist works he must be able to measure and adapt his results, and to recognize and correct the various faults which appear. A brief resume' of these techniques seemed necessary to an understanding of the present problem.

Since this experiment was concerned with coloring oxides, it was required also that some attention be given to the action and capacities of these colorants. Finally, the culminating activity of the ceramist, that of firing, was treated.

It has been stated that a review of related experiments showed no instance of a similar study. The experiments reviewed, however furnished a useful yardstick against which to measure when the present experiment was set up, since the maximum and minimum of absorption by crystals had to be known before the proportions of the colorants could be tried.

Five preliminary tests were run using varying amounts of the coloring oxides, to prevent one colorant's blacking out the other in any line. When a satisfactory color

resulted the proportions thus established were used throughout the present experiment. The problem was limited to the use of nine coloring oxides in a glaze made from a prepared frit (Ferro #3496) and ball clay, firing all the tiles at cone 04. The kiln used was one built by the writer, and all procedures and techniques were kept simple enough so that the conditions paralleled those found in the average classroom. A total of about four-hundred-fifty test tiles were prepared before the actual experiment began, and the basic glaze was mixed in 275 gram batches, with the colorants added as needed.

In each experiment each colorant was used in combination with another, varying in proportions of .2 through a line blend from one color to the other. Each glaze was used in combination with all of the others, resulting in nine experiments. When the resulting 189 tiles were completed they were placed on a chart and a color photograph taken.

Generally speaking, the dominant colorant in each line was reflected in the resulting color, with the exception of the nickle, which was assumed to be in too large proportion. All the lines containing rutile were flecked, and in all tiles where the proportion of manganese carbonate was larger there was bubbling. This bubbling may

have been the result of too thick a coating rather than too large a proportion.

### Recommendations

It is recommended first of all that a test be remade with the cobalt to determine, if possible, whether flecking is a natural result of the oxide or whether it was a result of faulty mixing or insufficient grinding, and that the lines using nickle be redone using that oxide in smaller amounts.

Secondly, it is recommended that each of the colorants be tested separately in varying proportions to determine what amounts may be safely used without blacking out.

A third experiment should be made using manganese carbonate in the same and smaller amounts to determine the cause of the bubbling. Firing two tiles with the same proportions of the oxides, one coat brushed on thinner than the other, should help in fixing the reason for the bubbling.

It is hoped that the present experiment, limited as it was to elementary procedures and fixed ingredients, will prove helpful as a teaching aid, and that it opened an avenue to related experiments which will add to the literature of ceramics and glazes.



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