A STUDY OF MACROCRYSTALLINE GLAZES

by

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INTRODUCTION

Glazes that are used to form a more or less vitreous coating on the surfaces of ceramic objects are actually a rather special type of glass. These glasses or glazes must by necessity have thermal characteristics closely akin to the ceramic bodies for which they are intended. They are securely bonded to the ceramic ware by the proper application of heat in a kiln.

There are many types of glazes, designed for a variety of applications and for firing at different temperature ranges. There is also a wide variance in the appearance of finished glazes. The type of glaze which is central to this study is the macrocrystalline glaze or, more commonly, the crystalline glaze.

Parmelee makes the following classification of crystalline glazes:

> 1) Macrocrystalline in which the crystals are large enough to be readily distinguished by the naked eye. There are two kinds:
> > a) Aventurine glazes where the crystals are sufficiently large and separated so as to be easily observed as minute scales or "flitters" suspended below the surface of the glaze; or, they may be very small and so numerous and oriented as to reflect light rays from the internal surfaces of the suspended crystals, producing an effect similar to the mineral, "catseye."
> > b) Crystalline glazes (the typical crystalline glaze) where the surface may be covered completely or partially with well developed individual crystals (some, perhaps, projecting above); or where the crystals may be

> below the surface, immersed in the glassy
> matrix. The crystals are usually in clusters,
> frequently covering considerable areas.
>
> 2) Microcrystalline, in which the crystals are not
>   individually visible except under magnification.
>   The typical example is the matt glaze. This has
>   a surface which, in the best examples, has the
>   soft, pleasing appearance of a glimmering resinous
>   luster similar to that exhibited by jade and chert.
>   Less satisfactory surfaces are semi-glossy, dull
>   and greasy.[1]

Although aventurine glazes were first produced in the Orient many centuries ago[2], the production of the more typical type of crystalline glaze is a comparatively recent development. The first scientific discussion of the preparation of these glazes was apparently made by Ebelman in the mid-nineteenth century[3]. At the Royal Copenhagen factory, crystalline glazes were first produced by the factory chemist, Clement, in 1886, and were later developed for production purposes by V. Englehardt[4]. In the United States a crystalline "tigereye" glaze had been introduced in 1884 by the Rookwood Pottery, Cincinnati[5]. During this period successful crystalline glazes were also produced at Sevres and in Berlin.

Crystalline glazes became quite popular during the Art Nouveau period and were widely used during the first decade of

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[1] Cullen W. Parmelee, Ceramic Glazes, (Chicago: Industrial Publications, Inc., 1951) p. 189.

[2] Ibid.

[3] Ibid.

[4] Hugh Wakefield, "The Modern World," WORLD CERAMICS, ed. by Robert J. Charleston (New York: McGraw-Hill Book Co., 1968) Part VIII, p. 302.

[5] Ibid.

EXPLANATION OF PLATE I

Porcelain 'mushroom' form with zinc silicate
crystalline glaze, white with gold crystals (height 5").

PLATE I

this century. The use of these glazes declined with the fortunes of
Art Nouveau and since this time they have remained primarily an oddity
among glazes. One person in particular who has done much to revive
current interest in crystalline glazes is Dr. Herbert H. Sanders of
San Jose State College.

PURPOSE OF THIS STUDY

Initially there were two reasons for undertaking a study of
crystalline glazes. This researcher has been interested in these
glazes for some time, since viewing published photographs of crystal-
line glazed ware and also actual pots with crystal formations in their
glazes. These glazes are quite unique in their appearance and, as
such, are a technical curiosity. It was also felt that an in-depth
study of crystalline glazes would yield insights into the technical
aspects of a glaze composition generally. This would have a broad
relevance to all types of glazes since the chemical components and
mechanics of formulation are basically the same for all types of
glazes.

A third purpose of this study emerged during the process
of experimentation and research. It gradually became more obvious
to this researcher that much of the published data regarding crystal-
line glazes, particularly in the more widely circulated books and
periodicals, does little more than reveal the author's ignorance on
the subject. Indeed, in some cases statements are made which are

completely false and in others conflicting statements and omissions promote incomprehension. It is obvious that the subject needs to be treated in some detail and although this paper certainly does not purport to be a definitive work on crystalline glazes, it is felt that a firm foundation has been established and guidelines extended for further profitable investigation into this fascinating subject.

THEORY OF CRYSTALLINE GROWTH IN GLAZES

Since there is a distinct similarity between common micro-crystalline matt glazes and macrocrystalline glazes, the two will be discussed jointly here for purposes of familiarity and clarity.

There are two basic types of matt glazes, those which are not completely vitreous due to actual underfiring (i.e., a complete, homogeneous melt is not achieved) and those which are matt because of partial devitrification in the form of a large number of tiny crystals. Macrocrystalline glazes are closely akin to the latter type. Loss of mattness in glazes that are fired above their ordinary terminal temperature is a common studio experience. Very often the results are a more or less transparent, glossy glaze quite different in appearance than what was intended. In the case of a glaze of the type which is matt due to underfiring, loss of mattness and resultant transparency and shine is due to true or actual maturity of the glaze melt. In the case of the second type of matt glaze, those which owe their mattness to the growth

of minute crystals within the glaze magma, transparency and gloss
are due to the dissolution of the crystal nuclei in the glaze melt.
This is caused by excessive thermal agitation and the eventual
breakdown of the nuclei at the higher than normal temperature. The
presence of suitable nuclei is a precondition for crystal develop-
ment in the glaze.

It can also be stated that matt glazes of the microcrystal-
line type ordinarily form more fluid melts than do glazes of the
underfired or partially vitrified type. The reason for this dif-
ference in viscosity is the result of two factors: first, glazes
become more fluid as the temperature is raised relative to the
point of complete vitrification and since matt glazes of the under-
fired type do not reach this point, they remain more viscous than
glazes which fully mature. Secondly, glazes of the crystalline
matt variety must be less viscous than ordinary in order to achieve
a degree of crystalization sufficient to produce the characteristic
mattness. The reason for this will become clear later.

The only physical difference between a microcrystalline
glaze and a macrocrystalline glaze that produces large, indivi-
dually discernible crystals is found in the viscosity of the glaze
melt, the latter being the less viscous of the two. Of course,
to achieve this difference in viscosity it is necessary to alter
the chemical structure of the glaze, minimizing those components
which act to stiffen the glaze melt.

There are also necessary differences in the treatment of the
two glazes. These differences become clear if a comparison is made
in terms of the firing cycle. When glazes are heated in a kiln they
go through a number of chemical and physical changes prior to reach-
ing the point of complete vitrification. These changes are quite
similar in all types of glazes and are not of immediate concern in
this discussion. Glazes which have crystallizing tendencies, how-
ever, reach a point in the heating cycle at which the viscosity be-
comes low enough to allow considerable mobility of the ions in the
glaze melt. Beyond this there is a continuous breaking and forming
of bonds between the various ions present in the melt and as a re-
sult, a large number of random cells are formed which are potential
nuclei for the growth of crystals. If at this point the heating
phase is concluded and the kiln allowed to cool, a large number of
microscopic crystals would grow around the nuclei present in the
glaze. This is, in fact, what happens during the firing of a typical
microcrystalline matt glaze. Virtually the same thing would happen
if the heating phase of a macrocrystalline glaze was terminated at
this point and allowed to cool at the same rate. At this point
the only important difference between the two glazes would be
the rate of crystalline growth. In an identical time-temperature
setting this would be entirely a function of glaze viscosity, the
more fluid glaze having the higher rate of crystallization. Assum-
ing that the number of nuclei present in the two glaze melts was

approximately the same, there would be little discernible physical difference between the two glazes.

In actual practice, however, the heating phase of a macro-crystalline firing is not terminated in the same manner as that of an ordinary matt glaze. The heating phase is prolonged and the temperature advance is accompanied by increased thermal agitation of the ions and molecules present in the glaze melt. The object of this continued heating is to almost or completely pass through the temperature zone of nucleation. This zone of nucleation can be described theoretically as beginning at a heat point where potential nuclei are just starting to form, extending to a point that represents the maximum rate of nucleation and upward to a heat point where thermal agitation has become so great that not only are no new nuclei being formed but all the nuclei previously formed are completely dissolved in the glaze magma. In actual practice, of course, the upper and lower limits of this zone of nucleation are not distinct points since there are no sudden changes in the character of the melt, only a gradual evolution.

The purpose of continued heating of the glaze melt through the zone of nucleation is to either severely limit the number of nuclei available for crystal growth or eliminate the natural nuclei completely. In the latter instance, artificial "seeds" would be introduced into the glaze which would function as crystal nuclei. This procedure makes possible some control over the eventual position

of crystalline growths in the glaze surface. Seeds can be intro-
duced into either the unfired glaze coating or directly into the
molten glaze and consist of particles of materials which either
do not completely dissolve in the glaze magma or, if they do dis-
solve, alter the viscosity of the glaze at the point where they
have dissolved and encourage the formation of suitable nuclei.
Norton reports on the use of sodium carbonate, calcium carbonate,
zinc oxide and silica particles as seeds[6].

When the upper limit of the zone of nucleation (which for
this type of glaze can be considered the point of maturity) is
reached, the kiln is ordinarily turned off and the temperature is
allowed to drop to the point at which crystalline growth will be-
gin to occur around the available nuclei. It is important to note
that significant nucleation does not recur as the temperature is
lowered. If this was not the case it would be virtually impossible
to produce anything but a matt glaze of the microcrystalline type.
It can be noted, as well, that for each different glaze there is
a distinct relationship between the temperature of maximum nucleation
and the temperature of maximum crystal growth rate. In some cases
this temperature may be the same; in others one may be higher or
lower than the other. Since there does not appear to be a recur-
rence of nucleation as the temperature is lowered, this relation-
ship does not appear to be of immediate significance.

[6]F. H. Norton, "The Control of Crystalline Glazes," Journal
of the American Ceramic Society, 20:222 (1937).

EXPLANATION OF PLATE II

Close-up of crystals grown in glaze ZT-8 between
2100° and 1900° F. The glaze contains one-half percent
cobalt carbonate as a colorant and the crystals are a
soft blue on a pale beige background (magnification
8.3X).

PLATE II

The rate of crystal growth in a particular glaze is a function of time and temperature and for each different glaze there is a temperature at which the growth rate is at its maximum. With the proper equipment this temperature can be determined experimentally. The time factor also plays an important role in determining the ultimate degree of crystallization and this can also be determined experimentally. With the optimum time-temperature relationship thus established it would be a simple matter to cool the kiln to the proper growing temperature and hold it at this point for the specified period of time. This procedure is complicated, however, when glazes of differing composition are fired at the same time since each may have a slightly different temperature for the maximum rate of crystal formation. In actual practice this problem is solved by using a controlled rate of cooling through the zone of crystallization rather than a fixed soaking temperature. In this manner each glaze passes through its optimum growth temperature at some time during the controlled cooling phase and if the rate of cooling is sufficiently slow, significant crystallization will take place.

It is important to note at this juncture that crystals of different shape and orientation will grow in the same glaze at different temperatures. Generally speaking, crystals that are oriented along a longitudinal axis are produced at the higher temperatures while at the intermediate and lower temperatures of

the growing range, crystals of a radial configuration are produced. This has been discussed in some depth by Norton[7].

The net effect of a crystal growth in a glaze that has been cooled slowly can be quite interesting since there are sudden definite changes in the growth pattern as the temperature is lowered. In the initial stages of formation at the upper end of the growth range the crystal may be oriented along a longitudinal axis and somewhat resemble a bow-tie since it is wider at its outer extremities than it is toward the middle. Then the growth may suddenly change to a radial configuration that is concentric to the nuclei. Further growth continues in the essentially radial pattern but may include one or more bands or halos which are of different color. As the temperature continues to drop toward the lower end of the zone of crystallization, the energy level of the different crystal growths being successively formed approaches that of the vitreous magma and the rate of the crystal growth becomes less as the cooling glaze becomes more viscous. There is not sufficient evidence to determine whether or not the chemical composition of the subsequent crystal formations changes. A change in the energy level could accompany both a change in the composition and a simple rearrangement of the ionic bonding.

Once the cooling phase has progressed to the lower limits of the zone of crystallization, the rate of cooling need not be regulated further and the kiln may be turned off and allowed to cool

[7]Norton, op. cit., p. 219, 220, 222, 223.

at its normal rate.

FACTORS AFFECTING THE GROWTH OF
CRYSTALS IN GLAZES

The Composition of the Glaze

It has been mentioned previously that the principal physical difference between macrocrystalline glazes and ordinary microcrystalline matt glazes is a difference in the viscosity of the glaze melt. This is achieved by compounding a glaze that is relatively low in the materials which cause a glaze to be viscous and relatively high in those materials which act as powerful fluxes in promoting a fluid melt. Basically the materials are the same as ordinarily found in more conventional glazes. The difference is in the proportions used.

Basic Components

The basic components act as fluxes in the glaze melt and the principal ones used in crystalline glazes are lead oxide, zinc oxide and the alkalis, all of which are powerful fluxes. Zinc oxide is the most important of these since it is a crystal-former, having the unusual property of crystalizing out of a super-saturated solution as a silicate rather than as an oxide[8]. It is by no means exclusive in this regard since under special conditions both magnesium and calcium (and a few other materials) will also form

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[8]CERAMIC INDUSTRY, January, 1967, p. 153.

crystalline silicates. At the usual range of firing temperatures, however, zinc has proven to be the most useful.

The alkalis (the oxides of sodium, potassium and lithium) and lead oxide are used as auxilliary fluxes although the use of lead is restricted as it has a tendency to volatilize out of glaze melts at high temperatures. It is difficult to state the maximum useful temperature of lead since this depends to some extent on the other components of the glaze. The temperature is approximately 2100° F, however. The alkalis are useful as fluxes throughout the normal range of temperatures.

The other fluxes which are commonly used in glazes, calcium, magnesium and barium, seem to have few, if any, beneficial effects on crystalline glazes. There seems to be some disagreement concerning the use of calcium, but this researcher is inclined to agree with Lehnhäuser who states that calcium is detrimental to crystallization and should not be present in amounts beyond 0.1 molecular equivalents[9]. Additions of magnesium have the property of increasing the viscosity of glaze melts and therefore have a definite effect on the rate of crystal growth[10]. There seems to be a consensus of opinion in regard to the use of barium. It does not appear to offer any beneficial characteristics to crystalline glazes and should be kept quite low, if not entirely absent.

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[9] Werner Lehnhäuser, Glasuren und ihre Farben (Dusseldorf: Wilhelm Knapp Verlag, 1959) p. 62.

[10] Ceramic Industry, op. cit., p. 118.

Amphoteric Components

Amphoteric oxides are those which may act either as a base or an acid, depending upon their particular circumstance. Aluminum is the principal of these and since it is the material which acts as a chief stiffening agent in glaze melts, it is kept low in crystalline glazes. It is usually present in amounts one half to one quarter of what is normal in more conventional glazes.

Boric oxide is classified as an amphoteric oxide because of its chemical composition and ability to act both as a flux and as a glass-former. Although in glaze melts it is ordinarily employed as a powerful flux, there seems to be some disagreement concerning its usefulness in crystalline glazes. Some researchers state that boron is detrimental to crystallization while others recommend its use because of its property of causing fluidity in siliceous melts[11]. The inclusion of boric oxide in a number of published crystalline glaze formulas would seem to support the latter contention.

Acid Components

Silica is, of course, the principal acidic oxide and the basis of all glazes since it is a glass-former. In crystalline glazes it functions as it does in conventional glazes and is proportioned to control the melting temperature of the glaze. Silica

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[11] Parmelee, op. cit., p. 191.

also combines with zinc to form the crystalline structure.

Mineralizing or Crystallizing Agents

There are a number of materials that are commonly added to crystalline glazes because they tend to facilitate the growth of crystals. These materials could be classified and discussed under the previous headings; however, they are mentioned separately here because of their unique function in the glaze.

The most important crystallizing agents are reported to be: titanium, molybdenum, tungsten, beryllium, bismuth, manganese, vanadium, copper and cobalt. The effectiveness of titanium is well known. Purdy and Krehbiel emphasize the effectiveness of manganese[12], while Lehnhäuser promotes the use of molybdenum and tungsten[13]. Koerner reports on the usefulness of bismuth in promoting crystallization in conjunction with uranic acid[14]. This researcher has found beryllium to be quite effective. Many more references could be cited; however, this is unnecessary. It should be stressed that these materials are not indispensable to successful crystalline glazes but they have the ability to promote and facilitate crystalline growth where it might not otherwise occur.

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[12]R. C. Purdy and J. F. Krehbiel, "Crystalline Glazes," Transactions of the American Ceramic Society, 9:319 (1907).

[13]Lehnhäuser, loc. cit.

[14]J. Koerner, "New Crystalline Glazes," Transactions of the American Ceramic Society, 10:61 (1908).

The Problem of Colorants

Crystalline glazes have the unique and interesting property of preferential absorption of colorants. This means that a colorant added to a base glaze may ultimately tint either the crystals or the magma. Iron and nickel, for instance, seem to lend their coloration to the magma while the colors of copper and cobalt seem to go primarily to the crystal. While complete color separation depends on the complex relationship between the amount of colorants added to the base glaze and the degree to which potential crystallization is realized, it should be apparent that interesting color contrasts can be achieved as a result of preferential absorption.

It is interesting to note that the impurities in commercially supplied glaze colorants often become apparent when introduced into crystalline glazes. A typical example is cited by Singer, " . . . when trade nickel oxide, which invariably contains a trace of cobalt oxide, is used to colour a zinc silicate crystalline glaze buff. . . the crystals are blue, having attracted the entire cobalt content of the glaze[15]."

The problem of colorants does not concern their chromatic effects, however, but rather their effect on the melting properties of the glaze. It is well known that certain of the common colorants act as fluxes in the glaze melt, some have little or no effect and

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[15] Felix Singer and Sonja S. Singer, _Industrial Ceramics_ (New York: Chemical Publishing Co., Inc., 1963) p. 593.

EXPLANATION OF PLATE III

Close-up of crystallization occurring in
glaze ZT-8 between 2100° and 1900° F. The glaze
contains one-quarter percent cobalt carbonate
and one-half percent iron oxide and the crystals
are grey-blue on a brown streaked beige back-
ground (streaking indicates direction of glaze
flow) (magnification 8.5X).

PLATE III

some have a tendency to make glazes more refractory. In more conventional glazes the influence of coloring oxides on the glaze melt occasionally causes problems. Additions of large amounts of iron oxide to produce saturated iron reds in a reduction fire, for instance, may cause the glaze to become too fluid at the end point of the heating phase. The production of black glazes through the introduction of relatively large quantities of cobalt, copper and iron is likely to be an even more troublesome situation. Conversely, relatively large additions of chromium, nickel or titanium compounds have the effect of seriously hardening a glaze and cause it to be underfired at the intended temperature. In all of these instances it is often found necessary to alter the composition of the glaze in order to achieve the desired degree of melting at a particular temperature.

In crystalline glazes this problem becomes somewhat more acute. It will be remembered from an earlier discussion of the firing procedures for a crystalline glaze that the heating phase is continued to the upper limits of the zone of nucleation. This is undoubtedly the most critical part of the firing cycle if subsequent crystallization is to be brought under any semblance of control. The objective is to dissolve all but a few potential nuclei in the case of random crystallization and all the naturally formed nuclei in the case of artificially seeded crystallization. It should be obvious that the addition of significant amounts of fluxing or refractory colorants to a base crystalline glaze can cause a serious

loss of control. Depending upon the manner in which the colorants affect the glaze melt, there might be either a loss of crystalliza- tion or too profuse a crystalline growth.

Although the addition of colorants to a base glaze may have a significant effect on the number of crystals finally produced, this is quite easily controllable. Either a slight alteration in the glaze formula or a slight change in the firing cycle will bring the desired results. Of these two possibilities, the former seems to be more workable since a multiplicity of firing schedules would potentially be more confusing than a number of glaze formulas that yielded distinctly different colors. Altering the glaze formulas would also allow several glazes to be fired at the same time using a standard firing procedure.

It should be noted that the foregoing observations are of a somewhat theoretical nature and in actual practice the problems of repeatedly duplicating an exact firing schedule are such that the same base glaze will vary in appearance from firing to firing. This tends to make the effects of colorants less obvious unless the same glaze with and without colorants is fired at the same time.

The Composition of the Ceramic Body

All glazes react chemically to some degree with the ceramic body on which they are fired. The higher the maturing temperature of the glaze and the lower its viscosity, the greater this interface

reaction becomes. Indeed, in microscopic examinations of a section of high temperature porcelain it has been noted that there is no distinct line of demarcation between the glaze and the body[16]. This solution of the body by the fluxing action of the glaze creates a vitreous material that gradually changes in composition from the surface of the glaze through the interface to the interior of the ceramic body.

This tendency of the glaze to eat into and dissolve a portion of the ceramic body is particularly significant in relation to crystalline glazes since they are highly fluxed and quite fluid at their top temperatures. What happens, of course, is that the composition of the glaze changes in relation to the amount of the material dissolved by the glaze. The high degree of thermal agitation of the ions in a crystalline glaze causes a thorough mixing of the dissolved portion of the ceramic body with the base glaze. This is of no direct concern as long as a particular glaze is restricted to use on the body for which it was originally developed. However, if the glaze is fired in a body of differing composition, the effect on the finished glaze may be quite noticeable. The composition of the finished glaze may be different than usual due to a variance in the materials dissolved into it during the firing. This remains basically a theoretical concept since little direct work has been undertaken on the subject. Spectrographic

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[16] Daniel Rhodes, _Stoneware and Porcelain_ (Philadelphia: Chilton Company, 1959), p. 73.

analysis of the same base glaze fired on a variety of ceramic bodies
would undoubtedly confirm the theory although the investigation would
be greatly complicated by the absence of a distinct point of separa-
tion between the glaze and the ceramic body.

Firing: The Heating and Cooling Phases

The heat treatment of crystalline glazes has been discussed
previously in several connections and there is little to be added
at this point. However, it should be emphasized that both the
heating and cooling phases of the glaze fire are important to the
ultimate appearance of the glaze and that it is necessary to closely
follow a standard firing procedure in order to achieve anything
approaching uniformity from firing to firing. Even if a rather
rigid plan is followed there will be sufficient variations in sub-
sequent firings to avoid tedium.

It is curious to note that most of the published material
concerning crystalline glazes tends to concentrate on glaze formula-
tion and does not sufficiently discuss firing techniques. Norton
presents one of the better discussions on firing techniques although
he lends little importance to the heating phase and directs the bulk
of his remarks to crystal formation in the cooling phase[17].

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[17] Norton, op. cit., p. 220.

EXPERIMENTAL PROCEDURES, PROCESSES AND RESULTS

Experimental Procedure

As this project was originally conceived, it was to involve the development and examination of several crystalline glazes that utilized slightly different materials in their chemical structure. However, as work progressed it became obvious that the scope of the undertaking was beyond reasonable expectations for the alloted time. It was decided, therefore, to limit the study to the development of a 'family' of glazes that utilized the same basic ingredients in their composition and were all related to the same "base" formula, each representing a controlled variation of the formulation thereof. In addition, a number of short test series would be conducted utilizing various other materials that are reported to be of some use in the production of crystalline glazes. These tests would serve to verify the reports and establish guidelines for future work in these areas.

In an effort to lend the greatest weight to the test results it was decided to standardize the testing procedures as much as possible. This matter of standardization and the resulting control of many variables proved during the course of experimentation to be of utmost importance in the production of successful crystalline glazes and to the validity of the conclusions reached from an analysis of the experimental results and observations.

Additionally, an effort was made to follow as closely as possible usual studio practices in the preparation, application and

EXPLANATION OF PLATE IV

Close-up of crystals grown in glaze ZT-8 between
2100° and 1900° F. The glaze contains one and one-half
percent copper carbonate as a colorant and the crystals
are a pale luminous green with successive coronas of
pale pink, grey-blue and reddish brown. The back-
ground glaze is grey with very pale tints of magenta
and green (magnification 8.4X).

PLATE IV

firing of glazes, since it was felt that unduly complex procedures would not only be inordinately time consuming but would have a discouraging effect on future investigation. From this standpoint it can be stated that this work is, in part, a study of the feasibility of producing crystalline glazes in a studio situation.

The ceramic body used for the production of test tiles and pottery forms was one developed by Mr. Henry F. Serenco as part of his preliminary thesis research conducted at Kansas State University during the Spring semester of 1968. It is a relatively low temperature porcelain throwing body that matures in the range of cone eight to ten (approximately 2250°-2300°F). The test tiles and pottery forms were produced, dried and bisque fired in line with normal studio practice.

All firings were conducted in a small Cress electric kiln that has a maximum recommended operating temperature of 2300° F. This particular brand of kiln has the important advantage of a continuously variable switching arrangement and as a result makes possible minute changes in the heat input to the firing chamber. The net effect is a greater degree of control throughout the firing cycle and some relief to the operator since a complicated switching sequence is avoided.

Pyrometric cones were used in all firings to determine the end point of the heating phase and an Amaco pyrometer was used to determine and regulate the rates of heating and cooling.

Development of the Principal Glaze

Initially it was decided to develop a glaze that would mature
properly at cone eight (approximately 2250° F), as during a firing,
this would place the top working temperature close to the maximum
recommended for the kiln. The porcelain body to be used matured
satisfactorily at this temperature, developing a degree of trans-
lucency when it was potted sufficiently thin.

It was also decided to originate glaze formulas rather than
begin working with formulas found in various publications. It was
felt that although this might not lead as quickly to the production
of a successful glaze, it would in the long run have the greatest
educational value.

The glaze formulas to be evolved would be kept as simple as
practical in order to limit the number of variables and the same raw
materials would be used in each glaze to avoid problems arising from
the different melting characteristics of related but different com-
pounds.

The selection of raw materials was made in light of several
considerations, both chemical and physical. Generally speaking, it
is unwise to use water soluble materials in compounding a glaze
since the glaze materials are mixed with water for purposes of appli-
cation and normal application to a porous ceramic body will allow the
soluble materials to soak into the body while the other components
remain on the surface. The result is a change in the composition of
the glaze. These soluble materials may also flux the ceramic body
and cause it to become overfired at normal peak temperatures. And

they also may alter the coefficient of thermal expansion of the body and seriously affect the "fit" of the glaze. Soluble materials are often hygroscopic, readily absorbing moisture from the air, which leads to indeterminate inaccuracies when weighing out these materials for a glaze batch.

Feldspars and commercially prepared glaze frits (various combinations of materials that are fused in a furnace, chilled and fractured by pouring the molten mass into a water bath and finely ground for use in compounding glasses and glazes) are the only relatively insoluble sources of the alkaline fluxes, sodium and potassium, and since feldspars ordinarily contain a fairly large amount of alumina, it was decided to select and utilize a suitable frit. This frit would necessarily be high in alkaline content and low in alumina. If the alumina content was low enough, an added advantage would be gained as the main portion of the alumina to be used could be added to the glaze batch in the form of clay. Raw clay added to a glaze batch in small quantities tends to improve the working qualities of the glaze slip. An excellent frit for these purposes is manufactured by the Pemco Division of the Glidden Company. Designated glaze frit P-283, it has the following molecular formula[18]:

$$Na_2O \quad 0.92$$
$$CaO \quad 0.02 \qquad Al_2O_3 \quad 0.20 \qquad SiO_2 \quad 4.37 \qquad mol. \ wt. \ 343$$
$$MgO \quad 0.06$$

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[18] Technical Data on Pemco Glaze Frits, Technical Bulletin #5011, Pemco Division, The Glidden Company, Baltimore, Maryland.

This frit has the added advantage of containing all its
alkali content in the form of sodium which is reported to be more
conducive to crystallization than potassium[19].

The remaining components of the glaze would be filled with
whiting, magnesium carbonate, kaolin and flint. Since titanium
is the most commonly used mineralizing agent in promoting crystal-
lization, it was decided to incorporate this material in the glaze
and use as a source the slightly impure mineral form, rutile.

From an inspection and analysis of a number of published
formulas for crystalline glazes an initial glaze was formulated
as follows:

Na_2O	0.30				
CaO	0.18			SiO_2	2.00
MgO	0.02	Al_2O_3	0.10		
ZnO	0.50			TiO_2	0.20

From this initial base glaze, a large number of variations
were derived, in each case varying the quantity of one component
of the glaze while changing the other components as little as
possible. The purpose in this approach is to observe what effect
each component has on the functioning of the glaze as a whole.
Due to the mechanics of the molecular formula, however, it is not
possible to make a change in one component of the RO column (basic
or flux materials) without making a compensating change in at least
one other component. The reason for this is that the sum of the
molecular equivalents of the RO column must always equal one. The

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[19] Parmelee, loc. cit.

EXPLANATION OF PLATE V

Close-up of crystallization in a zinc silicate
glaze containing beryllium as a mineralizing agent. No
colorants were added to the glaze and the crystals are
silver-white on an off-white background. The crystals
at the bottom of the photograph are typical of the type
grown near the upper limits of the zone of crystalliza-
tion, while the radially-oriented crystal at the top is
typical of the medium and lower growing temperatures
(magnification 8.8X).

PLATE V

formula must be at unity. Since it was felt that of the four components of the RO column, variations in the amount of calcium would affect the glaze the least, it was decided to use this to compensate for changes in other components. As it turned out, however, variations in the amount of calcium had a more significant effect than was originally anticipated.

Each of the various glaze formulas was converted to a batch recipe and weighed out in 100-gram samples. Although 100 grams of dry ingredients produces more wet glaze than is necessary to coat a single test tile, it was felt that in the interests of accuracy this was the smallest weight that should be attempted on the available scales. Each glaze sample was dry mixed, wet mixed and carefully screened using a ninety-four mesh sieve. A thick coat of glaze was applied to the tiles using a large brush.

It should be mentioned at this juncture that a small amount of a thick methocel solution was added to each glaze sample during the mixing procedure. This was added to the glazes to prevent cracking of the glaze coat during drying, a common problem with high zinc containing glazes. Cracking of the glaze coating can bring about crawling during the glaze fire. Methocel seemed to work quite well in this regard and the only severe cracking that was observed seemed to stem from the use of an excessive amount of water in the glaze mix. Very little crawling was observed on samples taken from the kiln. This experience is in marked contrast to that cited by Hansen, who reports having difficulties with a

glaze of similar composition. He found egg white to be the most efficient binder in preventing cracking of the glaze coating and subsequent crawling[20].

During the glaze firing each related group or 'family' of glaze tests was fired at the same time in order to insure identical heat treatment. Due to the extremely fluid nature of the glaze, the tiles were fired in ceramic trays especially made for this purpose and designed to prevent the flowing glaze from causing damage to the interior of the kiln. Although the test tiles were scored on their back side to snap out of these trays, considerable trouble was experienced in removing them in one piece and several required gluing.

Although an excellent glaze most fortunately came to light during the first firing, the testing was carried forward since it was felt that a related group of glazes should be developed that accurately reflected the influence of each chemical component of the glaze on the total melt. After several attempts this was realized in the last group to be fired, a 'family' of forty-three separate glazes. Each of the components in the molecular formula (except calcium) was added in small increments from an amount too low for proper melting of the glaze to an amount too great for proper melting. The effect of each material on the melting and crystallizing characteristics of the glaze could thus be readily

[20] Marc Hansen, "Zinc Silicate Crystal Glazes," *Ceramics Monthly*, Vol. 14:4 (April, 1966), p. 15.

seen and the glazes having the most pleasing crystalline structure
were 'centered' in the group and did not occur on the fringes. The
molecular formulas for this final series of glazes are presented in
Diagram 1. The most pleasing glazes resulting from the variations
of each material are marked with an asterisk (*). In all cases,
except magnesium, the highest and lowest amounts of each material
yielded a glaze which did not melt properly. Magnesium apparently
can be completely left out of the glaze, with no detrimental effects.
It is present here because it is an unavoidable component of the
frit used and it does seem to have some value if used in small amounts
as a replacement for calcium.

Relative to this series of tests, the following observations
can be made: the best results were obtained when zinc was present
in the glazes in an amount just below the point of causing the glaze
to become refractory and sodium (and the other alkali fluxes, as
well) should be held to a point just below that which shows signs
of causing significant crazing. The remainder of the RO can be
filled with calcium and magnesium although both of these materials
should be held to low amounts. Some small amount of alumina seems
necessary and approximately 0.1 molecular equivalents seems to be
about right. Silica should be added to the glaze in order to
strike a compromise between insufficient melting and excessive
fluidity which allows the glaze to largely run off the ware. The
proportion of titanium dioxide does not appear to be especially
critical and the best results were obtained in the area of 0.2
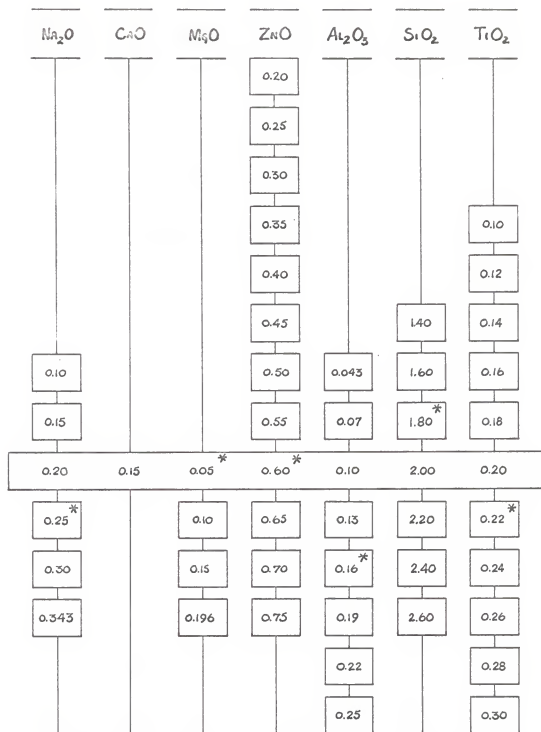molecular equivalents.

Na$_2$O	CaO	MgO	ZnO	Al$_2$O$_3$	SiO$_2$	TiO$_2$
			0.20			
			0.25			
			0.30			
			0.35			0.10
			0.40			0.12
			0.45		1.40	0.14
0.10			0.50	0.043	1.60	0.16
0.15			0.55	0.07	1.80*	0.18
0.20	0.15	0.05*	0.60*	0.10	2.00	0.20
0.25*		0.10	0.65	0.13	2.20	0.22*
0.30		0.15	0.70	0.16*	2.40	0.24
0.343		0.196	0.75	0.19	2.60	0.26
				0.22		0.28
				0.25		0.30

Diagram 1.--A group or 'family' of glazes derived from the same base formula. The quantities of CaO vary inversely to changes in Na$_2$O, MgO and ZnO since the sum of these four components must always equal 1.0. (Stated in molecular equivalents.)

The glaze that was fired with excellent results a number of times, both with and without colorants, is one that was developed during the early stages of the research. The molecular formula and batch recipe for this glaze, designated ZT-8, is as follows:

$$Na_2O \quad 0.30$$
$$CaO \quad 0.08$$
$$MgO \quad 0.02 \quad Al_2O_3 \quad 0.10 \quad \begin{array}{l} SiO_2 \quad 2.00 \\ TiO_2 \quad 0.20 \end{array}$$
$$ZnO \quad 0.60$$

Pemco P-283 Glaze Frit	50.1%
Whiting	3.3
Zinc Oxide	21.8
Kaolin	4.0
Flint	13.6
Rutile (Light Tone)	7.2
	100.0%

When this glaze was fired without added colorants the result was large golden crystals scattered on a white background. On close examination it was apparent that the white background was vertically streaked in the direction of the glaze flow, producing a textural effect similar to wood graining. However, when pure titanium dioxide was used in the glaze in place of rutile no streaking could be observed, indicating that the impurities in the rutile (mostly iron) were responsible. Since this streaking was not felt to be unattractive, the use of rutile was continued in subsequent glaze batches.

A number of colorants were added to this base glaze and some striking results were recorded. The oxides of copper, cobalt, iron and nickel were used alone and in combination with one another. The amount of contrast between the crystal and the background glaze depended to a great extent on the preferential absorption of the predominant colorant. Contrast is greatest when the predominant colorant goes to the crystal rather than to background glaze.

The results of these color tests are of a preliminary nature and more research is necessary to become thoroughly familiar with both the color response of the glaze and the effect of colorants on the characteristics of the glaze melt.

During the firing of the tests an attempt was made to establish a set routine in the management of the kiln so that a maximum amount of relevance could be established between tests from different firings. This proved to be something of a problem. For each firing the kiln was loaded and fired overnight at a fairly low rate. The average morning temperature was 1100° F. At this point, the kiln was switched to its highest control setting and allowed to advance until pyrometric cone eight was down. The rate of temperature advance during the latter stages of the heating phase was approximately 225° F per hour, although this varied somewhat depending upon the mass of material in the kiln. Indeed, during one firing when the kiln was largely filled with test tiles, the temperature climbed at a higher than normal rate and the result was a much more profuse crystallization than had been previously observed

in the same glazes. Obviously more nuclei were present in the cooling glaze but the reasons for this are not clear since pyrometric cones melt in direct relation to heat input in the same way as do glazes. Although the reasons for this behavior are not clear, the results indicate that the temperature rise should be as closely controlled as is the cooling phase.

One possible way to control the temperature rise during the heating phase would be to load the kiln with the same weight of material for each firing. Extra pieces of kiln furniture could be included to provide the proper balance. This would result in approximately the same amount of heat absorption from firing to firing and would tend to stabilize the temperature rise.

When the heating phase had advanced to cone eight (at a temperature rise of 225° F per hour this is approximately 2280° F) the kiln was switched off and allowed to cool normally to a pyrometer reading of 2100° F. At this point the kiln was switched on again. During the first firing, the kiln was held at approximately 2100° F for a period of three hours and then turned off again and allowed to cool normally to room temperature. The results of this firing were not satisfactory and an examination of several of the test tiles indicated that the crystals were of the high temperature type (see Norton[21]). In subsequent firings it was decided to use a controlled rate of cooling of 50° F per hour from 2100° F to 1900° F. This schedule proved to be quite workable and was used throughout the remainder of the testing.
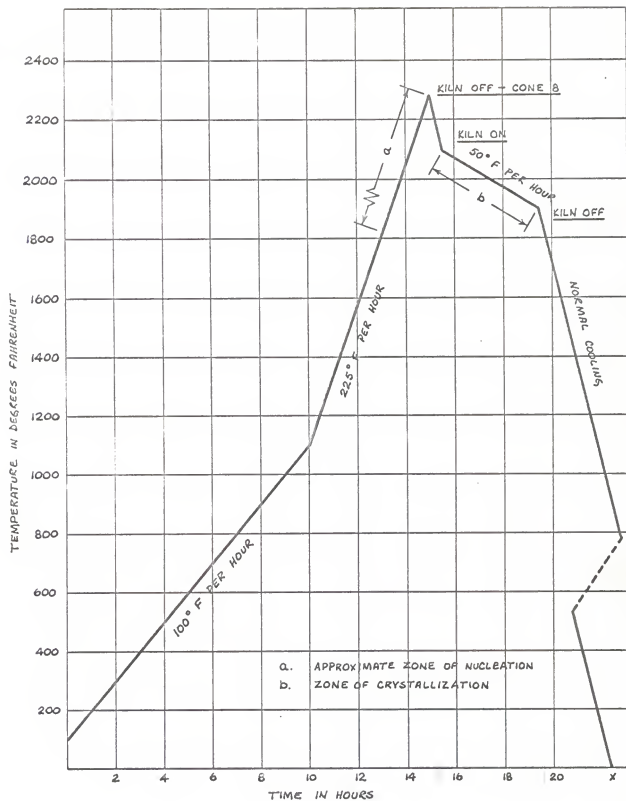
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[21] Norton, op. cit., p. 222.

Diagram 2. A typical firing schedule.

Other Tests

In addition to the tests conducted utilizing titanium as a mineralizing agent, a series of short tests were undertaken to verify the reported usefulness of lithium, molybdenum, tungsten, and beryllium in crystalline glazes. Since lithium is an alkaline flux it was used as a substitute for sodium in the formation of a group of glazes that contained no other specific mineralizing agent. Although crystalline growth was observed in many of the tests fired, the usefulness of lithium relative to sodium is yet to be determined.

Molybdenum, tungsten and beryllium were introduced separately to the same base glaze in small increments. All of these materials exhibited a definite tendency to promote crystallization. No comparison of the relative value of these materials can be made at this time since all three had a refractory influence on the base glaze and only small additions could be made before the glaze melt was seriously stiffened. Molybdenum was the most refractory of the three and beryllium the least. The latter observation came as something of a surprise since beryllium compounds are reportedly quite refractory and ordinarily are used only at very high temperatures. Verification tests on several other of the mineralizing agents were not completed due to the lack of sufficient time.

PROBLEMS ENCOUNTERED IN THE PRODUCTION OF
CRYSTALLINE GLAZED WARE

Many of the special problems encountered in dealing with
crystalline glazes have been already discussed. There is one
additional consideration, however, that deals specifically with
the production of crystalline glazed ware.

It has already been mentioned that due to the low viscosity
of crystalline glaze melts, the glaze tends to flow quite freely
at the maximum firing temperature. In the firing of crystalline
glazed ware it is necessary to provide some means of collecting
the glaze which flows off the ware to prevent damage to the in-
terior of the kiln and the kiln furniture. This is usually
accomplished by firing the ware over a small bowl which will contain
the flowing glaze. It is also necessary to elevate the ware on
some type of firing support so the glaze will run free of the pot
and not collect around the foot ring. If a correctly designed fir-
ing support is used, the chances of destroying the ware while remov-
ing the support and the excess glaze are minimized.

Hansen recommends the use of insulating fire brick, cut to
the size and shape of the foot and sealed to it with a thick solution
of alumina hydrate and laundry starch[22]. As long as the seal be-
tween the pieces is not broken, allowing the entrance of the glaze,

[22] Hansen, _loc. cit._

EXPLANATION OF PLATE VI

Close-up of profuse crystallization in a zinc
silicate glaze utilizing titanium as a mineralizing
agent. Crystals are golden yellow in color with no
background glaze visible (magnification 8.5X).

PLATE VI

little difficulty will be encountered in separating the two. The
raw edge of fractured glaze resulting from the separation can be
easily smoothed on a grinding wheel.

The mushroom-like forms used in this study presented a special
problem. The extreme shape of the forms required structural support
during the glaze firing in order to avoid slumping. Since the 'stem'
or footing of the mushroom would have to hang down inside the firing
support without touching, the use of insulating firebrick seemed im-
practical as it would be very difficult to cut it into a thin, knife-
edged cylinder without excessive crumbling. It was decided, there-
fore, to make cylindrical supports from the porcelain body. These
would have the added advantage of shrinking during the glaze firing
at the same rate as the forms being supported. The 'stems' of the
mushroom were glazed with a conventional transparent glaze and a
narrow band was left unglazed to accept the firing support. Alumina
hydrate was used to provide a seal and prevent fusion.

Generally speaking, this approach worked well. The molten
glaze flowed smoothly off the upper portion of the forms and down
the firing supports to collect in the bowls provided. Considerable
difficulty, however, was found in maintaining a glazed-tight seal be-
tween the mushroom forms and the firing supports. In one instance
attempts to separate the two led to the complete destruction of the
mushroom. It must be emphasized that even the smallest crack will
allow the highly fluid glaze to seep between the two pieces. The
closer the fit between the two, the easier it will be to affect

separation. As long as no glaze is allowed to bind the two pieces together, only a minimum of grinding will be necessary to smooth the raw edge of the glaze after separation.

CONCLUSION

Although crystalline glazes are of considerable technical interest, it must be recognized that the active, jewel-like surfaces that they present make them unsuitable for all but the most simple pottery forms. The unique technical problems they present and the profound restrictions on expressive form largely explain the limited use these glazes have had since the early years of the century.

Crystalline glazes are in themselves quite interesting and attractive, but combining them with forms to produce a total expressive unity is a challenging problem, indeed.

ADDENDUM

Subsequent to the writing of the foregoing text, a color
response series was run utilizing the base glaze ZT-8. Uniformly
excellent results were recorded. Diagram 1a outlines the colorants
used for the tests and the quantities that were employed.

The main portion of the tests involved the use of seven common
colorants. These were added to seven separate glaze batches, mixed
and screened and applied to porcelain test tiles. Each glaze was also
individually wet blended with each of the other six glazes and all the
possible fifty-fifty combinations were exhausted. This produced a test
series of twenty-eight tiles.

The results obtained with the glazes containing compounds of
iron, cobalt, copper and nickel were very similar to a short series
of tests that have already been discussed. Of the three other
colorants used, vanadium pentoxide was the least effective. Used
alone it had only a slight effect on the color of the base glaze,
causing the crystals to change from a golden yellow color to a beige
brown. In combination with the other colorants, vanadium appeared
to cause subtle variations in the colors of both the crystals and
the vitreous magma.

The use of chromium oxide produced some interesting results.
The oxide used alone in the amount of one percent caused the glaze
to become too refractory to melt properly and the result was some-
thing akin to an ordinary matt glaze. In combination with the other
glazes, however, the mix causing the chromium content to be reduced
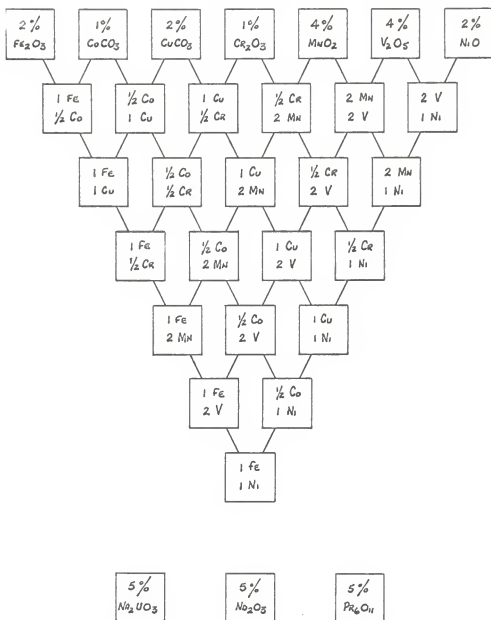by one half, large crystalline growths were apparent. The

Diagram 1a. Color response series and supplemental tests utilizing the base glaze ZT-8. (Nd_2O_3 and Pr_6O_{11} were added to a beryllium containing glaze.)

appearance of these growths was quite extraordinary since none of
the usual internal structural pattern of the crystal could be ob-
served with the naked eye. The amount of color contrast between
the crystals and the background glaze was unusually low while the
relative difference in the surface textures of the two (and thus
the degree of gloss) was quite pronounced. The areas of crystalline
growth appeared much as would an ordinary matt glaze while the magma
was considerably brighter.

Manganese dioxide, both used alone and in combination with
the other colorants, produced some striking results. The character-
istic effects of preferential absorption are not fully operative
with manganese since it lends color to both the crystals and the
magma. Although this causes the color contrast to be reduced, the
crystals remain quite clearly defined and their structural pattern
distinct.

Three single tests were also prepared to determine the
effectiveness of some of the more unusual colorants. Five percent
sodium uranate was added to the base glaze ZT-8 with excellent
results. The vitreous magma, which without colorants is white,
was tinted a subtle cream yellow. This reduced the contrast with
the crystals somewhat but the overall effect was quite rich.

The other two tests utilized the rare earth oxides neodymium
and praseodymium. These were added to a base glaze containing
beryllium rather than titanium as a mineralizing agent and the results
were disappointing. Through the process of preferential absorption,

both of these colorants lent their tints to the vitreous magma and caused the crystals to become less visible. Neodymium oxide produced a light lavender hue and praseodymium a very pale yellow.

Although these tests certainly do not exhaust all the possible combinations and quantities of colorants, they do provide a valuable reference for the preparation of a wide variety of colored crystalline glazes.

ACKNOWLEDGMENTS

REFERENCES

Green, David. Understanding Pottery Glazes. London: Faber and Faber Limited, 1963.

Hansen, Marc. "Zinc Silicate Crystal Glazes." Ceramics Monthly, XIV (April, 1966).

Koenig, J. H., and Earhart, W. H., eds. Literature Abstracts of Ceramic Glazes. Philadelphia: College Offset Press, 1951.

Koerner, J. "New Crystalline Glazes." Transactions of the American Ceramic Society, X (March, 1908).

Lehnhäuser, Werner. Glasuren und ihre Farben. Düsseldorf: Wilhelm Knapp Verlag, 1959.

Nelson, Glenn C. Ceramics. New York: Holt, Rinehart and Winston, 1960.

Norton, F. H. "The Control of Crystalline Glazes." Journal of the American Ceramic Society, XX (July, 1937).

_____. Elements of Ceramics. Cambridge: Addison-Wesley Publishing Company, 1952.

Parmelee, Cullen W. Ceramic Glazes. Chicago: Industrial Publications, Inc., 1951.

Purdy, R. C., and Krehbiel, J. F. "Crystalline Glazes," Transactions of the American Ceramic Society, IX (August, 1907).

Rhodes, Daniel. Clay and Glazes for the Potter. Philadelphia: Chilton Company, 1957.

_____. Stoneware and Porcelain. Philadelphia: Chilton Company, 1959.

Singer, Felix and Sonja S. Industrial Ceramics. New York: Chemical Publishing Co., Inc., 1963.

Wakefield, Hugh. "The Modern World," World Ceramics. Edited by Robert J. Charleston. New York: McGraw-Hill Book Co., 1968.

Weyl, Woldemar A., and Marboe, Evelyn Choster. The Constitution of Glasses, Vol. I: Fundamentals of the Structure of Inorganic Liquids and Solids. New York: Interscience Publishers, 1962.

A STUDY OF MACROCRYSTALLINE GLAZES

by

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B. B. A., Washburn University, 1966
B. A., Washburn University, 1967

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of

the requirements for the degree

MASTER OF ARTS .

Department of Art

KANSAS STATE UNIVERSITY
Manhattan, Kansas

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The purpose of this study was to investigate the chemical formulation and firing characteristics of a unique type of ceramic glaze which develops large crystalline growths in the glaze surface.

Sources for this study include published technical data regarding crystalline glaze formulation and firing procedures and personal experience.

A low temperature porcelain body was used to produce tiles and pottery forms for use as vehicles for the test glazes. All test firings were conducted in a small electric kiln in an oxidizing atmosphere.

Several successful glazes were developed as a result of the research.

Test results indicated that the more successful crystalline glazes tended to be quite high in both zinc and the alkaline fluxes, and low in the other common fluxing agents. The alumina content must be kept low in order to provide a fluid glaze melt, necessary for the growth of large crystals. Silica functions as it does in more conventional glazes. The use of several mineralizing agents which promote crystalline growth was also investigated with positive results.

Experience gained in the heat treatment of crystalline glazes indicates that the entire firing cycle must be closely regulated to insure consistent results from firing to firing.

Production problems caused by the extremely fluid nature of crystalline glaze melts were also considered.

Although this study is of a preliminary nature, it is felt that a firm foundation has been established and guidelines extended for further profitable investigations.