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LOW-COST GLAZES FOR STRUCTURAL CLAY PRODUCTS

By

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P R E F A C E

The general method of making glazes for structural clay products has been, first, to develop a clear or colorless one called the "base glaze," then to add certain oxides, salts, or stains to produce colors. The base glaze requires high-grade ceramic materials—such as white-burning clay, feldspar, and potter's flint—totaling about 40 to 75 percent of the raw materials.

When color is not of primary importance, costs may be reduced by use of local clays in place of the more expensive materials. Most clays used in the products to be glazed contain the proper ratios of silica to alumina for glaze-making purposes, and good glazes can be made from them by adding suitable fluxes to control fusibility. When used in this manner, such clays can displace all of the white-burning clay and the feldspar and most of the potter's flint.

The purpose of this Circular is to show how such low-cost glazes can be produced, in order to assist the practical glaze maker as well as the beginner. Part of the subject matter is essentially elementary, and terms common to the industry are used in preference to those of a more technical nature.

LYMAN J. BRIGGS, *Director.*

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By Ray T. Stull and Paul V. Johnson

ABSTRACT

Three groups of clays, consisting of three shales, three surface clays, and two fire clays, were investigated to determine their glaze-making properties when used as integral parts of glaze compositions. The clay-whiting (CaCO_3) composition which deformed at the lowest temperature was determined for each clay and served as the major portion of the glaze composition applied to tile made of that clay. Fluxing materials and potter's flint, when needed to control fusibility, texture, and glaze fit, were incorporated. Six different fluxes and eight different materials for producing glaze colors were investigated. The data are presented in 3 figures and 19 tables.

CONTENTS

	Page
Preface.....	II
I. Introduction.....	2
II. Glaze fundamentals.....	2
1. General discussion.....	2
2. Silica-alumina ratios of mat and bright glazes.....	3
(a) Forms of expression for the silica-alumina ratio.....	4
(b) Mat glazes.....	4
(1) Types.....	4
(2) Silica-alumina ratios recommended for mat glazes.....	4
(c) Bright glazes.....	5
(1) Types.....	5
(2) Silica-alumina ratios recommended for bright glazes.....	5
(d) Importance of the silica-alumina ratio of the clay.....	5
III. Materials investigated and methods employed.....	6
1. Clays.....	6
2. Materials for controlling fusibility, texture, and color.....	7
(a) Whiting (CaCO_3).....	7
(b) Lead-silica frit.....	7
(c) Galena (PbS).....	7
(d) Colemanite and frit substitute.....	7
(e) Zinc oxide (ZnO).....	8
(f) Potter's flint (SiO_2).....	8
(g) Materials used for glaze colors.....	8
3. Method of developing low-cost glazes.....	9
(a) Member having lowest deformation temperature (LD) defined.....	9
(b) Clay-whiting LD member.....	9
(c) Methods of reducing deformation and maturing temperatures and controlling texture.....	9
4. Preparation of the deformation and glaze trials.....	10
(a) Forming the deformation test specimens.....	10
(b) Forming the glaze trials and applying the glaze.....	11
5. Heat treatment of the trials.....	11
(a) Determination of the deformation temperatures.....	11
(b) Kiln treatment of the glaze trials.....	11

	Page
IV. Results, discussion, and conclusions.....	13
1. Deformation temperatures of clay-whiting compositions.....	13
(a) Effect of additions of galena to the S2 clay-whiting LD member.....	14
(b) Effect of replacement of part of the whiting by zinc oxide on the C2 clay-whiting LD member.....	15
(c) Effect of replacement of part of the clay by flint on the S1 clay-whiting LD member.....	15
(d) Effect on the C3 clay-whiting LD member by equivalent combining-weight substitutions of PbO in lead-silica frit for CaO in whiting.....	15
2. Glazes of good texture substantially free from defects.....	16
3. Conclusions.....	20

I. INTRODUCTION

This report on low-cost glazes for structural clay products consists of three parts. A general discussion of glaze fundamentals is given in section II, a description of the materials investigated and methods employed appears in section III, and the results, together with a discussion and the conclusions reached, are given in section IV.

The investigation was undertaken to illustrate how such glazes can be produced and also to demonstrate a simplified method of producing them independently of the so-called empirical glaze formula. A substantial portion of the general information on glazes has been taken from the private notes and practical experiences of the authors. In order to be understandable and useful to the beginner and to those of limited glaze-making experience, much of the subject matter treated must necessarily be elementary. Terms familiar to the industry are used as far as possible in preference to those of a more technical nature.

II. GLAZE FUNDAMENTALS

1. GENERAL DISCUSSION

Glazes applied to structural clay products are of two kinds, known by the trade as the "salt glaze" and the "ceramic glaze." The method of producing the salt glaze consists, briefly, in placing the dried ware in the kiln and vaporizing common salt on the kiln fires during the latter part of the firing process. The salt vapor enters the kiln chamber and forms the glaze in combination with the clay on the surface of the ware. The salt glaze cannot be applied successfully to all clays inasmuch as a clay may be either too aluminous or too siliceous to be salt-glazed successfully. Since the glaze is formed by the reaction between salt vapor and clay, the composition of the clay must be within limits favorable to the formation of a glaze,¹ and the clay must also withstand a kiln temperature sufficiently high to produce the reaction between the salt vapor and the clay. Practice indicates that the kiln temperature at the time of "salting" should be at or above the equivalent of pyrometric cone 1 (approximately 1,125° C), a temperature at which some clays become overfired, as indicated by bloating or by deforming under the load of the kiln setting.

The ceramic glaze is composed of suitable ceramic materials in the proper proportions to form the "batch" or "glaze mix," which is ground wet to form a free-flowing glaze slip. The slip is usually

¹ L. E. Barringer, *The relation between the constitution of a clay and its ability to take a good salt glaze*, Trans. Am. Ceram. Soc. 4, 222 (1902).

applied to the freshly formed or to the bone-dry ware by spraying or by dipping. The ware, when dry, is heated in the kiln to the temperature at which both body and glaze are matured, or the glaze may be applied to the ware after it has once been fired, and is given the second firing for development of the glaze. The practice generally followed in making the ceramic glaze is to develop a clear or colorless glaze, called the "base glaze", whose composition is adjusted to fit the clay body and kiln temperature at which the ware is to be treated. Where colored glazes are required, they are generally made by adding to the base glaze suitable coloring materials, such as metallic oxides, salts, or ceramic stains.

The ceramic glaze, although higher in production cost than the salt glaze, has certain advantages which may offset the difference in cost, and there is a growing tendency among manufacturers to replace the salt glaze by a ceramic glaze, especially when uniformity of color, ornamental features, durability, and higher market value are considered. Ceramic glazes may be applied to those clays capable of taking a good salt glaze and to many clays which do not salt-glaze readily. They are smoother, more uniform in color and texture than the salt glaze, and can be produced in a variety of colors and textures.

In order to be substantially free from color, the base glaze requires the use of materials comparatively free from the different forms of iron and other color-imparting materials. The glaze ingredients, therefore, are confined largely to the high-grade ceramic materials—such as white-burning clay, potter's flint, and feldspar—which constitute about 40 to 75 percent by weight of the glaze batch.

Where a white or colorless glaze is not required, the cost of the glaze material may be substantially reduced by use of local clays. Frequently the same clay as that used in making the ware, or some other clay in close proximity to the plant, is favorable in composition and thus can reduce glaze costs materially by replacement of all or a substantial part of the more expensive materials. The famous Albany slip is, in fact, a clay whose composition is such that it forms a bright glaze under favorable kiln conditions and has been used for generations for the production of the familiar brown glaze on household and chemical stoneware.

Clays containing the proper proportions of alumina and silica for glaze-making purposes are abundant, but they are generally deficient in fluxes. By the addition of the proper kind and amount of fluxing material to such clays, both bright and mat glazes may be produced in the temperature range used for the production of structural clay products.

The method of determining the batch composition of the glaze by application of the so-called "empirical glaze formula", as employed by the technically trained glaze maker, is more or less complicated. It requires a knowledge of elementary chemistry, at least, and also considerable practical experience in the art of glaze making.

2. SILICA-ALUMINA RATIOS OF MAT AND BRIGHT GLAZES

Whether the texture of the glaze will be mat or bright depends essentially upon the glaze composition and its heat treatment. The principal difference in composition between the mat and the bright glaze is that the ratio of silica to alumina of the mat glaze is lower than that of the bright glaze, and bright glazes can be made from mats

by the addition of flint to increase their silica-alumina ratios. Where all of the silica and the alumina of the glaze is derived from the clay, the silica-alumina ratio of the glaze is obviously the same as that of the clay.

(a) FORMS OF EXPRESSION FOR THE SILICA-ALUMINA RATIO

The silica-alumina ratio of a clay or of a glaze may be expressed in two different forms. In the ceramic literature the ratio is invariably expressed as the molecular (molar) ratio. This is the ratio expressed by the values for the silica and the alumina in what trade usage commonly terms the "empirical formula." The ratio may be expressed also as the "gravimetric" or weight ratio, defined as the ratio of the silica to the alumina according to their respective values as determined by chemical analysis.

In order to distinguish between the two different expressions for the silica-alumina ratio, the molar ratio is designated in this report as Rm and the gravimetric ratio as Rg (see table 1). For purposes of comparison, one ratio may be converted to that of the other by application of a simple conversion factor. Inasmuch as the approximate molar (or combining) weight of silica (SiO_2) is 60 and that of alumina (Al_2O_3) is 102, the molar-weight ratio of silica to alumina is 60/102, or 1 to 1.7. Then

$$Rg \times 1.7 = Rm. \quad (1)$$

For example, if the chemical analysis of a clay shows that the silica content is 75.5 parts and the alumina 14.8 parts, then $Rg = 75.5/14.8 = 5.1$, and $Rm = 5.1 \times 1.7 = 8.67$.

(b) MAT GLAZES

(1) *Types*.—There are two generally recognized types of mat glazes, known as the "true mat" and the underfired or "pseudomat." In the former type the composition and firing temperature are such that most, if not all, of the glaze materials have been liquefied by fusion. If it is cooled quickly (as by air-quenching), the glaze may have a smooth, glossy surface; but if it is cooled slowly (under normal kiln conditions), considerable crystallization takes place somewhat after the manner of blast-furnace slag, and the glaze becomes opaque and the surface mat in texture.

The composition of the pseudomat glaze may be either that of a true mat or that of a bright glaze which is underfired. It is similar in appearance to a highly vitrified slip in which the opacity and texture are due to the presence of a considerable portion of unfused material mixed with a small amount of crystalline material and some glass.

If fired at temperatures high enough and cooled slowly, the texture of the true mat composition will still be mat, while that of the other type tends to lose its matness and become more or less glossy. The temperature range of the true mat glaze is longer than that of the pseudomat and its texture and quality are generally more desirable.

(2) *Silica-alumina ratios recommended for mat glazes*.—For a glaze of pleasing mat texture² in a group fired to cone 05, the Rm value was 3.60. The Rm value when calculated for a mat glaze reported by Charles F. Binns³ as the best of a group fired to cone 01 was 3.00. For a mat glaze used by Hewitt Wilson⁴ as a base glaze for making a series

² Unpublished data.

³ *The development of the mat glaze*, Trans. Am. Ceram. Soc. 5, 53-55 (1903).

⁴ *Note on overglaze colors at cone 6-7*, Trans. Am. Ceram. Soc. 19, 657 (1917).

of overglaze colors for terra cotta at cone 6 to 7, the Rm value was 5.48. The Rm values of these mat glazes (selected from a large number reported as "good") range from 3.00 to 5.48. Although mat glazes may be produced in which the ratios are outside of this range, it appears to be sufficiently broad for most purposes.

(c) BRIGHT GLAZES

(1) *Types*.—There are two well-recognized types of bright or gloss glazes. These are (a) the clear glaze, which is more or less transparent, so that its apparent color is influenced largely by the color of the body underneath; and (b) the opaque glaze, in which the color of the body is masked owing to undissolved material suspended in the glaze, to segregated material, or to the addition of opacifying agents, such as tin oxide (SnO_2), titanium oxide (TiO_2), or zirconium oxide (ZrO_2).

A glaze rendered opaque by the addition of one or more of the above opacifying materials is known generally under the term "enamel." Bristol glazes applied to stoneware household utensils are glazes made partially opaque by zinc oxide (ZnO) in excess of that which enters into solution or combination.

(2) *Silica-alumina ratios recommended for bright glazes*.—The silica-alumina ratio limits of the bright glazes are broader than those of the mats. This is especially true for glazes such as those of the raw-lead type which mature at comparatively low temperatures. According to Walter M. Fickes,⁵ the probability of forming a perfect (raw-lead) glaze lies between Rm values of 8 and 15 when fired at temperatures from cone 04 to 02. Charles F. Binns⁶ lists a glaze maturing at cone 06; used for studio work, which has a calculated Rm value of 9.00. A bright glaze fired to cone 4, in an investigation of terra cotta glazes by R. B. Keeler,⁷ was reported as "perfect." Its Rm value is 6.86. Gordon D. Phillips⁸ gives the composition of a bright glaze, maturing at cone 6, as the base glaze to which coloring materials were added for making different colored glazes for terra cotta. Its Rm value is 9.02.

The raw-lead glazes reported by Fickes (see footnote 5) were fired in a small laboratory test kiln under a short-time heating and cooling period. The upper Rm value of 15, therefore, may be too high for satisfactory glazes when fired in a commercial kiln, because a glaze containing an excess of silica is liable to become more or less "dull" when heated and cooled slowly under regular kiln practice. For the range of temperatures ordinarily used for the production of structural clay products, satisfactory bright glazes may be obtained over the Rm range of 6.80 to about 11.00.

(d) IMPORTANCE OF THE SILICA-ALUMINA RATIO OF THE CLAY

Irrespective of the method of development of the glaze, more or less experimenting by "trial and error" is necessary to produce a glaze of desirable texture and color and which will fit the body to which it is applied and be free from defects. Although glazes may be developed from a clay without having its chemical analysis, the analysis

⁵ *The permissible variation in the silica and alumina contents of raw lead glazes*, Trans. Am. Ceram. Soc. **3**, 112 (1901).

⁶ *The Potter's Craft* (D. Van Nostrand Co., New York, N. Y., 1922).

⁷ *Influence of variable silica and alumina on terra cotta glazes*, Trans. Am. Ceram. Soc. **18**, 295-6 (1916).

⁸ *Terra cotta bodies, slips and glazes*, Trans. Am. Ceram. Soc. **16**, 171 (1914).

is helpful in reducing the amount of work involved. Inasmuch as the ratios of the silica to the alumina of good glazes fall within certain limits, considerable time may be saved if the glaze maker confines his trial-and-error experiments to those limits. It is, therefore, important to know at least the silica and alumina contents of the clay, from which its silica-alumina ratio (*Rm* value) can be calculated, since the clay may constitute the major part of the glaze and frequently represents the entire source of the silica and alumina.

III. MATERIALS INVESTIGATED AND METHODS EMPLOYED

1. CLAYS

Eight clays from different manufacturers of structural clay products were included in the investigation for determination of their glaze-making properties. Each glaze was applied to tile made of the same clay, respectively, as that used in the glaze composition. The identification number of each clay, its kind, the State from which it was obtained, the products made from it, its approximate chemical composition,^a and the *Rm* value are given in table 1. These compositions show not only the silica and alumina but also the fluxes lime, magnesia, potash, and soda, and the iron oxide, which also serves as a flux besides imparting color to the glaze.

TABLE 1.—Clays

No.	Description			Chemical composition					
	Clay	Source (State)	Commercial products	Ignition loss	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Ferric oxide (Fe ₂ O ₃)	Lime (CaO)	Magnesia (MgO)
				Percent	Percent	Percent	Percent	Percent	Percent
S1	Shale.....	Illinois.....	Red brick.....	7.0	59.2	19.3	7.0	0.7	2.1
S2	do.....	Ohio.....	do.....	6.8	58.1	19.8	8.7	.5	1.8
S3	do.....	Pennsylvania.....	do.....	6.1	60.2	20.7	6.5	.8	1.4
C1	Clay.....	Maryland.....	Buff brick and tile.....	5.9	73.2	16.6	1.7	.0	0.6
C2	do.....	do.....	Red brick.....	5.2	69.9	15.1	6.9	.0	.8
C3	do.....	do.....	Buff brick.....	5.9	75.4	14.8	1.4	.0	.5
F1	Fire clay.....	Ohio.....	Buff structural tile.....	9.4	57.2	28.3	1.4	.0	.8
F2	do.....	Pennsylvania.....	Buff brick and tile.....	7.0	63.7	24.1	1.9	.0	.7

No.	Description			Chemical composition—Continued			SiO ₂ -Al ₂ O ₃ ratios	
	Clay	Source (State)	Commercial products	Potash (K ₂ O)	Soda (Na ₂ O)	Total	<i>Rg</i> ^a	<i>Rm</i> ^b
				Percent	Percent	Percent		
S1	Shale.....	Illinois.....	Red brick.....	2.8	1.5	99.6	3.07	5.21
S2	do.....	Ohio.....	do.....	3.3	.8	99.8	2.93	5.00
S3	do.....	Pennsylvania.....	do.....	3.0	.6	99.3	2.91	4.94
C1	Clay.....	Maryland.....	Buff brick and tile.....	1.9	.2	100.1	4.41	7.60
C2	do.....	do.....	Red brick.....	2.1	.2	100.2	4.63	7.87
C3	do.....	do.....	Buff brick.....	1.7	.1	99.8	5.09	8.66
F1	Fire clay.....	Ohio.....	Buff structural tile.....	1.9	.2	99.2	2.01	3.44
F2	do.....	Pennsylvania.....	Buff brick and tile.....	2.4	.4	100.2	2.64	4.49

^a Gravimetric ratio (*Rg*).

^b Molar ratio (*Rm*).

(See p. 4 for definitions of *Rg* and *Rm*.)

⁹ The chemical analyses were made by the Chemistry Division, National Bureau of Standard

From table 1, it is seen that the *Rm* values are close for the three *S* clays, ranging from 4.94 to 5.21. The values for the fire clays *F1* and *F2* are lowest (3.44 and 4.49). All are within limits for good mat glazes. The highest *Rm* values (7.60, 7.87, and 8.66) are those for the *C* clays and are well within the limits required for making bright glazes without the addition of flint.

2. MATERIALS FOR CONTROLLING FUSIBILITY, TEXTURE, AND COLOR

Although there are a number of ceramic materials used for controlling fusibility and texture of glazes, only six were investigated and substitutes, which function equally well, are recommended for four of these. These six materials and the four substitutes and also eight materials which were used for coloring glazes are described below.

(a) WHITING (CaCO_3)

The carbonate of lime used as a flux is a fine-grained precipitate, marketed as a byproduct from certain chemical processes, and is substantially free from deleterious impurities. Where a sufficiently pure grade of limestone is available locally, it may be substituted if preground to pass a 100- to 120-mesh sieve.

(b) LEAD-SILICA FRIT

Lead-silica frit is an effective flux for reducing fusion temperature. The material used had the approximate composition of about 84.8 percent of PbO and 15.2 percent of SiO_2 . Although somewhat water-soluble, this frit is not considered liable to cause lead poisoning where workmen exercise proper care in the preparation and application of the glazes. As a substitute, 87 parts of red lead (Pb_3O_4) and 15 of flint by weight can replace 100 parts of the frit. The red lead and flint may be added to the glaze batch "raw," that is, without fritting.

(c) GALENA (PbS)

The lead-bearing mineral galena (PbS) has been used in Europe for a number of years and in America to a limited extent as a flux for glazes maturing at low temperatures. Its water solubility is practically nil and, according to H. A. Wheeler,¹⁰ it is not conducive to lead poisoning. Nearly all forms of lead, however, are more or less dangerous if taken internally. One objectionable feature to the use of galena as a glaze material is its tendency to settle in the glaze slip, owing to its high density (7.5). The glaze slip therefore requires frequent stirring during its application to keep the materials in suspension. As a substitute, 96 parts of red lead by weight may replace 100 parts of galena.

(d) COLEMANITE AND FRIT SUBSTITUTE

The mineral colemanite, a hydrated calcium borate, is practically insoluble in water. It not only functions as an effective flux, but serves also as a means of supplying the glaze with boric oxide in an insoluble form, and therefore fritting is unnecessary.

The colemanite was an impure variety which was marketed in powder form as a ceramic material. After the laboratory work in

¹⁰ *The use of lead ores in the ceramic industry*, Trans. Am. Ceramic Soc. 4, 131 (1902).

connection with the glaze investigation had been completed, it was learned from the company operating the colemanite properties that their colemanite operations had been discontinued in favor of other sources of material for the production of their refined products.

An approximate chemical analysis of the colemanite sample was therefore obtained (table 2) and a frit substitute made which has a composition substantially the same as that of the colemanite (less ignition loss, table 3). When tested in five different glazes, it produced results equally as good as those obtained from the colemanite.

TABLE 2.—Approximate chemical composition of the colemanite ^a

	Percent
Ignition loss.....	27.1
Silica (SiO ₂).....	12.5
Ferric oxide and alumina (R ₂ O ₃) ^b	2.3
Lime (CaO).....	20.8
Magnesia (MgO).....	4.4
Soda (Na ₂ O).....	3.4
Boric oxide (B ₂ O ₃).....	• 29.5

^a Chemical analysis made by Glass Section, National Bureau of Standards.

^b Mostly alumina (Al₂O₃).

^c By difference.

TABLE 3.—Batch composition and method of preparing the frit ^a substitute for colemanite

	Percent
Whiting (CaCO ₃).....	30.5
Magnesium carbonate (MgCO ₃).....	7.5
Borax (Na ₂ B ₄ O ₇ ·10H ₂ O).....	17.1
Kaolin (Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O).....	4.8
Boric acid (B ₂ O ₃ ·3H ₂ O).....	32.1
Flint (SiO ₂).....	8.0
Total.....	100.0

^a The frit batch was mixed dry by 1 hour's ball-mill grinding, fusing the mixture in a crucible at 1,050° to 1,100° C, quenching by pouring the melt into water, drying, and grinding in a ball mill to pass a 100-mesh sieve.

(e) ZINC OXIDE (ZnO)

The zinc oxide (ZnO) was the calcined variety prepared for the ceramic trade. It is more effective than whiting for lowering the fusion temperature, but less effective than lead- or boron-bearing materials.

(f) POTTER'S FLINT (SiO₂)

Potter's flint (SiO₂) is marketed in the form of finely ground, nearly pure quartz. It was used principally in mat glazes to improve texture or to increase the silica-alumina ratios sufficiently to form bright glazes. Under favorable conditions it also acts as a mild flux.

(g) MATERIALS USED FOR GLAZE COLORS

The color imparted to a glaze depends upon the quantity and purity of the coloring material used, the composition of the glaze, the firing temperature, and the atmospheric condition of the kiln. For example, in a mat glaze containing sufficient quantities of lime and iron to produce an olive-green color, if the proper amount of flint is added to the glaze, the color is changed to a dark buff or brown and the glaze becomes glossy. Within limits, the color deepens with increase in the

amount of some coloring agents added, while for others the color darkens, changing to either a gun metal or black. The depth of some colors increases with increase in firing temperature, while other colors are made paler, apparently because of partial volatilization of the coloring material. A ceramic coloring material may produce one color when fired in an oxidizing kiln atmosphere, and an entirely different one when fired in a reducing atmosphere. The names and chemical symbols ¹¹ of the materials used in this investigation for the production of the colored glazes are as follows:

Material	Chemical symbol
Cobaltous oxide.....	CoO
Cupric oxide.....	CuO
Ferric oxide.....	Fe ₂ O ₃
Lead chromate.....	PbCrO ₄
Manganese dioxide.....	MnO ₂
Rutile (titania).....	TiO ₂
Tin oxide.....	SnO ₂
Uranium oxide.....	UO ₂

3. METHOD OF DEVELOPING LOW-COST GLAZES

The method of developing low-cost glazes consists, first in determining the composition of that member of a series of clay and flux mixtures which softens and deforms at the lowest temperature, and second, adding to that member such ceramic materials as are needed to control fusibility, glaze fit, texture, and color.

(a) MEMBER HAVING LOWEST DEFORMATION TEMPERATURE (*LD*) DEFINED

When two unlike ceramic materials, such as a clay and a flux, are intimately mixed in different proportions, forming a series of members, and these members are then heated under uniformly rising temperature, that member softening and deforming at the lowest temperature is called the "lowest deformation member" of the series. For convenience, this will be termed the *LD* member.

(b) CLAY-WHITING *LD* MEMBER

Inasmuch as whiting (CaCO₃) is a flux, low in cost, and can be used in comparatively large quantities in glazes, it was used with the clays investigated to determine their clay-whiting *LD* members. These members constituted the major portions of the glaze compositions.

(c) METHODS OF REDUCING DEFORMATION AND MATURING TEMPERATURES AND CONTROLLING TEXTURE

There are three methods by which the deformation temperature and maturing temperature of the glaze may be reduced and the glaze texture controlled. Eighteen different series were made with the different clay-whiting *LD* members, using these methods. However, for the purpose of illustrating the three methods, and to avoid unneces-

¹¹ A. I. Andrews, Ceramic Tests and Calculations, pp. 130-139 (John Wiley & Sons, Inc., New York, N. Y., 1928).

sary repetition, the results of only four of the series are reported. The three methods employed are described as follows:

Method 1. By addition of the flux, in regular steps, to the *LD* member (table 6).

Method 2. By substituting for part of the whiting, on an equal weight basis, a flux producing a lower melting temperature (table 7). Also, by substituting flint, on an equal weight basis, for part of the clay to control texture, such as the conversion of a mat to a bright glaze (table 8).

Method 3. By substitution of one flux for another on the basis of combining weight equivalents (table 9).

4. PREPARATION OF THE DEFORMATION AND GLAZE TRIALS

The several clay-flux deformation series were made by preparing the two end members of each series and blending the proper dry-weight proportions of the corresponding end members to produce 150 g for each intermediate member. The end members were made by weighing the materials in proper proportions, grinding them separately in ball mills for 2 hours with sufficient water to form free-flowing slips, passing the slips thus formed through a 150-mesh sieve, allowing the slips to settle overnight, decanting the supernatant water, drying at about 95° to 100°C, and crushing the dry material to powder in a mortar.

Table 4 gives the general method of forming the intermediate members of a series. The weighed materials for each member were placed in a beaker and about 100 cm³ of water added, the materials thoroughly stirred, the slips thus formed passed through a 150-mesh sieve and dried to a stiff plastic condition in plaster of paris cups.

The different members of each glaze series were prepared in the same manner as described for the members of the clay-flux deformation series, except that 400 g of material were provided for each glaze member, to which 240 to 250 cm³ of water (about ½ pint) were added. After thorough stirring and sieving, the slips thus formed were ready for application to the glaze trial pieces.

TABLE 4.—Method of blending the end members to form the intermediate members of a series

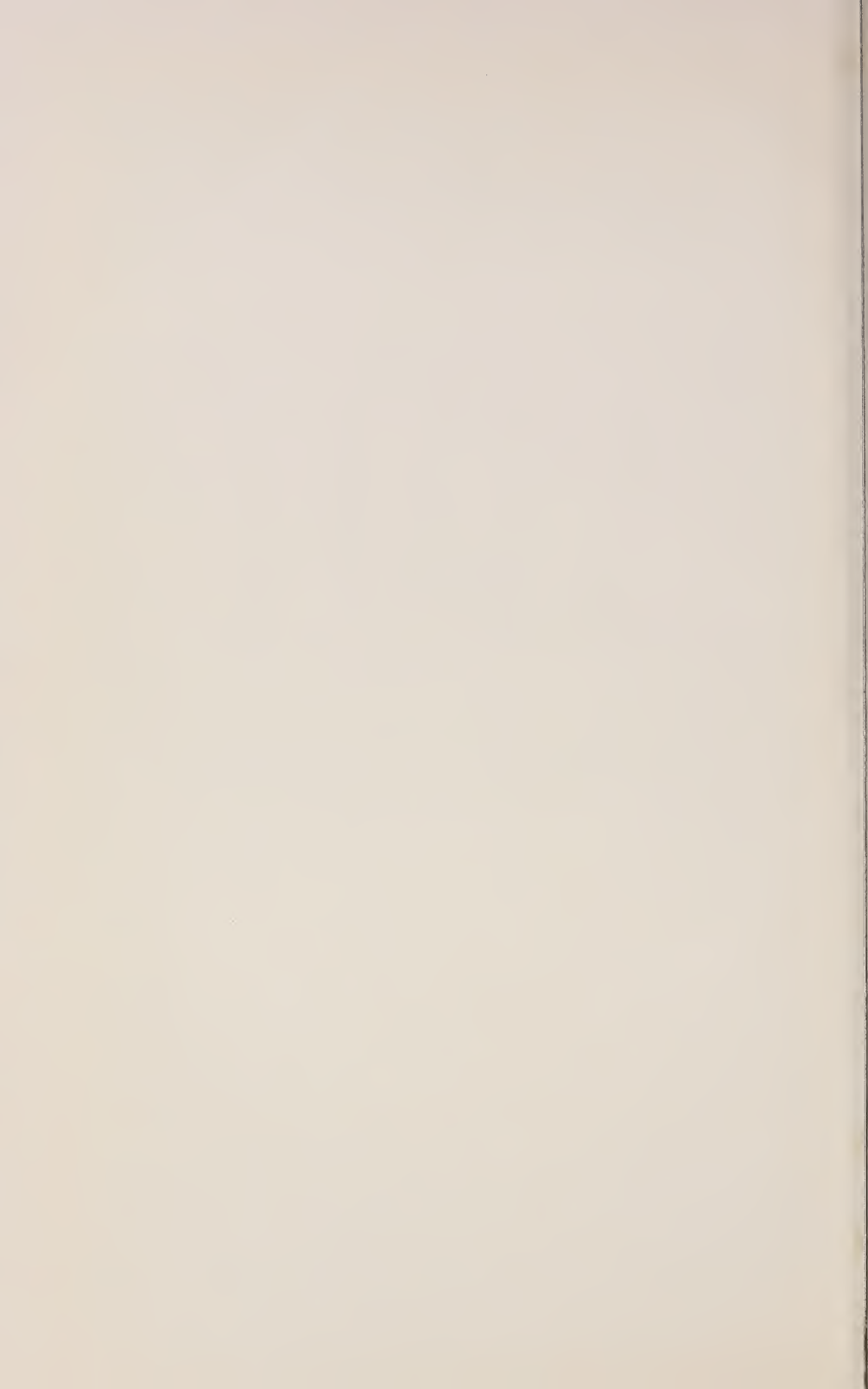
Member	Weight of end members 1 and 6 to produce members 1 to 6, inclusive		Composition		Member	Weight of end members 1 and 6 to produce members 1 to 6, inclusive		Composition	
	No. 1	No. 6	Clay	Whiting		No. 1	No. 6	Clay	Whiting
1.....	150	0	76	24	4.....	60	90	70	30
2.....	120	30	74	26	5.....	30	120	68	32
3.....	90	60	72	28	6.....	0	150	66	34

(a) FORMING THE DEFORMATION TEST SPECIMENS

The clay-flux deformation test specimens were made in the form of "tetrahedral cones" by moistening the plastic material with a few drops of gum tragacanth and pressing the material in a mold, thus forming cones 1¼ in. high with triangular bases of ¼ in. sides. The cones of each series when dry were set in a fire-clay plaque, as shown in figure 1, for determination of the deformation temperatures.



FIGURE 1.—Arrangement of specimens for determination of deformation temperatures.



(b) FORMING THE GLAZE TRIALS AND APPLYING THE GLAZE

Two different sizes of trial pieces to which the glazes were applied were made from each of the eight clays (table 1). For the earlier tests, tiles $\frac{1}{2}$ by 2 by $3\frac{3}{4}$ in. were hand-pressed from the clay in the stiff-mud condition. Later, when a laboratory-size deairing auger machine became available, the clay was deaired under a pressure of approximately $\frac{1}{15}$ atmosphere,¹² extruded from a $\frac{1}{2}$ - by $2\frac{3}{4}$ -in. die, and the column thus formed cut into 8-in. lengths.

The glazes were applied to the tiles immediately after they were formed, by spraying on a layer of glaze material approximately 0.03 to 0.04 in. in depth. The tiles were then dried to a leather-hard condition under paper at laboratory temperature to prevent uneven drying and warping, and the drying was completed in an oven at 90° to 100° C.

5. HEAT TREATMENT OF THE TRIALS**(a) DETERMINATION OF THE DEFORMATION TEMPERATURES**

The deformation temperatures of the cone specimens were determined by heating them in an electrical resistance furnace. The current was regulated to produce a temperature of about 1,000° C overnight, after which the temperature rise was maintained at approximately 30° C per hour.

Temperatures were determined by means of a potentiometer and a platinum-10-percent rhodium thermocouple. The temperature reading, taken with the junction of the thermocouple close to the base of the cone specimen as it began to deform, was considered as the deformation temperature when the specimen had softened and deformed so that its tip just touched the plaque. When two cones deformed within an interval of about 2 minutes, they were arbitrarily assumed to have deformation temperatures differing by 1° C.¹³

(b) KILN TREATMENT OF THE GLAZE TRIALS

Where coal or coke is used for firing the kiln, it is essential that the glazes be protected from direct contact with the kiln atmosphere to prevent injury which may result from fine ash dust. A method of setting brick in benches in which the glazed surfaces are protected by "boxing in," so that only the backs or other unglazed portions of the brick are exposed directly to the kiln atmosphere, has been described by R. T. Stull.¹⁴

In this study the glaze trials were heated either in a gas or an electrically heated kiln and, since injury to the glazes from ash dust was not a factor, the trials were set "open fire"—that is, they were neither contained in saggars nor boxed in. The color trials (see table 19) were heated in the electrically heated tunnel kiln¹⁵ designed by R. F. Geller, and all other glaze trials were heated in a gas-fired kiln.

The gas-fired kiln was operated under oxidizing conditions to produce a clear kiln atmosphere, an important factor in the development of glazes of the type under investigation. Six different firings of the kiln were made. The time-temperature rate of heating was practically

¹² In the plant this would be called deairing under evacuation of 28 in. of mercury.

¹³ Approximate deformation temperatures may be determined by comparison with standard pyrometric cones in any suitable kiln or furnace.

¹⁴ *Notes on the manufacture of enamel brick with some investigations on enamel brick slips*, Trans. Am. Ceram. Soc. 12, 721-2 (1910).

¹⁵ *Some factors affecting the properties of ceramic talcose whiteware*, J. Research NBS 26, 216 (1941) RP1371.

the same up to the desired pyrometric-cone temperature for each firing and, when the cone began to deform, the gas burners were regulated to hold the temperature substantially constant for about 2 to 3

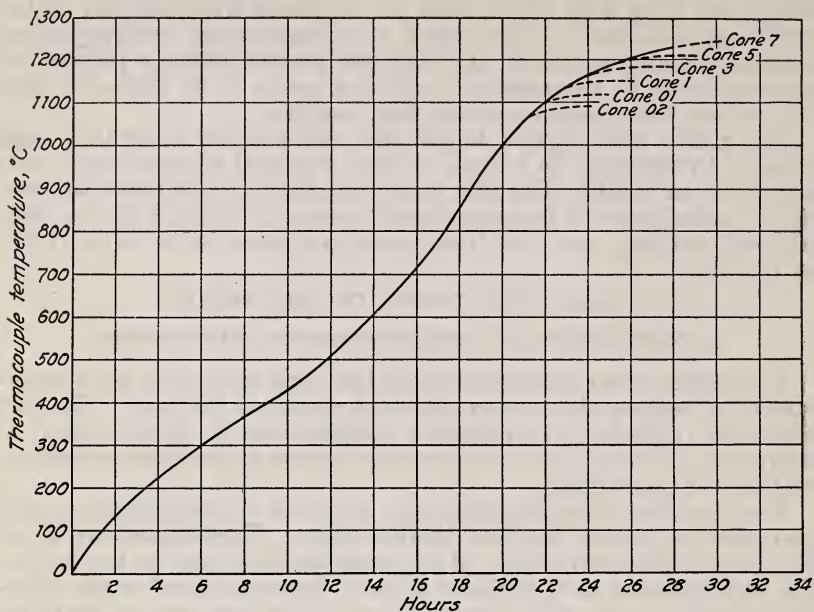


FIGURE 2.—Time-temperature relation for heating the gas-fired kiln.

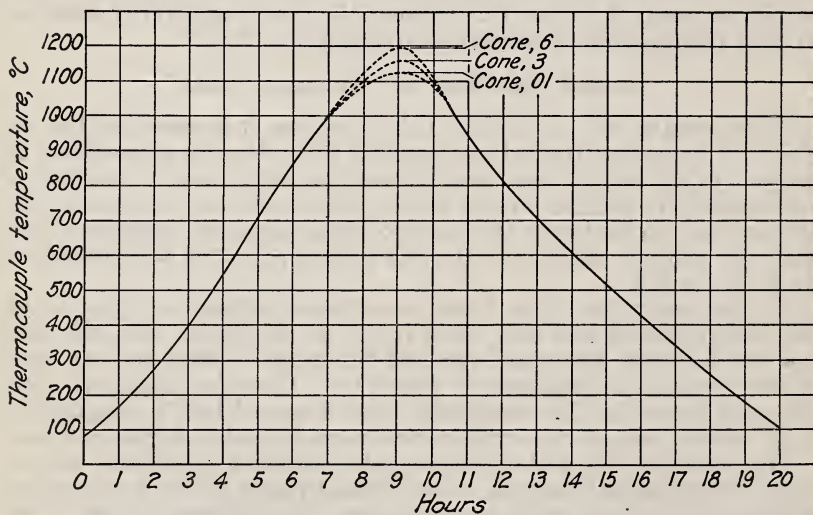


FIGURE 3.—Time-temperature relation for heating the electrically heated tunnel kiln.

hours. The burners were then shut off and the kiln allowed to cool for about 36 hours. The pyrometric cones to which the six different firings were made and the time-temperature graphs up to the time the burners were shut off are indicated in figure 2.

The color trials were developed at heats corresponding to pyrometric cones 01, 3, and 6 in the electrically heated tunnel kiln,¹⁶ which was operated on a schedule of 20 hours for the heating and cooling for all three heat treatments. The time-temperature graphs are shown in figure 3.

IV. RESULTS, DISCUSSION, AND CONCLUSIONS

1. DEFORMATION TEMPERATURES OF CLAY-WHITING COMPOSITIONS

Compositions of the different clay and whitening mixtures are plotted against their respective deformation temperatures in figure 4, and

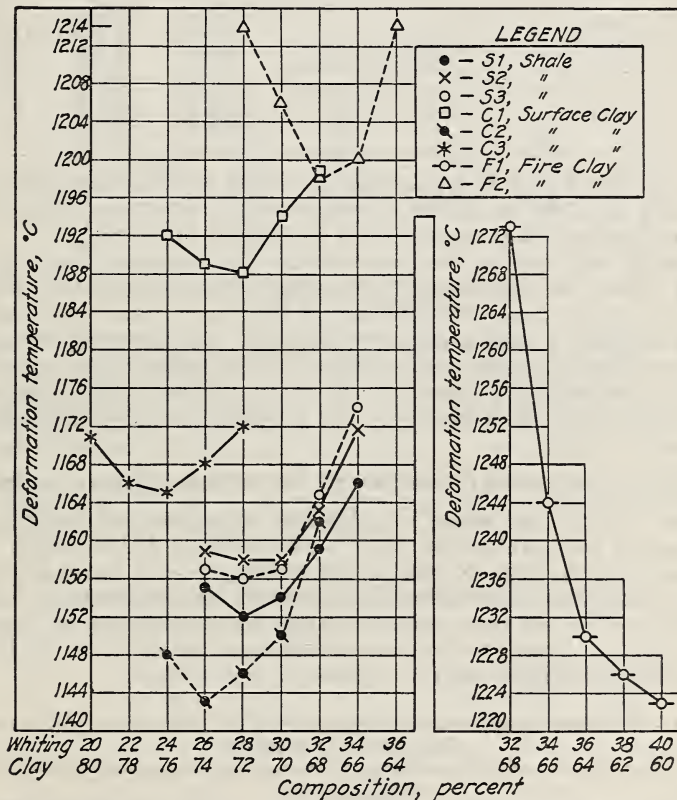


FIGURE 4.—Relation between clay-whitening compositions and their deformation temperatures.

their range in *LD* compositions and deformation temperatures are given in table 5.

Even though clays *S1*, *S2*, and *S3* came from widely different localities, the differences in their chemical compositions, *Rm* values (table 1), and *LD* compositions are small. The whitening contents of

¹⁶ When the color glaze trials were ready for the kiln treatment, the electrically heated tunnel kiln was in operation in connection with another investigation. The opportunity was taken to save both time and fuel by putting the color trials through this kiln.

their *LD* members all occur within the range of 26 to 30 percent, and their deformation temperatures range from 1,152° to 1,159° C.

Clays *C1*, *C2*, and *C3*, when compared with the *S* clays, show a greater spread in their *LD* compositions and deformation temperatures. The *LD* members for the *C* clays range in whiting content from about 22 to 26 percent for *C3*, to 24 to 28 percent for *C1*, and their deformation temperatures from 1,143° to 1,192° C, a difference of 49° C.

TABLE 5.—Ranges within which clay-whiting lowest deformation (*LD*) member compositions occur and their deformation temperatures

Clay	Clay	Whiting	Deformation range
	Percent	Percent	° C
<i>S1</i>	74 to 70	26 to 30	1,152 to 1,155
<i>S2</i>	74 to 70	26 to 30	1,158 to 1,159
<i>S3</i>	74 to 70	26 to 30	1,156 to 1,157
<i>C1</i>	76 to 72	24 to 28	1,188 to 1,192
<i>C2</i>	76 to 72	24 to 28	1,143 to 1,148
<i>C3</i>	78 to 74	22 to 26	1,165 to 1,168
<i>F1</i>	Below 60	Above 40	Below 1,220
<i>F2</i>	68 to 66	32 to 34	1,198 to 1,200

The *LD* member of *F2* was obtained with 32 to 34 percent of whiting, deforming at 1,198° to 1,200° C, whereas that of *F1* was approached but not obtained up to a content of 40 percent of whiting.

Although any one of the clay-whiting *LD* members forms a good glaze if heated to the proper temperature, that temperature may be too high for the best development of the clay product to which the glaze is applied. Such a glaze composition can, however, be applied to some other clay product of sufficiently high refractivity to meet the maturing-temperature requirement of the glaze, or the maturing temperature may be lowered by the introduction of suitable fluxing material.

(a) EFFECT OF ADDITIONS OF GALENA TO THE *S2* CLAY-WHITING *LD* MEMBER

Table 6 gives the effect of additions of galena on lowering the deformation temperature of the *S2* clay-whiting *LD* member. The addition of 47.0 parts of galena by weight to 53.0 parts of *S2-16*, forming the composition *S2-26*, has lowered the deformation temperature by 84° C, or from approximately the equivalent of cone 3+ to cone 03—. Since the *Rm* value of all members of the series is 5.00, it is evident that they can form glazes of mat texture.

TABLE 6.—Influence on deformation temperature of *S2* clay-whiting *LD* member by direct additions of galena

Glaze	Composition			<i>Rm</i> value	Deformation temperature	Pyrometric-cone equivalent
	Clay <i>S2</i>	Whiting (CaCO ₃)	Galena (PbS)			
	Parts	Parts	Parts		° C	Cone
<i>S2-16</i>	37.0	16.0	0	5.00	1,158	3+
<i>S2-19</i>	37.0	16.0	5.0	5.00	1,138	2+
<i>S2-20</i>	37.0	16.0	11.0	5.00	1,130	1+
<i>S2-21</i>	37.0	16.0	17.0	5.00	1,115	1+
<i>S2-22</i>	37.0	16.0	23.0	5.00	1,094	02
<i>S2-23</i>	37.0	16.0	29.0	5.00	1,088	03+
<i>S2-24</i>	37.0	16.0	35.0	5.00	1,086	03+
<i>S2-25</i>	37.0	16.0	41.0	5.00	1,077	03—
<i>S2-26</i>	37.0	16.0	47.0	5.00	1,074	03—

(b) EFFECT OF REPLACEMENT OF PART OF THE WHITING BY ZINC OXIDE ON THE C2 CLAY-WHITING LD MEMBER

Table 7 gives the effect obtained on the deformation temperature by replacement of part of the whiting by zinc oxide. The deformation temperature of C2-2 has been reduced from 1,144° C (cone 3) to 1,117° C (cone 01+) by the substitution of 6 parts zinc oxide for 6 of whiting. The *Rm* value is 7.87 for all members of the series; therefore their compositions are within the limits for the production of bright glazes.

TABLE 7.—Influence on deformation temperature of C2 clay-whiting LD member by replacement of part of the whiting by zinc oxide

Glaze	Composition			<i>Rm</i> value	Deformation temperature	Pyrometric-cone equivalent
	Clay C2	Whiting (CaCO ₃)	Zinc oxide (ZnO)			
	<i>Parts</i>	<i>Parts</i>	<i>Parts</i>		° C	<i>Cone</i>
C2-2.....	74.0	26.0	0	7.87	1,144	3
C2-7.....	74.0	25.0	1.0	7.87	1,142	3-
C2-8.....	74.0	24.0	2.0	7.87	1,133	2
C2-9.....	74.0	23.0	3.0	7.87	1,124	1
C2-10.....	74.0	22.0	4.0	7.87	1,122	1-
C2-11.....	74.0	21.0	5.0	7.87	1,121	1-
C2-12.....	74.0	20.0	6.0	7.87	1,117	01+

(c) EFFECT OF REPLACEMENT OF PART OF THE CLAY BY FLINT ON THE S1 CLAY-WHITING LD MEMBER

The influence on the deformation temperature and glaze texture of the S1 clay-whiting LD member by the replacements of part of the clay by flint is shown in table 8. The temperature has been lowered from 1,156° C (cone 4-) to 1,150° C (cone 3+) by a 15-percent replacement, then increased again to 1,156° C by a 25-percent replacement. The increase in silica by the flint has increased the *Rm* value from 5.21 in S1-6 to 10.11 in S1-17, and has changed the glaze texture from mat through semimat to bright.

TABLE 8.—Influence on deformation temperature and glaze texture of the S1 clay-whiting LD member by replacement of part of the clay by flint

Glaze	Composition			<i>Rm</i> value	Deformation temperature	Pyrometric-cone equivalent	Texture
	Clay S1	Whiting (CaCO ₃)	Potter's flint (SiO ₂)				
	<i>Parts</i>	<i>Parts</i>	<i>Parts</i>		° C	<i>Cone</i>	
S1-6.....	70.0	30.0	0	5.21	1,156	4-	Mat.
S1-13.....	65.0	30.0	5.0	5.89	1,154	3+	Semimat.
S1-14.....	60.0	30.0	10.0	6.68	1,153	3+	Bright.
S1-15.....	55.0	30.0	15.0	7.62	1,150	3+	Do.
S1-16.....	50.0	30.0	20.0	8.74	1,151	3+	Do.
S1-17.....	45.0	30.0	25.0	10.11	1,156	4-	Do.

(d) EFFECT ON THE C3 CLAY-WHITING LD MEMBER BY EQUIVALENT COMBINING, WEIGHT SUBSTITUTIONS OF PbO IN LEAD-SILICA FRIT FOR CaO IN WHITING

In table 9 are given the results of substituting lead-silica frit for part of the whiting of the C3 clay-whiting LD composition on the basis of molecular equivalents of PbO and CaO (see table 10). Table 9 indicates that the substitution of 36.8 parts, by weight, of lead-silica

frit for 14 of whiting (columns 3 and 4) has lowered the deformation temperature from 1,179° to 1,068°C, or from about cone 5 to cone 04+. The silica content of the glaze has been increased by the silica in the lead-silica frit, thus increasing the *Rm* value from 8.66 to 9.54 (column 5, table 9). The *Rm* values indicate that the members all fall within limits for bright glazes.

TABLE 9.—Influence on deformation temperature of the C3 clay-whiting LD member by substitution of lead-silica frit for part of the whiting on an equivalent combining-weight basis (see table 10)

Glaze	Composition			<i>Rm</i> value	Deformation temperature vertically °C	Pyrometric-cone equivalent
	Clay C3	Whiting (CaCO ₃)	Lead-silica frit			
	Parts	Parts	Parts			
C3-11.....	74.0	26.0	0	8.66	1,179	5
C3-20.....	74.0	24.0	5.3	8.79	1,170	4+
C3-21.....	74.0	22.0	10.5	8.91	1,158	4-
C3-22.....	74.0	20.0	18.8	9.04	1,153	3+
C3-23.....	74.0	18.0	21.1	9.16	1,146	3
C3-24.....	74.0	16.0	26.3	9.29	1,128	1+
C3-25.....	74.0	14.0	31.6	9.41	1,100	02+
C3-25.....	74.0	12.0	36.8	9.54	1,068	04+

TABLE 10.—Equivalent or combining weights of several fluxes expressed in proportion to unit weight for each different flux ^a

Row	Whiting (CaCO ₃)	Galena (PbS)	Lead-silica frit (3PbO:2SiO ₂)	Colemanite	Frit ^b substitute	Zinc oxide (ZnO)	Magnesium carbonate (MgCO ₃)	Barium carbonate (BaCO ₃)	Red lead (Pb ₂ O ₄)
1.....	1.00	2.39	2.63	1.87	1.36	0.81	0.84	1.97	2.28
2.....	0.42	1.00	1.10	0.78	0.57	.34	.35	0.82	0.96
3.....	.38	0.91	1.00	.71	.52	.31	.32	.75	.87
4.....	.53	1.28	1.41	1.00	.73	.43	.45	1.05	1.22
5.....	.73	1.75	1.93	1.37	1.00	.60	.62	1.45	1.67
6.....	1.23	2.94	3.23	2.30	1.68	1.00	1.04	2.42	2.81
7.....	1.19	2.84	3.12	2.22	1.62	0.97	1.00	2.34	2.71
8.....	0.51	1.21	1.33	0.95	0.69	.41	0.43	1.00	1.16
9.....	.44	1.05	1.15	.82	.60	.36	.37	0.86	1.00

^a Use of the table for determining the amount of a flux to be substituted for that of another is illustrated by the following concrete examples:

1. To replace 20 parts of whiting of a glaze by lead-silica frit: Row 1 of the table shows that the combining weight of lead-silica frit is in the proportion of 2.63 to 1.00 of whiting. Then $20 \times 2.63 = 52.6$ parts of lead-silica frit are required.
2. In a similar manner, if 20 parts of colemanite are to be replaced by frit substitute, then in row 4 of the table it is seen that the combining weight of frit substitute is in the proportion of 0.73 to 1.00 of colemanite. Therefore, $20 \times 0.73 = 14.6$ parts of frit substitute are required.

By the same method, any one flux may be substituted for another.

^b See table 3.

2. GLAZES OF GOOD TEXTURE SUBSTANTIALLY FREE FROM DEFECTS

Tables 11 to 18, inclusive, which list a total of 45 glazes matured in the gas-fired kiln, give the results obtained for the 8 glaze groups applied to the 8 clays investigated. Table 19, which lists 26 colored glazes matured in the electrically heated tunnel kiln, includes some of the more pleasing colors obtained without adding coloring material and also some colors obtained by adding coloring material to the glaze compositions. All glazes reported in tables 11 to 19, inclusive, were

of good quality and substantially free from defects. They all withstood the autoclave test for crazing,¹⁷ showing no signs of failure. When examined after storage in the laboratory for more than a year after the autoclave test, they showed no evidence of crazing, spalling, or other defects.

TABLE 11.—Glazes applied to S1 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition						Texture
		Clay S1	Whiting	Galena	Flint	Colemanite	Lead-silica frit	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
G1	3	72.0	28.0	0	0	0	0	Mat.
G2	3	52.8	23.0	24.2	0	0	0	Do.
G3	3	37.0	16.0	47.0	0	0	0	Do.
G4	3	54.0	29.0	0	17.0	0	0	Bright.
G5	3	51.0	21.6	0	16.0	11.4	0	Do.
G6	3	48.2	15.2	0	15.2	21.4	0	Do.
G7	01	35.3	13.7	51.0	0	0	0	Mat.
G8	01	52.4	20.2	0	0	27.4	0	Do.
G9	01	31.8	12.4	45.8	10.0	0	0	Bright.
G10	01	45.0	17.5	0	14.2	23.3	0	Do.
G11	02	35.3	13.7	0	5.2	0	45.8	Do.

TABLE 12.—Glazes applied to S2 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition						Texture
		Clay S2	Whiting	Galena	Flint	Colemanite	Lead-silica frit	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
H1	5	72.0	28.0	0	0	0	0	Mat.
H2	5	52.8	23.0	24.2	0	0	0	Do.
H3	5	37.0	16.0	47.0	0	0	0	Do.
H4	5	55.0	28.0	0	17.0	0	0	Bright.
H5	3	45.6	19.8	0	12.4	0	22.2	Do.
H6	1	39.8	17.2	0	8.6	0	34.4	Do.
H7	01	34.2	14.8	51.0	0	0	0	Mat.
H8	01	59.6	12.3	0	0	28.1	0	Seminat.
H9	01	30.3	13.1	45.1	11.5	0	0	Bright.
H10	01	49.3	10.1	0	17.4	23.2	0	Do.

TABLE 13.—Glazes applied to S3 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition						Texture
		Clay S3	Whiting	Galena	Flint	Colemanite	Lead-silica frit	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
J1	5	72.0	28.0	0	0	0	0	Mat.
J2	3 and 5	52.8	23.0	24.2	0	0	0	Do.
J3	3 and 5	52.0	28.0	0	20.0	0	0	Bright.
J5	3 and 5	44.0	19.0	20.4	16.6	0	0	Do.
J7	01	50.3	19.6	30.1	0	0	0	Mat.
J10	01	49.7	19.3	0	12.4	12.4	0	Bright.
J11	01	44.7	17.4	0	13.1	0	24.8	Do.

¹⁷ Resistance to crazing (autoclave test), Am. Soc. Testing Materials, Standards, pt. 2, 928-929 (1939).

TABLE 14.—Glazes applied to C1 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition			Texture
		Clay C1	Whiting	Galena	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
N4.....	7	72.0	28.0	0	Bright.
N5.....	5	63.2	24.5	12.3	Do.
N6.....	3 and 5	58.1	22.6	19.3	Do.

TABLE 15.—Glazes applied to C2 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition					Texture
		Clay C2	Clay F1	Whiting	Galena	Lead-silica frit	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
P1.....	5	21.2	18.8	15.6	44.4	0	Bright.
P2.....	5	17.2	15.4	12.8	54.6	0	Do.
P3.....	01	14.6	13.2	10.8	61.4	0	Do.
P4.....	5	72.0	0	28.0	0	0	Do.
P5.....	3	53.0	0	20.6	0	26.4	Do.
P6.....	1	44.0	0	17.0	0	39.0	Do.

TABLE 16.—Glazes applied to C3 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition			Texture
		Clay C3	Whiting	Colemanite	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
M4.....	7	74.0	26.0	0	Bright.
M5.....	5 and 7	71.2	21.1	7.7	Do.
M6.....	5	70.0	18.8	11.2	Do.

TABLE 17.—Glazes applied to F1 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition				Texture
		Clay F1	Whiting	Flint	Colemanite	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
K4.....	7	42.0	26.0	32.0	0	Bright.
K5.....	5 and 7	38.9	24.1	29.6	7.4	Do.
K6.....	5 and 7	37.5	23.2	28.6	10.7	Do.

TABLE 18.—Glazes applied to F2 clay tile which were good when heated at the pyrometric-cone equivalent indicated

Glaze	Pyrometric-cone equivalent	Composition				Texture
		Clay F2	Whiting	Flint	Lead-silica frit	
	<i>Cone</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
L5.....	5	35.0	24.0	18.0	23.0	Bright.
L6.....	3 and 4	31.7	22.5	16.2	29.6	Do.

TABLE 19.—Compositions, heating temperatures (pyrometric-cone equivalent), and textures of glazes, and colors of glazed tile

Glaze	Pyro-metric-cone equivalent	Clay ^a	Clay	White- ing (CaCO ₃)	Col- e-manite	Flint (SiO ₂)	Lead- silica frit	Man- ganese oxide (MnO ₂)	Cop- per oxide (CuO)	Cobalt oxide (CoO)	Tin oxide (SnO ₂)	Zinc oxide (ZnO)	Ura- nium oxide (UO ₂)	Iron oxide (Fe ₂ O ₃)	Rutile (TiO ₂)	Chrome tin stain ^b	Texture	Color
H8	01	S2	59.6	2.3	28.1	5.5	46.4									%	Mat.	Gray green.
H11	01	S2	33.6	14.5	15.3	13.1	24.8									%	Bright.	Light brown. ^e
J8	01	S2	61.0	23.7	17.4	39.0										%	Semimat.	Light gray green.
J11	01	S2	44.7	17.0	3.0											%	Bright.	Dark chocolate. ^e
P6	01	C2	44.0	17.0	3.0											%	Mat.	Dark brown. ^e
H12	03	S2	69.6	26.5	3.0			1.0								%	Bright.	Olive green.
H12A	3	S2	68.9	26.2	3.0											%	do.	Dark brown.
H15	3	S2	68.9	26.5	3.9	15.7										%	Bright.	Dark greenish brown. ^e
J15	3	S2	67.6	26.5	3.9					1.0						%	Mat.	Green.
J15A	3	S2	67.0	26.2	3.8											%	do.	Blue green.
J15B	3	S2	49.0	26.5	3.9	18.6										%	Bright.	Brown. ^e
J15C	3	S2	48.0	26.0	3.9	18.1					10.2					%	Semimat.	Light brown.
F10	3	S2	50.0	26.4	5.1	14.3										%	Mat.	Dark ecru.
L8D	3	C2	69.0	27.0	4.0											%	Bright.	Dark brown. ^e
L10A	6	F2	60.0	19.0	17.5	16.1		1.9								%	Mat.	Dark green.
L10B	6	F2	47.6	15.4	11.4	23.3										%	Bright.	Light brown.
L10R	6	F2	44.2	14.7	11.1	21.2										%	Mat.	Dark ecru.
N4-7	6	CI	65.4	25.5	9.1											%	do.	Dark brown. ^e
N4-12	6	CI	62.6	24.4	8.9					1.8						%	do.	Dark blue. ^e
N4-7A	6	CI	64.3	25.0	8.9					4.2						%	do.	Black.
N4-12E	6	CI	61.4	23.8	8.5											%	do.	Light yellow.
N4-12B	6	CI	57.6	22.4	8.0											%	do.	Light brown. ^e
N4-12C	6	CI	61.0	23.8	8.5											%	do.	Green. ^e
N4-12F	6	CI	60.4	23.6	8.4											%	do.	Green. ^e
N4-12K	6	CI	52.9	20.8	7.4											%	do.	Chrome-tin red.

^a Clay used in the glaze composition and also used in making the tile to which the glaze was applied.

^b Batch composition, chrome-tin stain: Whiting (CaCO₃), 46.5 percent; lead chromate (PbCrO₄), 10.0 percent; flint (SiO₂), 12.4 percent; tin oxide (SnO₂), 31.1 percent. The batch was mixed dry by ball-mill grinding for 1 hour, calcined in a sagger to cone 2, and then reduced to a powder by 2 hours ball-mill grinding.

^c Glaze more or less transparent. The apparent color results from a combination of the true glaze color and the reflected color from the contact surface of the tile and glaze.

3. CONCLUSIONS

The results obtained in this investigation of low-cost glazes for structural clay products indicate that shales, surface clays, and low-refractory fire clays can be used successfully as constituents of glaze compositions. Both mat and bright glazes were produced which were substantially free from defects and which withstood the auto-clave test for crazing without showing signs of failure.

Considering the shales, surface clays, and fire clays as three distinct groups, good glazes were obtained with the three shales within the pyrometric-cone temperature range of 02 to 5; with the three surface clays, from 1 to 7; and with the two fire clays, from 3 to 7.

Shales, surface clays, and low-refractory fire clays can be used for glaze-making purposes because of their low refractory values due to their natural content of fluxes and to their favorable silica-alumina ratios. In such glazes these clays can displace the white-burning clays and feldspars, some potter's flint, and part of the fluxes now in general use for glazes applied to structural clay products.

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