ASH GLAZES AND THE EFFECT OF COLORANTS AND FIRING CONDITIONS

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ASH GLAZES AND THE EFFECT OF COLORANTS AND FIRING CONDITIONS

Volume I

Text

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CHAPTER I

INTRODUCTION

The final step or procedure in producing a piece of pottery is that of applying a glaze and firing. It is the glaze that gives a ceramic piece its most dominant characteristic beyond the basic shape. Although there are many types of glazes, they are all basically nothing more than a thin glass-like coating fused to the clay surface of the pot by the heat of the kiln (2, p. 161).

Glazes may be categorized according to Norton in the following four ways: (1) transparency, (2) surface, (3) color, or (4) composition (3, pp. 229 and 230). Although the classifications of glazes vary, all contain certain oxides in common.

To better understand this common basis to all glazes, one should think of a glaze as a completed melt, containing only oxides as they have resulted from the combining and melting of raw materials (4, p. 78). For better communication, it is necessary to set up a method of recording the amount of these oxides found in a specific glaze and to identify which materials will yield these oxides in a given quantity. This is done by means of the empirical formula. "The empirical formula is a method of representing a finished or melted glaze in terms of the relative amounts of the various oxides which are present" (4, p. 78). The empirical formula is used to show the relationship between oxides in a glaze and the organization of the oxides into three specific groups. These groups are known as RO, R_2O_3, and RO_2. Each group contains oxides that perform the same or similar function in the creation of the glaze.

The RO, or base group, acts as the fluxing agent. The middle group, R_2O_3, is chemically neutral and assists in the reaction of RO on RO_2; it does not act as a flux yet it influences the melt of the glaze. RO_2, the acid, contains mainly silica and is the refractory part of the glaze. Although glazes may contain many materials, all the elements will serve one of these three group needs in a glaze.

Although it is possible to calculate precisely the composition of a glaze so that it will meet a specific need, most potters work in a less scientific way. Through the ages, many of the most beautiful glazes have been created in a trial-and-error manner. Some materials contain the necessary glaze-making oxides in varying amounts so that it is not possible to calculate exactly what the glaze will be. One of these materials which may be used to produce outstanding glazes is the ash of various vegetable materials.

The Problem and Its Purpose

The study being undertaken was to ascertain the effect or effects of different firing conditions and colorants on glazes composed of wood ash from two trees indigenous to Texas. The problem was divided into two parts: first, to identify the best mixtures using the selected vegetable ash; second, to alter successful glazes with set percentages of colorants.

The main objective of the study was to evaluate findings resulting from the variation of elements, firing conditions, and colorants used and to select successful glazes.

Experimental Plan

The study was limited in three ways. A limitation was set on the number of raw materials used in producing glazes. Ash, feldspar, and whiting were the raw materials chosen because their component parts are known to produce satisfactory glazes. "A suggested starting point for a stoneware ash glaze test would be 40 parts ash, 40 parts feldspar and 20 parts whiting" (2, p. 167). Of these three ingredients, ash was the basic variant. Both types of wood were collected and reduced to ash by burning in an open pit. "Ashes contain alkaline in more or less soluble form together with silica, alumina, and small percentages of other elements" (5, p. 160). The wood collected for the study was obtained in Denton County and each variety was taken from one tree or one group of trees respectively. This step was taken to insure uniformity of the ash. Ashes vary widely in composition and even the ash from two examples of a given variety of tree will vary, depending on the soil in which they grew (4, p. 188).

The second limitation was set in the different types of ash to be used, mesquite ash and hackberry ash. Another variant was established in the firing conditions with all testing conducted in both oxidation and reduction firings. The third and final limitation was the number of colorants to be added to successful glazes. The colorants chosen were red iron oxide, copper carbonate, cobalt carbonate, vanadium stain, and manganese dioxide.

Definitions

Components--In the introduction to the study it was cited that all glazes have a common basis. This basis being the empirical formula of RO, R_2O_3, and RO_2. The components of feldspar, ash, and whiting combined account for these necessities. Variation of the proportion of the components affects the character of the glaze.

Feldspar is used both as a fluxing agent and for its silica content. Feldspars are considered a cheap source of glaze flux and have the additional advantage of being non-soluble (2, p. 211). The feldspar used in this study was a potassium feldspar with the theoretical formula of K_2O-AL_2O_3-$6SiO_2$; this was purchased locally.

"Whiting, calcium carbonate ($CaCO_3$), is the major high-fire fluxing agent, although it has a minor use in bodies where a small amount will lower vitrification temperature and reduce porosity" (2, p. 218).

Two different wood ashes were employed in this study. Hackberry (Celtis occidentalis) and mesquite (Porsopis glandulosa) were the two plants chosen for the study because both were plentiful in the local area. Hackberry thrives in various regions, but more commonly in rich soil. Its wood is heavy but soft and weak, and decays rapidly when exposed (6, p. 27). Mesquite is found mainly in hilly pastures west of the Trinity River. Mesquite wood is heavy, hard, close-grained, and durable in soil (6, p. 240).

Firing conditions.--In this study all glazes were tested in two firing atmospheres. All glaze samples were fired in both an oxidizing atmosphere and a reduction atmosphere. The oxidation firing was conducted in an electric kiln where the atmosphere was static and neutral. An oxidizing fire is one during which the kiln chamber retains an ample supply of oxygen. For this to take place, the combustion in the fire box of a fuel-burning kiln must be perfectly adjusted. An electric kiln will normally give an oxidizing fire.

Reduction firing was done in a gas kiln. The term reduction fire as used in this study refers to the chemical reaction by which, under great heat, free carbon in the kiln will unite with the oxygen combined in ceramic compounds (2, p. 239).

Both atmospheres mentioned above were used in firing these ash glazes because of the differences that can be obtained. "In oxidation most glazes made with ash will tend to be somewhat tan in color, due to the small amounts of iron normally present in the ash. In reduction the prevailing color will be gray or gray-green" (5, p. 162).

<u>Colorants</u>.--Five colorants were added to the satisfactory base glazes so that the variation might be observed. Red iron oxide (Fe_2O_3) in glazes produces colors ranging from amber through tan to deep red brown or gray to green, depending on the quantity of iron and the atmosphere of the kiln. Between five per cent and ten per cent by weight of iron oxide should be used (1, p. 192). Copper carbonate ($CuCO_3$) has been used since antiquity to produce colors of blue and green in glazes (4, p. 130). In a reduction atmosphere it also produces reds. A suggested amount of copper carbonate to be used would be two per cent by weight. "Cobalt carbonate ($CoCO_3$) is the most stable and reliable glaze colorant. It gives a similar shade of blue in almost all types of glazes and under various firing conditions" (4, p. 131). Cobalt is the most powerful of coloring oxides and for this reason, only one-half of one per cent by weight is needed for color.

Vanadium oxide added to a base glaze will produce a yellow color. Vanadium is usually used in glazes as a stain which is prepared by combining vanadium pentoxide, (V_2O_5), with tin oxide (4, p. 133). Because there is only a small amount of vanadium oxide in vanadium stain, a larger percentage is needed for color. "Five per cent will usually give a weak yellow, and eight to ten per cent, a strong yellow"(4, p. 133).

Manganese gives a brown or purple color to a base glaze. Manganese dioxide (MnO_2), compared to cobalt or copper, is a weak colorant, and 2 or 3 per cent by weight is usually required to give a pronounced color (4, p. 132).

Conclusion

Chapter I has given the reader background information on the formation of glazes and their classifications. The problem undertaken in this study was stated and related information to the problem was defined.

Chapter II will be a step-by-step recording of procedures used in solving the problem. Information, terms, and procedures covered in Chapter I will be directly applied to the problem in Chapter II.

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CHAPTER II

PROCEDURE

Testing in this problem was divided into two steps. Step one was the formulation of compounds excluding colorants and step two was the testing of the satisfactory glaze formulae with the addition of colorants.

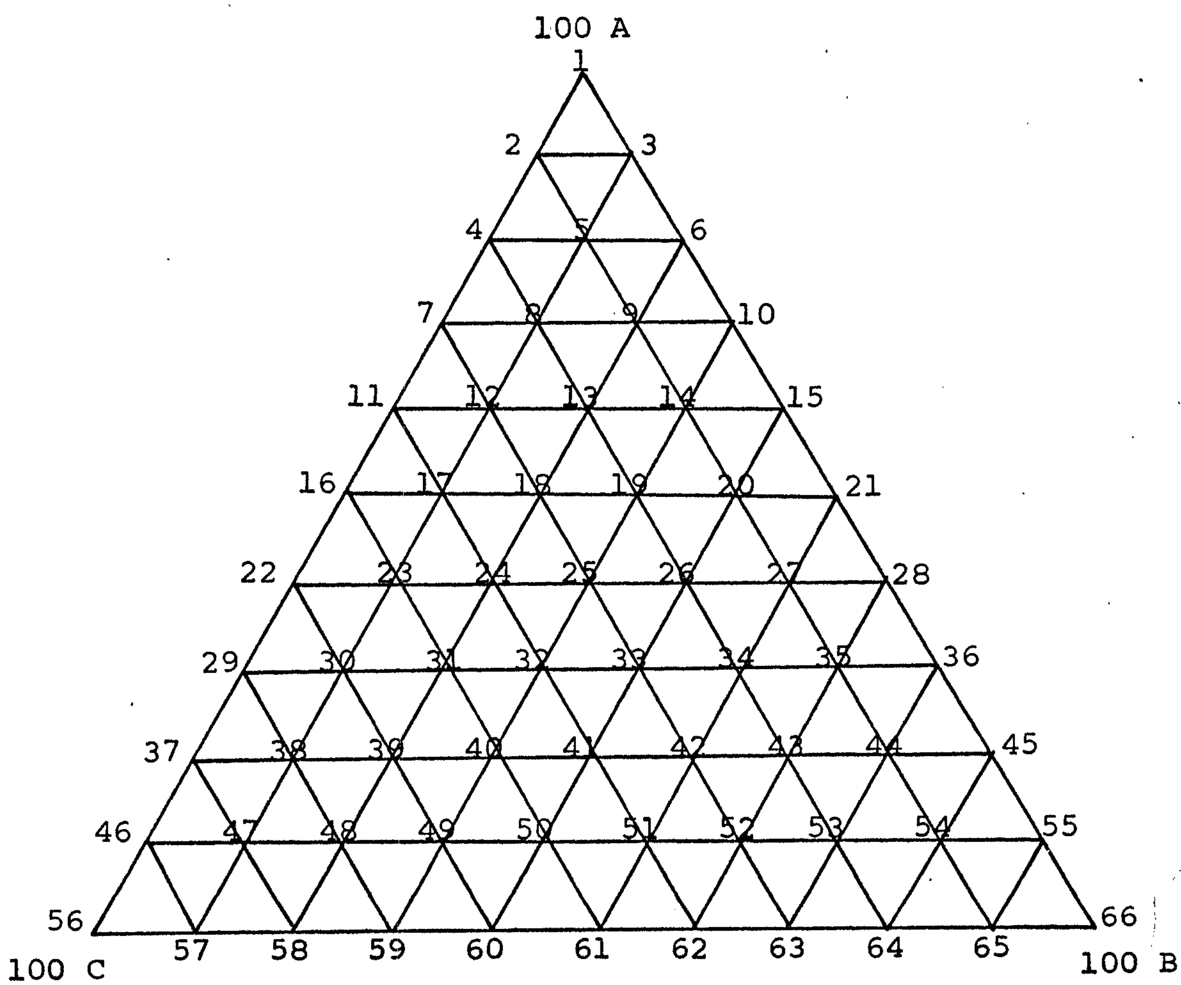
Because the major variant of the study was wood ash, it was necessary first to collect and to process the two different woods. As mentioned in Chapter I, the two woods selected were mesquite (Prosopis glandulosa) and hackberry (Celtis occidentalis). These plants were chosen for two basic reasons: both are indigenous to Texas, and both are readily available in the local area.

Mesquite wood was gathered in Denton County near the city of Lewisville, Texas. Both dead wood and green wood were collected. After gathering, the wood was reduced to ashes by burning in an open pit. The hackberry wood was collected in Denton County in Denton, Texas. Once again, both dead wood and green wood were gathered and reduced to ashes by burning in an open pit.

In processing the ash of each wood, it was decided that neither a washing nor a decanting procedure would be undertaken. This decision was made in consideration of the fact that each washing of an ash removes alkalies and makes the glaze less fusible (3, p. 161). It is possible to use wood ash in a glaze without washing. This unrefined ash often produces a finish with a more mottled and interesting effect than that produced with refined materials because of the particles and unburned matter removed by washing. Both the mesquite and the hackberry ashes were passed through a 30-mesh screen to remove any lumpy or large unburned pieces of material. After this one step of processing, the ash was weighed out directly for the glaze. "The general practice is to first run the dry ash through a very coarse sieve to remove unburned particles. The ash is then soaked in water that is decanted and screened through a 60-100 mesh sieve and dried" (1, p. 167). In this type of processing, the glaze is more likely to be smooth and refined in character.

Tri-Axial Blend Mixtures

The system chosen for determining combinations of the three glaze ingredients was by tri-axial blending of the materials. To calculate the combinations by use of a tri-axial, an equilateral triangle diagram was drawn with points A, B, and C. Each point on the triangle represents 100 grams of one of the materials being used. In this case, A represents ash, B represents feldspar, and C represents whiting. This is shown in Fig. 1. On line A-B of triangle ABC ten equal units were marked off by points. This was also done on lines B-C and C-A respectively. Next, lines were drawn parallel to lines A-B, B-C, and A-C from each of the points crossing at a total of 66 points on and within the boundry of triangle ABC. Each point made by the connecting of lines was given Arabic numbers from 1 through 66, denoting the combinations of the three basic raw materials to be used. In this way A was identified as number 1, B as number 66, and C as number 56.



A--Ash
B--Feldspar
C--Whiting

Fig. 1--Tri-axial blend

As stated, A represents 100 grams of ash, B represents 100 grams of feldspar, and C represents 100 grams of whiting. The midway point of line A-B represents one-half or 50 grams of ash and one-half or 50 grams of feldspar. Other points on line A-B will contain different amounts of ash and feldspar. If a point on line A-B is closer to A than B, it will contain more ash than feldspar, if closer to B than A, it will contain more feldspar than ash. The composition of a point on the inside of triangle ABC will depend on its distance away from the points at the corner. Mixture 26 will contain 20 per cent of whiting since it is eight spaces removed from C, and 40 per cent or grams of feldspar since it is six spaces removed from B. It will also contain 40 per cent or grams of ash since it is six spaces removed from A. Similarly, the composition of any other point in the diagram can be determined (2, p. 137). Because this study covers only those combinations including the raw material ash, combinations 56 through 66 were disregarded because all are on line C-B and contain only feldspar and whiting. (See Fig. 1.).

In Table I, pages 13-14, the numbered mixtures are identified as to gram weight of feldspar, whiting and ash in each combination.

Formulation of Compounds Excluding Color

The next step in preparing the mixtures was to weigh out raw materials for each mixture. These were weighed in grams,

TABLE I

ANALYSIS OF TRI-AXIAL BLEND

Tri-Axial Combination	Feldspar Content	Whiting Content	Ash Content
1			100
2		10	90
3	10		90
4		20	80
5	10	10	80
6	20		80
7		30	70
8	10	20	70
9	20	10	70
10	30		70
11		40	60
12	10	30	60
13	20	20	60
14	30	10	60
15	40		60
16		50	50
17	10	40	50
18	20	30	50
19	30	20	50
20	40	10	50
21	50		50
22		60	40
23	10	50	40
24	20	40	40
25	30	30	40
26	40	20	40
27	50	10	40
28	60		40
29		70	30
30	10	60	30
31	20	50	30
32	30	40	30
33	40	30	30
34	50	20	30
35	60	10	30
36	70		30
37		80	20
38	10	70	20
39	20	60	20
40	30	50	20
41	40	40	20
42	50	30	20
43	60	20	20

TABLE I--Continued

Tri-Axial Combination	Feldspar Content	Whiting Content	Ash Content
44	70	10	20
45	80		20
46		90	10
47	10	80	10
48	20	70	10
49	30	60	10
50	40	50	10
51	50	40	10
52	60	30	10
53	70	20	10
54	80	10	10
55	90		10
56		100	
57	10	90	
58	20	80	
59	30	70	
60	40	60	
61	50	50	
62	60	40	
63	70	30	
64	80	20	
65	90	10	
66	100		

mixed, and placed in plastic bags until applied to the test tiles. The mixtures were identified with numbers 1 through 55 in relation to their position in the tri-axial. The percentages used could represent any measured weight; in this study one gram was used to represent one per cent.

After weighing and combining the mixtures, two test tiles were made for each combination. Test tiles were made of stoneware clay since successful glazes would later be used for stoneware pottery. Each test tile was cut approximately 1½" by 2" in measurement, numbered 1 through 55 by scratching with a dissecting needle, and fired to cone 09 (930° Centigrade or 1706° Fahrenheit). Each test tile was also coded according to the ash used, either hackberry or mesquite, and the firing atmosphere in which it was tested. The letter C designated hackberry, M designated mesquite, O designated oxidation, and R designated reduction. Because each combination was to be tested in both oxidation and reduction firings, the total number of test tiles made for this first test was 220 as follows: 55 tiles using mesquite in a reduction atmosphere, 55 tiles using hackberry in a reduction atmosphere, 55 tiles using mesquite in an oxidation atmosphere, and 55 tiles using hackberry in an oxidation atmosphere.

Each mixture from the tri-axial blend was then applied to two test tiles, one for oxidation firing and one for reduction firing. In mixing each combination for application, water was added to the dry material until a thick, creamy consistency was reached. The mixture was then applied to each of two bisque test tiles identified with the mixture number. One group of test tiles numbered 1MR through 55MR were then fired in a reduction atmosphere and one group numbered 1MO through 55MO were fired in an oxidation atmosphere. This same process was used with mixtures containing hackberry ash. One group of test tiles numbered 1CR through 55CR was fired in the gas kiln and one group numbered 1CO through 55CO was fired in the electric kiln. Mixtures were fired to cone 9 (1250° Centigrade or 2282° Fahrenheit).

Mixtures proving satisfactory as a glaze will be evaluated in Chapter III. At this point in the experiment, mixtures which did not prove satisfactory as a glaze were discarded and only those proving useful were tested with colorants.

Satisfactory Glazes with Colorants Added

One hundred grams of each of the twenty acceptable mixtures were then weighed out. When thoroughly mixed, each sample was divided into five smaller samples weighing 20 grams. To each of these 20 gram units was added

1. Red iron oxide--5 per cent or 1. gram
2. Copper carbonate--1 per cent or .2 gram
3. Cobalt carbonate--one-half of 1 per cent or .1 gram
4. Vanadium stain--5 per cent or 1. gram
5. Manganese dioxide--2 per cent or .4 gram

Each 20 gram unit with its colorant was placed in a plastic bag and labeled according to mixture number and the type of ash used. Each colorant was also given a letter for identification as follows:

1. Red iron oxide--V
2. Copper carbonate--W
3. Cobalt carbonate--X
4. Vanadium stain--Y
5. Manganese dioxide--Z

The identification code then consisted of the following:

1. M or C for the ash used
2. Arabic number for the base glaze used
3. O or R for the atmosphere tested in
4. V, W, X, Y, or Z for the colorant added

Each mixture containing colorants was applied to bisque test tiles and tested in both oxidation and reduction atmospheres. The number of tiles needed in this second part of testing was 400. All glazes in this part of the problem were fired to cone 9 (1250° Centigrade or 2282° Fahrenheit).

Summary

In Chapter II the steps in formulation of glaze mixtures using both hackberry and mesquite ashes has been traced. Part one was concerned with finding satisfactory base glazes using only feldspar, ash, and whiting. The second part recorded how each of the twenty acceptable glazes was altered by adding set percentages of five different colorants.

In Chapter III the evaluation of findings from these tests will be discussed and compared.

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CHAPTER III

TESTING RESULTS

As stated in Chapter I, the problem being studied is to formulate satisfactory glazes using ashes from two trees indigenous to Texas. Different colorants were added to these satisfactory glazes and were tested in two firing atmospheres. Early in the study it was evident that a system of combining the raw materials was necessary. The system used was that of a tri-axial blend. From the sixty-six combinations that were produced by the tri-axial, only a small number was deemed acceptable as glazes and their potential qualities tested further.

It was found that the ratio of feldspar to whiting to ash was more important in producing a glaze base than the kind of ash used or the firing atmosphere. Usually, any combination of raw materials that proved useful as a glaze did so in both oxidation and reduction atmospheres and regardless of the type of ash used. The only exceptions were in mixtures 14 and 37. (See Table I)

Mixture 14 proved unsatisfactory as a glaze when the ash used was mesquite and the testing atmosphere oxidizing. Mixture 14 proved satisfactory in both oxidation and reduction atmospheres when the ash used was that of hackberry.

This mixture also proved acceptable as a glaze using mesquite in a reduction atmosphere. The other exception to this basic trend was that of mixture 37. Mixture 37 proved unsatisfactory in both oxidation and reduction firings when mesquite ash was used. It proved acceptable as a glaze in both oxidation and reduction fire when hackberry ash was used. The mixtures that proved satisfactory as base glazes were

10--70 ash, 30 feldspar
14--60 ash, 30 feldspar, 10 whiting
15--60 ash, 40 feldspar,
20--50 ash, 40 feldspar, 10 whiting
21--50 ash, 50 feldspar
27--40 ash, 50 feldspar, 10 whiting
28--40 ash, 60 feldspar
29--30 ash, 70 feldspar
33--30 ash, 40 feldspar, 30 whiting
34--30 ash, 50 feldspar, 20 whiting
35--30 ash, 60 feldspar, 10 whiting
36--30 ash, 70 feldspar
37--20 ash, 80 whiting
42--20 ash, 50 feldspar, 30 whiting
43--20 ash, 60 feldspar, 20 whiting
44--20 ash, 70 feldspar, 10 whiting
51--10 ash, 50 feldspar, 40 whiting
52--10 ash, 60 feldspar, 30 whiting
53--10 ash, 70 feldspar, 20 whiting
54--10 ash, 80 feldspar, 10 whiting

These combinations proved acceptable as base glazes in that they produced satisfactory qualities of a glaze such as hardness, glossiness or mattness of surface, and fit. The mixtures mentioned above possessed one or more of these desirable qualities. Those combinations from the tri-axial blend not mentioned were discarded because they lacked the qualities desired for good base glazes. The combinations that were not considered as possible base glazes usually turned into a crumbly powder on the test tile or had rough, uneven surfaces that appeared underfired at cone 9. Plates I, VI, and XI in Volume II show typical satisfactory mixtures from the tri-axial blend. Of the twenty acceptable base glazes, there were distinctive qualities for both of the ashes used and the atmosphere in which the samples were fired.

Base Glazes in Reduction Firing

"The exact degree of reduction is hard to control, and it is this factor which introduces uncertainty into the process" (3, p. 153). Although the reduction fire is variable and can be uncertain if the potter does not know his kiln and its operation, certain characteristics are common in reduction firing. Most of the qualities obtainable in reduction testing cannot be reached in oxidation firing. The two most important basic colors of glazes obtainable in reduction firing are the copper reds and the gray-green celedons. More important than the colors obtainable from reduction firing however, are the surface qualities. "In surface quality, reduction glazes tend to be softer, more lustrous, and more pleasant to the touch than oxidation glazes, especially when the glaze is mat" (3, p. 155). As mentioned in Chapter I, the prevailing color to be expected in reduction firing of ash glazes is gray or gray-green. Although this fact proved true in this study, there were also instances where the base glazes were ochre, brown, taupe, or white. Approximately one-half of the base glazes were predominately gray or gray-green in color.

Mesquite ash used in base glazes produced more green tones than gray tones. It can be noted in Table II that over one-half of the base glazes tested using mesquite in a reduction atmosphere produced tones of green, gray-green, greenish white, and yellow-green. Although gray-green was the predominant color, some glazes having green tones lacked a gray color. Base glazes with hackberry ash as a raw material tended to have a more dominant gray coloring in reduction than those made with mesquite ash. This gray color ranged from gray and gray-green to gray-white. As recorded in Table II, the gray-toned base glazes employing hackberry in reduction firing were more apt to be speckled than those glazes which were predominantly white or green. These specks, brown in color, appeared more often in hackberry base glazes than in mesquite base glazes. In mesquite glazes, the speckles appeared in approximately one-fourth of the twenty successful base glazes and most often appeared in gray-green or white glazes.

Table II shows that approximately eight to nine base glazes produced colors ranging from milky-white to taupe. As shown in Table I, pages 13 and 14, those glazes producing neutral tones contain from ten to thirty per cent ash, but never more than thirty per cent.. It was also obvious that

TABLE II

ANALYSIS OF BASE GLAZE COLOR

Base Glaze	Ash	Reduction	Oxidation
10	Mesquite	Speckled Gray-Green	Ochre
	Hackberry	Mottled Ochre-Green	Speckled Ochre
14	Mesquite	Gray-Green with Brown Transparency	Unmatured
	Hackberry	Speckled Gray-Green	Mottled Tan-Green
15	Mesquite	Transparent Green over Gray	Ochre
	Hackberry	Gray-Green	Ochre
20	Mesquite	Transparent Green over Gray	Mottled Orange-Ochre
	Hackberry	Greenish-Ochre	Mottled Orange-Ochre
21	Mesquite	Gray-Green	Ochre with Brown Specks
	Hackberry	Gray with Brown Specks	Milky-Tan with Brown Specks
27	Mesquite	Gray-Green	Gray-Ochre
	Hackberry	Gray-Green with Brown Specks	Ochre with Brown Specks
28	Mesquite	Gray-Green with Dark Brown Specks	Milky-White with Brown Specks
	Hackberry	Gray-Green	Milky Gray-White
29	Mesquite	Taupe with Brown Specks	Milky-White with Brown Specks
	Hackberry	Gray-Green	Milky Gray-White
33	Mesquite	Yellow-Green	Dark Ochre
	Hackberry	Gray-Green	Dark Ochre
34	Mesquite	Beige-White with Brown Specks	Light Ochre with Brown Specks
	Hackberry	Gray-Green with Brown Specks	Light Ochre with Brown Specks
35	Mesquite	Gray-Green	Taupe with Brown Specks
	Hackberry	Gray-Green with Brown Specks	Light Ochre with Brown Specks
36	Mesquite	Brownish-Green	Taupe
	Hackberry	Gray-White	Milky-White

TABLE II--Continued

Base Glaze	Ash	Reduction	Oxidation
37	Mesquite	Brownish-Green	Unmatured
	Hackberry	Taupe	Taupe
42	Mesquite	Dark Gray-Green	Ochre with Brown Specks
	Hackberry	Greenish-White with Brown Specks	Ochre with Brown Specks
43	Mesquite	White	Milky-White with Brown Specks
	Hackberry	Gray-White with Brown Specks	Milky-White with Brown Specks
44	Mesquite	White	Taupe
	Hackberry	White	Milky Taupe-White
51	Mesquite	Ochre-White	Dark Ochre
	Hackberry	Milky-Green	Milky-Ochre
52	Mesquite	Gray-Green	Light Ochre with Brown Specks
	Hackberry	Gray-Green	Light Ochre with Brown Specks
53	Mesquite	White with Brown Specks	Taupe with White Areas
	Hackberry	Milky Gray-White	White with Brown Specks
54	Mesquite	Taupe	Taupe
	Hackberry	Taupe	White-Taupe

those base glazes which produced colors of white and taupe usually contained more feldspar than whiting or ash.

A crazing or crackle effect was noted in both mesquite and hackberry base glazes in reduction firing. Crazing in a glaze is the end result of tensions developed when a glaze and a clay body expand and contract at different rates (2, p. 168). Although crackles appeared in both types of base glazes in reduction firing, they were different in two ways. The crackles in mesquite base glazes were very definite and usually appeared in a transparent area of the glaze, while in the hackberry base glaze the crackles were found in a finer pattern and were usually present in opaque glazes.

Both mesquite base and hackberry base glazes were glossier and more lustrous in reduction firing than were the same base glazes in oxidation firing.

In Table III, pages 26 and 27,the surface qualities of the twenty acceptable base glazes in both reduction and oxidation firings are recorded. It can be noted from this table that reduction firing of the acceptable base glazes gave more transparency and glossiness than did oxidation firing of the same glazes.

Base Glazes in Oxidation Firing

Just as there are certain characteristics of color and surface in reduction firing of glazes, there are dominant characteristics for glazes fired in an oxidation atmosphere. Due to the fact that an oxidizing fire is more stable, the findings from tests in this type of atmosphere will be more consistent than findings from reduction testing.

It was expected in testing ash glazes in an oxidation atmosphere that the predominant color would be tan, this coloring being the result of small amounts of iron usually found in an ash. From the findings recorded in Table II, the basic color from both mesquite and hackberry in oxidation firing in this study was ochre more often than tan. The three dominant colors resulting from oxidation firing

TABLE III

ANALYSIS OF BASE GLAZE SURFACES

Base Glaze	Ash	Reduction	Oxidation
10	Mesquite	Opaque, Semi-Mat	Opaque Mat
	Hackberry	Opaque, Mat	Opaque, Mat
14	Mesquite	Crackle Opaque, Gloss	Unmatured
	Hackberry	Opaque, Semi-Gloss	Opaque, Mat
15	Mesquite	Opaque, High-Gloss	Opaque, Mat
	Hackberry	Opaque, Mat	Opaque, Mat
20	Mesquite	Crackle Opaque, Gloss	Opaque, Mat
	Hackberry	Opaque, Mat	Opaque, Mat
21	Mesquite	Crackle Opaque, Gloss	Opaque, Dull Gloss
	Hackberry	Crackle Opaque, Mat	Opaque, Mat
27	Mesquite	Opaque, Mat	Opaque, Mat
	Hackberry	Opaque, Mat	Opaque, Mat
28	Mesquite	Opaque, Gloss	Opaque, Mat
	Hackberry	Crackle Opaque, Gloss	Opaque, Mat
29	Mesquite	Transparent, Gloss	Opaque, Gloss
	Hackberry	Crackle Opaque, Gloss	Opaque, Dull Gloss
33	Mesquite	Opaque, Semi-Gloss	Opaque, Dull Gloss
	Hackberry	Opaque, Simi-Gloss	Opaque, Dull Gloss
34	Mesquite	Opaque, Mat	Opaque, Mat
	Hackberry	Opaque, Mat	Opaque, Mat
35	Mesquite	Crackle Transparent, Gloss	Opaque, Mat
	Hackberry	Opaque, Dull Gloss	Opaque, Mat
36	Mesquite	Transparent, Gloss	Semi-Opaque, Gloss
	Hackberry	Opaque, Dull Gloss	Semi-Opaque, Mat
37	Mesquite	Opaque, Semi-Gloss	Unmatured
	Hackberry	Transparent, Gloss	Transparent, Gloss
42	Mesquite	Crackle Transparent, Gloss	Opaque, Mat
	Hackberry	Crackle Opaque, Dull Gloss	Opaque, Mat
43	Mesquite	Opaque, Mat	Opaque, Mat
	Hackberry	Opaque, Mat	Opaque, Mat
44	Mesquite	Transparent, Gloss	Opaque, Gloss
	Hackberry	Semi-Opaque, Mat	Semi-Opaque, Mat

TABLE III--Continued

Base Glaze	Ash	Reduction	Oxidation
51	Mesquite	Opaque, Mat	Opaque, Mat
	Hackberry	Crackle Opaque, Dull Gloss	Opaque, Mat
52	Mesquite	Crackle Transparent, Gloss	Opaque, Mat
	Hackberry	Crackle Opaque, Semi-Gloss	Opaque, Mat
53	Mesquite	Opaque, Mat	Semi-Opaque, Gloss
	Hackberry	Opaque, Mat	Opaque, Mat
54	Mesquite	Transparent, Gloss	Semi-Opaque, Gloss
	Hackberry	Transparent, Gloss	Semi-Opaque, Gloss

were ochre, taupe, and white. Most of the hackberry base glazes were ochre, while the mesquite glazes were usually white or taupe in color. These neutral colors were usually speckled with brown while the ochre colors were not. In checking Table I, it can be seen that those glazes producing neutral rather than dominant colors in oxidation firing tend to have 40 per cent or less ash in their make-up. It can also be seen that the major component of these neutral glazes is usually feldspar rather than ash or whiting. This trend does not follow in base glazes 36 and 37 where the major component is whiting, yet the color of the glaze is a neutral taupe in oxidation firing.

A variation in surface texture and quality was noticed between glazes tested in an oxidation and a reduction firing. Where there had been several cases of crackle in reduction fire, there were no crackle glazes in oxidation. Glazes were "fat" or "buttery" in oxidation firing while those tested in a reducing atmosphere appeared either crackled or slick. There was a larger number of glossy glazes obtained from a reduction fire than from an oxidation fire.

Base Glazes with Colorants Added

The second part of the experiment consisted of testing the acceptable base glazes from the tri-axial blend with colorants added. In this phase, also, all satisfactory base glaze formulae were tested in both oxidation and reduction atmospheres. To glazes which had proved satisfactory, colorants were added as described on pages 6 and 7.

Base Glazes with Colorants in Reduction Firing

Although all glazes had colorants added to obtain specific colors, a definite difference could be seen between examples of the same combination in oxidation and reduction firing. In glazes fired in a reduction atmosphere there was a brownish-green cast to the individual colors. This color was consistent regardless of formula, ash used, or colorant added. Glaze colors obtained in the reduction firing were usually deeper, and more intense than those obtained in an oxidizing atmosphere. Regardless of base glaze or ash used, when colorants were added, specific color characteristics were evident. These color characteristics in reduction firing were as follows:

1. Red iron oxide--dark green
2. Copper carbonate--soft green to dark red, depending on the amount of reduction obtained.
3. Cobalt carbonate--deep blue
4. Vanadium stain--light yellow to greenish-yellow
5. Manganese dioxide--brown to brownish-green

Not all colorants proved satisfactory in all base glazes. In Table IV, pages 30 and 31, all base glazes in both oxidation and reduction firing using mesquite and hackberry ashes and with colorants added are analyzed. Also the colorants most acceptable to each base glaze are identified in Table IV.

As mentioned earlier, the majority of acceptable base glazes tested contained brown specks in both oxidation and reduction firing using both mesquite and hackberry ash. This speckled characteristic also appeared in both hackberry and mesquite glazes with colorants added.

The greatest color differences between hackberry and mesquite glazes in reduction firing were the addition of copper carbonate and vanadium stain. Copper reds were obtained more often with hackberry ashes in base glazes than with mesquite ashes. With the addition of vanadium stain to both ash glazes, it was noticed that more true yellows were gained with the use of mesquite than with hackberry.

The most noticeable difference in the testing of base glazes with and without colorants was surface appearance.

TABLE IV

ANALYSIS OF BASE GLAZES WITH COLORANTS ADDED

Base Glaze	Ash	REDUCTION Satisfactory Colors	REDUCTION Evaluation	OXIDATION Satisfactory Colors	OXIDATION Evaluation
10	Mesquite	*Z	Poor	None	Poor
	Hackberry	None	Poor	None	Poor
14	Mesquite	None	Poor	None	Poor
	Hackberry	None	Poor	None	Poor
15	Mesquite	None	Poor	None	Poor
	Hackberry	None	Poor	*Y	Poor
20	Mesquite	None	Poor	Z	Poor
	Hackberry	None	Poor	Y	Poor
21	Mesquite	Z	Fair	*W,Z	Fair
	Hackberry	W,Y	Fair	None	Poor
27	Mesquite	W,Y,Z	Fair	*X,Z	Poor
	Hackberry	Y	Fair	Y	Poor
28	Mesquite	*V	Fair	V	Fair
	Hackberry	W,Y,Z	Good	V,X,W	Fair
29	Mesquite	V,W,X,Y	Good	V,W,Y	Good
	Hackberry	V,W,X,Y,Z	Good	Y	Fair
33	Mesquite	None	Poor	X,Y	Poor
	Hackberry	None	Poor	None	Poor
34	Mesquite	Y,Z	Poor	None	Poor
	Hackberry	Y	Poor	Y	Poor
35	Mesquite	Y,Z	Fair	W,X,Y	Fair
	Hackberry	W,Y	Fair	W,Y,Z	Fair
36	Mesquite	None	Poor	None	Poor
	Hackberry	None	Poor	None	Poor
37	Mesquite	None	Poor	None	Poor
	Hackberry	None	Poor	None	Poor
42	Mesquite	None	Poor	Y,Z	Poor
	Hackberry	Y	Poor	Y,Z	Poor
43	Mesquite	V,W,X,Y,Z	Excellent	W,X,Y,Z	Excellent
	Hackberry	V,W,X,Y,Z	Excellent	W,X,Y,Z	Excellent
44	Mesquite	W,X,Y,Z	Good	Y	Good
	Hackberry	V,W,Y	Good	W,X,Y	Good
51	Mesquite	W,Y,Z	Good	X,Y	Good
	Hackberry	None	Fair	Y	Poor
52	Mesquite	V,X,Y	Good	X,Y	Fair
	Hackberry	W,Y,Z	Good	X,Y	Good
53	Mesquite	V,W,X,Y,Z	Excellent	V,W,X,Y,Z	Excellent
	Hackberry	V,W,X,Y,Z	Excellent	V,W,X,Y,Z	Excellent

TABLE IV--Continued

Base Glaze	Ash	REDUCTION Satisfactory Colors	REDUCTION Evaluation	OXIDATION Satisfactory Colors	OXIDATION Evaluation
54	Mesquite	V,W,X,Y,Z	Excellent	V,X,Y,Z	Excellent
	Hackberry	V,W,X,Y,Z	Excellent	V,W,X,Y,Z	Excellent

*V--Red iron oxide
*W--Copper carbonate
*X--Cobalt carbonate
*Y--Vanadium stain
*Z--Manganese dioxide

Many of the original twenty base glazes proved unsatisfactory with colorants added because of excessive crawling of the glaze. Crawling is a glaze defect in which irregular areas of the clay surface remain unglazed or partially glazed. This defect may result from application of a glaze over unclean bisque ware or from a weak bond between glaze and body. This weak bond may stem from shrinkage of the applied glaze during drying and before firing (1, p. 72). Crawling was more common in glazes which contained from 30 to 70 per cent ash. Most of the glazes that crawled contained less than 30 per cent whiting in their composition. Glazes that did prove satisfactory in reduction firing were slick to the touch and had a high gloss.

Base Glazes with Colorants in Oxidation Firing

Colors obtained in oxidation firing of the glazes were usually more pale than the deep, intense colors obtained in a reduction firing of the same glazes. Where the dominant color in reduction had been greenish-brown, the dominant color in oxidation firing was a yellow-tan. It was evident that each colorant added produced a specific color, but a cast of yellow-tan was noticeable in the majority of the glazes. This yellow-tan cast was attributed to the effect of the oxidizing atmosphere on iron present in the ash where as the greenish-brown cast of the same glazes was attributed to the effect of the reduction atmosphere. Once again, this cast of color did not vary from the use of mesquite ash to hackberry ash or from base glaze to base glaze. The specific colors obtained from the different colorants added in oxidation firing were

1. Red iron oxide--dark brown to yellow-tan
2. Copper carbonate--light green to dark gray-green
3. Cobalt carbonate--pastel blue to dark blue
4. Vanadium stain--ochre to yellow
5. Manganese dioxide--taupe to beige

Classification of Glazes

All base glazes with colorants added were classified as either poor, fair, good, or excellent. This classification of glazes was the system used to denote surface and color of base glazes in both firing atmospheres with both ash and all colorants added. Table IV, pages 30 and 31, uses this system to classify and evaluate each glaze in terms of their acceptability for further use.

Poor Glazes

The term poor was used in cases where the final base glaze was powdery, chalk-like, or crawled excessively with all colorants. The evident crawling left an irregular color finish of dull unglazed areas in contrast to shiny glazed areas. Many of the samples appeared to be underfired. This was especially evident in formulae 36 and 37 in both oxidation and reduction testing with both of the ashes. In checking Table IV, it can be seen that from nine to twelve of the base glaze formulae proved poor with colorants added. This classification was given to the majority of the glaze formulae tested.

Fair Glazes

A classification of fair was given to glazes that proved satisfactory with at least two of the colorants added. This acceptability of glazes was usually not uniform in more than two colors within a specific glaze. An example of this classification can be seen in Table IV, with glaze number 21. It can be seen here that glaze 21 proved satisfactory in reduction firing using hackberry ash with copper carbonate and also with the addition of vanadium stain. The same glaze proved acceptable using mesquite ash with copper carbonate and manganese dioxide. The glazes classified fair proved more acceptable than those classified poor, but were not of a high enough quality to pursue further in this study.

Good Glazes

Good glazes were those that proved satisfactory with the addition of at least three colorants using either hackberry or mesquite and tested in either atmosphere. Those glazes proving good were approximately the same in number as those classified as fair. In checking Table IV, it can be seen that glaze 29 proved good except in the use of hackberry ash in oxidation firing, where it proved only fair. Glaze 44 proved satisfactory with all colorants, with both of the ashes, and in both atmospheres, but did not rate a classification of excellent.

Excellent Glazes

Numbers 43, 53, and 54 were the only glazes which were satisfactory under all of the variations; therefore they were classified as excellent. It can be seen in Table I, that all three glazes are relatively close in formulation of raw materials. All three have 10 or 20 per cent whiting, 10 or 20 per cent ash, and from 60 to 80 per cent feldspar.

Glaze 43.--Glaze number 43 has a combination of 20 per cent whiting, 20 per cent ash, and 60 per cent feldspar. It can be seen in Volume II, Plate I, that the basic difference in samples of the glaze with no colorant added was a gray color obtained in reduction firing as opposed to a beige-white in oxidation firing. In both the variation of the ashes and of testing atmospheres the brown speckles, a dominant characteristic of most glazes tested, were produced. When glaze 43 was tested with no color all variations of ash and atmospheres resulted in a mat, opaque surface. When fired in an oxidizing atmosphere with colorants, semi-gloss glazes were produced (Plates II and III). The glazes with the highest gloss were those in which mesquite ash was used with vanadium stain and those with hackberry ash plus cobalt carbonate. Red iron oxide with both mesquite and hackberry ash in oxidizing fire proved the least satisfactory of this group. When copper carbonate was added to glazes made with both ashes, a metalic-like film appeared which seemed to float upon a transparent green glaze. This same effect appeared with the addition of manganese dioxide, where the color was opaque taupe over brown. With glaze 43 more glossy samples were produced in reduction firing than in the oxidizing fire (Plates IV and V). Crawling occurred when mesquite ash was used with red iron oxide. While a copper red was produced with copper carbonate in glazes made with both ashes, it was more intense and glossy with mesquite than with hackberry. The addition of cobalt carbonate to glaze 43 produced a dark glossy blue that was uniform with both ashes whereas the addition of vanadium stain resulted in a yellow color with mesquite ash and green with hackberry. The glazes containing manganese dioxide were green in reduction as compared to the taupe-brown of oxidation firing.

In this glaze combination (number 43), copper carbonate proved to be the most acceptable colorant when fired in a reduction atmosphere; glazes containing cobalt carbonate, vanadium stain, and manganese dioxide were acceptable in oxidation while those containing red iron oxide were unsatisfactory in both atmospheres.

Glaze 53.--The composition of glaze 53 was 10 per cent ash, 70 per cent feldspar and 20 per cent whiting. The high percentage of feldspar probably accounts for the slick, buttery appearance of the glazes to which colors were added. Plate VI shows number 53 as it appeared when fired in both atmospheres with no colorants added. The differences in color between oxidation and reduction firing of glaze 53 with no color added was less than that in similar samples of glaze 43. The overall color in 53 with no colorant was taupe-white. Although only 10 per cent ash was used, the brown speckles common to ash glazes were present, but were not as prominant as those found in glaze 43.

As with number 43, number 53 in an oxidizing atmosphere with color produced semi-gloss surfaces (Plates VII and VIII). The least gloss of the five colorants added was produced in the glazes containing red iron oxide. There was a different appearance in glazes made with mesquite and hackberry ash and containing copper carbonate. Glaze 53 made with hackberry with copper carbonate added had the same appearance as did glaze 43 with both hackberry and mesquite, a transparent green with a metalic-like flotation on top. With the use of mesquite, however, the glaze was a soft green with the clay body showing through. Glazes containing cobalt carbonate were blue when made with either ash, but the color was not as intense in oxidation as in reduction firing. The use of vanadium stain resulted in a strong yellow with brown speckles in the case of both kinds of ashes. A light brown glaze was obtained with the addition of manganese dioxide, with little variation because of the ash used.

Reduction firing of glaze 53 resulted in much more intense colors than did oxidation firing (Plates IX and X). The major variation of color with the use of the two ashes was in those glazes to which vanadium stain or manganese dioxide were added. The use of vanadium stain in the mesquite ash glaze resulted in a greenish-yellow, while in glazes made with hackberry ash a clear medium green was produced. With manganese dioxide in the mesquite ash glaze, a beige-tan was gained; when manganese dioxide was added to glaze 53 using hackberry ash a brownish-green resulted. A brownish-green was produced with red iron oxide; a red with copper carbonate, although uneven in color; and blues with cobalt carbonate. These blues were more intense in glazes made with mesquite ash than in those made with hackberry.

<u>Glaze 54</u>.--Base glaze 54 contained equal amounts of ash and whiting (10 per cent) and 80 per cent feldspar. Plate XI shows the difference between the use of mesquite ash and hackberry ash with no colorant added. It can be seen that in oxidation firing a somewhat transparent taupe was

obtained with both ashes while a more opaque white-taupe was produced in reduction firing. The use of hackberry ash in oxidation firing of number 54 with colorants resulted in more glossy glazes than did mesquite ashes. Less crawling of the glaze was evident with oxidation firing than with reduction firing of number 54 with colorants. The most satisfactory glaze produced with base glaze 54 in an oxidation firing was with the addition of copper carbonate to hackberry. The surface of this glaze was exceptionally smooth and glossy, the color, clear and very uniform (Plate XII). The use of red iron oxide with glazes made of both hackberry and mesquite produced similar color and glaze surface. Copper carbonate used in the mesquite glaze gave a result which was poor in color and surface when compared to the same glaze with hackberry. Cobalt carbonate, vanadium stain, and manganese dioxide produced colors and surfaces of semi-gloss deep blue, yellow-gold, and brown, respectively, with the use of both kinds of ashes in glaze 54 in an oxidizing atmosphere (Plates XII and XIII).

In a reducing atmosphere (Plates XIV and XV) glaze 54 produced glossy surfaces and intense colors with both kinds of ash. The addition of red iron oxide produced a crawling glaze with both ashes. Just as in oxidation firing of this glaze, copper carbonate produced a far more satisfactory glaze with the use of hackberry ash than with mesquite ash. Blues produced by cobalt carbonate were harsh and less acceptable from a reduction firing than when fired in an oxidizing atmosphere. Unlike the clear yellow-gold obtained in the oxidation firing of vanadium stain, reduction firing produced a yellow-brown with brown speckles more evident. With both ashes and the addition of manganese dioxide, reduction fired samples of glaze 54 produced tones of greenish-brown. An overall evaluation of glaze 54 indicated that hackberry ash was more acceptable than mesquite ash in both atmospheres.

The classifications and evaluations discussed in this chapter were based on the acceptability of glaze color and surface qualities. Although findings from the study were discussed in this chapter, more detailed conclusions will be discussed in the next chapter. Chapter IV, therefore, will be concerned with a summary of the study, conclusions, and recommendations for further study of ash glazes.

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CHAPTER IV

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary

In this study, the problem was to investigate the usefulness of certain ashes as glaze material and to evaluate their acceptability both with different colorants and when fired in reduction and oxidation atmospheres.

Three raw materials were chosen to be used in formulating mixtures that might prove satisfactory as base glazes. This selection of only three basic raw materials, ash, feldspar, and whiting, was the first of three limitations set in the study. The second limitation was the type of ashes used. Hackberry and mesquite wood ashes were selected because both were readily available locally and both were indigenous to Texas. The final limitation set in the study was the choice of colorants and the percentages of these colorants to be added to base glazes which proved satisfactory. Those colorants and percentages were

1. Red iron oxide--5 per cent or 1. gram
2. Copper carbonate--1 per cent of .2 gram
3. Cobalt carbonate--one-half of 1 per cent or .1 gram
4. Vanadium stain--5 per cent or 1. gram
5. Manganese dioxide--2 per cent or .4 gram

These colorants and percentages were chosen to give a wide range of colors and were used in percentages known to produce satisfactory color in most glazes.

The system selected for combining the three raw materials in several combinations was that of a tri-axial blend. This system produced sixty-six possible mixtures. Table I in Chapter II gives an analysis of the sixty-six combinations. The first step in testing the mixtures in both oxidation and reduction atmospheres resulted in approximately twenty of the original sixty-six as satisfactory base glazes. The others were rejected due to unfavorable surface characteristics. Analyses of base glaze colors and surfaces were shown in Tables II and III in Chapter III.

The second step in testing was the addition of the selected colorants to the acceptable base glazes using both mesquite and hackberry ashes and firing in both oxidation and reduction atmospheres. An evaluation of the glazes with specific colorants and an overall analysis of base glazes with all colorants added are recorded in Table IV.

Glazes were classified as poor, fair, good, or excellent according to the results of tests in which there were variations in colorants, ashes, and firing atmospheres. Results of these tests were discussed; glazes that proved excellent were discussed in detail.

Conclusions and Recommendations

In the combining of the three raw materials through a tri-axial blend it was found that twenty of the sixty-six combinations could serve as a base glaze for colorant. These proving acceptable were:

1. Glaze 10--70 ash, 30 feldspar
2. Glaze 14--60 ash, 30 feldspar, 10 whiting
3. Glaze 15--60 ash, 40 feldspar
4. Glaze 20--50 ash, 40 feldspar, 10 whiting
5. Glaze 21--50 ash, 50 feldspar
6. Glaze 27--40 ash, 50 feldspar, 10 whiting
7. Glaze 28--40 ash, 60 feldspar
8. Glaze 29--30 ash, 70 feldspar
9. Glaze 33--30 ash, 40 feldspar, 30 whiting
10. Glaze 34--30 ash, 50 feldspar, 20 whiting
11. Glaze 35--30 ash, 60 feldspar, 10 whiting
12. Glaze 36--30 ash, 70 whiting
13. Glaze 37--20 ash, 80 whiting
14. Glaze 42--20 ash, 50 feldspar, 30 whiting
15. Glaze 43--20 ash, 60 feldspar, 20 whiting
16. Glaze 44--20 ash, 70 feldspar, 10 whiting
17. Glaze 51--10 ash, 50 feldspar, 40 whiting
18. Glaze 52--10 ash, 60 feldspar, 30 whiting
19. Glaze 53--10 ash, 70 feldspar, 20 whiting
20. Glaze 54--10 ash, 80 feldspar, 10 whiting

It was found that any of the above combinations could be used as a glaze, made with either hackberry or mesquite ashes, and fired in either reduction or oxidation firing without the addition of any colorant. With the addition of colorants, many of the base glazes proved less satisfactory than without colorants. With this in mind, additional pleasing colors might be obtained with the addition of varying percentages of colorants, or by combining two or more colorants in one glaze. Vanadium stain was an acceptable colorant most often when added to glazes of either ash or fired in either atmosphere. The order of acceptability of colorants was:

1. Vanadium stain--forty-five satisfactory glazes
2. Manganese dioxide--twenty-seven satisfactory glazes
3. Copper carbonate--twenty-seven satisfactory glazes
4. Cobalt carbonate--twenty-four satisfactory glazes
5. Red iron oxide--eighteen satisfactory glazes

Three of the glazes, numbers 43, 53, and 54 proved excellent or near excellent with both ashes, in both testing atmospheres, and with all colorants. Most variations of these glazes are recommended for use without further research. Samples from this group which were not satisfactory are as follows:

1. Glaze 43 with red iron oxide as a colorant.
2. Glaze 53 with red iron oxide as a colorant.
3. Glaze 53 with copper carbonate and mesquite ash in an oxidizing atmosphere.
4. Glaze 54 with red iron oxide as a colorant.
5. Glaze 54 with copper carbonate and mesquite ash in an oxidizing atmosphere.

In base glazes without colorants, those made with mesquite ash and fired in reduction atmosphere produced green tones, while those made with hackberry ash produced tones that were predominantly gray. In oxidation firing, glazes containing hackberry ash were usually ochre and those containing mesquite either taupe or white. Other possibilities which might prove satisfactory using this study as a pilot would be a greater variation of ashes used in the acceptable base glazes. Instead of hackberry and mesquite, the ashes of various grasses or weeds might be substituted as a raw material.

As mentioned in Chapter III, all base glazes with colorants added were classified poor, fair, good, or excellent. It is recommended that various glazes proving good, but not excellent, be tested further with different ashes and different percentages of colorants. Because this study contained several variants, it is felt that through the altering and changing of these variants, many satisfactory glazes could be produced.

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