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EXPERIMENTAL SEPARATION OF IRON-BEARING MINERALS FROM CERTAIN KANSAS CLAYS

By

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CONTENTS

TABLE

TABLE 1.—*Size distribution of clays and certain mineral fractions from them based upon total weight of crude clay*

Size	Gray clay from Cloud County		Black clay from Cloud County			Cherokee County clay	
	Weight, percent of total	Pyrite, percent of total weight	Weight, percent of total	Pyrite, percent of total weight	Lignite, percent of total weight	Weight, percent of total	Sink product, percent of total weight
18-13 mm	0.06	0.055	0.11	0.107			
13- 9 mm	0.09	0.079	0.03	0.030			
9 mm-3 mesh	0.11	0.066	0.01	0.008			
3- 4 mesh	0.10	0.037	0.02	0.019			
4- 6 mesh	0.07	0.014	0.03	0.027			
6- 8 mesh	0.06	0.017	0.02				
8- 10 mesh	0.05		0.02	0.049	0.078		
10- 14 mesh	0.04	0.040	0.04				
14- 20 mesh	0.03		0.05			0.53	0.286
20- 28 mesh	0.05		0.12			0.55	0.330
28- 35 mesh	0.09		0.24		0.120	0.74	0.506
35- 48 mesh	0.10	0.100	0.34			1.37	1.077
48- 65 mesh	0.13		0.37			1.99	1.692
65-100 mesh	2.35		1.66			2.17	1.715
100-150 mesh	2.49		3.80	0.007		1.00	0.659
150-200 mesh	9.32		9.30			1.09	0.462
200-270 mesh	7.02		4.96			0.72	0.198
-270 dry screening	4.43	0.002	3.11			0.80	
-270 wet screening	73.44		75.77			89.04	
Totals	100.00	0.410*	100.00	0.250*	0.198**	100.00	6.925*

*Includes only material coarser than 270 mesh.
**Includes only material coarser than 65 mesh.

ABSTRACT

Two light-firing clays from Cloud County and one from Cherokee County were investigated in an effort to devise methods for the elimination of dark spots which appear upon firing caused by coarse pyrite or siderite. The clays were sized and fractionated to determine the occurrence and distribution of the iron minerals. Various methods for the removal of the iron minerals were tested and fired bricks were made from the purified clay products. All three clays were found to be amenable to improvement by simple beneficiation methods involving some combination of screening, classification, or magnetic separation.

INTRODUCTION

Several plants in Kansas make light-colored, buff, tan, or nearly white facing bricks, and other light-colored ceramic products. In some places the clay from which light-colored bricks and other ceramic articles may be made contains small amounts of coarse iron minerals, primarily pyrite, that cause difficulties in manufacture. The iron in each particle fluxes the clay around it during firing, and if it is located near the surface, a black spot appears. Also the iron particles may expand on firing and cause blisters or "broken-out" places. The size of the resulting black spot depends upon the size of the pyrite particle, but since clays are usually ground only to about 8 mesh, the spots may be very noticeable on a light-colored surface.

The present investigation was undertaken in an effort to determine if a relatively low-cost type of beneficiation would produce a significant removal of iron minerals from raw clay. Three light-firing clays examined in order to determine the type and distribution of the iron mineral were subjected to several types of treatment. Two of the samples are from adjacent beds in the Janssen member of the Cretaceous Dakota formation in Cloud County near Aurora, Kansas (Plummer and Romary, 1947; Plummer and Hladik, 1953). At the place where it was sampled (SE¼ sec. 32, T. 7 S., R. 2 W.) the Janssen member is 40 feet thick; the samples are from the upper 18 feet. Both of these clays are light firing, but their unfired appearance is quite different. One is light gray, the other is black owing to fine lignite deposited with the clay. The two clays are used together, but were investigated separately because of differences in their appearance. The third sample is from the underclay below the Mineral coal in the Pennsylvanian Cherokee group in Cherokee County near Weir, Kansas (SW¼ sec. 34, T. 31 S., R. 24 E.).

Each clay was sized and fractionated to determine, at least partially, its mineralogical composition. Following this, certain tests were made to indicate how the objectionable minerals might be removed. Small bricks were made by the Geological Survey's Ceramics Division from the test products in order to indicate the quality of fired ware that could be produced.

SIZING AND FRACTIONATION OF CLAY SAMPLES

Each of the three clays in this investigation was sized and fractionated to determine its mineralogical composition. The details were varied with each sample, but in general, the procedure consisted of wet and dry screening followed by heavy liquid separation with magnetic separation of the specific gravity fractions. The final fractions were examined with a low-power binocular microscope, and with either a petrographic or a metallographic microscope after proper mounting and preparation.

Gray clay from Cloud County.—The large sample of gray clay from the Cloud County locality was crushed to finer than 1¼ inches and mixed thoroughly. The laboratory sample consisted of 10 kg of the large sample. The laboratory sample was soaked in water and stirred until the lumps of clay and sand disintegrated and became suspended in the water. This slurry was screened at 20 mesh and the plus 20-mesh sand was washed free of fine material. The minus 20-mesh pulp was further sized by wet screening at 100 and 270 mesh. Dry screen analyses on each sand fraction were made and these data were used to calculate the size distribution of the clay as shown in Table 1.

The coarse pyrite was separated by hand sorting each size fraction down to 8 mesh. The sand from 8 to 20 mesh was panned to separate pyrite from lighter material. These data together with information gained by fractionating the finer sand were used to calculate the pyrite distribution shown also in Table 1.

Samples of the 20- to 100-mesh and the 100- to 270-mesh fractions were treated with tetrabromoethane to separate particles with specific gravity greater than 2.96 from ones of lower specific gravity. The sink product (those particles with a gravity more than 2.96) from the 20- to 100-mesh material was mainly pyrite and attached quartz grains. A sample of the sink product mounted in bakelite was ground and polished to reveal the cross section of the particles. Nearly all the pyrite in this clay is in the form of irregular spheres ranging in size from more than 13 mm in diameter to about 100 mesh. Most of the finer pyrite lumps are coated with attached grains of quartz, and many of the pyrite particles as seen in the polished section, contain occluded quartz grains.

The sink product from the 100- to 270-mesh fraction contains a variety of minerals besides pyrite. This material was separated at high magnetic intensity by passing it through a Frantz Isodynamic separator (Gaudin and Spedden, 1943). A petrographic examination of the magnetic and nonmagnetic fractions revealed the presence of tourmaline, zircon, brookite, staurolite, rutile, pyrite, and unidentified black and white opaque minerals. The quantity of these minerals is very small, however, because the sink fraction amounts to only 0.125 percent of the crude clay.

The sandy part of this clay contains muscovite in noticeable quantities. The float material (those particles with a gravity less than 2.96) from the 100- to 270-mesh fraction was separated into mica and quartz products on the Isodynamic separator, and from these data the crude clay was estimated to contain 0.5 percent muscovite. A product containing a high proportion of this mica was prepared by flotation of the 100- to 270-mesh material using amine as the collector. This product was fired in a crucible to check the possibility that the mica might expand and cause cracks in the finished ware. No expansion was noted.

Black clay from Cloud County.—A sample of the black clay from the Cloud County locality was sized and fractionated in much the same way as was the sample of gray clay. A 10 kg sample of the crushed and mixed clay was pulped in water and wet screened at 20 and 270 mesh. The oversize portions were dry screened and the size distribution of the clay was calculated as shown in Table 1. A sample of the 20- to 270-mesh material was segregated in tetrabromoethane, and the sink fraction was separated into two parts on the Isodynamic separator. Petrographic examination of the sink fractions showed the presence of tourmaline, zircon, rutile, pyrite, opaque minerals, and very minor amounts of several others. These heavy minerals amount to only 0.106 percent of the clay. The float fraction is more than 99 percent quartz.

The pyrite distribution shown in Table 1 was calculated from data obtained by hand sorting and panning of the plus 20-mesh material, and from fractionation of the minus 20-mesh material. The pyrite in the black clay seems to have replaced pieces of lignite or wood, as much of the pyrite is in the form of fossilized wood. This is in distinct contrast to the concretionary form of the pyrite in the gray clay.

The lignite, which gives the clay its black color, ranges in size from about 8 mesh to much finer than 270 mesh. The quantity and distribution of coarse lignite was noted during the dry screening as shown in Table 1. The quantity of plus 270-mesh lignite amounts to only about 0.2 percent of the clay. Although no determination of the quantity present was made, only a small proportion of very fine lignite is required to color the clay.

Clay from Cherokee County.—A sample of clay collected near Weir was received as ground clay in which any lumps of pyrite or other mineral coarser than 8 mesh had been broken. Examination of the sample indicated that the original clay probably contained no pyrite coarser than 8 mesh; hence, the size analysis of the ground material is probably the same as would be obtained from lump clay. A 1 kg sample of the ground material was pulped in water and wet screened at 270 mesh. The oversize was dry screened and the size distribution of the clay calculated as shown in Table 1. A sample of the plus 270-mesh sand was separated in tetrabromoethane to give float and sink products. The sink product amounting to about 7 percent of the clay was screened; its distribution is shown in Table 1.

The 65- to 100-mesh fraction of the sink product was separated into three portions with the Isodynamic separator. More than 93 percent of this fraction is quite magnetic; about 6.4 percent is nonmagnetic. The intermediate portion amounts to only 0.3 percent. The strongly magnetic and the nonmagnetic parts were mounted in bakelite, ground, and polished so that the cross section of the particles could be seen. Examination with a metallographic microscope revealed that the magnetic portion consists of rough spheres of siderite pseudomorphic after pyrite. Many of the particles contain cores of unaltered pyrite. The nonmagnetic fraction contains spheres of pyrite that have not been altered. Examination with a stereoscopic microscope revealed that at all sizes the sink product consists almost entirely of spheres of siderite and pyrite.

BENEFICIATION

As all the clays considered in this investigation fire to light colors, the contained pyrite or siderite particles cause black spots which are objectionable.

If the iron minerals could be removed economically, these clays would be more desirable for brick making, and additional uses for which the crude clays are unsuited, such as pottery, wall tile, quarry tile, or refractories, might be found for the beneficiated clays. With these objectives in mind a number of tests were made to remove pyrite and/or lignite from the clay. Part of these tests were made on a sample containing both gray clay and black clay from Cloud County in about the same proportions as they occur in the pit. Test bricks from the beneficiated clay samples were made and fired in order to indicate by their color and properties the results of the tests.

Screening and Flotation Tests

Mixed gray and black clay from Cloud County.—The fractionation of a mixed sample of gray and black clay from the Cloud County locality showed that the pyrite they contain is relatively coarse. By passing the material through a 20-mesh screen it was possible to remove 75 percent of the pyrite from the gray clay and 96 percent of it from the black clay. Sizing of the gray clay at 100 mesh will remove 99.5 percent of the pyrite. Thus the objectionable material may be removed by simple wet screening or classification. Accordingly, tests were made in which the clay was pulped in water and wet screened at 20 and 100 mesh.

Only part of the lignite is removed by screening the clay, the rest passing even the finest screens to contaminate the clay. Several flotation tests to remove lignite that passed the 20- or 100-mesh screens were made. Best flotation results were obtained by dispersing the clay with calgon (sodium hexametaphosphate) and using oleic acid, kerosene, and pine oil as flotation reagents. Test bricks made from samples prepared by screening alone and by screening and flotation indicate that the latter method gave no improvement over screening alone. Screening of the clay at 20 mesh eliminated all but a few small black spots and screening at 100 mesh eliminated all visible spots.

Black clay from Cloud County.—Flotation of lignite was included in three tests on the black clay from Cloud County. The gray clay contained almost no lignite. In one test the lignite was floated by using calgon, oleic acid, kerosene, and pine oil, followed by screening the nonfloat at 100 mesh to remove coarse material. In the other two tests flotation was applied to part of the minus 270-mesh pulp from the sizing and fractionation work. In one of these, the clay was further refined by sedimentation and decantation as discussed later. Test bricks show that removal of pyrite by screening is all the treatment necessary to produce clay from which objects without black spots may be made.

Clay from Cherokee County.—Much of the iron mineral in the clay from the Cherokee County locality is in the form of pyrite altered to siderite. Inasmuch as siderite is quite magnetic, the logical method of treatment was wet magnetic separation. A series of tests compared the effect of screening alone with screening and magnetic separation in the Frantz Ferrofilter. Test bricks show that wet screening at 20 mesh or finer eliminates the particles that cause blisters and relatively large dark spots in the fired ware. Bricks made from clay screened at 20 mesh show a multitude of easily visible black spots, and those from minus 100-mesh clay have many barely visible spots. Screening at 270 mesh eliminates all visible specks. Magnetic separation of the screened clay eliminates all visible specks from minus 100-mesh material and all but a few of those from minus 20-mesh material. These latter spots are attributed to pyrite particles that cannot be removed by magnetic separation.

Sedimentation and Decantation Tests

All three clays considered contain considerable amounts of sand or silt, which is almost entirely quartz. Although the clay with this quartz is acceptable for the manufacture of brick, there are other possible uses in which the excess quartz would be detrimental.

The possibility of producing a refined light-firing clay for uses other than brick making was checked. Part of the minus 270-

mesh pulp from the sizing test of the gray clay from Cloud County was dispersed and permitted to settle for 2 hours in a pan about 4 inches deep. The unsettled clay was decanted, and the process repeated twice with the clay and silt that settled to the bottom. Thus a clay fraction containing particles finer than 5 or 10 microns was obtained. The black clay from Cloud County was separated in the same manner in one test, and in addition sedimentation and decantation were tried on a sample of this clay from which part of the lignite had been removed by flotation. A sample of the clay from Cherokee County was treated in the same way after it had been pulped and wet screened at 100 mesh followed by magnetic separation in the Ferrofilter.

Test bricks show that the fine fractions from the Cloud County clays are relatively light in color, having a pronounced yellowish-green color when fired. Flotation of the lignite made no noticeable difference in the black clay. The fine fraction from the Cherokee County clay burns to a definite red color, the iron that gives the buff color to bricks from this clay being concentrated in the extreme fines.

SUMMARY

Sizing and fractionation tests on the three clays revealed the minerals present and their distribution in the size fractions coarser than 270 mesh. In the gray clay from Cloud County pyrite occurs as round balls or concretions ranging in size from about 13 mm in diameter to about 100 mesh and amounting to about 0.4 percent of the sample. About 75 percent of this pyrite is coarser than 20 mesh and about 99.5 percent is coarser than 100 mesh. A heavy mineral fraction coarser than 270 mesh and amounting to about 0.13 percent of the sample contains a variety of minerals including tourmaline and zircon. It is estimated that about 0.5 percent of the clay is muscovite, which because of its platelike structure is quite noticeable.

The black clay from a bed overlying the gray clay contains about 0.25 percent pyrite. In this clay the pyrite is pseudomorphic after lignite, with 96 percent of it being coarser than 20 mesh. This clay is black due to fine lignite; lignite coarser than 270 mesh amounts to 0.2 percent of the clay. The heavy mineral fraction coarser than 270 mesh amounts to only 0.11 percent of the

clay. Both the gray and the black clay from Cloud County contain large amounts of quartz sand or silt. About 25 percent of each is coarser than 270 mesh, and there is a large amount of fine sand in the minus 270-mesh part. In fact, in sedimentation and decantation tests intended to make a separation at 5 to 10 microns, the fine portion amounted to only 28.4 percent of the gray clay and 35.5 percent of the black clay.

The clay from Cherokee County contains about 10 percent siderite pseudomorphic after pyrite and unaltered pyrite. Of this more than 80 percent is coarser than 100 mesh. This clay contains less coarse sand than the Cloud County clays, but even so, only 31.3 percent of it was recovered as a fine fraction after sedimentation and decantation.

Separation tests on the Cloud County clays showed that wet screening at 20 mesh eliminated all but a few dark spots from fired test bricks, and wet screening at 100 mesh eliminated all visible black spots. Flotation of the lignite in the screen undersize pulp made no change in appearance of the test bricks. The clay mineral fractions from these clays are light firing and might be useful as ball clay in ceramic bodies or in refractories.

Separation tests on the Cherokee County clay showed that screening at 20 or 100 mesh eliminated nearly all the dark spots. Magnetic separation in combination with screening eliminated all visible spots. The clay mineral fraction of this clay fires quite red, and this fact would make it unsuitable for some purposes.

ECONOMIC CONSIDERATIONS

The wet screening of all the clay used in the manufacture of brick is not feasible because of the cost of the process. There is a possibility, however, that a large proportion of the pyrite and siderite in the larger particles could be removed by partial wet screening, and at a reasonable cost. In the dry pans commonly used in brick plants for grinding clay the ground clay passes through coarse slots in the bottom to a vibrating 8-mesh screen and the oversize is returned to the pan for further grinding. Due to the cushioning effect of the clay in the mill, hard particles are reduced in size very slowly, and in some cases must be removed from the mill pan by hand. It is probable that much of the pyrite and siderite will be found in the oversize, and if this material were blunged in an equal weight of water, with a dispersing agent, a large amount of the pyrite and other hard particles could be removed by wet screening through a 20- or 30-mesh sieve. The slip, or slurry, could then be fed to the pug mill and used for tempering water. If the oversize did not exceed 20 percent of the total weight of clay being processed the amount of water used for blunging, or pulping, would not be excessive for tempering the clay used for extrusion. If barium carbonate were used in the clay it could be added to the water in the blunging process, and if sodium carbonate were used for dispersion some clays would be benefitted by its use (Plummer and Hladik, 1953).

The sedimentation and decantation process produces two potentially useful products. The clay fraction is essentially a very fine-grained ball clay, and in the case of the Cloud County (Dakota formation) clays, light-firing. The silt fraction contains some clay and, except for the pyrite and siderite, is a relatively pure material. If the slip, or slurry, were screened through a 20-mesh or finer sieve much of the pyrite and siderite could be removed from the clay, thus producing two types of material adapted to special uses. Magnetic separation could be combined with the screening with beneficial results.

The fine clay portion, essentially a very fine-grained ball clay, could be used as the plastic clay addition to pottery bodies or floor and wall tile bodies. Its range of usefulness would be limited only by the slight color. The light greenish-yellow color in the fired Cloud County clay would show up only as a slight tinting in vitrified ware.

The silt fraction in all three clays fires to a very light color. In the case of the Cloud County clays the color is almost white, and the material is refractory. This silty material contains enough clay for forming into bricks either by the plastic or dry-press method, and is well suited to the manufacture of highly siliceous or "semi-silica" fire bricks of the type in demand for heat regenerator checker work in steel mills.

The data obtained on the clays tested should not be considered valid only for those mentioned. Both the Cloud and Cherokee County clays tested are typical of wide-spread deposits in their respective areas.

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ELECTRON MICROSCOPY OF FIRED GLAZE SURFACES

By

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ILLUSTRATIONS

ABSTRACT

A standard replica technique of electron microscopy is applied to the study of the finer surface features of a black glossy submetallic glaze. Electron micrographs indicate the presence of large plane glossy areas, broad flat-topped plateaus, narrow rough-textured ridges, areas of fine wrinkles, rough jagged regions, crystals, bubbles, and intersecting grooves or cracks. Detailed interpretation is deferred until further studies are made.

INTRODUCTION

The general appearance of a glaze depends largely upon the character of the glaze surface and its effect upon the light which is reflected from it. Some of the surface features of glazes are so small that although their effect is readily discernible, their true character is not known. The overall inadequacy of light microscopy in the study of glaze surfaces is illustrated by the old controversies in the literature concerning the character of mat glazes (*viz.* Binns, 1903; Pence, 1912, 1913; Purdy, 1912; Staley, 1912).

The purpose of this paper is the description of a well-known technique of electron microscopy as applied to one particular glaze. Interpretations of the various features observed are only tentative, and perhaps raise more questions than they answer.

The idea of the microscopic study of the surfaces of finished ceramic products by replica methods is not new; it was suggested by Hillier (1946) as a promising field for electron microscopy. A Faxfilm replica technique was used in light microscopy by Allen and Friedburg (1948) in examination of scratches and thermal cracks on enamels, glazes, and glass. The low resolving power of light restricts observation in a light microscope to the gross character of features coarser than 1 or 2 microns. Published data on crystallite sizes in glazes are rare; Insley (1927) describes some glazes with maximum length of mullite crystals ranging from 5 to 20 microns. Pence (1913) describes crystals having dimensions of about 1×6 microns, at the surface of a glaze and throughout the mass. Crystals smaller than 5 microns come within the range suitable for electron microscopy. Although Allen and Friedburg (1948) report that extensive electron microscope studies of surfaces are being conducted in ceramics and related fields, few or no descriptions of electron microscopy of glaze surfaces have reached the publication stage.

Thanks are expressed to C. C. McMurtry who made the electron micrographs in the Department of Oncology, University of Kansas Medical School, in 1951.

LABORATORY TECHNIQUE

Various methods of replication for electron microscopy are described in standard textbooks (i.e., Cosslett, 1951). The type of replica used for the present study is a single-stage collodion film. The method is briefly summarized here so that the reader who is not familiar with techniques of specimen preparation for the electron microscope can more readily interpret the micrographs.

A few drops of a dilute (ca. 2 percent) solution of collodion in amyl acetate are poured on the clean glaze surface and the excess is drained off. After the amyl acetate has evaporated the glazed surface is immersed in water and the film of collodion is teased off so that it floats on the surface of the water. It is then transferred to a specimen screen. Before placing the replica in the microscope the surface relief and contrast are accentuated by evaporating chromium onto the specimen *in vacuo* at a low angle (in this case 5:1). The projections on the surface receive heavy deposits of the metal, while the area on their lee sides is protected. This gives the effect of a shadow five times as long as the projection is high, and makes possible the measurement of the depth or height of the irregularities.

The single-stage replica is of necessity a negative replica; that is, a projection on the replica represents a depression in the glaze surface, and vice versa. This fact must be kept in mind for proper interpretation of the micrographs.

A replica suitable for electron microscopy must be thin (less than 0.2 micron), and such exceedingly thin films cannot be stripped from a very rough surface. Cosslett (1951, p. 223) indicates that the surface irregularities should be less than 1 micron in elevation, and that more rugged surfaces should be replicated by a nonstripping process. The process of stripping may also pro-

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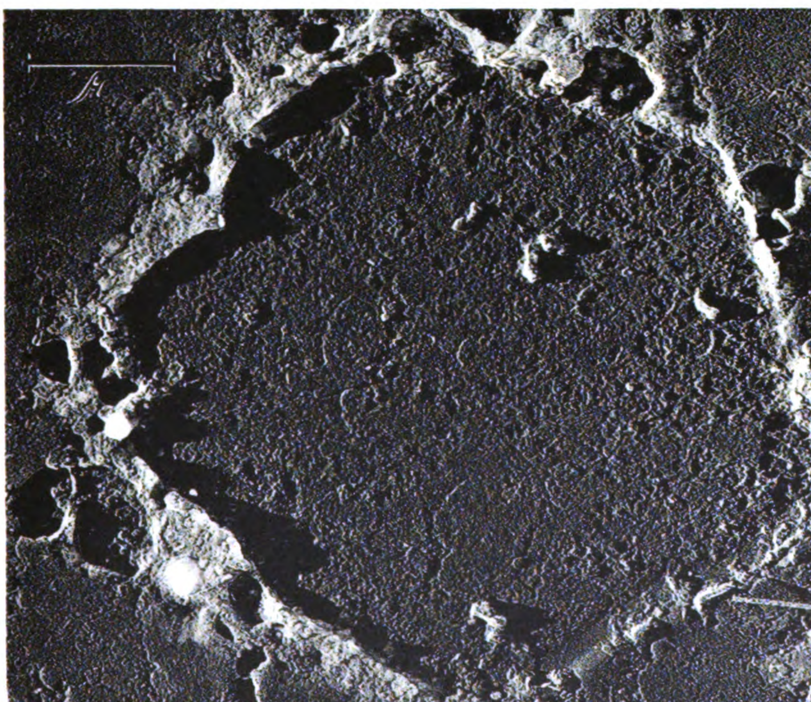
PLATE 1. Electron micrographs showing fired glaze surface replica shadowed with Cr at ca. 18°

A. Smooth, nearly featureless surface of glassy area. × 28,000.

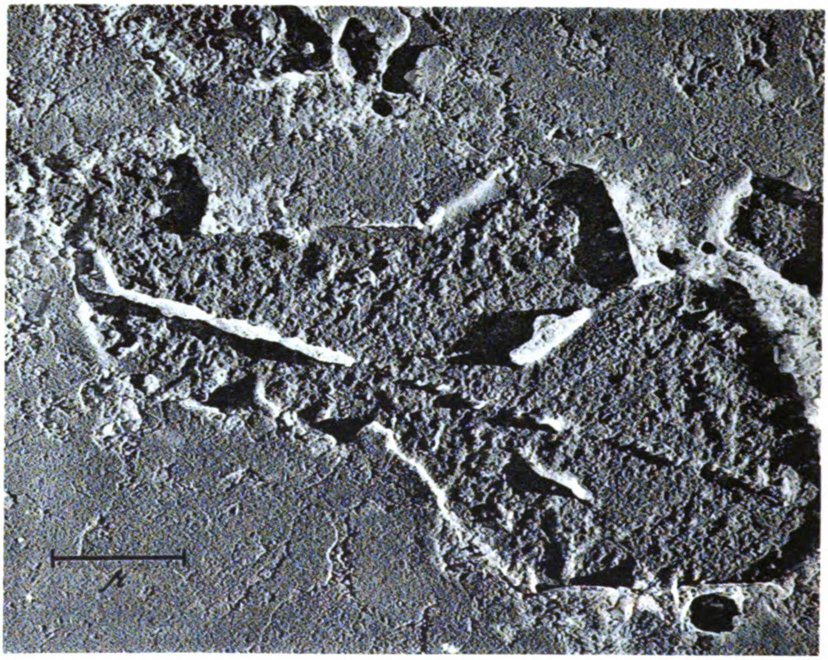
B. Level plateau 4 microns in diameter, 0.07 micron in elevation. Note depressed perimeter, rough "reaction rim." × 19,500.

A

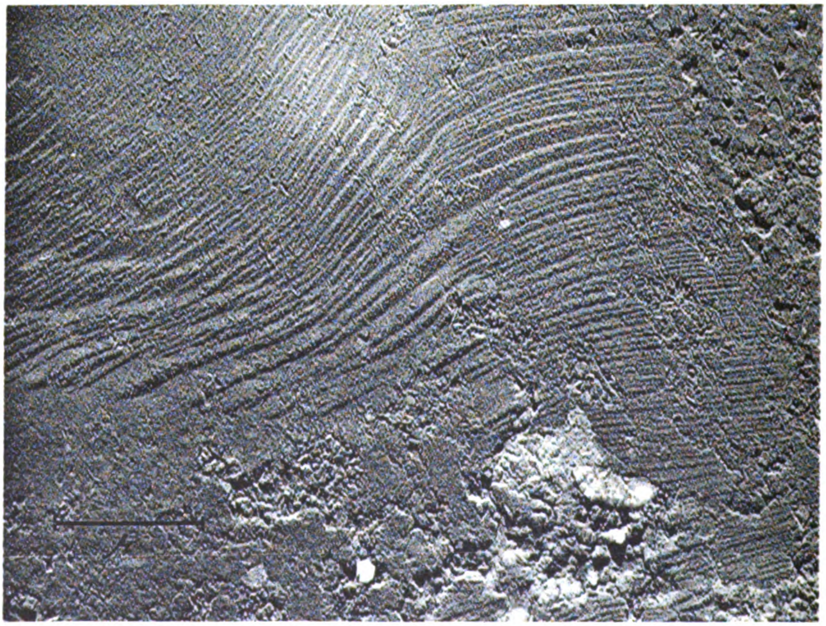


B

SWINEFORD AND PLUMMER — Electron micrographs of glaze replicas.



A



B

SWINEFORD AND PLUMMER — Electron micrographs of glaze replicas.

duce strain lines or tears in the film which can be misinterpreted as structures in the glaze.

The resolution obtainable from a replica in the electron microscope, although much better than that in a light microscope, is worse than the resolving power of the instrument. This is because the collodion itself has a grainy structure, the units being about 100 A in diameter. Thus the resolution in collodion replicas is of the order of 200 to 300 A (Cosslett, 1951, p. 219). The grain of the collodion and possible granulation of the chromium coating must be recognized as such and not interpreted as grain on the glaze surface.

CHARACTER OF THE GLAZE

The specimen examined is a black glaze with a glossy surface speckled with minute frosty areas (ca. 50 to 300 microns in diameter) which are visible to the naked eye and seem to have a submetallic sheen. The composition is as follows:

Eagle Picher frit	37.61 percent
Feldspar	15.05
Whiting	3.91
Zinc oxide	2.12
Barium carbonate	5.14
Clay	13.05
Flint	23.12
	100.00

Add black stain: DF-576 . . . 5.5 percent

The equivalent formula of the base glaze without the black stain is:

PbO	.5500				
K_2O	.0751				
Na_2O	.0231	Al_2O_3	.2230	SiO_2	3.0000
CaO	.1518				
ZnO	.1000				
BaO	.1000				

The exact composition of the black stain is not known, but such stains commonly contain at least four of the oxides of cobalt, copper, iron, manganese, or chromium. The following black stain is

PLATE 2. Electron micrographs showing fired glaze surface.

A. Level plateau with groove. Note rough surface of plateau as compared with smooth surface of surrounding glass. × 17,500.

B. Wrinkled surface and crystalline area (upper right-hand corner). Wrinkles are judged to be replicas of glaze, but may possibly be artifacts. × 19,500.

in commercial use: CuO, 18 percent; CoO, 18 percent; FeO, 10 percent; MnO_2, 36 percent; and Cr_2O_3, 18 percent. If this black stain were calculated into the glaze the empirical formula would be:

PbO	.4526				
K_2O	.0618				
Na_2O	.0190				
CaO	.1249				
ZnO	.0823	Al_2O_3	.1835	SiO_2	2.4685
BaO	.0823	Cr_2O_3	.0206		
CuO	.0392				
CoO	.0417				
FeO	.0242				
MnO	.0720				

The coloring metallic oxides present in black stains of this type are so proportioned that the colors produced by the silicates of the metals completely neutralize each other. A true gray can be produced from a good black glaze by mixing it with a white glaze. If an excess of the black stain—more than can be combined as silicates—is present in the glaze, the black oxides will be suspended in the glass. The submetallic sheen is commonly attributed to this excess of metallic oxides. If the above black stain were increased to 10 percent, for example, the glaze would be a definite "gunmetal."

The Eagle Picher frit consists of about 15 percent SiO_2 and 85 percent PbO. The clay is a ball clay from the Dakota formation of central Kansas; its mineralogical composition is about 40 percent kaolinite, 30 percent quartz, 20 percent illite and muscovite, a trace of feldspar, and a slight but definite indication of a mixed-layer mineral. The glaze was fired to cone 01 (2030°F.).

The glaze surface seems entirely smooth to the touch, and study of a Faxfilm replica under the light microscope reveals less detail than can be seen by direct observation of the glaze.

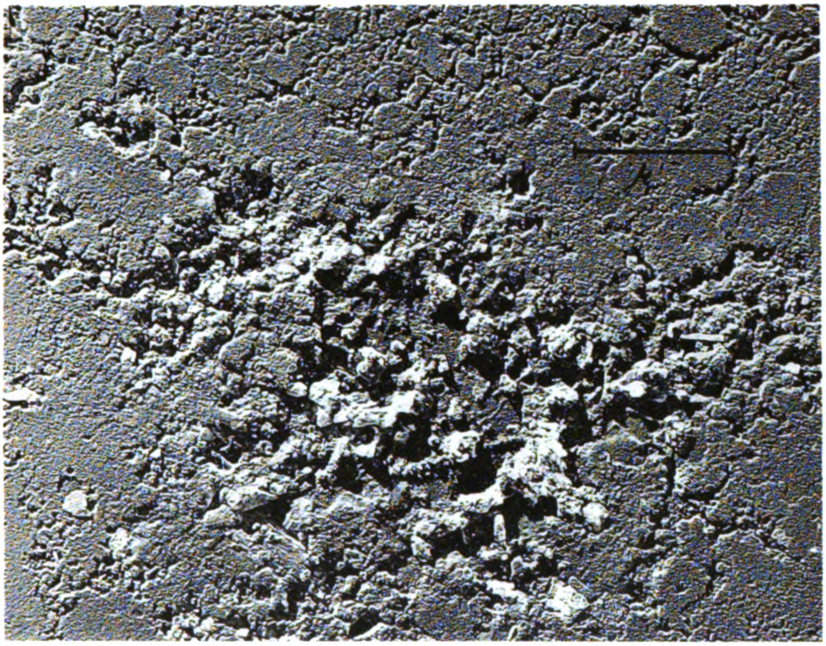
The electron microscope shows several types of surface features, most of which are considerably less than a micron in order of magnitude (Pls. 1 to 4). The various types are listed below.

1. Large plane glassy areas, showing almost nothing which cannot be attributed to collodion structure (Pl. 1A).

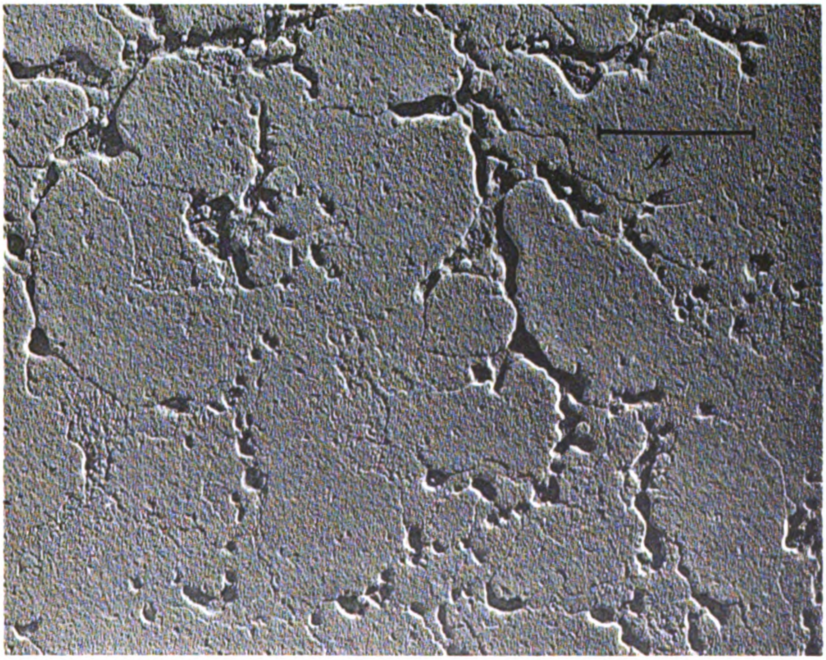
PLATE 3. Electron micrographs showing fired glaze surface.

A. Rough jagged surface; possibly unabsorbed refractory part of glaze. × 20,000.

B. Dendritic pattern of rough narrow ridges. × 20,000.



A



B

Swineford and Plummer — Electron micrographs of glaze replicas.

Swineford and Plummer — Electron micrograph of a glaze replica.

2. Broad, flat-topped projections or plateaus. These appear as flat-bottomed depressions in the negative replicas (Pls. 1B and 2A). The tops of the plateaus are rougher than the other surfaces, and they seem to be surrounded by a depressed area. Immediately adjacent to the foot of a typical plateau is a disturbed or bubbly area.

3. Narrow, rough-textured ridges (some discontinuous) having dendritic pattern, with smooth flat intervening "lowland" (Pl. 3B).

4. Areas of fine wrinkles, generally adjacent to some more rugged feature (Pls. 2B and 4). Some of the wrinkles have a chevron pattern.

5. Rough jagged regions (Pl. 3A).

6. Crystals. Crystals having triangular faces are suggested in the upper right corner of Plate 2B. These are approximately 0.1 micron in diameter. Another crystal (possibly an octahedron) appears in Plate 4, just below the micron mark.

7. Bubble. The replica of an unbroken bubble about 1.2 microns in diameter is clearly shown in Plate 4.

8. Intersecting grooves (Pl. 4). These grooves range in diameter from 0.05 to 0.2 microns and strongly resemble craze features.

Detailed interpretation of the micrographs must be deferred until more data are available. In conclusion it should be noted that there are two general levels to the glaze: a somewhat rough upper level and a more extensive smooth glassy lower level. The total relief (except for the "craze" cracks) is much less than 0.1 micron. The rough areas are judged to be parts which did not melt completely and become assimilated into the glass, and the bubbly areas around the perimeters of some of them are probably reaction rims.

The wrinkles may indicate rapid cooling or flowage of the glass after a thin scum had developed on its surface. On the other hand they may not be part of the glaze at all, but perhaps were formed in the collodion during the production of the replica. Further study may determine whether or not these wrinkles are artifacts.

PLATE 4. Electron micrograph of glaze surface, showing curved intersecting grooves (craze pattern?), wrinkles, crystal, and bubble. × 15,000.

CONCLUSIONS

The minute frost-speckled appearance of the black glaze is judged to be due to incomplete melting of the raw material. The submetallic sheen is not explained, but it may be an effect of the total surface relief, which is between 0.05 and 0.1 micron.

Electron microscopy of surface replicas is judged to be a promising method for the study of relatively smooth glaze surfaces. The internal structure of fired glaze batches could also be examined by replication of fracture surfaces.

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