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SPECIFIC GRAVITIES AND FLUIDITY FACTORS OF GLAZE SLIPS

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Introduction

Early this year an order restricting the use of lead-bearing chemicals was issued by the War Production Board, reducing the amount allowed the ceramic industries to 50% of 1944 consumption. This shortage necessitated the immediate reduction in the lead content of several glazes.

At about this same time changed body composition and plant process required adjustments in the glaze composition and application.

The laboratory began the investigation of these problems: First - to determine the changes necessary in the chemical composition of the glazes (because of the lead order and also the new body). Second - to determine the best methods of application of these new glazes to the new body. And, third, to establish control methods for plant use to insure satisfactory and consistent results.

Preliminary Laboratory Work

The formulae were re-calculated and the lead content was reduced. The glaze slip is a suspension of clays, feldspar, whiting, white lead, flint, aluminum hydrate, coloring oxides and other glass forming materials in water. The slip was milled and applied by dipping, to small cones cast of the new body. These prepared pieces were fired through the laboratory kiln with a simulative fire, approximating conditions in the commercial kilns. These preliminary investigations resulted in glazes maturing at required temperatures. The colors were developed and the surface textures adjusted.

Early Plant Experiments

The new processes were then tested at the plant. Batches of the new glazes were ground with normal plant procedure, and casts were prepared for fire. The glazes matured, and the colors and textures were good, but several glaze faults developed. Some pieces exhibited crawling, a fault characterized by shrinkage of the glaze at various spots on the body, leaving naked zones with rounded edges. Some revealed body scars and blisters where the walls of the ware had split slightly. With these problems in view, laboratory investigation was resumed.

Further Laboratory Investigation

Crawling starts at the beginning of fire, revealing lack of compatibility between the raw glaze and body. The glaze coating dries rapidly during this period and is likely to crack and shrink prior to melting. If the glaze is not extremely fluid in the molten state, the cracks will not heal. Rather, the surface tension of the glaze causes the broken edges to roll back still further, leaving the surface of the body bare.

Crawling can develop, too, if the surface of the body is dusty when the glaze is applied. Like other liquids, the molten glass will not cling to a surface which it cannot wet, and will recede from the dust covered areas.

Since proper precautions against dust were observed, the trouble was considered to lie in the glaze film itself. In this particular instance, due to material restrictions, it was more feasible to increase the strength of the raw glaze film than to increase the fluidity of the molten glaze. The bonding agents used in the glaze are normally ball clays, such clays showing a maximum subdivision and the highest degree of plasticity, possessing a great bonding power and toughness in the unfired state and vitrifying at comparatively low temperatures as compared to the kaolins. The indicated increase in the glaze eliminated the crawling.

The phenomenon of wall splitting was more difficult to control. An extensive search of ceramic literature failed to reveal much of real help. It did, however, support our own observation that the fault arose during application and was caused both by the condition of the ware and that of the glaze slip.

The work was carried out with unfired ware, which had lost its plasticity due to drying and also a great deal of the toughness and strength imparted by the plastic clay. Addition of water does not restore these properties, but weakens the body.

When an excess of water from the glaze was absorbed, saturating the surface of the ware, it divided the walls into strata. The swelling of the outside layer caused it to rise and finally to burst outward, leaving a star shaped tear which was further aggravated by the stresses of firing.

Investigation of the Effect of Moisture in the Ware

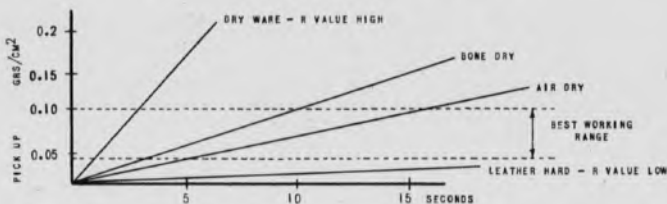
The effect of various water contents of the ware was first investigated. Normal glaze, milled with water containing no electrolyte, and thinned with water to dipping consistency, was applied to pieces of ware leather hard (containing 10% moisture), air dry (6% moisture), bone dry (4% moisture), and dry.

Tests were made on ware in these conditions with 5-, 10-, and 15-second immersions. The leather hard ware, already containing 10% water, had a low receptivity value. That is, it did not quickly absorb further water into its surface. The receptivity value is a measure of the amount of water absorbed per unit area per unit time, and influences the glaze thickness on dipping. The surface of the ware in this condition failed to absorb water fast enough to give a proper thickness of glaze. Increasing the immersion time beyond practical limits only caused enough water to be taken up to bring about wall splitting.

The air dry and bone dry tests gave similar results. The R value here was considerably greater and consequently water was absorbed more rapidly and a thicker deposition resulted. Still too much water was absorbed in normal dipping time, to give good results.

The glaze was deposited on the dry ware too rapidly, building up an extremely thick coating during a very short immersion. The R value of the dry ware was extremely high, and again the excess water caused wall splitting.

TYPICAL CURVE RELATING TIME OF IMMERSION, COHERENCE VALUE AND CONDITION OF THE WARE



Since control of the moisture content of the body did not show promise, attention was directed to the glaze slip itself.

INVESTIGATION OF FLUIDITY FACTORS IN GLAZE SLIPS

The problems here appear to be control of the following factors through control of the slip consistency:

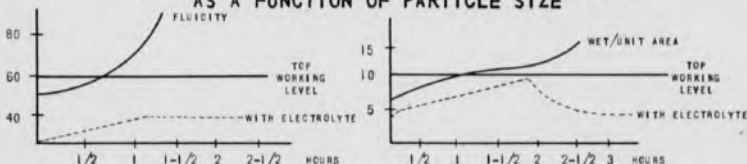
- (1) the weight of glaze deposited per unit area per unit time (coherence value)
- (2) the character of the deposition
- (3) the quantity of water absorbed per unit weight of the deposition (controlled by water content of the glaze and receptivity of the ware).

The three factors were found to be so closely related that it is impractical to separate them for discussion. They were in turn influenced by the particle size, fluidity, pH value, and specific gravity of the slip.

A glaze which showed poor behavior in respect to wall splitting was chosen as the basis for the tests.

The effect of particle size was investigated. Studies of the dipping behavior of the glaze milled for varying lengths of time with no electrolyte addition showed that the milling time affected glaze consistency, dipping characteristics, fluidity and pH value. Until the glaze reached the optimum particle size distribution, its characteristics improved, dipping nicely with a good fluidity, drying rapidly and having a good smooth texture. Further increase in grinding time resulted in the glaze becoming quite viscous and in the tendency toward poor drainage, slow drying and severe cracking on drying, which became progressively worse with further reduction of particle size. The fluidity of the slip decreased rapidly and the amount of glaze adhering to the surface per unit time increased. The pH value increased as the particle size became smaller. The glaze dried slowly because of the clogging of pores by the fine particles, thus reducing the capillary action.

TYPICAL CURVES SHOWING WORKING PROPERTIES AS A FUNCTION OF PARTICLE SIZE



The fluidity of the slip was found to change with age. On standing, thinning was pronounced, and might be explained by progressive solution of the salts, resulting in increased alkalinity.

The addition of an electrolyte to the glaze slip produced definite changes in its behavior. "N" Brand sodium silicate was chosen and added to the mill batch in order to accelerate its action. The water content was cut to about 75% of that formerly used, resulting in a slip of high specific gravity. This was held constant and the glaze deflocculated almost to the settling point with sodium silicate. Thus the specific gravity could be held fairly constant, while the fluidity could be varied from a heavy paste at one extreme, to a watery consistency at the other extreme.

Starting with a five drop addition of the reagent, we increased it at five drop intervals to 40. The following results were gained:

Drops	Glaze Characteristics
5 ..	Too viscous. Deposition too thick. Poor draining, slow drying and cracks on drying.
10 ..	Still too viscous, with poor draining, slow drying.
15 ..	A little too viscous, dips fairly well, dries a little faster, no cracks.
20 ..	Dips well, drains well giving a uniform coating, dries rapidly, strong smooth feel.
25 ..	Dips well. A little too fluid, dries a little too rapidly. Grainy feel.
30 ..	Dips well but too fluid. Curtains (dried before smoothing out well). Grainy feel.
35 ..	Too fluid. Glaze coating too thin. Curtains badly. Cracks.
40 ..	Watery. Coating very thin. Curtains badly. Severe cracks on drying.

Working above the optimum silicate content, it was found that fairly satisfactory physical dipping characteristics could be regained by adding acetic acid. This apparently caused the formation of a gel which retarded the drying rate and thus reduced curtaining. The glaze coating, although it appeared thick enough in the raw state because of the gel-like character, was still far too thin on firing. Therefore, silicate alone was indicated for plant use.

Plant Control Procedure

Since the glaze preparation at the plant is carried out in close co-operation with the laboratory, most of the control work was instituted during this operation. The changes in clay content were made here. The optimum time schedule for milling each separate glaze was determined and put into effect. The initial water was measured, and the accurately measured silicate was added to the batch. These factors, which were the variables throughout the tests, were now set values when the glaze was delivered to the dippers. All that remains is to thin the slip slightly with water

to bring it to the specific gravity specified for each separate glaze and each size ware, calculated simply from the weight in grams of 1000 cc of the slip, and to select air dry ware for dipping. Some of the dippers become quite skilled at judging a glaze by the feel, but all are required to make the weight test several times during the dipping period to insure proper control.

Some of the glazes require an ageing period of 24 to 48 hours before dipping. These are ground ahead of the dipping schedule and stored under the supervision of the dipper who records the time of delivery and then waits for the specified time before using the glaze.

With these controls being conscientiously used in the plant, glaze troubles have been reduced and ware quality improved.

