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RED GLAZES

ΒY

SIDNEY AUSTIN PEER

A

THESIS

submitted to the faculty of the SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI in partial fulfillment of the work required for the Degree of BACHELOR OF SCIENCE IN CERAMIC ENGINEERING

Rolla, Mo.

March 30, 1940

7. Herold Approved by

Professor of Ceramic Engineering

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# RED GLAZES

Red glazes are extremely difficult to produce on pottery except at relatively low temperatures, or under conditions which can only be regarded as largely accidental. For many years ceramists have demanded a red glaze maturing at cone 4. To produce this glaze, much time and research is required.

In obtaining a red glaze, many factors must be considered; First of all, the glaze must have a pleasing shade of red. Secondly, the glaze must mature at cone 4 or higher. Thirdly, the glaze must be reasonable cheap to manufacture.

In the actual manufacture of pottery and tiles, most glazes may be applied and fired at the same temperature at which the ware is vitrified. In the case of red glazes, the ware must be fired at one temperature and the red glaze applied and then fired at enother temperature. This involves the expense of having two separate firings; One for the vitrifying of the ware, and the other for the maturing of the glaze.

For this reason, many attempts have been made to obtain a red glaze which could be fired at the same temperature at which the ware is normally fired.

The preparation of the colored glazes is quite important and the final quality of the glaze depends almost entirely upon the preparation of the glaze. There are four important steps to be taken in the manufacture of a glaze:

(1) Weighing. In weighing out the ingredients to be used in the glaze, care must be exercised in order to get the exact amount of each material. A little variation either way, in weight, will cause a decided variation in the final color of the glaze. Any water contained in the materials weighed should be included in the calculations. If this weight of water is not taken into consideration, the true weight of the materials cannot be tabulated. For this reason, it is best that all materials used be perfectly dry when they are weighed.

(2) Mixing and Grinding. To insure an even color in the final product, the materials used in the glaze should be ground to a fine state and mixed thoroughly so that there will not be a concentration of any one material in any certain spot in the glaze. If the material is not mixed thoroughly, the final result will not be an evenly colored glaze but one that is spotty. Care must be taken in the mixing of the glaze to evoid any introduction of air to the slip. If the glaze contains air bubbles, the final fired glaze will contain pinholes.

(3) Application. To obtain a satisfactory application of the glaze, it is necessary for the glaze to have the correct specific gravity. That is, the specific gravity of the glaze must be of such a nature that it will apply evenly to the ware. There are two main methods of applying the glaze to the ware. These two methods are dipping and spraying. In dipping, the part of the article to be coated is passed quickly through the slip with

a single motion of the hand, care being taken that the article does not stop. Any superfluous glaze slip is allowed to drain off or is shaken off of the ware by a dexterous turn of the wrist. The thickness of the application is determined by the duration of the immersion and the specific gravity of the slip. Spraying, consists in applying the glaze in the form of a fine spray by means of an atomiser. serograph or similiar device, in which a current of eir is blown on to the slip in such a manner that a small quantity of it is drawn up a tube an injected. along with the air, in the form of a fine mist or The thickness of the application in the case spray. of spraying is dependent on the duration of the time that the spray gun is held on the ware and to a smaller extent, due to the specific gravity of the slip. Care must be taken that all particles of the materials used are ground fine enough so that they do not clog up the atomiser.

(4) Firing. The firing of a glaze is an important item in the manufacture of a glaze. Care must be exercised in the controlling of the temperatures so that a uniform rate of heating, and also

a uniform rate of cooling is maintained. Quite often the colors of the glazes are affected by the rates of cooling and heating to which the glazes are subjected. The maturing temperature of the glaze must be reached but not over run. If the glaze is overfired, the color will change or else the glaze will spoil in some way. It may lose its luster or it may blister. If the maturing temperature of the glaze is not reached. then the color will not be brought out and the glaze will be dull and without luster. Kiln conditions are an essential factor in the firing of If the glaze requires reducing conditions glazes. and the kiln operates under an oxidizing condition. then the glaze will either be spoiled altogether or else the glaze will have an entirely different final color than that which is desired.

# MATERIALS USED

The materials used for the body glaze were; white lead, and silica.

The coloring oxides used in an attempt to get a red glaze were; Cr2O3, MoO3, MnO, WO3, CuSO4, SnO2, SiC.

Tiles used for the application of the glazes were vitreous tiles.

All glaze trials were fored in a globar electric furnace.

SCOPE OF INVESTIGATION

The object of this study was to produce a commercial red glaze at cone 4 from different oxides in a base glaze of white lead and silica.

#### METHOD OF INVESTIGATION

Since PbMoO4, PbOr2O4, and MnO.WO3 were not available for use, the oxides were added in such proportions as to give the same oxide ingredients as the desired compounds would have given, had they been available.

A clear glaze was used for the body of the red glaze. This clear glaze was composed of 85 parts of white lead and 15 parts of silica. This clear glaze matured at cone O15 and was used in experimenting for a red glaze in order to save time. The glaze used, matured at a low temperature and yet gave the same results that would have been given by a glaze that would have matured at a higher temperature.

The glazes were applied to vitreous tiles and fired to the desired temperature, of 805°C, at a uniform rate.

Each of the oxides used was applied to the glaze in different percentages to find the result

of concentration as well as the results obtained from the oxides themselves.

#### PROCEDURE

A clear, transparent glaze was made up of 85 parts of white lead and 15 parts of silica. The oxides from which these components were made, were finely ground and sifted through a 150 mesh sieve. All of the oxides added to the body glaze were ground and sifted through a 150 mesh sieve and then weighed accurately to the desired amount.

The oxides added and the amounts in which they were added were as follows:

> 1, 3, 5, and 7 percent Cr203 8. 1, 3, 5, and 7 percent MoO3 Ъ. 1 percent MnO plus 3 percent WO3 C. ð. 3 percent MnO plus 9 percent WOz l percent MnO plus 5 percent WO3 e. 5 percent MnO plus 5 percent WOg f. 8 percent WO3 g. 0.3 percent copper plus 0.3 percent tin h.

plus 0.5 percent carborundum

1 percent copper plus 1 percent tin plus
1.5 percent cerborundum

The trial labeled (a) consisted of four separate trials in which the Cr<sub>2</sub>O<sub>3</sub> was added to the clear glaze in the four different percentages that are listed. In the trial labeled (b) this same condition existed and the trial was broken up into four separate trials in which the different percentages were added. The rest of the trials tabulated, were all complete trials in themselves.

Each of the vitreous tile test blocks were marked with a cobelt pensil. This was done in order to keep track of the various trials upon completion of the firing.

The glaze body was made up from its constituents and the coloring oxides added in the desired percentages.

Next, the vitreous tiles were dipped in the prepared colored glazes. Care was taken not to get the glazes on the tile blocks too heavily for this would have influenced the final color of the glazes to some extent. Any superfluous glaze slip was drained off of the trials. Two trials of each colored glaze were made in order to get truer results. By having two trial tiles, of each separate trial, the chances of obtaining the true results were raised. If one trial was ruined in some unforseen way, the other trial would give the desired information. When the glaze trials were placed in the kiln, one set of each glaze occupied a different part of the kiln than the other. In this way neither of the two trials would have the identical conditions while firing.

All of the trials were fired to cone 015 in five hours time, at a uniform rate of firing. The trials were allowed to cool slowly so that the cooling would not affect the final results.



Much in U. S. A. Printer Form No. 5780E-20 Squares per Inch

## DISCUSSION OF RESULTS

The glazes in which the chromium was added produced colors ranging from an orange to a deep red color. The trial in which 1 percent of the glaze was chromium gave a light orange color. The trial in which 3 percent chromium was added gave a bright red on one trial an gave a yellow red on the other trial block. In the glazes in which 5 and 7 percent were chromium, the glaze became a dull and dark red matt.

In the glazes in which MoO3 was added to the glaze body, a light ivory to a yellow was obtained. The trials containing 1 and 3 percent MoO3 gave a light ivory color. The other trials, which contained 5 and 7 percent MoO3, a yellow tint was imparted to the glaze.

When copper, tin, and carborundum were added to the body glaze, all results gave a green color to the glaze. This was a good green with no signs of a red present. An increase in the percentages

of the coloring oxides gave a darker green color.

In the glazes in which MnO and WO3 oxides were added, the colors obtained as final results ranged from a brown to a deep brown red. The trials which contained 1 percent MnO and 3 percent WO3, gave a light brown glaze. The trials in which the glaze contained 3 percent MnO and 9 percent WO3 gave a dark red brown. In the glaze in which 5 percent MnO and 5 percent WO3 was used, a real dark brown matt resulted. The glaze containing 1 percent MnO and 5 percent WO3 tended to craze quite a bit and gave a dull brown matt color. In trials which contained WO3 as the sole coloring agent in the glaze, a good white glaze resulted. In this last trial the WO3 was present as 8 percent of the raw batch.

#### CONCLUSIONS

It is concluded that;

Chromium will give a red glaze under the right conditions. By experiment it was found that 3 percent of the raw batch as chromium would give a bright red glaze. The body glaze used must be a lead glaze so that the chromium may combine with the lead to form PbCr<sub>2</sub>O<sub>3</sub>. When fired to cone Ol5, this glaze gave a good red and when an additional amount of the chromium was added the red became a deep, dull, red matt glaze. When the percentage of the chromium coloring oxide added was less than 3 percent, the color became an orange.

A glaze in which MoO3 was added as the coloring oxide a yellow was obtained. With an increasing perdentage of the coloring oxide, the color of the glaze became a deeper yellow. MoO3 would probably give a red if the percentage added was great enough but due to the cost of this oxide, the glaze could not be made on a paying basis and be used in the ceramic industry commercially. For this reason, further work on obtaining a red thru the use of MoO3 would be unadvisable.

In the glazes in which WO3 and MnO were tried, the only combination that gave any indication of a red was the combination in which 3 percent MnO and 9 percent WO3 was added to the glaze. The color resulting from the use of this percentage, gave a deep red brown glaze. This glaze is likely to give a good red if further work is done with it.

The glazes in which combinations of copper, tin, and carborundum were used gave no indications of a red. This was probably due to the wrong conditions in the kiln. A fairly good red has been obtained by using this combination of oxides in the past. Reducing conditions were required in the kiln at the time of firing.

The use of the oxide WO3 alone will not give a red glaze. By using very high percentages of this oxide in the glaze, a red might be obtained. This last fact would eliminate this oxide from the list of possibilities due to the fact that this oxide would involve a tremendous amount of money at such high percentages.

#### RECOMMENDATIONS

For further work on obtaining a red glaze, it would be advisable to try more work on the combination of the two oxides; MnO and WO<sub>3</sub>. These oxides gave a very good indication of giving a red glaze. Further experimentation with the oxide, chromium might give the desired glaze also.

By using these oxides in different tempconditions a good red might be obtained. That is, if the rate of firing and the rate of cooling of the glazes is varied it might be that a more favorable set of conditions could be found. By using the oxides in different percentages and by altering the conditions under which the trials are fired, a red glaze may be obtained.

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