A COBALT-URANIUM GREEN GLAZE FOR TERRA COTTA.

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We were confronted with the problem of developing a commercial green glaze having a deeper shade than any of the yellow-greens we had produced by the use of chromium stains in glazes fired to cones 6 or 7.

The characteristics and methods of producing green colors in glazes may be outlined as follows:

1. Copper greens are used extensively. At cones 6 or 7, however, the greater part of the copper is volatilized and the resultant shades of green are light and uneven.

2. Chromium and chromium stains when used in most glazes of the Bristol type give greens which appear yellow when compared with deep greens. The chromium can only be used in glazes in which the zinc content is very low. A reduction of the zinc content necessitates either a higher maturing temperature for the glaze or the use of lead compounds or frits. Chromium compounds are unstable in the kiln. In the proximity of even small amounts of chromium, glazes containing zinc oxide fade to brown and glazes containing tin are apt to be streaked with pink.

3. The nickel green colors are variable.

4. Iron compounds, if used alone, are volatilized at cones 6 or 7.

5. Uranium compounds, if used alone, produce variable yellow-green colors.

6. Greens may be produced by the blending of blue and yellow colors.

(a) It is reported that mixtures of iron and cobalt compounds have produced good greens. This has not been our experience—our trials giving browns and brown-greens.

(b) Orton notes the preparation, by roofing-tile manufacturers, of a green sulphate from antimony and cobalt oxides. Various yellow stains—some of which derived their yellow color from

antimony—were blended with cobalt and produced yellow and greenish browns which shaded into blues.

(c) Mixtures of cobalt oxide and titanium compounds are reported to have produced greens.

(d) Several investigators¹ have produced greens from mixtures of soluble uranium and cobalt compounds which were added to the glaze as insoluble frits.

In our attempt to develop the shade of green desired the procedure was as follows:

Series A.

Using a dull matt glaze as a base, uranium oxide and a cobalt stain were added to this glaze in varying amounts.

The formula of the glaze was as follows:

This glaze matures at from cones 3 to 7 in a commercial kiln. The blue stain added to the glaze had the following composition:

	Per cent. (Raw).
Cobalt oxide.....	16.0
English ball clay.....	53.0
Zinc oxide.....	31.0
	<hr/> 100.0

The commercial uranium oxide was supplied by the Carnotite Reduction Co. of Chicago. A rectangular series of 45 members was prepared by the addition of the cobalt stain and uranium oxide to the matt glaze. The corner glazes of the series were as follows:

- Glaze No. 1—Matt glaze + 7.0% uranium oxide + 0.0% blue stain
 Glaze No. 9—Matt glaze + 7.0% uranium oxide + 6.0% blue stain
 Glaze No. 37—Matt glaze + 3.0% uranium oxide + 0.0% blue stain
 Glaze No. 45—Matt glaze + 3.0% uranium oxide + 6.0% blue stain

¹ F. H. Riddle, *Trans. Am. Ceram. Soc.*, **8**, 210 (1906); R. H. Minton, *Ibid.*, **9**, 777 (1907); B. S. Radcliffe, *Ibid.*, **16**, 209 (1914); *La Céramique*, **1907**, No. 225, S. 25; *Tonind. Ztg.*, **1907**, S. 1412.

Each glaze was sprayed upon 3" X 5" terra cotta tile to which a coating of white underslip had been first applied.

The glazed tiles were placed in a commercial terra cotta muffle kiln and burned to between cones 6 and 7. The burning period was 70 hours and the cooling period 80 hours.

The appearance of the glazes of this series is noted as follows:

Glazes Nos. 1, 10, 19, 28, and 37, containing no cobalt stain, developed the characteristic uranium colors. 3.0 per cent. of

		Uranium Oxide Per cent.				
		7.0	6.0	5.0	4.0	3.0
Cobalt Stain - Per cent.	0	1	10	19	28	37
	0.75	2	11	20	29	38
	1.5	3	12	21	30	39
	2.25	4	13	22	31	40
	3.0	5	14	23	32	41
	3.75	6	15	24	33	42
	4.5	7	16	25	34	43
	5.25	8	17	26	35	44
	6.0	9	18	27	36	45
		Series A Matt Glaze as Base				
		Series B Bright Glaze as Base				

the stain produced a brownish yellow color, changing to green as the uranium content increased. The glaze containing 7.0 per cent. uranium oxide, although green, had a decided yellow cast.

Glazes Nos. 2, 11, 20, 29 and 38 were of deeper green shades and showed the influence of the stain but slightly.

Glazes Nos. 3, 12 and 21 were as green as any of the glazes of the series, but were not uniform when applied on large surfaces.

Glazes Nos. 30 and 39 were mottled by patches of yellow.

Glazes Nos. 4 to 9, 13 to 18, and 22 and 23 were uniformly deep green in color.

Glazes Nos. 24 to 27 developed a distinct blue-green color. The green color faded and the blue became stronger with increasing amounts of the cobalt stain.

Glaze No. 40 contained the smallest amount of the cobalt stain to show blue tints. When the uranium addition was lowest (3.0 per cent.), the blue shades were obtained with the lowest amounts of blue stain.

The glazes listed above as good deep greens were somewhat defective on account of the occurrence of yellow patches on the surfaces. There was no regularity in the occurrence of this yellow surface mottling. This mottling was very prominent in several of the good green glazes which were applied to full sized pieces of terra cotta. The appearance of the mottling was not very objectionable—in fact was pleasing—although not desired.

Series B.

Using a bright glaze of the following formula as a base, another series was prepared by the addition of the uranium oxide and cobalt stain in the same proportions as in Series A:

Bright Glaze:

This glaze matures at from cones 4 to 7 when fired either in a small or large kiln.

The appearance of the glazes of Series B is noted as follows:

The colors developed were in general the same as those of the Series A glazes, although not as distinct. The green colors tend toward the brown and drab shades. The blue and yellow colors are less pronounced. The addition of uranium oxide alone tends to produce fine dark specks.

The yellow mottling developed by some of the glazes of Series A was not observed in any of the glazes of Series B. The mottling of the glazes of Series A may be explained as follows:

Since the uranium compound is partially soluble, a greater proportion of the yellow material was deposited near the surface of the glaze as the water evaporated in drying. The yellow color of the uranium partly masked the blue color of the insoluble stain and produced the mottled effect. Although the uranium does not come to the surface as a scum, it tends to take possession of the surface and the upper portion of the glaze—leaving a greater proportion of the blue stain next to the underslip. Any particles of blue stain which do appear on the surface are coated with sufficient uranium to appear green. Under the microscope, a cross section of the glaze coating shows that in places where the yellow-green does extend into the mass of the glaze a darker and bluer green results close to the underslip. As the bright glaze used in Series B produced no mottling, we may assume that it had greater solvent power than the matt glaze used in Series A.

Series C.

From the information secured from Series A and B a third series was prepared as follows:

In order to avoid the mottling of the matt glaze, a soluble blue stain was employed—the cobalt being added as soluble cobalt sulphate. Maintaining the uranium content constant at 6.0 per cent., the cobalt sulphate was added to the matt glaze (Series A) in varying amounts. The addition of 3.0 per cent. gave a reliable color, the proportion of uranium to cobalt sulphate in this case being 2 : 1. The matt glazes to which the cobalt sulphate was added were more vitreous than those in which the insoluble cobalt stain was used.

No signs of mottling were in evidence in the glazes of series C and the 3.0 per cent. cobalt sulphate glaze was used in the coating of 200 sq. ft. of terra cotta surface. A green glaze of this description can be burned in proximity to other glazes without danger of discoloring them.

By calcining or fritting the cobalt and uranium to a homo-

geneous mixture and by subsequent fine grinding a similar green can no doubt be obtained.

COMMUNICATED DISCUSSION.

R. L. CLARE: 1. I wish to state that whenever possible we have avoided the use of uranium compounds in terra cotta glazes on account of their excessive cost and we have usually been able to produce the various shades of green desired without the use of these materials.

2. We have used chromium alone in glazes and have found it to be very unstable and unsatisfactory. It, however, in some cases gives a very deep green color, deeper and better in fact than any which we have been able to secure by the use of a stain. It appears that the materials used in a stain with the chromium tend to dilute the green shade. Materials such as iron, cobalt or uranium when used in a stain change the shade to a brown-green, blue-green or a yellow-green.

3. It is very interesting to note that Mr. Wilson has produced a good green by the use of a mixture of uranium oxide and a cobalt stain. It is not clear in my mind whether his resultant green is of the same shade as the typical chromium green. We have produced greens by the use of mixtures of iron and cobalt stains and manganese and cobalt stains, but in each case they have developed yellow-green, blue-green or brown-green colors and in no case were the typical deep grass-greens of the chromium produced.

Mr. Wilson's theory of the cause of the mottling on the glaze surface is very interesting and plausible. We have often noticed scumming on the surfaces of some of our colored glazes and we have attributed it to the solubility of some of the colorants and the consequent concentration of salts on the surfaces of the pieces—due to evaporation. It has already been shown that colors can be produced by painting or spraying certain soluble salts in solution on the surfaces of the unburned terra cotta glazes.

D. F. ALBERRY: I wish to note the following in reference to the methods of producing green colors in terra cotta glazes:

1. Copper oxide is satisfactory in glazes fired from approximately cone 04 to cone 2.

2. Chromium alone is too unstable to be recommended for the production of the green colors.

3. Chromium stains when properly compounded, calcined and washed, produce very stable and uniform greens of practically any desired shade. These green shades may be varied from deep blue-greens to brown-greens by the addition of cobalt oxide, iron oxide or burnt umber. The composition of the stain influences its color and shade considerably. For instance, it is possible to vary the shade of a given glaze by substituting plaster of paris for whiting in the stain. The composition of the glaze also has a decided influence on the stability of the color produced by a given stain.

We have made name panels by using a green glaze for the background and a white glaze—containing about 6 per cent. tin oxide—for the raised letters. The white glaze did not show the slightest discoloration even though it was in contact with the green glaze in a line at the base of the letters. It is largely a matter of glaze composition. Our green glazes are not fritted and do not contain zinc or lead.

4. I have never known of an iron compound producing a green color when used alone in a glaze at any temperature.

5. I have produced an unstable yellow-green by the introduction of a high percentage of uranium.

6. I have produced good blue-greens with cobalt-rutile combinations in glazes maturing at from cone 03 to cone 2.

Although good green colors may be obtained by cobalt-uranium combinations, it would appear that the cost of the high percentage of uranium oxide necessary would discourage the extensive use of this method.

R. H. MINTON: Those who have had experience in the manufacture of architectural terra cotta will appreciate the value of a dependable green coloring agent which is not affected by zinc oxide, and which will not affect, or be affected by, other colors. White, greens, browns and tans are widely used in polychrome work and a combination of these colors has always presented difficulties if the green was produced by the use of chromium compounds—the usual practice. Terra cotta white matt glazes

usually contain a high percentage of zinc oxide and, if used next to a chromium green, an unsightly line of tan or brown results at the juncture. For this reason, a green produced from a mixture of uranium and cobalt greatly simplifies the factory operation.

My experience with the use of uranium compounds for yellows and greens has covered its use in both fritted and raw, bright and matt glazes, and has shown that in order to produce a good yellow from uranium in a matt glaze, the zinc oxide should be eliminated as it tends to the development of greens. I have found that in order to produce uniform uranium colors, either yellow, orange or green in a matt glaze, it is of great advantage to use a small amount of rutile. The rutile appears to "set" the color and prevent the irregularity of color so often produced by uranium. An excellent green may be produced by the use of cobalt and rutile with the addition of a small amount of oxide of iron, although the color is not quite so bright as that secured with the presence of some uranium.

The mottling of the color in the matt glaze is undoubtedly due to the failure of the glaze to dissolve the uranium and the consequent crystallization or segregation, upon cooling. This difficulty is almost always encountered in producing uranium yellow matt glazes, where reducing conditions may occur, the result being a mottled green-yellow. The addition of rutile will entirely overcome this defect and the color will be improved if the content of zinc oxide is kept very low. A high zinc content and reducing atmosphere in the kiln are favorable for the production of greens. The use of the soluble form of the cobalt, rather than the difficultly soluble stain, as stated by Mr. Wilson, probably caused the formation of the green color by solution of the cobalt and uranium instead of by suspension.

HEWITT WILSON: The uranium-cobalt greens developed in the above study are not of the same shade as the typical chromium greens. The color is a deeper green than that afforded by the majority of the chromium greens burned in terra cotta muffle kilns to cone 6. While it is true that the cobalt-uranium greens do not match the characteristic chromium greens, it is likewise

true that it would be difficult to match some truly acceptable uranium-cobalt green shades with chromium combinations.

There is no question as to the practicability of producing green colors from cobalt and uranium mixtures. They have been produced in regular terra cotta work in a quantity sufficient to insure the uniformity required.

The disadvantages of the high cost of uranium is not so great when the comparatively small amount of green glazed terra cotta produced is considered. We do not know of any single component for colored glazes which has caused more terra cotta trouble than chromium.

The advantages of the above uranium oxide-cobalt sulphate green are as follows:

1. Ease of preparation. No calcining, washing or extra grinding necessary.
2. So far as noted, there was almost no discoloration of adjoining glazes—regardless of their composition.
3. A greater range of glaze composition in which green colors can be produced. It can be used in zinc and tin glazes.

Although it is not claimed that uranium-cobalt greens will replace the chromium greens, they have a place in terra cotta work in which uranium shades are desired and the complexities of chromium troubles are to be avoided.

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