NICKEL OXIDE IN GLAZES¹

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ABSTRACT

Colors produced from NiO.—The literature on this subject published in the Transactions of the Society is briefly reviewed.

Effects of variations of RO in cone 6 glazes on colors from nickel oxide.—*Red* colors are produced when ZnO and BaO are used in certain proportions. *Blues* and *purples* of varied shades and hues are developed with varied combinations of ZnO, CaO and BaO. *Grays* are possible in presence of CaO and MgO.

The transactions of our Society contain a few references to the colors produced by nickel oxide in glazes. These references are scattered through a number of volumes. To gather up the data and present it together with any new developments which might be obtained is the purpose of this paper. Furthermore, it was desired to determine, if possible, the influence exerted by each RO oxide on colors produced by oxide of nickel.

The conditions outlined make necessary, therefore, some overlapping with work previously done. This repetition, however, serves a useful purpose in emphasizing and strengthening conclusions already drawn.

Geijsbeck² states that Le Chatelier and Chaupuy in Paris reported the following colors obtained from nickel oxide in oxidizing fire: violet, blue, green, yellow, red and brown. Many of these colors are familiar to most of us. Some no doubt are unusual. Browns and yellows are the usual colors in lead glazes and under ordinary conditions. Blues and greens, more or less familiar colors, were once attributed to traces of cobalt in with the oxide of nickel.

Pence, however, in his study,³ "Colors Produced by Nickel Oxide in Ceramic Mixtures Containing Zinc," demonstrates that nickel oxide of the highest purity gives colors changing from

¹ Received March 10, 1921.

² *Trans. A. C. S.*, **6**, 195.

³ *Trans. A. C. S.*, **14**, p. 144.

brown through purple, reddish purple to blue as ZnO replaces BaO and CaO, and further that the blues thus obtained can not be duplicated by the use of cobalt oxide.

Nothing more red than the reddish tone of purple obtained by Pence had ever come under my observation. Hence the possibility of producing a red color from NiO was quite alluring. In paper presented¹ last year it was demonstrated that gray colors are produced by NiO in the presence of MgO.

Experimental

Inasmuch as this work is a continuation and enlargement of that previously reported, the base glaze used was the same and much of the present investigation was based on the results obtained at that time. The work was so planned that as each RO oxide replaced another the effect on the color produced by NiO could be noted.

The following base glaze was used:

The amount of NiO used was kept at 0.025 equivalent except in Series X; it was a straight addition to each glaze.

Series 1—ZnO vs. BaO.—This is a continuation of a series in the previous paper² in which ZnO replaces BaO. In the present instance the ZnO replaces BaO by 0.05 equivalent until the latter is eliminated from the formula.

Series 2—CaO vs. K₂O.—With no BaO in the RO, CaO replaces K₂O by 0.05 equivalent until the latter is eliminated from the formula. It will be noted here that the final 0.05 K₂O was replaced by 0.05 ZnO making the last glaze of the series have an RO of 0.5 ZnO, 0.5 CaO.

Series 3—ZnO vs. CaO.—We start this series with the original RO formula, 0.25 K₂O, 0.30 CaO, 0.45 BaO. ZnO replaces CaO by 0.05 equivalent until CaO is eliminated from the formula. We may compare this with Series 1 wherein ZnO replaces BaO.

¹ *J. Am. Ceram. Soc.*, 1920, 663.

² *Loc. cit.*

Series 4.—ZnO vs. K₂O.—Wishing to parallel the high CaO-ZnO glaze of Series 2, the K₂O in glaze 6 of Series 3 was replaced by ZnO in increments of 0.05 equivalent until the content of 0.5 ZnO is reached. The remaining 0.05 K₂O is then replaced by 0.05 BaO and we have glaze 5 with an RO content of 0.5 BaO, 0.5 ZnO.

In order to determine the different effects produced when MgO replaced each of the other RO oxides, the four following series were constructed:

Series 5.—With an RO consisting of 0.15 K₂O, 0.40 ZnO, 0.45 BaO as in glaze 2, series 4, MgO replaces BaO by 0.05 equivalents up to and including 0.20 MgO. ZnO and K₂O do not change.

Series 6.—With the same RO as in Series 5, MgO replaces ZnO in like manner, the BaO and K₂O remaining unchanged.

Series 7.—Starting with an RO consisting of 0.15 K₂O, 0.45 CaO, 0.40 ZnO, MgO replaces CaO by 0.05 equivalents until a content of 0.20 MgO is reached. ZnO and K₂O remain unchanged.

Series 8.—Using the same RO as in series 7, MgO replaces ZnO in like manner, the K₂O and CaO remaining constant.

When the results of these eight series were noted and it was found that a red color was obtained in glaze 2, series 4, the two following series were added to indicate what effect, if any, variations in the Al₂O₃ and NiO content might have on the red color.

Series 9.—Starting with glaze 2, series 4, Al₂O₃ was reduced by 0.05 equivalents to 0.10 equivalent, keeping the oxygen ratio constant at 1:2.

Series 10.—With the same glaze, the nickel oxide was varied from 0.025 to 0.10 equivalent.

Materials.—Formulae and batch weights of all the glazes are found in table 1. The materials used in this investigation were taken from regular factory stock and include the following: Eureka Feldspar, English Cliffstone Whiting, Red Seal Oxide of Zinc, Oxide of Nickel, Granville Flint, Cornwall Stone, Precipitated Barium Carbonate, Calcined Magnesite, Calcined N. C. Kaolin.

TABLE 1

Series 1

Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

Glaze No.	Formulae				Batch Weights						
	K ₂ O	CaO	BaO	ZnO	Feldspar	Stone	Whiting	Barium Carb.	Oxide Zinc	Calc. Clay	Nickel Flint Oxide
1	0.25	0.30	0.20	0.25	83.4	84.3	30.0	39.4	20.25	14.43	1.87
2	.25	.30	.15	.30	83.4	84.3	30.0	29.55	24.30	14.43	1.87
3	.25	.30	.10	.35	83.4	84.3	30.0	19.70	28.35	14.43	1.87
4	.25	.30	.05	.40	83.4	84.3	30.0	9.85	32.40	14.43	1.87
5	.25	.30	.00	.45	83.4	84.3	30.0	...	36.45	14.43	1.87

Series 2

Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

1	0.20	0.35		0.45	83.4	42.15	35.0	...	36.45	29.41	19.74	1.87
2	.15	.40		.45	55.6	42.15	40.0	...	36.45	40.51	31.74	1.87
3	.10	.45		.45	55.6	...	45.0	...	36.45	55.50	54.00	1.87
4	.05	.50		.45	27.8	...	50.0	...	36.45	66.60	66.00	1.87
5	.00	.50		.50	...	...	50.0	...	40.50	77.70	78.00	1.87

Series 3

Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

1	0.25	0.25	0.45	0.05	83.4	84.3	25.0	88.65	4.05	14.43	...	1.87
2	.25	.20	.45	.10	83.4	84.3	20.0	88.65	8.10	14.43	...	1.87
3	.25	.15	.45	.15	83.4	84.3	15.0	88.65	12.15	14.43	...	1.87
4	.25	.10	.45	.20	83.4	84.3	10.0	88.65	16.20	14.43	...	1.87
5	.25	.05	.45	.25	83.4	84.3	5.0	88.65	20.25	14.43	...	1.87
6	.25	.00	.45	.30	83.4	84.3	...	88.65	24.30	14.43	...	1.87

Series 4

Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

1	0.20		0.45	0.35	83.40	42.15	...	88.65	28.35	29.41	19.74	1.87
2	.15		.45	.40	55.60	42.15	...	88.65	32.40	40.51	31.74	1.87
3	.10		.45	.45	55.60	...	...	88.65	36.45	55.50	54.00	1.87
4	.05		.45	.50	27.80	...	...	88.65	40.50	66.60	66.00	1.87
5	.00		.50	.50	...	...	...	98.50	40.50	77.70	78.00	1.87

Series 5

Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

Glaze No.	Formulae				Batch Weights							
	K ₂ O	BaO	ZnO	MgO	Feldspar	Stone	Barium Carb.	Oxide Zinc	Calc. Magnesite	Calc. Clay	Flint	Nickel Oxide
1	0.15	0.45	0.40	0.00	55.60	42.15	88.65	32.40	...	40.51	31.74	1.87
2	.15	.40	.40	.05	55.60	42.15	78.80	32.40	2.015	40.51	31.74	1.87
3	.15	.35	.40	.10	55.60	42.15	68.95	32.40	4.030	40.51	31.74	1.87
4	.15	.30	.40	.15	55.60	42.15	59.10	32.40	6.045	40.51	31.74	1.87
5	.15	.25	.40	.20	55.60	42.15	49.25	32.40	8.060	40.51	31.74	1.87

*Series 6*Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

1	0.15	0.45	0.35	0.05	55.60	42.15	88.65	28.35	2.015	40.51	31.74	1.87
2	.15	.45	.30	.10	55.60	42.15	88.65	24.30	4.030	40.51	31.74	1.87
3	.15	.45	.25	.15	55.60	42.15	88.65	20.25	6.045	40.51	31.74	1.87
4	.15	.45	.20	.20	55.60	42.15	88.65	16.20	8.060	40.51	31.74	1.87

*Series 7*Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

CaO					Whiting							
1	0.15	0.40	0.45	0.00	55.6	42.15	40.0	36.45	...	40.51	31.74	1.87
2	.15	.35	.45	.05	55.6	42.15	35.0	36.45	2.015	40.51	31.74	1.87
3	.15	.30	.45	.10	55.6	42.15	30.0	36.45	4.030	40.51	31.74	1.87
4	.15	.25	.45	.15	55.6	42.15	25.0	36.45	6.045	40.51	31.74	1.87
5	.15	.20	.45	.20	55.6	42.15	20.0	36.45	8.060	40.51	31.74	1.87

*Series 8*Common to all glazes: 0.35 Al₂O₃; 2.00 SiO₂; 0.025 NiO

CaO					Whiting							
1	0.15	0.40	0.40	0.05	55.6	42.15	40.0	32.40	2.015	40.51	31.74	1.87
2	.15	.40	.35	.10	55.6	42.15	40.0	28.35	4.030	40.51	31.74	1.87
3	.15	.40	.30	.15	55.6	42.15	40.0	24.30	6.045	40.51	31.74	1.87
4	.15	.40	.25	.20	55.6	42.15	40.0	20.25	8.06	40.51	31.74	1.87

Series 9

Common to all glazes: 0.45 BaO; 0.025 NiO

Glaze No.	Formulae				Batch Weights							
	K ₂ O	ZnO	Al ₂ O ₃	SiO ₂	Feldspar	Stone	Barium Carb.	Oxide Zinc	Calc. Clay	Flint	Nickel Oxide	
1	0.15	0.40	0.35	2.00	55.6	42.15	88.65	32.40	40.51	31.74	1.87	
2	.15	.40	.30	1.90	55.6	42.15	88.65	32.40	29.41	31.74	1.87	
3	.15	.40	.25	1.75	55.6	42.15	88.65	32.40	18.32	28.74	1.87	
4	.15	.40	.20	1.60	55.6	42.15	88.65	32.40	7.22	25.74	1.87	
5	.15	.40	.15	1.45	83.4	...	88.65	32.40	...	33.00	1.87	
6	.10	.45	.10	1.30	55.6	...	88.65	36.45	...	42.00	1.87	

*Series 10*Common to all glazes: 0.45 BaO; 2.00 SiO₂

Glaze No.	Formulae				Batch Weights							
	K ₂ O	ZnO	Al ₂ O ₃	NiO	Feldspar	Stone	Barium Carb.	Oxide Zinc	Calc. Clay	Flint	Nickel Oxide	
1	0.15	0.40	0.35	0.025	55.6	42.15	88.65	32.4	40.51	31.74	1.87	
2	.15	.40	.35	.050	55.6	42.15	88.65	32.4	40.51	31.74	3.74	
3	.15	.40	.35	.075	55.6	42.15	88.65	32.4	40.51	31.74	5.61	
4	.15	.40	.35	.100	55.6	42.15	88.65	32.4	40.51	31.74	7.48	

The glazes were weighed up separately, ground in small trial mills and applied, by dipping, to thin porous wall tile bisque ($1\frac{1}{2}'' \times 1\frac{1}{2}'' \times 0\frac{1}{8}''$).

All glazes except those of series 9 and 10 were fired at the same time in a commercial down-draft kiln. The fuel used was natural gas. Cones placed in each sagger of glazed tile indicated a temperature corresponding to cone 6.

The majority of the glazes were matured at this temperature although some of those high in MgO were somewhat immature. The glazes of series 9 and 10 were fired at another time but the cones indicated a heat treatment very similar to that of the first burn.

Results

Series 1.—Glaze 1, reddish purple; glaze 2, more blue than glaze 1; glaze 3, mingled blue and tan, the blue apparently consisting of crystals on a tan background; glaze 4, goes bright, blue where thickest, yellowish color on edges of tile where thinnest; glaze 5, greenish matt, tending to blue crystalline where thickest.

The odd behavior of glaze 4 which went bright was attributed to a mistake in weighing the glaze, but a new batch, carefully checked, was made up and upon firing gave very similar results. Evidently some peculiar action, similar to the formation of a eutectic, occurs with 0.05 BaO.

These results indicate that an increase of ZnO at the expense of BaO gives colors tending toward blues and greens and away from purple tones. This contradicts Minton's statement¹ in his discussion of my paper last year that "the effect of BaO produces blue green with NiO" and confirms my previous observations.

Series 2.—Glaze 1, crystalline blue, similar to glaze 5, series 1, from which it differs only by 0.05 CaO replacing 0.05 K₂O. The crystals are small but the effect is very pleasing; glaze 2, purplish blue of slightly mottled nature; glaze 3, similar to glaze 2; glazes 4 and 5, more of grey blue color. The increase of CaO at expense of the K₂O seems to intensify the resulting blue color.

¹ *J. Am. Ceram. Soc.*, 1920, 669.

High whiting and high zinc together gives light greyish blues. The surface of glaze 5 which contains only CaO and ZnO in the RO is of an unpleasant greasy nature.

Series 3.—Glaze 1, brown; glaze 2, purplish blue; glaze 3, purplish blue; glaze 4, purple; glaze 5, about like glaze 4; glaze 6, reddish purple.

The results of this series confirm Pence's statement that purples and blues are developed as ZnO increases at the expense of BaO and CaO. If we compare the results of this series with the results obtained in series 1 last year wherein ZnO was used to replace BaO, we see that BaO and CaO produce much the same colors when used in connection with ZnO.

Series 4.—Glazes 1 and 2, these glazes develop decided reds which have a more or less purplish tone; glaze 3, light blue, similar to glaze 4, series 2; glaze 4, similar to glaze 3; glaze 5, more reddish than glazes 3 and 4.

In this series, with high ZnO and BaO, the reddish tone frequently observed has developed into a red of a somewhat purplish tone. This red develops where the glaze is dipped rather heavy and seems to be a segregation on the surface of the blue. Where the glaze is dipped light, the blue color predominates with only here and there a fleck of red on the surface. This red color seems to be developed within the following narrow limits of RO composition:

0.15	0.20 K ₂ O
.35	.40 ZnO
.45	.40 BaO

Later experiments tend to confirm this action and indicate that a variation of only about 0.05 equivalent in any one of these three oxides is permissible.

Series 5.—Glaze 1, red; glaze 2, blue; glaze 3, blue; glaze 4, lighter blue; glaze 5, lighter blue, nearer to turquoise.

The replacement of BaO with MgO in presence of ZnO gives blues, but lightens the tone. No purple blues are noticeable. The glazes are hardened somewhat as the MgO increases.

Series 6.—Glaze 1, blue; glaze 2, light grey blue; glaze 3, faded lilac; glaze 4, more grey than glaze 3.

The MgO replacing ZnO in presence of BaO hardens the glaze more than in the previous series. Furthermore, greater changes in color occur. This is equivalent to saying that ZnO has a more powerful effect on the color produced by NiO than has CaO and BaO.

Series 7.—Glaze 1, medium dark blue; glaze 2, bright glaze, yellow brown with blue segregations (Compare glaze 4, series 1); glaze 3, light green semi-matt; glaze 4, lighter in color than glaze 3, semi-matt; glaze 5, still lighter than glaze 4.

In glaze 2 this series, with a content of 0.05 MgO, we observe the same phenomenon as in glaze 4, series 1, which contains 0.05 BaO. The glazes in this series are hardened when MgO replaces CaO and the colors are lightened and tend toward grey greens.

Series 8.—Glaze 1, light blue; glaze 2, mingled grey and blue; glaze 3, good grey; glaze 4, grey, slightly browner than glaze 3.

In this series, wherein MgO replaces ZnO in presence of CaO, nice greys are developed. Last year it was shown that greys were developed when MgO replaced BaO with no ZnO in the formula. This leads to the conclusion that greys are not developed when the ZnO is present in too large quantities and the tendency of ZnO is to produce greys of bluish tones.

Series 9.—All glazes of this series are reds of the same purplish tone as glazes 1 and 2, series 4. The reduction of Al_2O_3 does not destroy the red color. It does, however, soften the glaze and produces better surfaces.

Series 10.—The red color changes from purplish to brownish as the NiO is increased.

Discussion of Results

A study of these results brings out some interesting facts. In the first place, a very interesting red color has been produced using NiO as the coloring agent. This color seems to be confined to a very narrow range of glaze composition so far as the RO is concerned. A content of not less than 0.35 BaO and 0.35 ZnO seems necessary, but both must not be this low at the same time.

This red color seems to be a crystalline segregation on the surface of a blue color, the blue always predominating when the glaze is dipped light. Within the limits studied the Al_2O_3 content may vary at will. The content of NiO influences the shades of red produced.

In the second place, more data on the development of grey colors is noted. It appears that CaO is necessary to the formula in producing greys; that the ZnO should not exceed 0.30 equivalent; that the MgO should approximate 0.15 equivalent; that BaO is not necessary in the formula, but that its presence is not detrimental. BaO may replace a part of the CaO as was shown in the paper of last year.

Conclusions

We conclude, therefore, that the following statements are justified as a result of this study:

- (1) The dominant tendency of ZnO is to produce blue colors with NiO , as already reported by Pence.
- (2) ZnO is not necessary in the production of greys with NiO but may be present if it does not exceed 0.30 equivalent.
- (3) BaO with CaO and K_2O gives browns, with ZnO , purples, reddish purples and reds when the proper proportions are used.
- (4) BaO is not necessary to produce greys but may be present in the formula partly replacing CaO .
- (5) CaO with ZnO produces blues and must be present with MgO to produce greys.
- (6) MgO tends to produce greyish tints when used with other oxides. To produce neutral greys it should be used with CaO or a combination of CaO and BaO . Bluish tones of grey are obtained when ZnO is present.
- (7) The coloring influence of K_2O is slight but its presence promotes maturity and good surfaces.

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