Over the Nickel Rainbow

Carol Marians shares her research on her search for nickel blue

Looking through Emmanuel Cooper's *The Potter's Book of Glaze Recipes*, I became intrigued by the variety of colours in nickel-containing glazes. Blue being the rarest, I set out to find a great nickel blue. Rarely was a glaze journey as full of delightful surprises.

Inspired by Cooper's *#94*, I designed *Ana#1* – substituting strontium for barium and soda feldspar for potash feldspar. In a digital electric kiln, I investigated composition and cool down in achieving nickel blues. *Ana#1* applied to tiles, is a variegated, pointillist, temperamental robin's egg blue, [See image captions.] But how different is *Ana #1* from 'all ' other glazes? If it is, what makes it so? Where are its neighbouring blue glazes? And what would 'neighbourhood' mean?

Ana #1 stands out because of its 0.1 MgO molecular equivalent. This is a measured, discernible amount of magnesium, not the trace found in all glazes. Nor is it the 0.2 plus magnesium of classical magnesium glazes. It falls in between. *Ana#1* is a sensitive multi-phase assemblage, balancing between blue on one side, brown on the other. The volume fraction of matte to glossy varies, as does the colour. The strong blue concentrates in the matte phase, in firings with holds near 1500ºF. The glossy phase is mauve/taupe bordering on tan.

Colour is most intense with thorough intermixing of the two phases, suggesting holds are most relevant just where liquid and solid meet. Examined through a jeweller's loupe, *Ana #1* appears an almost fully glossy transparent second phase surrounding islands of sugary white. It is its small crystals that 'carry' the blue colour, so they are wanted in large numbers. (If instead, there were a small number of large crystals, a white glaze with a few small scattered deep blue dots would result.) Thickly applied, the glaze looks white, not blue.

The needed multitude of small crystals must be well dispersed throughout the glaze to achieve that elusive blue. Therefore a large number of particles must be obtained in the solidification of the glaze, or through slow growth of the second phase, near the end of solidification.

Magnification explains what is going on. At different points in heating, and again in cooling, specific ingredients melt and form rivulets, which may or may not converge with other rivulets. Glaze colours are most often achieved when particular rivulets are 'frozen' into the solidified glaze. When glazes 'break' at the edges it is because one 'rivulet' takes over from another. We see the sky as blue because of light rays, bouncing around and hitting molecules of air and bits of dust. Similarly, flint assumes many colours, because of light reflections trapped inside the rock. And the structures and conditions 'trapped' in the glaze give us the colours we see.

My first tests had a blue ground with variegated blue and violet dots. I went on to get many variations – tan, opaque white with blue specks, near gloss translucent taupe with no visible blue. I learned nickel blue requires a glaze composition allowing the formation of the blue coloured material. I had to find the conditions under which the blue particles could be seen.

A glaze's composition determines the starting point from which it assumes characteristics in cooling. A glaze is balanced between opposites: gloss/matte, opaque/transparent, fine on one side/coarse, with a lizard skin surface texture on the other. Fractional solidification during cooling pushes properties from one side to the other. As the glaze heats, solids interact and liquids form. Each reaction occurs at its 'own' temperature, so that at the maturing temperature, a melt with no remaining solid results. At top temperature, a fully moulten layer sits on the pot. Were the pot held at this temperature – for hours, even days – changes would continue and segregation and textures might develop. (Hare's fur, partridge feather iron glazes are examples, as are celadons.)

Then, as the glaze cools the first solid forms, changing greatly the composition of what remains liquid. What happens later is determined by what happens first. Empirical formulas tell us glazes are made up of bases, alumina, and silica. The bases divide into alkali: K_2O, Na_2O, Li_2O and alkaline earths: CaO, MgO, ZnO and SrO. A glaze's parameters cannot be changed arbitrarily.

Working with unity formulas requires the sum of the bases to be adjusted to 1 and means that when one base is increased, the others must be lowered. Meanwhile, the silica/alumina ratio influences balance of glossy and matt, as well as the maturation temperature. A 'finished' glaze results from a balancing of fluxes (bases) and silica/alumina.

I experimented with small variations in the proportions of the bases – CaO/MgO/SrO – changing as little in the empirical formula as possible while maintaining a cone 6 glaze. I focused on MgO and CaO. Lowering magnesium produced a lavender glaze *Ana#3* [Figure 6], which seems more stable than the blue in *Ana#1*. Raising MgO resulted in a brown glaze.

I checked out the role of strontium. Keeping the same alumina and silica content and proportion meant reducing SrO. This would raise CaO or MgO and might result in a more fluid glaze. I did not want another brown glaze but when I increased the calcium, that is what I had. Within the limits of my tests I never created a fully transparent nickel glaze that was anything but brown.

At this point I looked through all of my glaze notes and chose one from each glaze family. There I found *Jon* [Figure 7] which has neither SrO nor ZnO. Next I focused on the influence of CaO on the colour of Nickel in a glaze and compared colour to CaO content. Finally I achieved *RuthMeske#1*, [Figure 8], a saturated teal blue, breaking yellow on the edges. It was quite stiff, with high surface tension. I lowered Al_2O_3, kept the same SiO_2/Al_2O_3 ratio to achieve *RuthMeske#2* [Figure 9], a smooth teal blue.

Along the road to *Nickel Blue* I got the following results. (The starred glazes are those whose results were positive and whose recipes are given here.)

Figure 6. *Glaze: Ana#2, Firing #3.*

Figure 7. *Glaze: Jon, Firing #7.*

Figure 8. *Glaze: RuthMeske1, Firing #6.*

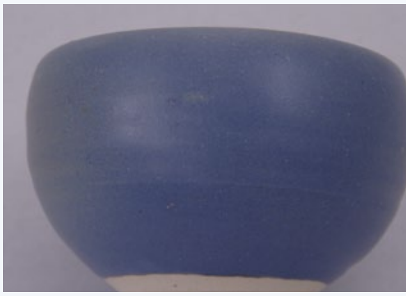

Figure 9. *Glaze: RuthMeske2, Firing #4.*

TABLE 1: Mol Fraction Calcia

0.030000 brown mauve tinge	0.390000 coffee brown
*0.150000 pale blue	0.400000 pale grey blue tinge
*0.180000 chartreuse	0.420000 greyed brown
0.200000 pale blue	0.420000 pale grey
0.200000 pinkish brown	0.420000 grey flecks blue
*0.210000 pale blue	0.480000 pale yellow
*0.270000 mauve	0.500000 pale grey
0.370000 brown	0.510000 light coffee

As can be seen, nickel blue is unlikely in a high CaO glaze. Next I wanted to learn the effect of controlled cooling and 'holds' on the glaze colour. The slower the kiln is cooled, or held at a given temperature, the more change can occur in the glaze. But kiln cooling times are sufficiently rapid that re-absorption of newly formed solids cannot take place. The composition of an already solidified material is set. The rate of cooling can affect glaze only up to complete solidification. For cone 6, 1400ºF seems a reasonable bottom temperature for slow cooling and 2000ºF an equally reasonable top temperature.

A short hold just after the top temperature is reached helps to even out the temperature in the kiln. A long hold at this point will only raise the effective cone of the firing.

From cone 6 (for me 2160ºF) to 1400ºF the following intervals were useful in interpreting my many firings.

1. 2000-1800ºF – The entire glaze is moulten, possible precipitation of crystals as in saturated iron glazes.

Figure 10. Glaze Silvia#1, Firing #3.

Figure 11. Glaze Silvia#2, Firing #3.

Figure 12. Glaze Silvia#3, Firing #7.

Figure 13. Glaze amHi, Firing #3.

Figure 14. Glaze am, Firing #3.

Figure 15. Glaze loCa, Firing #3.

2. 1800-1600ºF – In multi-phase glazes, segregation has begun, one or more phases may have begun to solidify.

3. 1600-1400ºF – The last phases present have begun to solidify.

My intervals were determined by dividing the total cooling into three phases. To illustrate the process: *Ana#1* in five firings, time given in hours (beyond normal kiln cooling)

Region 1	Region 2	Region 3	time above 1400 deg F
1. 0	0	0	0
2. 2.4	1.3	.67	4.4
3. 0	4	0	4
4. 0	2	5	7
5. 0	0	5	5

Fast cooling #1, gives a semi-transparent, semi-gloss taupe.

Firing #2, retarded moderate cooling gives a tan waxy matte.

Firing #3, with the time concentrated in Region 2, gives a pale waxy matte blue,with a sprinkling of deep blue spots.

Firing #4, more time in Region 3 – an exceedingly slow down fire – gives a dry densely opaque matte, with only a sprinkling of dark blue.

Firing # 5 yields that deep blue colour in a semi transparent waxy glaze with a little gloss (Figures 1-5)

Here are my cooling and hold schedules. In these firings only the firing down had any influence. [-----------] means fire down at a rate of 50ºF per hour in the interval contained between the brackets. Each '*' indicates 15 minutes of hold. [For example, Firing #4 has a slow down firing from 1700ºF to 1400ºF, with one hour hold at 1500ºF.]

	Top 1750 1700 1650 1600 1550 1500 1450 1400
#3	[------------------------]
#4	[------------------------------****---------------]
#5	[--------------****---------------]
#6	[**--------------------****-----------------------]
#7	[-------------****] [--------------***]

Having done all of that, I set out to find how the combination of nickel and other materials would influence colour. I began with rutile which resulted in a gorgeous buttery yellow, *Silvia#1* (figure 10), which started me on further quests to find the end of the Nickel Rainbow. So again using rutile resulted in *Silvia#2* and *Silvia#3* (Figures 11, 12) and *amHi* (figure 13). Adding rutile and iron resulted in *am* (Figure 14). Last, the glaze *loCa* gives a fabulous aqua if applied very thick (figure 15).

Glazes

Ana#1

Bentonite	4.0	Strontium Carbonate	18.7
Custer Feldspar	5.6	Talc	7.2
EPK Kaolin	31.7	Unispar	9.5
Lithium Carbonate	2.6	Whiting	9.7
Nepheline Syenite	33.6	Zinc Oxide	11.7
Silica	66.2	Nickel Oxide	2

Chemical Composition:

K_2O	0.0498	Al_2O_3	0.3983	SiO_2	3.4146
Na_2O	0.1195	B_2O_3	0.0000	P_2O_5	0.0009
CaO	0.2011	Fe_2O_3	0.0033	ZrO_2	0.0000
MgO	0.1002			TiO_2	0.0027
Li_2O	0.0613			SnO_2	0.0000
BaO	0.0000				
ZnO	0.2484				
SrO	0.2196				

Ana#2

Bentonite	4.0	Strontium_Carbonate	20.9
EPK Kaolin	29.9	Unispar	40.4
Lithium Carbonate	2.6	Whiting	13.2
Nepheline Syenite	13.2	Zinc Oxide	11.5
Silica	64.6	Black Nickel Oxide	2

Chemical Composition:

K_2O	0.0502	Al_2O_3	0.4003	SiO_2	3.4251
Na_2O	0.1205	B_2O_3	0.0000	P_2O_5	0.0009
CaO	0.2613	Fe_2O_3	0.0029	ZrO_2	0.0000
MgO	0.0060			TiO_2	0.0026
Li_2O	0.0625			SnO_2	0.0000
BaO	0.0000				
ZnO	0.2490				
SrO	0.2505				

RuthMeske#1

Bentonite	4.0	Strontium Carbonate	19.4
Custer Feldspar	6.4	Talc	6.5
EPK Kaolin	36.4	Whiting	2.1
Lithium Carbonate	2.4	Zinc Oxide	14.9
Nepheline Syenite	36.4	Black Nickel Oxide	4
Silica	71.8		

Chemical Composition:

K_2O	0.0500	Al_2O_3	0.4504	SiO_2	3.8494
Na_2O	0.1202	B_2O_3	0.0000	P_2O_5	0.0012
CaO	0.0701	Fe_2O_3	0.0041	ZrO_2	0.0000
MgO	0.0999			TiO_2	0.0034
Li_2O	0.0600			SnO_2	0.0000
BaO	0.0000				
ZnO	0.3497				
SrO	0.2500				

RuthMeske#2

Bentonite	4.0	Strontium Carbonate	21.2
Custer Feldspar	7.3	Talc	7.2
EPK Kaolin	32.0	Whiting	2.3
Lithium Carbonate	2.6	Zinc Oxide	16.3
Nepheline Syenite	39.8	Black Nickel Oxide	4
Silica	67.6		

Chemical Composition:

K_2O	0.0500	Al_2O_3	0.3996	SiO_2	3.4250
Na_2O	0.1199	B_2O_3	0.0000	P_2O_5	0.0009
CaO	0.0699	Fe_2O_3	0.0034	ZrO_2	0.0000
MgO	0.0998			TiO_2	0.0027
Li_2O	0.0600			SnO_2	0.0000
BaO	0.0000				
ZnO	0.3496				
SrO	0.2508				

Figure 1. *Glaze: Ana#1, firing #1.*

Figure 2. *Glaze: Ana#1, Firing #2.*

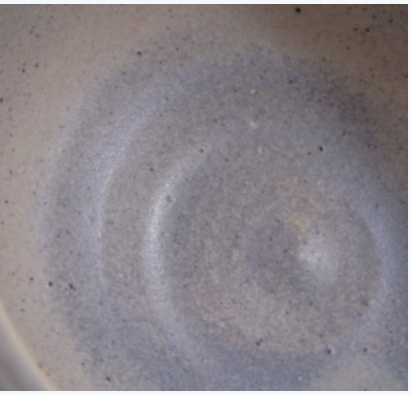

Figure 3. *Glaze: Ana#1, Firing #3.*

am

Bentonite	4.0	Red Iron Oxide	3.1
Custer Feldspar	20.3	Rutile	10.6
EPK Kaolin	30.4	Silica	29.0
Frit 3134	20.9	Whiting	22.3
Lithium Carbonate	11.2	Black Nickel Oxide	3
Nepheline Syenite	48.7		

Chemical Composition:	K_2O	0.0747	Al_2O_3	0.4203	SiO_2	2.6017
	Na_2O	0.1951	B_2O_3	0.1097	P_2O_5	0.0008
	CaO	0.4841	Fe_2O_3	0.0331	ZrO_2	0.0000
	MgO	0.0067			TiO_2	0.2124
	Li_2O	0.2395			SnO_2	0.0000
	BaO	0.0000				
	ZnO	0.0000				
	SrO	0.0000				

amHi

Bentonite	4.1	Rutile	10.6
EPK Kaolin	21.8	Silica	36.3
Frit 3124	34.8	Whiting	20.6
Lithium Carbonate	11.1	Nickel Oxide	4
Nepheline Syenite	61.1		

Chemical Composition:	K_2O	0.0536	Al_2O_3	0.4201	SiO_2	2.8109
	Na_2O	0.2150	B_2O_3	0.1100	P_2O_5	0.0006
	CaO	0.4844	Fe_2O_3	0.0023	ZrO_2	0.0000
	MgO	0.0070			TiO_2	0.2142
	Li_2O	0.2399			SnO_2	0.0000
	BaO	0.0000				
	ZnO	0.0000				
	SrO	0.0000				

Silvia#1

Bentonite	5.9	Talc	6.5
Custer Feldspar	12.3	Whiting	7.2
Lithium Carbonate	5.9	Zinc_Oxide	5.7
Nepheline Syenite	106.2	Zircopax	9.8
Rutile	8.5	Nickel Oxide	2
Silica	32.3		

Chemical Composition:	K_2O	0.1211	Al_2O_3	0.5100	SiO_2	3.5618
	Na_2O	0.3263	B_2O_3	0.0000	P_2O_5	0.0000
	CaO	0.1777	Fe_2O_3	0.0015	ZrO_2	0.0982
	MgO	0.1004			TiO_2	0.1963
	Li_2O	0.1472			SnO_2	0.0000
	BaO	0.0000				
	ZnO	0.1274				
	SrO	0.0000				

Silvia#2

Bentonite	6.4	Silica	22.9
Dolomite	13.3	Zinc_Oxide	6.2
Lithium Carbonate	6.5	Zircopax	10.6
Nepheline Syenite	125.3	Nickel Oxide	4
Rutile	9.3		

Chemical Composition:	K_2O	0.1041	Al_2O_3	0.5068	SiO_2	3.0011
	Na_2O	0.3400	B_2O_3	0.0000	P_2O_5	0.0000
	CaO	0.1489	Fe_2O_3	0.0013	ZrO_2	0.0979
	MgO	0.1328			TiO_2	0.1959
	Li_2O	0.1470			SnO_2	0.0000
	BaO	0.0000				
	ZnO	0.1273				
	SrO	0.0000				

Figure 4. Glaze: Ana#1, Firing #4.

Figure 5. Glaze: Ana#1, Firing #5.

loCa

Bentonite	4.0	Talc	8.3
Custer Feldspar	144.0	Whiting	4.3
EPK Kaolin	10.4	Zinc_Oxide	18.5
Lithium Carbonate	4.8	Nickel Oxide	4
Silica	6.0		

Chemical Composition:

K_2O	0.2442	Al_2O_3	0.4513	SiO_2	3.0195
Na_2O	0.1081	B_2O_3	0.0000	P_2O_5	0.0003
CaO	0.0979	Fe_2O_3	0.0026	ZrO_2	0.0000
MgO	0.0991			TiO	0.0009
Li2O	0.1003			SnO_2	0.0000
BaO	0.0000				
ZnO	0.3503				
SrO	0.0000				

Silvia#3

Bentonite	4.99	Rutile	10.6
Custer Feldspar	97.4	Talc	1.47
Dolomite	21.8	Black Iron Oxide	6
Lithium Carbonate	9.8	Nickel Oxide	4
Nepheline Syenite	53.9		

Chemical Composition:

K_2O	0.2000	Al_2O_3	0.4504	SiO_2	2.6042
Na_2O	0.2004	B_2O_3	0.0000	P_2O_5	0.0000
CaO	0.1996	Fe_2O_3	0.0016	ZrO_2	0.0000
MgO	0.2003			TiO_2	0.1998
Li_2O	0.1997			SnO_2	0.0000
BaO	0.0000				
ZnO	0.0000				
SrO	0.0000				

Jon

Bentonite	4.0	Nepheline Syenite	86.6
Dolomite	8.4	Silica	67.7
EPK Kaolin	12.5	Whiting	13.3
Frit 3134	3.1	Nickel Oxide	4
Lithium Carbonate	4.8		

Chemical Composition:

K_2O	0.0855	Al_2O_3	0.5020	SiO_2	4.3097
Na_2O	0.2866	B_2O_3	0.0199	P_2O_5	0.0004
CaO	0.3987	Fe_2O_3	0.0023	ZrO_2	0.0000
MgO	0.0998			TiO_2	0.0013
Li_2O	0.124			SnO_2	0.0000
BaO	0.0000				
ZnO	0.0000				
SrO	0.0000				

Carol Marians has been a potter since 1952 when she discovered clay in a craft course. She proceeded to earn two PhDs from MIT, one in Math, the other in Materials Science. Self-trained in clay, she studied the literature and took workshops with F. Carlton Ball and Tom Coleman. She has published in *Ceramics Monthly* and on the web site: http://vickihardin.com/articles/index.html. She currently is devoting her time to the study of glaze. (http://carol.knighten.org/)
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