Benefits of substituting borax pentahydrate with anhydrous borax in enamel glaze production

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Abstract: Substituting borax pentahydrate with anhydrous borax in enamel glaze production can improve the adhesiveness between iron substrate and glaze. The hypothesis of the adhesiveness improvement is proposed by studying the differences in the metal/glaze interface with SEM and EDS techniques. Up to 25.5% melting energy saving can be achieved in melting the batch containing anhydrous borax. Additional benefits are the reduction of boron emission, reduction of sodium nitrate dosage, and productivity improvement.

Keywords: enamel glaze, adhesiveness, anhydrous borax, sodium nitrate reduction, energy saving, boron emission

1. Introduction

Sodium borate plays a very important role in the production of enamel glaze. B_2O_3 acts as flux and network former, it lowers the melting temperature and the viscosity of the enamel frit. It helps to obtain a glaze of low thermal coefficient, sound heat and chemical resistance and good mechanical strength. During the production process of enamel, borax melts iron oxide and lowers the surface tension of the melt to increase the adhesiveness between the metal and glaze. Furthermore, borax can also be used as grinding agent to modify characteristics of the glaze slurry.

Borax pentahydrate and anhydrous borax are two common sodium borate chemicals used in enamel glaze production as compared in Table 1. Borax pentahydrate is white crystalline. Anhydrous borax is produced by dehydrating borax pentahydrate through heating in furnace. The dehydrated melt is cooled to solidify and then grinded to the required particle size distribution. Anhydrous borax is a non-crystalline, glassy material.

Table 1: Comparison between borax pentahydrate (*Neobor*®) and anhydrous borax (*Dehybor*®) produced by U.S. Borax.

	Borax pentahydrate *Neobor*	Anhydrous borax *Dehybor*
Oxide formula	$Na_2O{\cdot}2B_2O_3.5H_2O$	$Na_2O{\cdot}2B_2O_3$
Chemical compositions	B_2O_3 48.6-49.3 % Na_2O 21.6-21.9 % H_2O 28.8-29.8 % (by difference)	B_2O_3 68.5-69.4 % Na_2O 30.5-30.9 %
Structures	crystalline	non-crystalline glassy

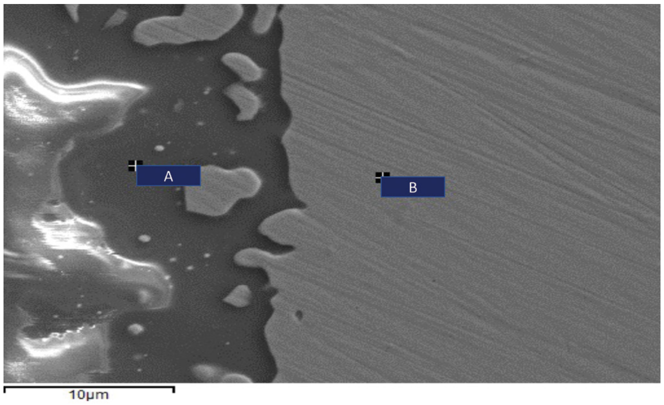
The typical B_2O_3 contents in *Neobor* (borax pentahydrate) and *Dehybor* (anhydrous borax) are 48.9% and 69.1% respectively. High B_2O_3 content and non-crystalline glassy structure of *Dehybor* make the melting easier leading to melting energy saving and increase in batch capacity.

2. Mechanism of adhesiveness between Ni/Co glaze and iron substrate

Batches can be prepared by substituting borax pentahydrate with *Dehybor*. Plant experiences have shown significant improvement in metal/glaze adhesiveness for cobalt and nickel ground coat glaze. It is believed that when cobalt/nickel ground coat glaze is applied to steel surface and then fired; the glaze melts when the temperature reaches 750°C. Electrochemical reactions occur between certain amount of Co_2O_3, Ni_2O_3, and Fe of steel as shown in equations (1), (2), (3), and (4).

$$Fe + Ni^{3+} \rightarrow Fe^{3+} + Ni^{2+} \text{-----------------} (1)$$
$$2Fe + 3Ni_2O_3 \rightarrow Fe_2O_3 + 6\,NiO \text{-------} (2)$$
$$Fe + Co^{3+} \rightarrow Fe^{3+} + Co^{2+} \text{---------------} (3)$$
$$2Fe + 3Co_2O_3 \rightarrow Fe_2O_3 + 6\,CoO \text{-----} (4)$$

The reactions above were supported by the SEM and EDS analysis. Figure 1 shows the cross section of the glaze and metal substrate interface of finished enamel product with scanning electron microscope (SEM). Darker area on the left side represents enamel glaze and lighter greyish area on the right represents the steel substrate. Element concentrations at points A and B were tested with Energy Dispersive Spectroscopy (EDS) and the results are listed in the table on the right. The Fe content at point A is 10.82%. Even EDS is a semi-quantitative tool to test the element concentration, the data is convincing enough that Iron (Fe) has diffused into the glaze layer, which is preferred to be in the form of Fe_2O_3. This conclusion is further supported by the EDS line scanning results shown in Figure 2.



Elements	% elements (point A)	% elements (point B)
C	0.02	0.02
O	51.11	
Na	6.73	
Al Si	1.14 24.57	
K	0.28	
Ca	2.90	
Mn	0.51	
Fe	10.63	99.98
Ti	1.01	
Zr	1.09	
Total	100	100

Figure 1. SEM image of the glaze and iron substrate cross section. EDS analysis was performed at point A and B with element concentrations listed in table on the right.

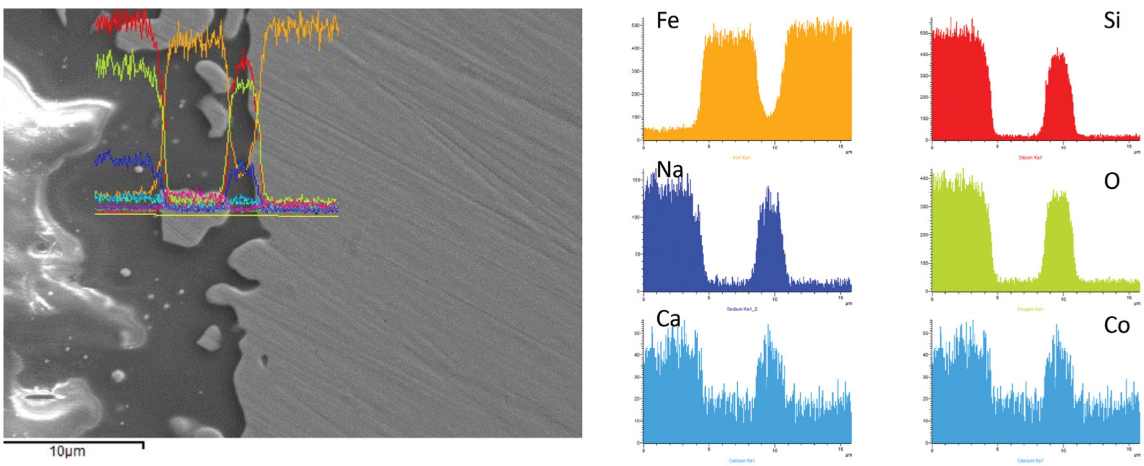


Figure 2. EDS line scanning along the cross section of the interface.

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3. Experimental results

Experimental works and plants trials have been conducted to compare the adhesion of the enamel products prepared with *Dehybor* (anhydrous borax) and borax pentahydrate. The adhesiveness tests were performed according to standard GB/T 31567-2015, and the results are shown in Figure 3. For glaze SGC 170 with firing time of 2 min 20 sec or 90 sec at temperature of 800°C shown in Figure 3(a), 3(b), and 3(c), the glaze prepared with *Dehybor* had much smaller peeling area, meaning its adhesiveness is much higher than that of glaze prepared with borax pentahydrate. Same results were achieved for glaze SGC 171 with firing time of 3 min at temperature of 800°C shown in Figure 3(d). Adhesiveness is one key criteria of enamel product, thus the quality of enamel can be improved with glaze prepared with *Dehybor*.

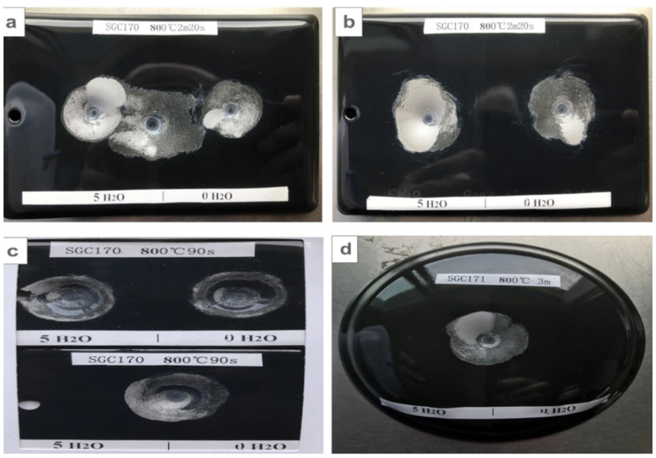


Figure 3. Adhesiveness results with drop test method of enamel glazes prepared from borax pentahydrate (left side) and *Dehybor* (right side); (a) and (b): glaze SGC 170 fired at 800°C for 2 min 20 sec; (c) glaze SGC 170 fired at 800°C for 90 sec; and (d) glaze SGC 171 fired at 800°C for 3 min.

4. Discussion on the results of adhesiveness test

In a gas firing furnace environment, the non-crystalline water of the enamel glaze batch materials will be vaporized first. Such non-crystalline water has less effect to flame and characteristic. As temperature increases, dehydration of borax pentahydrate occurs and proceeds as equation (5).

$$Na_2B_4O_7{\cdot}5H_2O \xrightarrow{80^\circ C} Na_2B_4O_7{\cdot}2H_2O \xrightarrow{200^\circ C} Na_2B_4O_7{\cdot}H_2O \xrightarrow{350\text{-}400^\circ C} Na_2B_4O_7 \text{ -------(5)}$$

Vapor of water of crystallization emitted at a higher temperature may increase the reducing characteristic of the flame thus reducing the formation of Ni_2O_3 and Co_2O_3 and subsequently the formation of Fe_2O_3 in equations (2) and (4). The strength of the metal/glaze adhesion is related to the quantity of the Fe_2O_3 in the glaze, the extent of crystal growth, the quantity and the proportions of other elements such as B, Li, K, and Na in the glaze. Roughness of the steel surface and the activity of the electrochemical reactions in the glaze melt also play important roles. Reactions in equations (1) and (3) indicate the strong relationship between the steel/enamel glaze bonding and the quantity of Ni_2O_3 and Co_2O_3 in the glaze melt.

Enamel glaze is a kind of borosilicate salt, up to 20% B_2O_3 can be added together with some metal oxides to achieve the objective of melting. Nickel oxide and cobalt oxide are usually added as $NiO_2 \cdot Ni_2O_3$ / $CoO_2 \cdot Co_2O_3$ mixture with metal content about 72%. It is evident that *Dehybor* performs better than borax pentahydrate in the adhesiveness between of the enamel glaze and the metal substrate.

5. Reducing or eliminating sodium nitrate

Furnace environment of the gas fired furnace used in enamel glaze production is usually reducing. Appropriate quantity of $NaNO_3$ is added to batch containing borax pentahydrate to ensure sufficient Ni^{3+} present in the glaze to facilitate the formation of Fe_2O_3. In addition, reducing $NaNO_3$ in formulations containing borax pentahydrate can also affect the colour of the glaze.

Producer X has replaced borax pentahydrate with *Dehybor* and eliminated the use of $NaNO_3$ in 90% of its nickel ground coat glaze. The dosage of the remaining 10% nickel base glaze is between 1 - 2%. The same producer has also eliminated $NaNO_3$ in 30% of its cobalt/nickel ground coat glaze; the dosage of $NaNO_3$ in the remaining formulations is below 2%. Amount of $NaNO_3$ in transparent glaze and top glaze has been reduced to between 0 - 2%.

6. Thermal behaviour and emission loss of borax pentahydrate and *Dehybor*

When borax pentahydrate crystal is heated, it will dehydrate and expand forming a low-density sphere which will burst into dust and flakes. In the environment of gas firing furnace, certain amount of boron containing dust will escape from the exhaust of the furnace as shown in Figure 4(a) and 4(b). *Dehybor* does not expand during heating, therefore the loss due to crystal bursting is greatly reduced.

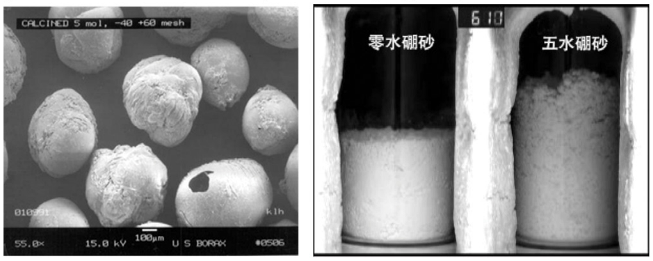


Figure 4. Volume change during the heating process. (a): expanded spheres of borax pentahydrate during dehydration; (b): comparison of batch volumes. Each batch contains 5% B_2O_3. Left crucible is a batch containing *Dehybor* and right crucible is a batch containing borax pentahydrate. Temperature recorded was 611°C.

Plant experiences have reported that the boron emission loss from gas firing furnace has been reduced from 10% to 4%. Reduction of boron emission loss can reduce costs and help the plant to meet environmental requirements. Reduction in boron volatility loss can also reduce furnace maintenance cost and reduce risk of refractory corrosion of the furnace.

7. Other benefits of *Dehybor* in enamel frit production

7.1 Batch capacity and productivity increase

The typical values of % B_2O_3 in *Dehybor* and borax pentahydrate are 69.1% and 48.9% respectively. The theoretical factor conversion factor is 69.1/48.9 = 1.41. This factor may be higher considering that boron volatility loss in borax pentahydrate is higher than *Dehybor*. Example of a typical nickel/cobalt ground coat glaze shows a theoretical increase batch capacity of 8%. Besides capacity increase, the maintenance frequency with *Dehybor* is only one third to one half of that with borax pentahydrate as *Dehybor* has much less B_2O_3 emission, which further increases productivity Plant experiences have reported 25% increase in productivity. It is worthy to note that the reduction of maintenance frequency is very welcomed by the plant operators as commented by nearly all enamel frit producers using anhydrous borax (*Dehybor*).

7.2 Energy saving

Thermal analysis data has shown the energy difference of heating borax pentahydrate and *Dehybor* from 25°C to 1200°C is 3884 MJ per mt B_2O_3 (see Figure 5). This is equivalent to heating one mt borax pentahydrate and will require nearly 1942 MJ energy more (borax pentahydrate and contains 48.9% B_2O_3). Assuming the theoretical efficiency of the furnace is 50%, the heat energy requirement difference will be doubled. This means every mt of borax pentahydrate will consume 3884 MJ more than *Dehybor*.

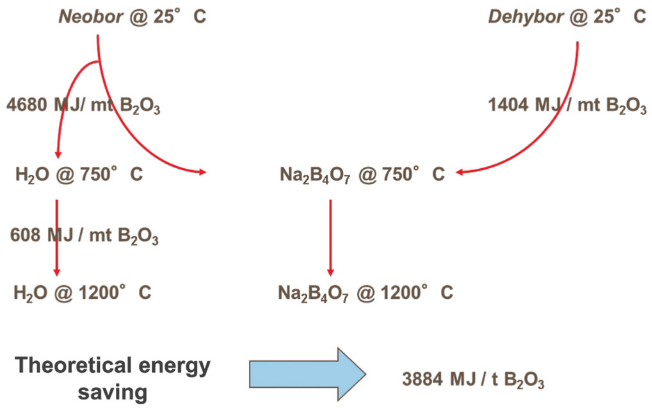


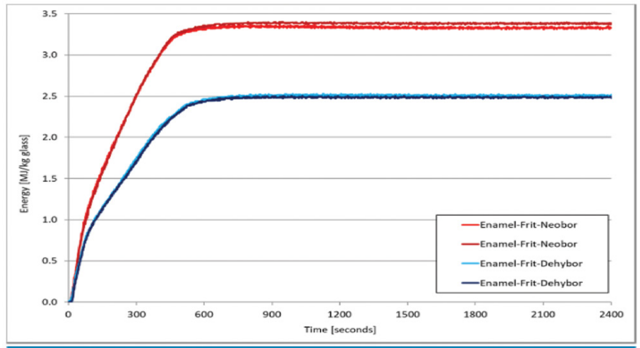
Figure 5. Heating energy difference between *Dehybor* and borax pentahydrate.

Further comparative works have been conducted with ground coat glaze batches prepared from these two types of sodium borate. The oxide composition of the frit and the batch formulations are shown in Table 2.

Table 2: Typical Ni/Co ground coat glaze composition and corresponding batch formulations with borax pentahydrate and *Dehybor*.

Composition	Weight percentage 1%	Batch formulations	With borax pentahydrate (1%)	With *Dehybor*
SiO_2	42.71	Sand	22.92	24.86
B_2O_3	15.53	Fluospar (CaF_2)	10.59	11.48
Al_2O_3	4.21	*Neobor* ($Na_2B_4O_7.5H_2O$)	26.87	
CaO	7.45	*Dehybor* ($Na_2B_4O_7$)		20.69
Na_2O	16.79	Potassium Feldspar	20.08	21.78
K_2O	3.5	Soda Ash	12.35	13.36
MnO	2.02	Sodium Nitrate	3.16	3.45
CuO	1.03	MnO_2	1.713	1.858
NiO	1.29	CuO	0.873	0.947
CoO	0.42	NiO	1.091	1.184
F	5.05	CoO	0.36	0.391
Total	100	Total	100.00	100.00

Experiment works were conducted in the laboratory to measure the energy required to heat 300g samples in silica crucible from 22°C to 1200°C. The technique was based on the principle of Drop Calorimetry. Results can be seen in Figure 6. The energy consumption to produce 1 kg frit glass is also listed. The energy consumption is around 3.356 MJ/kg frit glass for batch with borax pentahydrate (*Neobor*), while the energy consumption is 2.499 MJ/kg frit for batch with *Dehybor*, meaning there is an energy saving of 25.5% for batch formulation with *Dehybor*.



	Neobor	Dehybor	
Measurement 1	3.329	2.510	[MJ/kg Glass]
Measurement 2	3.383	2.487	[MJ/kg Glass]
Average	3.356	2.499	[MJ/kg Glass]
Difference compared to Neobor		-25.5	[%]

Figure 6. Energy requirement (MJ/kg frit glass) for batches with anhydrous borax (*Dehybor*) and borax pentahydrate.

8. Conclusions

Substituting borax pentahydrate with *Dehybor* without altering the oxides proportion, improves the adhesiveness between the cobalt/nickel ground coat and steel substrate. The dosage of sodium nitrate can be reduced or even eliminated therefore reducing the emission of NO_x during the melting stage. For an enamel frit containing 15.53% B_2O_3, substituting borax pentahydrate with *Dehybor* can save 25.5% of energy when the batch was heated from 22°C to 1200°C. Other benefits of *Dehybor* include reduction in boron emission loss, productivity improvement, reduction of refractory corrosion, and saving of logistic and warehouse costs.

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