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X Ray Diffraction Analysis of Processes in Specific Enamel Blend during Heat Treatment

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Abstract

The present work deals with the physicochemical processes occurring in the Na2O-SrO-BaO-B2O3-SiO2 system's theoretically envisaged enamel blends designed for coating copper.

X-ray analysis revealed that the processes in enamel blend while heat treatment can be conditionally presented in several stages. The first stage covers 383-773 (973) K temperatures, resulting in formation of the first portions of different stoichiometric sodium borates and the liquid phase. The second stage corresponds to 773 (973) -973 (1073) K temperature range where Sr and Ba borates and silicates are formed and in case of increased amount of liquid phase their triple compounds are formed. On the third stage refractory compounds are dissolved in the liquid phase, at 1173K roentgen-amorphous product, suitable for enamel production, and at 1373K glass are obtained.

Keywords: Blend, Composition, Diffractogram, Borates, Silicates, X-Ray Diffraction Analysis, Products.

Introduction

The method for predicting oxide compositions of enamels intended for coating copper was proposed by different scholars (Sarukhanishvili, Gordeladze, Andguladze, Ebanoidze, 2012). It involves determination of glass-forming ability of the compounds intended for producing specific enamels and obtained by eutectic merging in Na2O-SrO-BaO-B2O3-SiO2 system and defining the lowest eutectics in multi-component systems (Sheby, 2006, Royson, 1970, Appen, 1970, Berezhai, 1988).

Having considered the compounds of the above system, the compositions fully meeting the requirements for producing specific enamels were proposed in Table 1.

Table 1. *Estimated enamel compositions*

Composition №	$f_{Si,B}$	Oxide content, weight %				
		Na_2O	SrO	BaO	B_2O_3	SiO_2
9	0,305	10,75	8,19	32,96	18,93	29,17
10	0,356	13,62	10,99	26,74	9,52	39,13
21	0,367	15,66	5,98	17,49	11,96	48,91
27	0,371	20,42	5,98	17,49	11,96	44,15
30	0,328	15,32	5,98	16,24	15,93	36,53
32	0,367	15,32	9,62	25,89	5,29	43,88
34	0,351	16,66	11,96	24.00	8,04	39,34

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The goal of the present work is to determine the essence and sequence of the processes in enamel blends while heat treatment of the proposed enamel compositions.

Working Methodology

Four compositions: № 9, 10, 27, 32 (Table 1) were selected for investigation considering their oxide content. Composition №9 was selected due to minimum SiO_2 and maximum B_2O_3 content. Composition №10 contains maximum SrO at moderate content of other oxides. Composition №27 is distinguished by maximum content of Na_2O and SiO_2 and №32 - by minimum content of B_2O_3.

For obtaining selected compositions special materials intended for producing vitreous materials, Na, Sr and Ba carbonates, boric acid and silica sand (SiO_2> 99 weight %), were used (6). The results obtained with the same technology in accordance with the blend composing regulations are presented in Table 2.

Table 2. *Blend composition considering weight loss*

Material	Blend № and composition, mass fraction				Note
	9	10	27	32	
Na_2CO_3	18,97	24,04	36,04	27,04	The loss includes content of the main compound in the material under study, loss during blend preparation and the loss due to evaporation.
$SrCO_3$	11,75	15,76	8,58	13,80	
$BaCO_3$	42,95	34,84	22,79	33,74	
H_3BO_3	37,97	19,10	23,99	10,61	
SiO_2 (Quartz sand)	29,43	39,49	44,55	44,28	

For heat treatment of enamel blends electric and carborundum (silicon carbide heater) chamber furnaces were used. In the latter case, temperature was controlled and regulated by high precision temperature regulator (BPT-2). Enamel blend was placed in different capacity corundum pots.

Heat treatment modes of enamel blends have been established according to the data of differential-thermal analysis and contained seven central temperature points: 573, 773, 873, 973, 1073, 1173 and 1373 K, at which the blend was hold for 30 minutes. After holding, each sample was cooled to room temperature in a pot and then the sample of the obtained product was prepared for powder X-ray diffraction analysis.

The study was conducted with general-purpose X-ray diffractometer DRON-1,5 (anode Cu, λ = 1,54178Å, graphite monochromator, counting speed of 1^0C / min, current - 20mA). For the assessment of the amount of solid crystalline and solid amorphous states in samples microscope Labor-Lux-12 at different magnifications was used.

For recognition of diffractogram reflexes and discussion of the results certain data were used (Bragina, Zubekhin, Belila, at al. 2003, Nedoma, 1975, ICPD, 1985, Kondratieva, 1969, Winchell, A., Winchell, H., 1967, Toropov, Barzakovski, Lapin, Kurtseva, 1969, Toropov, Barzakovski, Lapin, Kurtseva, Boikova, 1972).

Results

Prior to discussion of the research methods, it must be noted that the selected compositions, as well as the rest, were obtained by combining invariant points of two and three component systems (Sarukhanishvili, Gordeladze, Andguladze, Ebanoidze, 2012). It is suggested that selected eutectic provide the system's liquid phase at low temperatures.

In our case combination of invariant points looks like (weight %):

In the compositions №9 and №10:

30%$SrO•BaO•2SiO_2$+30%$Na_2O•2SiO_2$(NS_2)+40%-$BaO•2B_2O_3$(B'B2) and 40%$SrO•BaO•2SiO_2$(S'B'S2)+40% $Na_2O•2SiO_2$(NS)+20%$BaO•2B_2O_3$(B'B_2), respectively.

In the composition №27:

30%$3BaO•3B_2O_3•2SiO_2$($B'_3B_3S_2$)+60%Na_2O•-$2SiO_2$(NS_2)+10%$SrO•B_2O_3$(B'B_2),

In №32:

20%$3BaO•3B_2O_3•2SiO_2$($B'_3B_3S_2$)+45%Na_2O•-$2SiO_2$(NS_2)+35%$SrO•BaO•2SiO_2$(S'B'S_2).

Generalizing the information obtained by dirificograms can be concluded as follows:

- At room temperature, all the enamel bled diphactograms are in satisfactory compliance with the reflexes of contained compounds and their amount;
- Na_2CO_3 and SiO_2 are the exceptions, reflexes of which are less intensive than those in the case of the corresponding amount. This inconsistency seems to be caused by high inclination of Na_2CO_3 to form the thinnest SiO_2 film on the grain surface;
- The peculiarities of the high temperature behavior of all four blend compositions led to the conclusion that the processes in these blends can be conditionally divided into several stages:

The first stage involves 383-773K temperature range basically distinguished by interaction between boric acid and its transformation products with Na_2CO_3. As a result the first portions of different stoichiometric sodium borates and the liquid phase are formed. The upper temperature of this interval can be moved to 973K.

On the second stage, covering 773-973K temperature interval, Na, Sr and Ba borates and silicates are formed and in case of increased amount of liquid phase their triple compounds are obtained. In this case, it is possible to increase the temperature range to 1073K.

At 973 (1073) K refractory compounds are dissolved in the liquid phase. As a result at 1173K and 1373K temperatures compounds suitable for production of enamel and glass are obtained.

Diffractograms of products derived as a result of processing the enamel blend composition №9 at five different temperatures are presented (Fig. 1).

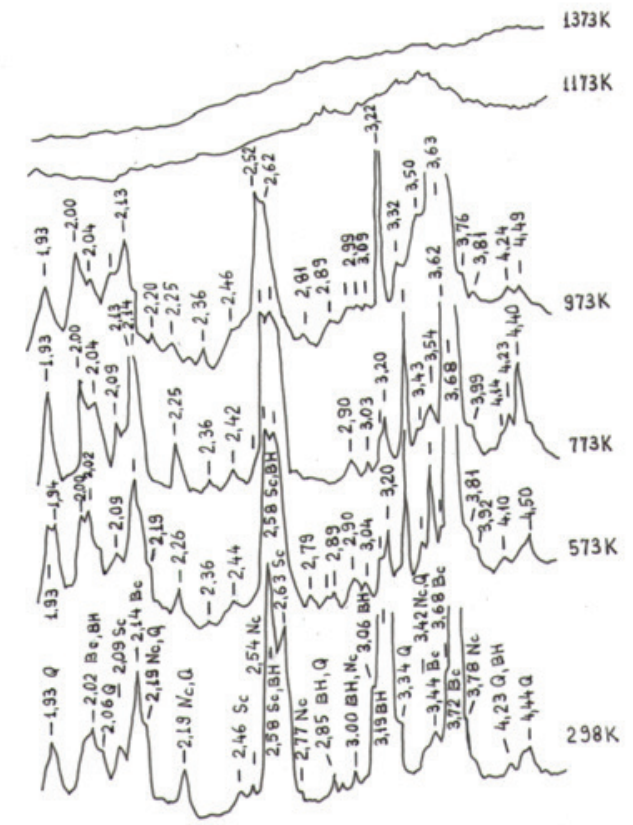

Figure 1. *Diffractograms of the enamel blend composition №9 and the products obtained as a result of processing the enamel blend at different temperatures. conventional signs: Q-β-SiO_2; Bc-$BaCO_3$; S'c-$SrCO_3$; Nc-Na_2CO_3.*

The diffractogram of the product obtained by processing blend №9 at 573K temperature indicates significant decrease in the intensity of H_3BO_3 dα/n lines and the appearance of reflexes of various stoichiometric sodium borates. From these borates clearly stand out $Na_2O•2B_2O_3$ dα/n -lines (4,50; 4,07; 3,97; 3,16). Formation of hydrous sodium borates is not excluded either. For example, sodium pentaborates (dα/n -lines: 4,65; 3,68; 3,21). Due to the emergence of eutectic and melting some of them the first portion of the liquid phase containing boric acid modifications appears in the range of 350-573 (673) K.

Phase composition was difficult to establish in the blend processed at 773K, due to the similarity of the reflexes of new formations. The dα/n lines, characteristic for not yet fully interacted $BaCO_3$, $SrCO_3$ and SiO_2, are clearly visible. However, signs of active interaction of these components are observable mostly at 873K. By a certain degree of authenticity, we can prove the existence of: $Na_2O•B_2O_3$, $Na_2O•2SiO_2$(dα/n -lines: 4,14; 3,94; 3,62; 3,42); $BaO•2B_2O_3$(dα/n -lines: 3,97; 3,34; 3,11; 2,90); $BaO•SrO•2SiO_2$(dα/n - lines: 3,60; 3,32; 3,11; 2,20) at this temperature. Liquid phase increase is evident seemingly stipulated by the formation of eutectic. For example: $Na_2O•B_2O_3+Na_2O•2SiO_2$ + liquid (793K); $Na_2O•B_2O_3+Na_2O•2B_2O_3$ O3 + liquid (793K); $BaO•4B_2O_3+B_2O_3+SiO_2$ + liquid (<723K).

On the diffractogram of the product obtained by processing of blends at 973K, except for the above, are observed compounds of $BaO•SiO_2$ (dα/n - lines: 3,69; 3,42; 3,34; 3,10) and $SrO•SiO_2$ (dα/n -lines: 3,57; 2,98; 2,04). The amount of liquid phase is increased due to the formation of dual and triple invariant points. For example: $Na_2O•B_2O_3+SiO_2$+ liquid + (803 K); $Na_2O•4B_2O_3+SiO_2$+ liquid + (948 K). In the range of 773-973K the bled is preparing for activation at 200K temperature increase. Indeed, after the processing at 1173K, the blend is almost completely transferred to the liquid state, which is observed on the diffractogram of the product obtained at this temperature - it reflects the roentgenamorphous solid body still containing submircroscopic regulated clasters. Supercooling of such melt is used in enamel production technology.

Data presented in Fig.1. do not allow to establish the solid phases that precede the formation of roentgen-amorphous state. To achieve this goal, it is necessary to choose the treatment temperature between 973K and 1173K, where the diffractogram of the product, obtained by processing, is quite sharp and reflects the solid phases existing before full melting. This temperature appeared to be 1073K, and the according diffractogram of the product, obtained through the processing at this temperature, is shown in Fig.2.

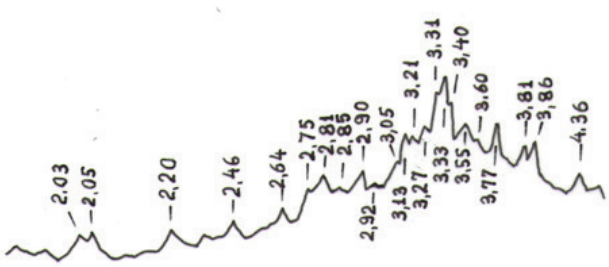

Figure 2. *Diffractogram of the blend №9 processed at 1073K.*

By identifying the reflexes on the diffractograms, it becomes clear that only three solid phases can be specified confidently. They include: $Na_2O•2SiO_2[NS_2]$ (dα/n- lines: 3,86; 3,77; 3,31; 2,64), $BaO•2B_2O_3$ [$B'B_2$] (dα/n -lines: 4, 36; 3,81; 3,55; 3,13) and SrO •BaO •$2SiO_2$[$S'B'S_2$] (dα/n - lines: 3,55; 3,21; 3,13; 2.20). It proves the presumed opinion (Sarukhanishvili, Gordeladze, Andguladze & Ebanoidze, 2012) when determining enamel composition.

Basically, the same processes are going in the other blends. However, each of them is peculiar.

E.g. on the diffractogram of the product obtained by processing blend №10 (which differs from the previous blend by more content of SiO_2) at 973K reflexes characteristic for this oxide are clearly shown, as well as on the diffractogram of the product obtained by processing at 1073K. However, on the second diffractogram above-mentioned compounds (NS_2; $B'B_2$ & $S'B'S_2$) prevail.

Diffractogram of the blend № 27, processed at 973K, (as well as of the one, processed at 1073K) more clearly indicates three compounds (different from the compounds in the blends №9 and №10): $Na_2O•2SiO_2$ [NS_2]; $SrO•2B_2O_3$[$S'B_2$] and $3BaO•3B_2O_3•2SiO_2$[$B'_3B_3S_2$] (Fig. 3).

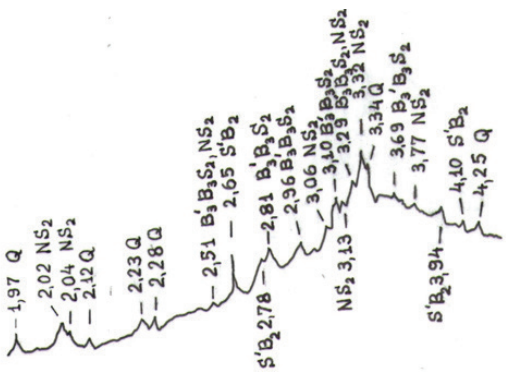

Figure 3. *Diffractogram of the blend №27 processed at 1073K*.

As for the blend № 32, it is characterized by the minimal content of H_3BO_3. Because of this, at low temperatures mostly boron depleted borates are obtained. On the diffractograms of this blend processed at 973K and 1073K (less clearly at 973K) mainly reflexes of $S'B'S_2$, $B'_3B_3S_2$ and NS_2 are revealed.

In the blends №27 and №32, in addition to the above-mentioned compounds, several unknown compounds and those of SiO2 with vague reflexes are observed. The expectations in the case of №27 and №32 (compared to № 9 and № 10) were less successful, but the main goals were reached – compounds suitable for enamel and glass production at 1173K and at 1373K respectively, were obtained in case of all blends.

Conclusion

According to the X-ray data, general scheme of glass (enamel) formation in several compositions of Na_2CO_3-$SrCO_3$-$BaCO_3$-B_2O_3-SiO_2 system in the range of 298-1373K may be displayed as follows:

In the range of 298-383K hygroscopic water is removed;

At 350-450 K following changes occur: conversion of boric acid, formation of HBO_2; formation of the first portions of liquid phases due to appearance of eutectic between H_3BO_3, HBO_2 and B_2O_3 and melting of H_3BO_3 and HBO_2;

In the range of 432-573(773) K - Na_2CO_3 interacts with boron compounds and sodium borates are formed. Interaction of $SrCO_3$ and $BaCO_3$ with boron compounds and formation of borates is started. The blend is a heterogeneous system composed of carbonates, quartz and liquid phase, composition of which can be displayed as Na_2O-nB_2O_3;

In the range of 573 (773) -773 (973) K SiO_2 is involved in the reactions; Na, Sr and Ba silicates and boron silicates are formed; Na and Sr carbonates are still in the system; double and triple eutectics are created; a number of compounds are melting;

In the interval of 773 (973) - 973 (1073) K in a number of blends primarily $BaO•2B_2O_3$+$SrO•BaO•2SiO_2$+$Na_2O•2SiO_2$ and in the rest $3BaO•3B_2O_3•2SiO_2$+$SrO•2B_2O_3$+$Na_2O•2SiO_2$ and $3BaO•3B_2O•2SiO_2$+$SrO•BaO•2SiO_2$+$Na_2O•2SiO_2$ are formed.

In the range of 973 (1073) -1173 (1373) K above-mentioned phases are combined, eutectics are formed and complex compounds are melting; the heterogeneous system is transformed into homogenous.

One more conclusion that can be drawn is that except the invariant points and despite existence of other components, the authors (Sarukhanishvili, Gordeladze, Andguladze, Ebanoidze, 2012) approach to the prediction of special enamel compositions is basically true.

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