



Examination of Vitreous Enamel Coating Properties Prepared from Different CaO-P₂O₅ Raw Material Sources

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Makale Bilgisi / Article Info

Sunulma / Received : 12.08.2021

Düzeltilme / Revised : 24.03.2022

Kabul / Accepted : 25.03.2022

Anahtar Kelimeler

Apatit
İnorganik Kaplama
Hammadde
Cam Seramik
Karakterizasyon

Keywords

Apatite
Inorganic Coating
Raw Material
Glass-Ceramic
Characterization

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Abstract

Ceramics, glass, and glass-ceramic coatings typically use calcium oxide (CaO) and phosphorus pentoxide (P₂O₅). Calcium (Ca) is used to increase viscosity as a melting aid whereas phosphorus (P) is used to reduce opacity and improve color balance. This study examined the impact of three distinct calcium and phosphorus sources on inorganic coating performance. Precursor glasses (PGs) were prepared as a glass-ceramic coating raw material. These PGs mostly included Ca and P, allowing us to explore the impact of these oxides on the coating performance and thermal characteristics. Calcium phosphate (Ca₃(PO₄)₂), and calcium hydrogen phosphate (CaHPO₄) were used to substitute commercial calcium (CaCO₃) and phosphorus ((NH₄)₃PO₄) sources in the PG structure. Melting and quenching method was used to produce PGs. To examine the features of the created PGs, they were compared to PGs produced from commercial Ca and P sources. X-ray fluorescence (XRF), X-ray diffractometer (XRD), differential thermal analysis (DTA), thermogravimetric analysis (TGA), heat microscopy, and dilatometer were used to characterize the chemical, structural, and thermal properties of the two glasses, respectively. The PGs were applied to steel substrates using a wet spray coating technique and fired at elevated temperatures (T=820 °C) to obtain a glass-ceramic coating. To investigate the change in inorganic coating product performance on the surface, color, gloss, and roughness measurements were conducted. A scanning electron microscope (SEM) was also used to evaluate the surface morphology, and XRD analysis was used to identify the crystal phases of the coating.

Farklı CaO-P₂O₅ Hammadde Kaynaklarından Hazırlanan Vitroz Emaye Kaplamaların Özelliklerinin İncelenmesi

Özet

Seramiklerde, cam ve cam seramik kaplamalarda genellikle kalsiyum oksit (CaO) ve fosfor pentaoksit (P₂O₅) kullanılır. Kalsiyum (Ca), ergitme ajanı olarak viskoziteyi artırmak için kullanılırken, fosfor (P) opaklığı azaltmak ve renk dengesini iyileştirmek için kullanılır. Bu çalışmada, üç farklı kalsiyum ve fosfor kaynağının inorganik kaplama performansı üzerindeki etkisini incelenmiştir. Öncü camlar cam-seramik kaplama hammaddesi olarak hazırlanmıştır. Bu öncü camların çoğunlukla Ca ve P içerikli olması oksitlerin kaplama performansı ve termal özellikler üzerindeki etkisini inceleyebilmemizi sağlamıştır. Öncü cam yapısındaki ticari kalsiyum (CaCO₃) ve fosfor ((NH₄)₃PO₄) kaynaklarının yerine kalsiyum fosfat (Ca₃(PO₄)₂) ve kalsiyum hidrojen fosfat (CaHPO₄) kullanılmıştır. Öncü cam üretimi ergitme ve su verme yöntemleri ile gerçekleştirilmiştir. Oluşturulan öncü camların özelliklerinin incelenmesi ticari Ca ve P kaynaklarından üretilen öncü cam yapılar karşılaştırılması ile sağlanmıştır. X-ışını floresansı (XRF), X-ışını difraktometresi (XRD), diferansiyel termal analiz (DTA), termogravimetrik analiz (TGA), ısı mikroskobu ve dilatometre sırasıyla iki camın kimyasal, yapısal ve termal özelliklerini karakterize etmek için kullanılmıştır. Öncü camlar, yaş püskürtme kaplama tekniği kullanılarak çelik altlıklara uygulanmıştır ve cam-seramik kaplama elde etmek için yüksek sıcaklıklarda (T=820 °C) pişirilmiştir. İnorganik kaplama ürün performansının yüzeydeki değişimini araştırmak için renk, parlaklık ve pürüzlülük ölçümleri yapılmıştır. Tarama elektron mikroskobu (SEM) yüzey morfolojisini değerlendirmek ve kaplamanın kristal fazlarını tanımlamak için XRD analizi kullanılmıştır.

1. INTRODUCTION

Vitreous enamel coatings are glass-ceramic based coating material. It is generally used in the coating of ferrous metal surfaces.¹ It is used in corrosive environments due to its resistance. It has high acid resistance and corrosion resistance. It is preferred in many areas of industry and daily life, such as boilers, kitchenware, ovens.^{2,3}

Vitreous enamel coatings are obtained by controlled crystallization or devitrification of a precursor glass (PG) called frit.^{1,3} Frit, obtained by mixing the raw materials that will provide the final chemical structure and obtaining them at high temperatures (1200-1400°C) is the glassy midproduct that forms the glass or glass-ceramic structure that will give the coating final product properties.^{1,4} Frits are milled with additives and applied on metal substrate.^{3,4} Frit coated metal is fired between 750-900°C depending on the structure and controlled cooled.¹ After the firing process, enamel-metal adherence occurs and coating is obtained after cooling.^{5,6}

Enamel frits consist of as many as 30 different oxides. These oxides consist of metal oxide or nonmetal oxide. It also includes enamel frits F₂ [1]. The oxides in the frit structure have many uses and raw material sources. These are summarized in Table 1.^{1,4}

Calcium oxide (CaO) is used as a melting aid to increase viscosity in enamel frit production.^{1,7} The main raw material source is calcium carbonate (CaCO₃). Phosphorus pentoxide (P₂O₅) is used to control opacity and improve color balance [1]. Mono ammonium phosphate ((NH₄)H₂PO₄) is used as the main raw material source.

Apatite (Ca₁₀(PO₄)₆(OH,F,Cl)₂) is known as the source of both oxides.^{8,9} There are forms of organic origin or mineral origin. The structure that provides the transparency of famous Chinese porcelain is apatite of animal origin.¹⁰

A study was conducted on the use of animal origin apatite in the production of enamel frit. As a result of this study, it was observed that although the chemical or crystal structure of the frit did not change, its thermal properties changed. In this study, the effect of raw material source change on frit properties and coating performance was investigated. Frits were obtained using laboratory grade calcium phosphate (Ca₃(PO₄)₂) and calcium hydrogen phosphate (CaHPO₄). The chemical and thermal properties of the frits obtained were compared with the frit sourced from industrial raw materials. The performances of the coatings were compared by obtaining coatings from the frits.

As a result of the studies, similar results were obtained to the examples in the literature. Although the change of raw material source did not affect the chemical composition, it did affect the thermal behavior. It has been observed that the frits originating from complex raw materials begin to lose mass at lower temperatures. In addition, it was observed that the crystals were closer to the surface in coatings where calcium oxide and phosphorus oxide were taken from a single source. Although there were changes in the properties, the raw material change did not significantly affect the coating performance.

Table 1 Mineral sources and function of oxides used in frit

Compound	Mineral	Function
SiO ₂	Quartz Feldspar	The refractory component is glass forming oxide. It increases the rigidity of the vitreous system, provides chemical resistance and increases the viscosity.
B ₂ O ₃	Borates	It is the flux that forms the vitreous matrix, lowers the viscosity and increases the surface hardness.
Na ₂ O K ₂ O Li ₂ O	Albite Feldspar Spodumene Petalite Lepidolite	They are alkaline components. By reducing the softening temperature of the glass, they increase the gloss while decreasing the elasticity.
Al ₂ O ₃	Feldspar Corundum	Increases viscosity, mechanical, chemical and thermal resistance. It reduces the expansion coefficient and provides an opaque surface.
F ₂	Fluorite	Influenced the opacity and provides a shiny surface. Also it is kind of flux, makes easier glass softening.

In this study, the effect of raw material source change on frit properties and coating performance was investigated. Frits were obtained using laboratory grade calcium phosphate (Ca₃(PO₄)₂) and calcium hydrogen phosphate (CaHPO₄). The chemical and thermal properties of the frits obtained were compared with the frit sourced from industrial raw materials. The performances of the coatings were compared by obtaining coatings from the frits.

2. METHODS

2.1 Raw Material Characterization

In the study, three different raw materials which are industrial raw material, calcium phosphate and calcium hydrogen phosphate, were used as calcium and phosphorous sources in the production of frits. CaCO₃ and ((NH₄)₃PO₄) was obtained from industrial raw material supplier. Calcium phosphate (Ca₃(PO₄)₂), and calcium hydrogen phosphate (CaHPO₄) were used. X-ray Diffraction (XRD) (Bruker D8 Advance Eco) analysis were investigated to determine the crystalline phases, X-ray Fluorescence (XRF) (Bruker AXS S8 Tiger) analysis were performed for the determination of chemical composition of raw materials. Thermogravimetric-differential thermal analysis (TG-DTA) (Netzsch STA 449F1A-0207-M) were performed to characterize their thermal decomposition behaviour.

2.2 Frit Preparation

Frits are used in the production of the glass-ceramic coating as a raw material for coating application. As the frit composition a commercial product of Akcoat, was used. Three different frits were prepared in the study. In the product coded as REF, industrial calcium carbonate and mono ammonium phosphate was used as Ca and P sources, calcium phosphate was used as Ca and P sources in glass coded as CP and

calcium hydrogen phosphate was used as Ca and P sources in glass coded CH. In order to achieve similar oxides composition, in the CH sample the amount of less calcium oxide was completed using CaCO₃. The mixtures were melted in a aluminosilicate-based crucibles at 1400°C for 60 minutes and cooled by quenching method. The frits were dried for 1 hour in a 110°C oven. The frits were milled in ring mill (Rocklabs BenchTop Ring Mill Pulveriser; WC-Co ring) for characterization tests and sieved through a 325 mesh (180 µm) sieve.

XRF analysis was performed to determine the chemical structures of the frits. In order to determine thermal decomposition behaviour of frits, TG-DTA analysis was carried out in nitrogen atmosphere.

2.3 Coating Application and Analysis

The milled frits prepared in the previous stage were applied on a low carbon steel plate with the code DC04EK, measuring 12x10 cm and having a thickness of 0.75 mm. The plate whose dimensions and features are specified has been selected in accordance with EN10209 norm. Before the application, the plate was degreased and cleaned with a chemical. The plate, which is ready for application, was coated with the wet spray method. Application amount is average 8 g/dm². Plates were dried in a 110 °C oven for 10 minutes after application. The dried plates were fired in a box furnace (Protherm PLF110) at 820° C for 4.5 minutes. After firing, the plates were allowed to dry at room temperature.

Coatings produced from their frits are coded same name. XRD analysis was performed to determine the crystal structures of the coatings. In order to determine the colors of the coatings, measurements were taken with a spectrophotometer (Spectrophotometer CM-700d, Konica Minolta) in SCE D65 mode according to ISO 7724. Coatings' gloss values were measured with a glossmeter (TQC Sheen Polygloss) at 60° according to ISO 2813. Adherence performance of the coatings to the metal surface was determined by the impact test in accordance with the EN10209 standard. The microstructures of the coatings were investigated by SEM-EDS method.

3. RESULTS AND DISCUSSION

3.1 Characterization of Raw Materials

Table 2 shows the results of the XRF analysis of calcium phosphate and calcium hydrogen phosphate. Those defined as LOI (Loss of Ignition) in the table are volatile products such as carbon dioxide (CO₂) and water. Oxides with a apart from CaO and P₂O₅ are not included in the table. As can be seen from the table, calcium phosphate raw material contains 53.02% CaO and 39.12% P₂O₅. When the examine calcium hydrogen phosphate raw material, this CaO-P₂O₅ percentage ratio changes slightly. Calcium hydrogen phosphate contains 43.47% CaO and 47.19% P₂O₅.

Table 2 Chemical Composition of Raw Materials

Calcium Phosphate		Calcium Hydrogen Phosphate	
CaO	53.02	CaO	43.47
P ₂ O ₅	39.12	P ₂ O ₅	47.19
LOI	5.75	LOI	8.4
*Balance (SiO ₂ +Na ₂ O+MgO)	-	*Balance (SiO ₂ +Na ₂ O+MgO)	-

The XRD patterns of the raw materials used are presented in Figure 2. Main phase in calcium phosphate is hydroxyapatite (PDF # 00-009-0432). Except for hydroxyapatite, monetite (PDF # 04-009-3755) phase was detected. In calcium hydrogen phosphate, the main phase was determined as monetite (PDF # 04-009-0080).

The TG-DTA analysis is shown in Figure 3. These results are from calcium phosphate analysis, which is used in CP frit and coating. According to TG analysis, the total mass loss of calcium phosphate is 3.41 percent. Moisture and the elimination of OH from the hydroxyapatite cause temperature losses of up to 400 degrees. The calcium phosphate decomposition reactions begin as the temperature rises over 800°C. Above this temperature, the calcium phosphate decomposition process resulted in the formation of calcium oxide and phosphorus pentoxide (see Equation1).¹¹⁻¹³

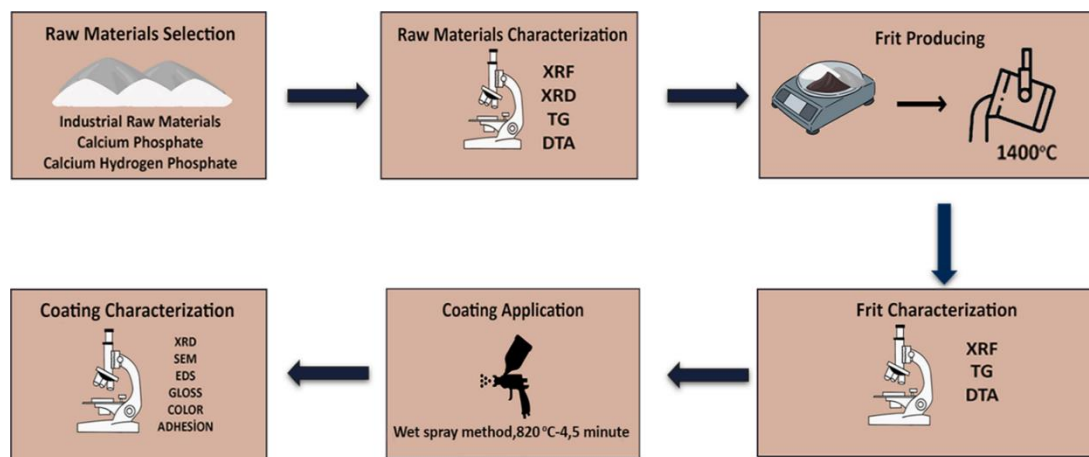


Figure 1. Experimental flowchart.

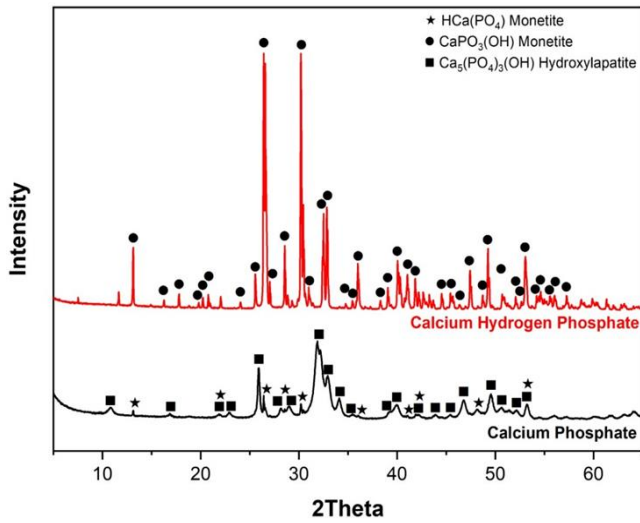


Figure 2. XRD Patterns of Raw Materials.

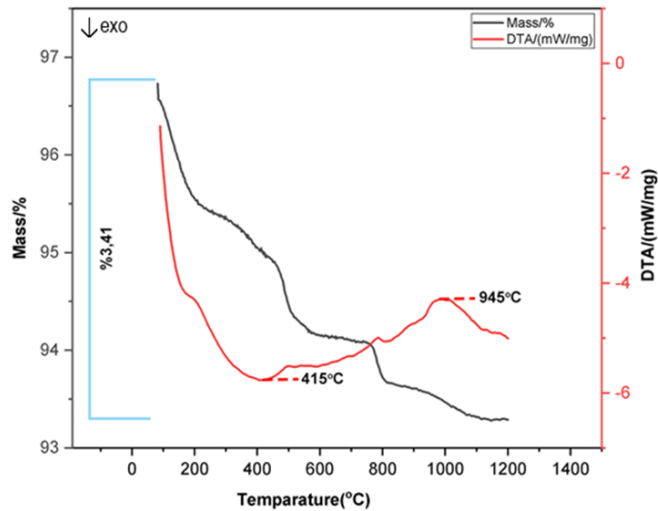


Figure 3. TG-DTA Analysis of Calcium Phosphate.

Calcium hydrogen phosphate's TG-DTA analysis is presented in Figure 4. Calcium hydrogen phosphate's total mass loss is %7.74 according to TG analysis. Water molecules in the structure of calcium hydrogen phosphate was removed in two steps. These processes took place at temperatures between 200 and 300 degrees Celsius, and the reactions were known as dehydration reactions. Monetite and water are generated as a result of these interactions. Equation 2 below describes the reaction. Monetite can be transformed in two different ways. Monetite converts into gamma monetite around 350°C. The following equation 3 explains the reaction. The second conversion process takes place as the temperature rises. The conversion of gamma monetite to beta emerges at a temperature of roughly 700°C. The following equation 4 explains the reaction.^{14,15}

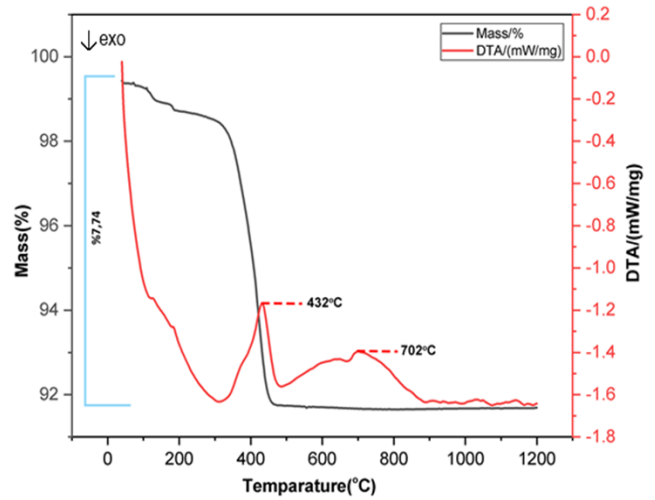
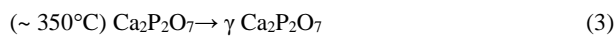
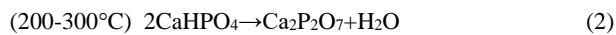


Figure 4. TG-DTA Analysis of Calcium Hydrogen Phosphate

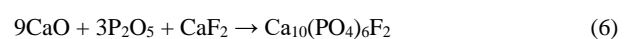
3.2 Frit Characterization

Target frit chemical compositions are given above in Table 3. Frit compositions were studied in accordance with Akcoat commercial product recipes. Only Ca and P sources were obtained from different raw materials without changing the proportions of the samples prepared with industrial raw materials. As a result of the XRF analyzes, it was observed that the chemical compositions of the frits were close to each other.

Table 3. Chemical Composition of Frits

	Oxide	wt%
	CaO	6.8
	P ₂ O ₅	5.0
RO	MgO + NiO + CoO + CuO	1.75
R ₂ O	Na ₂ O + K ₂ O	19.5
RO ₂	SiO ₂	43.83
R ₂ O ₃	Al ₂ O ₃ + B ₂ O ₃	20.97
R	F	2.15

The first analysis in Figure 5 belongs to the TG analysis, which measures the mass loss of the frits. Total mass losses for REF, CP and CH frits are 0.204%, 1.257% and 1.560%, respectively. The general reason for the mass loss is related to the moisture retention and fluoride release of these frits. In the literature, such glass structures are called is thirty glass structures [16]. CH frits' weight loss more than other 2 frits. This is because of raw material which is calcium hydrogen phosphate, 2 step decomposition reactions. This reactions leads to more softened frits. For the reason fluorides can easily remove from the structure. There are elements with high fluoride affinity in the structure. Calcium is the element with the highest fluoride affinity and forms the CaF₂ structure with free fluoride. Studies in the literature show that the calcium phosphate structure can remain intact at high temperatures and become amorphous [8][12]. CaF₂ tends to combine with apatite and calcium-phosphorous oxides to form fluorapatite (see Equation 5 and 6). It is thought that the differences in DTA analysis are due to the difference in the start and end temperatures of these reactions.



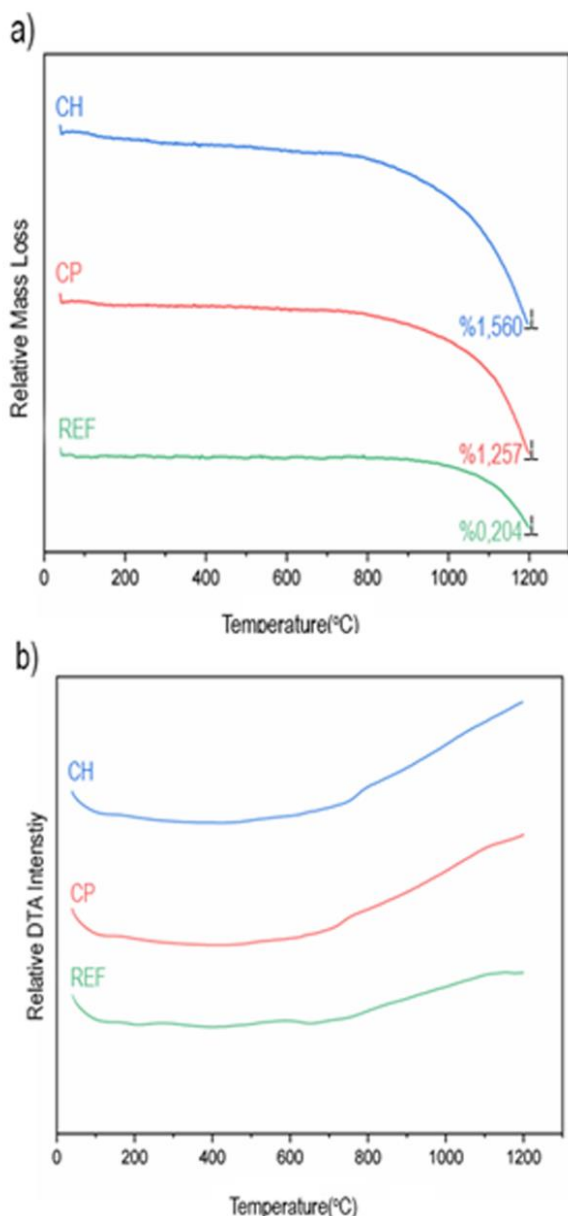


Figure 5. Thermal Analysis of Frits a)TG b)DTA

3.3 Coating Characterization and Performance Analysis

Figure 6 shows the XRD analysis of coating. No crystals were found in all coatings, except for fluorapatite (Ca₅(PO₄)₃F) (PDF#04-015-2186), which is a phase expected to occur in fluoride-containing glass-ceramics. It is seen that the change of CaO and P₂O₅ source does not change the crystal structure of the coating.

The images of the adherence test of the samples to the metal surface are given in Figure 7. In the samples, results such as separation from the surface and metal appearance are not observed. All samples showed the highest degree of adherence compared to the standard. No rupture was observed in the impacted areas of the CH sample. The CH sample appears to have better impact resistance compared to the reference and CP sample. The reason for this difference may be the difference in crystallinity ratio.

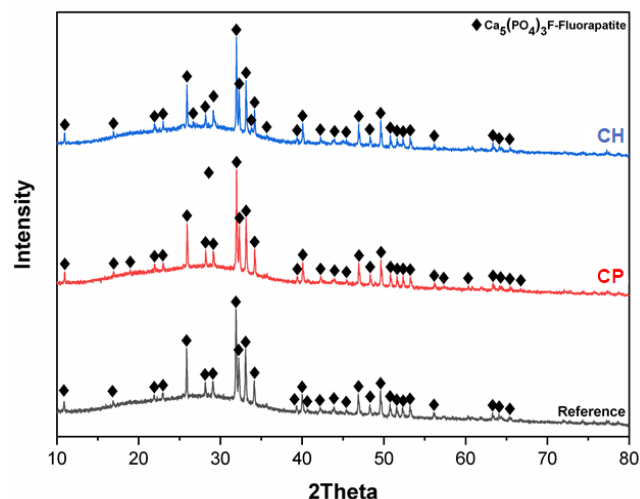


Figure 6. XRD Patterns of Coatings

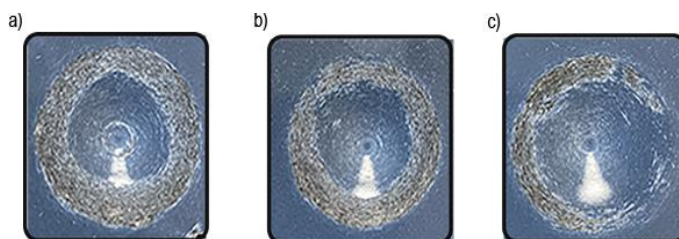


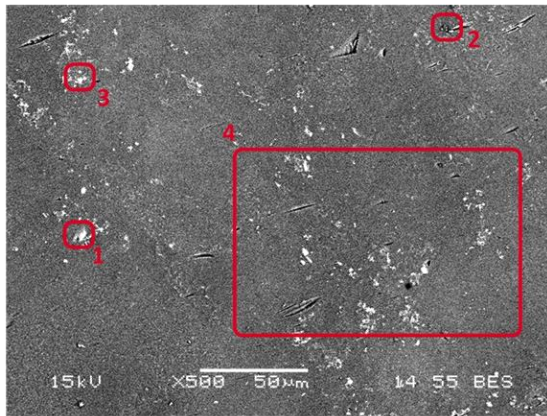
Figure 7. Coating Adherence Test Results a) REF coating b) CP coating c) CH coating

The color, brightness measurements of the coatings made of precursor glasses are given in Table 4. An L value close to 0 means blackness, if it is close to 90 it means whiteness. An A value more than 0 it means greenness, if it is less than 0 it means redness. An B value more than 0 it means blueness, if it is less than 0 it means yellowness. The L, a and b values of the REF sample, were measured 30.64, -0.7,-9.68; CP sample were measured 29.0, -0.83, -8.98 and CH sample were measured 31.3, -0.92, -9.85 respectively. There is no significant difference in gloss values, and the brightness value of CP is 0.5 points and CH brightness value is 1.5 points higher than the REF sample.

Table 4 Color and Gloss Measurements of Coatings

Sample	Gloss	L	A	B	ΔE
Reference	67	30.64	-0.79	-9.68	-
CP	67.5	29	-0.83	-8.98	1,80
CH	68.5	31.3	-0.925	-9.85	0,49

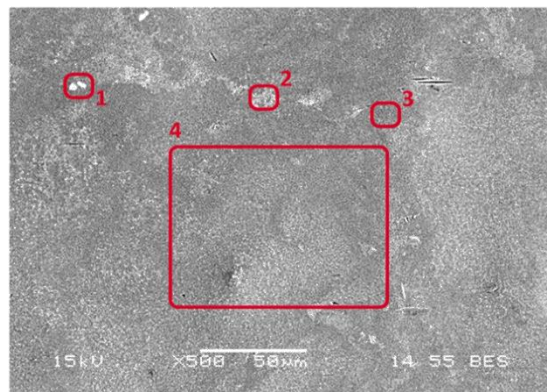
Figure 8 shows the results of the BSE image and EDS analysis of reference coatings EDS analysis of the REF coating. The dark regions appear to be the glassy phase due to high Si and Na. These regions appear to contain low amounts of Ca and P. White regions are Ca-P dense regions. These regions are thought to be fluorapatite detected in XRD analysis.



1		2	
Elt.	Atomic%	Elt.	Atomic%
C	6.957	O	50.212
O	54.304	Na	11.161
Si	9.137	Si	25.480
P	8.021	P	3.864
Ca	11.513	Ca	3.047

3		4	
Elt.	Atomic%	Elt.	Atomic%
C	6.405	O	51.354
O	50.467	Na	13.586
Na	7.700	Si	25.007
Si	15.721	P	2.814
P	7.592	Ca	1.249
Ca	8.416		

Figure 8. SEM Image and EDS Analysis of Reference Coatings



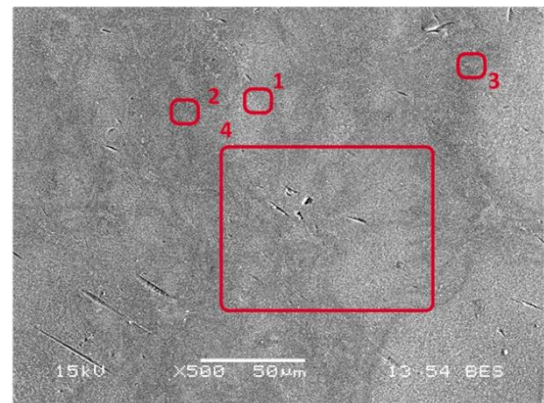
1		2	
Elt.	Atomic%	Elt.	Atomic%
C	2.589	O	49.761
O	52.930	Na	13.114
Na	6.101	Si	24.777
Si	8.077	P	3.615
P	11.663	Ca	3.728
Ca	15.740		

3		4	
Elt.	Atomic%	Elt.	Atomic%
O	51.504	C	1.208
Na	13.952	O	52.405
Ca	1.610	Na	13.899
Si	25.358	Ca	2.146
P	2.209	Si	23.338

Figure 9. SEM Image and EDS Analysis of CP Coatings

Figure 9 shows the BSE image and EDS analysis of the CP coating. It is seen that the calcium phosphate sourced sample has a similar structure to the reference sample. Si-Na dense dark regions indicate the glassy phase. The white regions are Ca-P dense and indicate the crystal phase. Unlike the reference sample, more crystals are seen near the sample surface.

Figure 10 shows BSE image and EDS analysis of the CH coating. The elemental analysis of the coating shows parallelism with the previous samples. The dark regions are the glassy phase containing dense Si-Na. White areas are Ca-P dense areas in fluorapatite form.



1		2	
Elt.	Atomic%	Elt.	Atomic%
O	51.714	O	52.172
Na	13.746	Na	12.676
Ca	2.343	Si	25.289
Si	24.214	P	2.250
P	2.531	Ca	2.778

3		4	
Elt.	Atomic%	Elt.	Atomic%
O	49.321	O	50.460
Na	13.726	Na	14.081
Si	27.569	Ca	2.462
P	2.418	Si	25.246
Ca	1.713	P	2.376

Figure 10. SEM Image and EDS Analysis of CH Coatings

4. CONCLUSIONS

In this study, the effects of different calcium and phosphorus sources on the thermal behavior, crystal structure properties and aesthetic properties of the final product on the vitreous enamel coating were investigated. The results obtained are as follows:

1. The use of different CaO-P₂O₅ sources does not affect the frit chemical composition and phase transformations.
2. Using different raw material source did not cause new phase formation in the coating crystal structure.
3. The adherence performance of the coating with higher crystallinity was better.
4. The use of complex raw materials affects the thermal behavior of the frit. Produced from complex raw materials starts to lose mass at lower temperatures.
5. The change of raw material affects the color and gloss properties only moderately.

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