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Effects of Acid Resistance on Migration Behavior of Vitreous Enamels

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Abstract:

A wide variety of cookware and utensils are continuously used throughout the world. Owing to the high mechanical and thermal properties, metallic surfaces such as cast iron, steel and aluminum are frequently used in this field. However, during cooking process, metal atoms can enter the food from the surface due to the pH of the food, relatively high cooking temperature and contact time of the processed food. This condition is called migration and when the human body gets more metal than it needs to take daily or the harmful elements enter the body, it causes many diseases, notably cancer. The enamel coating is an inorganic coating that has high heat capacity owing to the silicates in their chemical structure, high hardness and durability owing to their amorphous structure, chemical resistance and abrasion resistance. Hazardous compounds can be present in the enamel coatings which comes from the minor components used in production of frit compositions such as NiO and CoO to ensure chemical bonding in interface. Some regulations and standards have been developed since these compounds can leach or migrate into food and from there into human body. ISO 4531:2018 standard states an ICP analysis with limited release of 16 elements. However, some of these elements have a vital importance in the enamel coating technology hence it was aimed to replace the required oxides without causing a change in the enamel structure. In this study, the effect of weak organic acid resistance on migration behavior of of vitreous enamel coatings was investigated. The migration properties were investigated according to ISO 4531:2018 standard. It is stated that healthy and conforming to standards enamel compositions can be developed.

Keywords: Enamel Coating; Element Release; ISO 4531:2018; Food Contact.

1. INTRODUCTION

Vitreous or porcelain enamel coatings are inorganic coatings containing mainly oxides such as SiO_2, B_2O_3, Al_2O_3, Na_2O, K_2O, Li_2O, as well as smaller amounts of BaO, SrO, CaO, CuO, MgO, CoO, NiO, TiO_2, ZrO_2, etc. It is obtained by grinding the frits, which is the main raw material of the enamels, into powder and applying them to metallic surfaces such as steel, cast iron, copper or aluminum and firing at temperatures of 500 - 870°C. The application methods are generally electrostatic, spraying, electrophoretic, dipping and more recent thermal spray applications. Enamel coatings have superior engineering properties such as high temperature resistance, abrasion resistance, chemical resistance, and mechanical strength, as well as aesthetic properties, so that application examples can be observed in many areas such as heaters, fireplaces, gas and electric cookers, clock faces, cookware, hot water services, etc. When combined with the superior technical features, aesthetic appearance and numerous color options of enamel coatings, it is an indispensable coating for cookware [1-4].

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By definition, migration refers to the transfer of substances from one environment to another. On surfaces in contact with food, the contact base indicates the passage of elements from the surface to the processed food [5]. The migration of elements is a mathematically derived process of kinetic and thermodynamic control derived from Fick's law. The diffusion process is mathematically explained by time function, temperature, the thickness of the contacting surface, chemicals on the surface, coefficient of decomposition and coefficient of dispersion. Kinetics deals with the speed of migration behavior.

Thermodynamics concerns the balance between the food being cooked and the substrate. The important point here is that as the affinity of the oxides or chemicals in the substrate increases, more elements can pass into the cooked food even in a shorter period of time.

Conversely, low permeability oxide or chemicals migrate in low amounts. The content of cooked food, contact surface, contact time, temperature and pH are important parameters that affect migration. The movement of elements within the substrate is described in three headings: impermeable, permeable, and porous as shown in Fig. 1. Porous materials (e.g. paper and cardboard) have large voids, heterogeneous and open channels, so that the element transition is very easy. Permeable materials (e.g. plastics) exhibit a low resistance to migration and migration starts from the surface and inside the material. Impermeable materials (e.g. glass, ceramics and metals) form an absolute barrier between the substrate and the food. In this way, the migration occurs only from the surface and no migration occurs through the substrate [5-7].

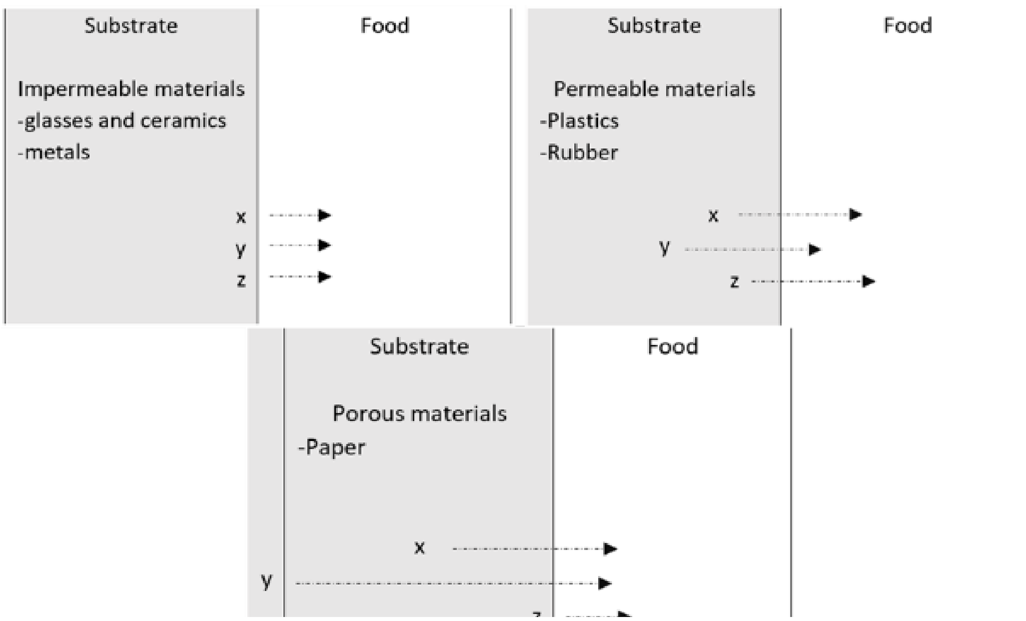

Figure 1. The movement of elements within the different substrates.

Elements exist in many different forms in nature and these elements are vital for the human body to perform cell functions at the biological, chemical and molecular levels. While 98% of the human body contains non-metallic elements, 1.89% is sodium, magnesium, potassium and calcium, which are the 4 main electrolytes. The remaining 0.02% are 11 trace elements and play a role in many vital biochemical reactions as cofactors or catalysts in the human body [8-10]. 29 elements necessary for human life can be classified into 5 main groups as follows:

•**Group 1:** It is a group of 4 basic organic elements that contain carbon, hydrogen, oxygen and nitrogen. These are essential components of carbohydrates, fats and proteins.

•**Group 2:** Nutritionally important minerals classified as macro elements. Sodium, potassium, chlorine, calcium, phosphate, magnesium and sulfur, and if the average daily intake of these elements below 100 mg/day fatal diseases can be developed.

•**Group 3:** This group of trace elements includes copper, iron, zinc, chromium, cobalt, iodine, molybdenum and selenium. In order for an element to be classified as a trace

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element, it must be less than 100 mg per day for the body and may be fatal if taken above this limit.

•Group 4: These group elements are called additional trace elements and may be mandatory for the body, although their functions are not fully known. Cadmium, nickel, silica, tin, vanadium and aluminum are the elements of this group.

•Group 5: These elements, whose functions are not fully known, can be toxic. Gold, mercury, cyanide and lead are the elements in this group [10, 11].

The intake of these elements in the body for a longer period of time than required leads to diseases and can be fatal. The excess copper element accumulates in the cell core fluid and causes oxidative stress, thus affecting many immune functions [12]. Nausea, vomiting and diarrhea occur when excess iron increases in the body. Chronic or prolonged iron accumulation occurs in the body, while liver failure, diabetes, testicular atrophy, arthritis, cardiomyopathy, peripheral neuropathy and hyperpigmentation diseases occur [13]. Prolonged exposure to chromium causes chronic ulcers of the skin [14]. Manganese increasing in the body over an extended period of time causes anorexia, apathy, headache, leg cramps, speech disorder, encephalitis syndrome and Parkinson syndrome [15]. Increased intake of selenium leads to acute and chronic cardiogenic shock, heart growth and arrhythmia, also known as Keshan syndrome [16]. Excess fluoride intake leads to bone diseases and tooth decay [17, 18]. Iodine overtakes in small amounts can be excreted with urea. However, it may cause hyperthyroid, chronic thyroid diseases and eventually thyroid gland cancer in long-term excessive intake [19].

ISO 4531: 2018 Standard was published in September 2018 under the title of Vitreous and porcelain enamels - Release from enameled articles in contact with food - Methods of testing and limits. The limit value for metal ions used in enamels is determined mainly because the passage of metal ions on surfaces in contact with food causes temporary and permanent diseases. These limit values were determined by ICP analysis of metal ions from enamel surfaces in acetic acid at different temperatures and times in different applications. This standard has begun to use in many countries due to international health concerns. The most challenging part of enamel producers here is that the limit values of some elements are very low. For example, although cobalt is the main element for adhesion between enamel and metal, the limit values are kept very low. Therefore, it can be said that its use is almost not allowed. The limit values specified by the standard are given in Table 1.

Table 1. Release limits of the elements according to ISO 4531:2018 Standard.

Element	**Release limits** (µg/l)
Al	5000
Ag	80
As	2
Ba	1200
Cd	5
Co	100
Cr	250
Cu	4000
Li	480
Mn	1800
Mo	120
Ni	140
Pb	10
Sb	40
V	10
Zn	5000

In this study, it is aimed to develop enameled surfaces which fulfill ISO 4531: 2018 Standard and are suitable for food contact. Within the scope of the study, 3 different frit compositions were developed, and standard enamel tests were applied for prepared coatings. Afterward, the samples were analyzed by SEM and EDS, and the enamel composition was selected which provided micro- and macro-structural integrity fulfilling the enamel standards. The enamel coating was sent to TÜV SÜD accredited laboratory in Germany and analyzed according to ISO 4531: 2018 Standard.

2. EXPERIMENTAL PROCEDURE

All frit compositions used in the study were produced in Gizem Frit R&D Center. Since it was aimed to provide the food contact standard ISO 4531: 2018, which is

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performed in acetic acid solution, it is thought that the enamel coatings to be prepared should have high acid resistance. In this context, three different frit compositions with high, medium and low acid resistance were prepared.

Table 2. Oxidic composition range of prepared frits of F1, F2 and F3.

Oxides	**F1**	**F2**	**F3**
	% Composition		
Na_2O	8 – 11	7 – 11	8 – 11
K_2O	2 – 4	4 – 6	2 – 4
Li_2O	2 – 3	2 – 3	1,5 – 2,5
CaO	1 – 1,5	0,1 – 0,2	1 – 1,5
MgO	0,01 – 0,05	0,01 – 0,05	0,01 – 0,05
BaO	1 – 2	2,5 – 3,5	1 – 2
NiO	0,5 – 1,5	0	0
CoO	1 – 1,5	0,75 – 1	0,95 – 1,15
CuO	0,5 – 0,7	0,7 – 0,9	0,7 – 0,9
MnO	2,75 – 3,0	2,5 – 3,5	1,75 – 2,25
Fe_2O_3	2,5 – 3	5 – 6,5	2,5 – 3
Cr_2O_3	0,25 – 0,5	0,1 – 0,3	0
Sb_2O_3	0,5 – 0,7	0	0,5 – 0,7
Al_2O_3	0,15 – 0,5	0,4 – 0,7	0,7 – 0,9
B_2O_3	12 – 16	12 – 16	10 – 13
SiO_2	45 – 55	45 – 55	50 – 65
TiO_2	3 – 4	4 – 5	3 – 4
ZrO_2	2,5 – 3,5	0,04 – 0,08	0
MoO_3	0	0,1 – 0,4	0,1 – 0,3
F	0,1 – 0,3	0,75 – 1,5	0,4 – 0,7

It is a known fact increase in alkaline oxide content such as Na, K, Li and Ba have a beneficial effect for acid resistance while B, Zr and Al have a negative effect. F1 frit composition was prepared with the concerns of a high amount of metal oxides with a high amount of alkaline oxides. Also, F1 and F2 compositions were consisted low amount of SiO_2 while F3 composition has high amount of SiO_2. The oxidic composition range of prepared frits is given in Table 2.

In this study, 10 cm x 30 cm low carbon steel plates were chosen as a substrate. In order to ensure the adhesion of the enamel and the metal surface, surface activation processes were carried out. All experiments were performed via the electrostatic spraying method. In order to provide electrostaticization, silicone oil was added to the frit compositions which were powdered in the mill. All experimental studies were conducted in a laboratory scale. For this reason, preheating was carried out by keeping the samples at a box furnace (Protherm PLF 110/30) at 550°C for 4 minutes 30 seconds. Afterward, the firing process was carried out in the box furnace (Protherm PLF 110/30) at 830°C for 4 minutes and 30 seconds.

Typical enamel tests, color measurement, impact resistance (ASTM B916-01 (2007) -Standard Test Method for Adherence of Porcelain Enamel Coatings to Sheet Metal) and acid resistance (ISO 28706-1: 2008 (Vitreous and porcelain enamels - Determination) and ETC (Easy-to-clean) tests were carried out since the enamel compositions should be suitable for contact with food. Impact resistance test was performed via dropping of 2268 g weighted hammer from 406.4 mm height which equals to 9.03 joules of impact energy. The acid resistance test examines the change of the affected surface visually after a 10 % solution of citric acid monohydrate ($C_6H_8O_7.H_2O$) in a specific area for 15 minutes. The ETC test is a common test among enamel manufacturers and users, and it is based on the fact that 0.5 grams of lithium nitrate is placed in an acid-tested area and kept for 30 minutes at 300°C. The cleaning is carried out by draining the water at room temperature over the lithium nitrated zone. Then, if there is no trace on the enamel coated surface, it is interpreted that the enamel is ETC.

SEM and EDS analyses were performed in the backscatter electron mode with an acceleration voltage of 15 kV and operating distance of 9.5 mm. (Phenom Pro Desktop SEM) after the tests. Mechanical and chemical adhesion between enamel and metal and microstructures formed on the surface were investigated. In addition, the surface SEM analysis of the acid-tested regions were done, and the damage caused by the acid was investigated. When the color, acid resistance, impact resistance, ETC test and SEM analyzes were compared, the sample which was given the best results was sent to ISO 4531: 2018 test to TÜV SÜD Industrie Service GmbH in Germany.

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3. RESULTS and DISCUSSION

3.1. Color Values

The L, a and b color values of the samples obtained by spectrophotometer are given in the Table 3.

Table 3. Color values of the studied samples according to CIELAB Color Space.

Color Channels	Color Values in D65 SCI		
	F1	F2	F3
L*	28,63	29,09	29,14
a*	0,02	-0,02	-0,1
b*	-0,69	-0,56	0,47

L* value indicates opacity, whiteness increases with increase and blackness increases with decrease. The a* value represents green and red colors. Negative values indicate green, positive values indicate red color. The b* value represents the yellowness and blueness. Negative values indicate blue, positive values indicate yellow color. It can be seen that all samples show similar color values.

3.2. Impact Resistance

Figure 2 shows a photograph of the impact test areas after the impact test has been performed under the standard scope of the samples. For all three samples, it can be stated that the adherence between metal and enamel is perfect. Only F1 sample consists NiO content in the oxidic composition while F2 and F3 samples show similar adherence oxides content. Due to the regulations of the food contact, the amount of NiO is zero in the F2 and F3 samples and the adherence tried to be achieved via other adherence oxides such as CuO and MoO_3.

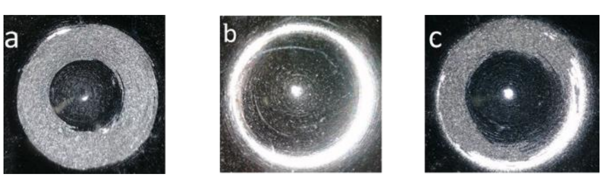

Figure 2. Photographs of studied samples after impact test: **a)**F1, **b)**F2, **c)**F3.

3.3. SEM Images

SEM analysis were made in order to investigate surface and surface related properties of the prepared enamel coatings and shown in Fig. 3. In the enamel coating prepared with F1 frit composition, it is observed that the glass structure on the surface increases excessively. The large number of glass formers in the composition makes this understandable. Therefore, micro cracks were formed on the sample surface. White structures appearing around the cracks are thought to be pigments. In the enamel coating prepared with F2 frit composition, round shaped structures are observed. It is understood that the enamel structure is provided in a basic sense. In the enamel coating formed with F3 composition, the surface is more accurate than other samples. It is also desirable that the structure formed on the surface remains as a trace only in terms of structure homogeneity. However, EDX analysis was needed in all 3 compositions in order to fully understand the main causes of the surface properties. EDX spot analysis was shown in Fig. 4. As expected in the EDX analysis for the F1 composition, it was found that the structures of different colors were Cr, Fe and Mn elements. The reason for this was found to be either pigment content or the metal oxides in the frit composition. As expected, it is understood from the high fluorine content with low SiO2 amount that there is also a high glassy structure. In the EDX analysis for the F2 composition, it was observed that the round shapes contained very low amounts of pigment, while the structurally visible shapes contained high levels of silicon. The high Si content is thought to occur during enamel application. In the application process, several enamel defects may occur due to the operator actions. The agglomeration of the particles can be occurred due to the splitting. In the composition F3, the regions seen as traces show the typical enamel structure. High titanium content is observed in white areas. So, of all three samples, it can be concluded that the best surface was achieved with F3 composition. After the acid resistance test according to the standard of ISO 28706-1, it was observed that the F1 and F2 compositions visually degraded via citric acid solution and the SEM images of the samples are shown in Fig. 5. The black color of the enamel coatings turned whitish because of the acidic degradation. However, no color change and acid resistance were observed in the F3 sample. SEM and EDS analyze were performed to investigate this situation better. White and round shapes are also shown in the F1 and F2 samples, but not in the F3 sample. When the EDS analysis is performed, it is observed that the iron (Fe) and carbon (C) ratio is high in these white round shapes. As a result, it was found that the enamel was almost completely eroded, and the steel surface was observed during the

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analysis. Typical enamel structure was still observed in the EDS analysis of the F3 sample. The glassy nature of the enamel coating was protected, and the whitish areas show Cr and Mn based pigments.

It can be stated that the high amount of SiO_2 content in the F3 composition showed a beneficial effect of acid resistance.

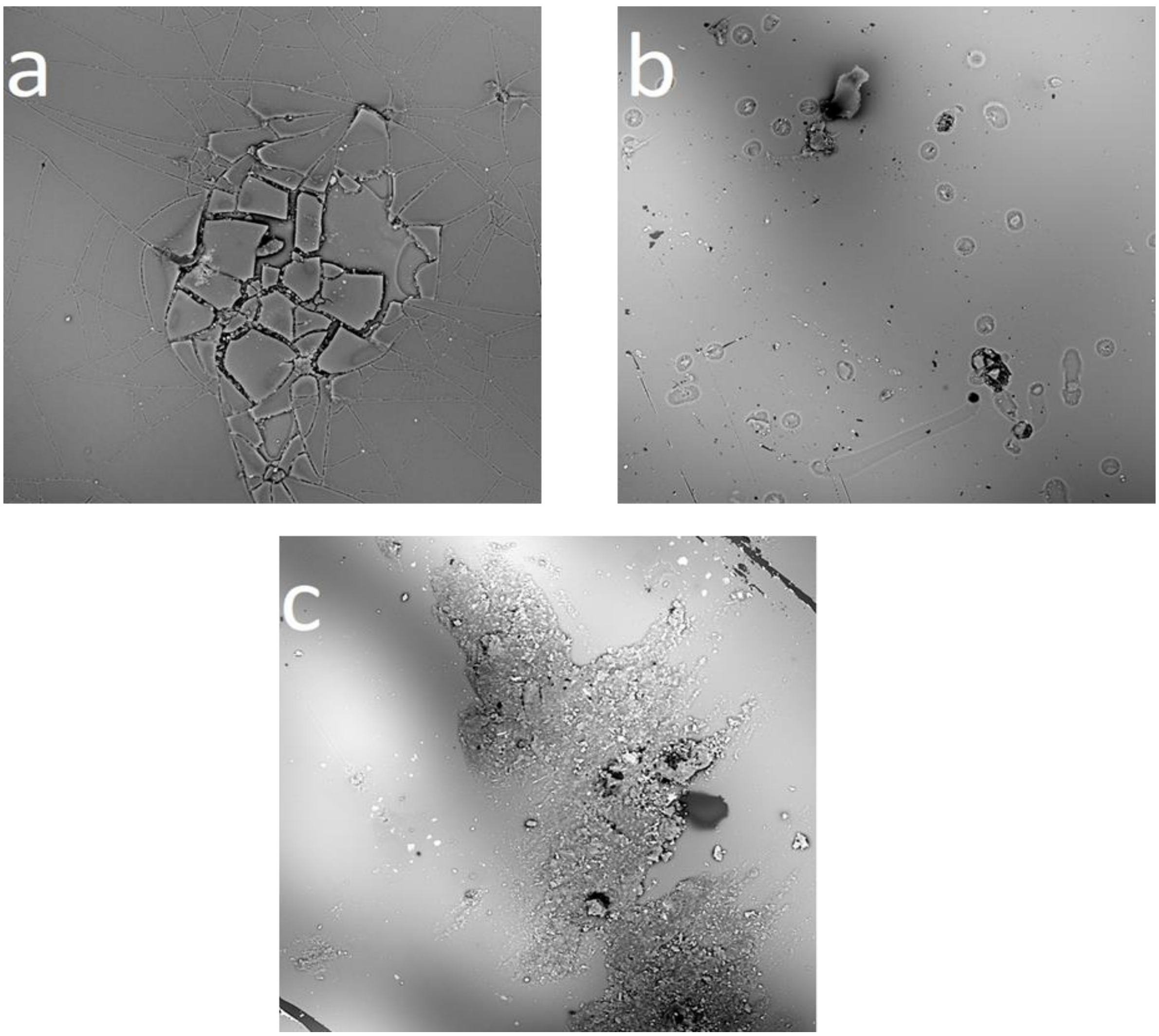

Figure 3. SEM images of the prepared vitreous enamel coatings: **a)**F1, **b)**F2, **c)**F3.

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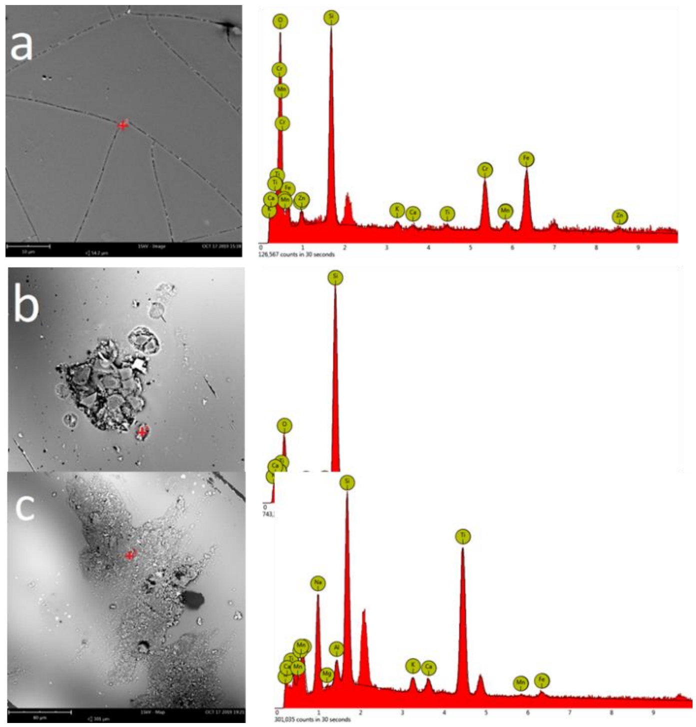

Figure 4. SEM and EDX analysis of the prepared vitreous enamel coatings: **a)**F1, **b)**F2, **c)**F3.

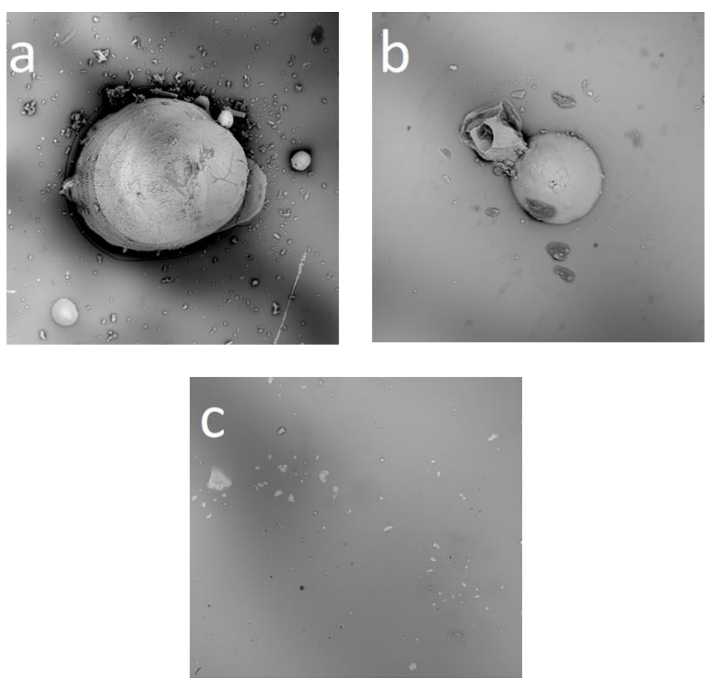

Figure 5. SEM images of the prepared samples after acid resistance test: **a)**F1, **b)**F2, **c)**F3.

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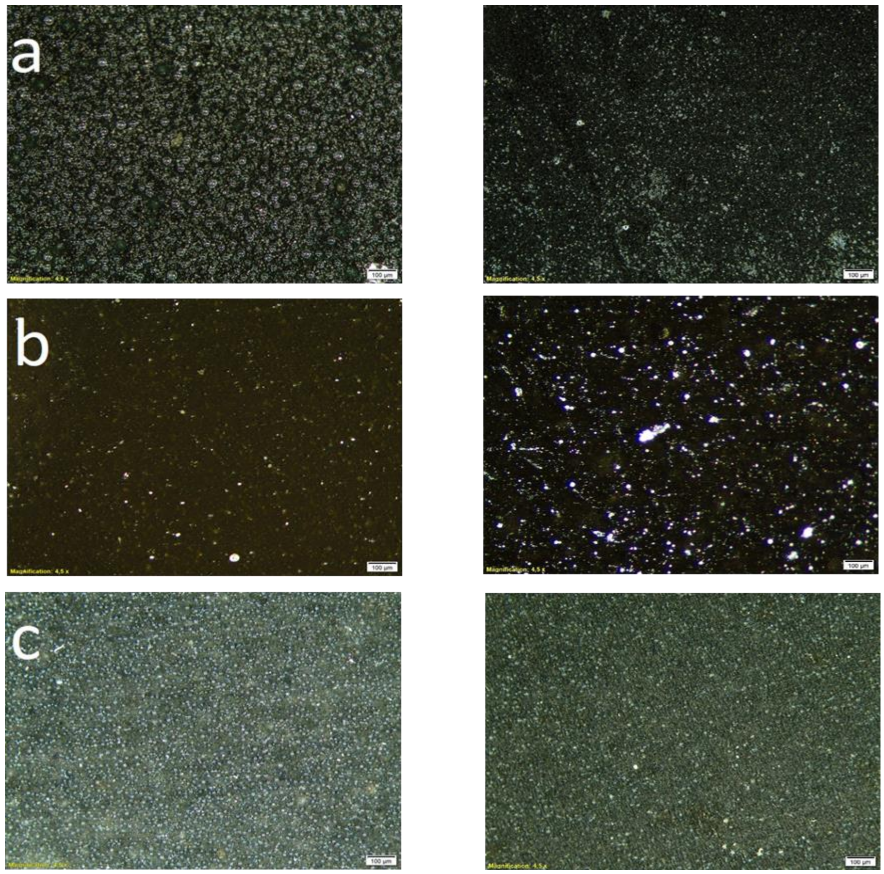

Figure 6. Optical microscope images of the enameled samples before the ETC test (left) and after the ETC test (right): **a)**F1, **b)**F2, **c)**F3.

4. ETC (Easy-to-clean) Test

Since the interpretation was made according to the trace formed after the ETC test, optical microscope images were taken before and after the test and it was shown in Fig. 6. Although the subject relates to interactions in which the lithium nitrate ($LiNO_3$) is exposed to the enamel surface at partially high temperature (300°C), the standard is concerned only with visible surface traces. However, different studies on this subject may be started with the show that glassy structures are gradually disappearing, and glowing structures are more visible. Both the bubble structure formed by the glassy structure and the bright crystals are observed in the F3 sample.

After the ETC test, it is observed that the structure is partially degraded, and the crystals are not damaged. concerns of elements diffused into the lithium nitrate. As seen in the F1 sample, many bubble structures have occurred in the glassy structure. However, almost all of these structures disappeared after the test and white scars appeared. Due to traces, the sample is visually interpreted as “not ETC”. In the F2 sample, it is observed that the crystal structures glow through the glassy structure even though the glassy structure containing the bubble is not so much as in the F1 example. However, after the ETC test, many flares

After all the tests and analysis described above, the F3 composition which gave the best results from acid resistance, impact resistance and ETC test results were sent to TÜV SÜD test center for analysis within the scope of ISO 4531-2018 standard.

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Table 4. Food contact test results of prepared enamel coating of F3 according to ISO 4531:2018 Standard

Parameter	Unit	Specific Release Limit	F3 Sample
Aluminium	µg/l	5000	15
Silver	µg/l	80	< 1
Arsenic	µg/l	2	< 1
Barium	µg/l	1200	36
Cadmium	µg/l	5	< 1
Cobalt	µg/l	100	23
Chromium	µg/l	250	4
Copper	µg/l	4000	62
Lithium	µg/l	480	35
Manganese	µg/l	1800	54
Molybdenum	µg/l	120	4
Nickel	µg/l	140	< 1
Lead	µg/l	10	< 1
Antimony	µg/l	40	8
Vanadium	µg/l	10	< 1
Zinc	µg/l	5000	12

3.5. ISO 4531:2018 Food Contact Test

The F3 sample prepared was successful under the test standards and the results are given in Table 4.

4. CONCLUSION

Today, enamels have become the indispensable coating material of cookware. However, national and international standards have been developed with the emergence of elemental migration from food contact surfaces causing health problems. In this study, it is aimed to prepare enamel compositions which do not compromise the standard enamel properties while meeting ISO 4531: 2018 standards. Since the standard performs the test procedure with acetic acid, it is considered that the acid resistance of the enamel coatings prepared should be high. It was stated that the high amount of SiO_2 content with low amount of F, shows a beneficial effect for acid resistance. Furthermore, the increased metal oxide ratio, especially Mn and Fe, increases the acid resistance. The presence of pigment does not affect acid resistance. As a result, in this study, enamel composition, which is suitable for contact with food, does not cause health problems and conforms to standards has been developed.

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