REPUBLIC OF TURKEY

YILDIZ TECHNICAL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE RESEARCH OF THE ENAMEL FRITS WITH LITHIUM EFFECT ON SURFACE CHARACTERISTICS OF VITREOUS ENAMEL COATINGS

Ahmet Murat ERAYVAZ

MSc. THESIS

Department of Chemical Engineering

Program of Chemical Engineering

Adviser

Assoc. Prof. Dr. Emek MOROYDOR DERUN

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A thesis submitted by Ahmet Murat ERAYVAZ in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE is approved by the committee on 09.05.2019 in Department of Chemical Engineering, Chemical Engineering Program.

Assoc. Prof. Dr. Emek MOROYDOR DERUN

Yildiz Technical University

Adviser

Approved by the Examining Committee

Assoc. Prof. Dr. Emek DERUN, Adviser

Yildiz Technical University _____

Assoc. Prof. Dr. Emel AKYOL, Member

Yildiz Technical University _____

Assist. Prof. Dr. Aslı Can KARAÇA, Member

Istanbul Technical University _____

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Ahmet Murat ERAYVAZ

Signature

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To dedicate my family for their endless help and support

and

to my best friends who appreciate me always

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LIST OF SYMBOLS

$	Dollar
±	Plus- Minus
ΔG	Gibbs (free) energy
a *	Expresses Redness and Greenness in Color Values
A/m^2	Unit Current Density
b *	Expresses Yellowish and Blueish in Color Values
Bayer	Enamel-Test-Sieve
Cm	centimeter
g/cm^3	Density
g/ml	Density
ga	Pressure
in.lb	Newton-Meter
J	Joule
Kg	Kilogram
Km	Kilometer
kV	Kilovolt
L *	Represents Lightness and Darkness in Color Values.
mA	Milliamp
mesh	Sieve Size
min.	Minute
ml	Milliliter
mm	Milimeter
N	Newton

nm	Nanometer
^{o}C	Celsius Degree
pH	Hydrogen Ion Concentration
Ppm	Parts Per Million
wt	Mass Versus Weight
µm	Micrometer

LIST OF ABBREVIATIONS

a.m.u	Atomic Mass Unit
ASTM	American Society for Testing and Materials
CIE	Corporación Interamericana de Entretenimiento
D65	Standard Illuminant
DC1107	Type of Silicon Oil
EK04	Type of Sheet steel
ETC	Easy to Clean
ICs	International Continence Society
ISO	International Organization for Standardization
LCE	Lithium Carbonate Equivalent
RHI	Rockwood Holdings, Inc
SEM	Scanning Electron Microscope
TS EN	Turkish Standards Institute
XRF	X-ray fluorescence
YTU	Yildiz Technical University

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ABSTRACT

The Research of The Enamel Frits with Lithium Effects On Surface Characteristics Of Vitreous Enamel Coatings

Ahmet Murat ERAYVAZ

Department of Chemical Engineering

M. Sc. Thesis

Advisor: Assoc. Prof. Dr. Emek MOROYDOR DERUN

Lithium is the lightest of all metals and the third element in the periodic table. Despite the fact that more than 150 lithium minerals are known in the land, very few are commercially available with approximately twenty-four industrial uses.

Since the early 2000s, lithium salts have become an important input for the energy industry. Lithium carbonate and hydroxides are the basic building blocks of Li-ion battery production. Lithium compounds usage areas not only limited to energy; heavy duty machines; in the aluminum industry; in nuclear power plants; defense and medical industries, glass, ceramic, frit and coating in industrial. Lithium has also been found to be very useful in the development of harder, smoother and more resistant low-temperature glasses, glazes and enamels.

It is also used in very low-melting vitreous compositions like aluminum enamels, color, fluxes and glass seals. Use of lithium also helps in the development of low expansion bodies, glazes and glasses. With increasing popularity in different sectors and at the same time with rare and cheap Lithium frit and enamel recipes, made it

possible to present cheaper products to the market, providing information on new projects, possible to achieve good adhesion.

In this study; understanding the surface characteristic of lithium in enamel, fulfilling the functions expected from the products and also aimed that investigate to behavior of interface layer. X-ray fluorescence (XRF) spectrometry was used for chemical characterization and Mastersizer for particular size, Impact test was used for understanding bond structure behaviors of different type of enamels. SEM analyses of the enameled materials has been made to see and define surface morphologies.

Keywords: Lithium, Glaze, Frits, Electrostatic Powder Enamel, XRF, Mastersizer

ÖZET

Emaye Fritlerin Camsı Emaye Kaplamalarında Lityumun Yüzey Özelliklerine Etkisinin Araştırılması

Ahmet Murat ERAYVAZ

Kimya Mühendisliği Bölümü

Yüksek Lisans Tezi

Tez Danışmanı: Doç. Dr. Emek MOROYDOR DERUN

Lityum tüm metallerin en hafifi ve periyodik tablodaki üçüncü elementtir. Dünya'da 150'den fazla lityum mineralinin bilinmesine rağmen, yaklaşık yirmi dört endüstriyel kullanımı bulunmaktadır.

2000'li yılların başından beri, lityum tuzları enerji endüstrisi için önemli bir girdi haline gelmiştir. Lityum karbonat ve hidroksit, Li-ion pil üretiminin temel yapı taşlarıdır. Lityum bileşiklerinin kullanım alanları sadece enerji ile sınırlı değildir; ağır makineler; alüminyum endüstrisinde; nükleer santrallerde; Savunma ve tıp endüstrisi, cam ve seramik endüstrisinde de kullanımları mevcuttur. Günümüz değişen teknolojisi ile birlikte Li bileşikleri daha önemli hale gelmiştir.

Ayrıca lityumun daha sert, daha pürüzsüz ve daha dirençli düşük sıcaklıktaki camların, sırların ve emayelerin geliştirilmesinde çok faydalı olduğu bulunmuştur. Aynı zamanda, alüminyum emayeler, renk ve cam contalar gibi çok düşük erime noktalı camsı bileşimlerde kullanılır. Lityum kullanımı ayrıca düşük genleşmeye sahip maddelerin, camların ve camsı materyallerin gelişimine yardımcı olur. Farklı sektörlerde artan popülerlik ile birlikte ucuz ve nadir bulunan lityum, frit ve emaye reçetelerinde

değişikliğe gidilmeye başlanmıştır. Bunun sonucu olarak lityumun emaye yüzeyindeki etkileri merak konusu haline gelmiştir.

Bu çalışmada; emayede lityum yüzey karakteristiğini anlamak, ürünlerden beklenen fonksiyonları yerine getirmek ve arayüz katman davranışını araştırmayı amaçlanmıştır. Kimyasal karakterizasyon için X-ışını floresans spektrometresi (XRF) ve tanecik boyut analizi için Mastersizer ve farklı tipte emayelerin bağ yapılarını anlamak için Darbe testi kullanılmıştır. Bunun yanı sıra, yüzey morfolojisini görmek ve tanımlamak amacıyla SEM analizleri yapılmıştır.

Anahtar Kelimeler: Lityum, Sır, Frit, Elektrostatik Toz Emaye, XRF, Mastersizer

1
Introduction

1.1 Literature Review

The enamel known as the most advanced coating technique in the history from the 6th century BC to the present day which was first used in the coloring and decoration of jewelry and ornaments in ancient times. Enamel; chemically is known as silica-based glassy material. It is a type of coating which is not affected by atmospheric conditions and has high corrosion resistance [1].

Enamel; is an inorganic coating used on metals used for protective, functional and decorative purposes. The enameling process is made with the aim of creating a new material by combining the resistance, formability and lightness of the metal used in the base material, the hygiene and hardness properties of the enamel coating [2].

The smallest structure forming the enamel is called frit. Frit is the glassy granule or pulp obtained by rapid cooling (roller or water) of the inorganic raw materials forming itself.

By changing the chemical composition of the enamel, the coating is provided with different functional properties. The most important advantages of enamel are; temperature resistance, thermal shock resistance (-50°C to 450°C), high corrosion resistance, high scratch resistance, acid and base are resistant to such chemicals. It can be applied as decoration because it is bright and it is possible to apply in different colors.

Enamel coating is widely used as protection for iron materials in industrial applications. In recent years, enamel coating has been spreading on aluminum, copper and stainless-steel base materials [1].

1.2 Objective of the Thesis

It is possible to make enamel which can be cleaned easily by changing the frit composition. Enamels with this composition are used on hob, oven and tray applications. Enamel coatings in different colors are used in pots, pans and utensils applications. They are used in chemical storage containers due to their resistance to chemicals such as acid and base.

Different properties of frit components are used to obtain different conditions in enamel. For example, the hard frit provides high resistance to abrasion and fine line defects and superior wear resistance. The soft frit melts in the smelting process and closes the metal and improves the adhesion and ensures that the edges are smooth. Thus, improved coating smoothness is obtained with suitable frit compositions [3].

Different from glass and porcelain, chemical composition, structure and properties of enamels, especially softening temperature and surface structure, affect enamel coating technology. The surface roughness of the base material, the type of the base material and the composition of the enamel are the most important parameters affecting the adhesion mechanism [2].

In addition to the traditionally used ceramic coating of lithium, it also has an important task in enamel and porcelain. Lithium is highly reactive and is not elemental in nature. It has three times more flux characteristics than sodium. Lithium also has different surface effects on enamel [1].

Gizem Frit manufactures frits and pigments used as intermediate raw materials for decorative and protective coating of materials such as sheet metal, stainless steel, aluminum, cast, ceramic tile, sanitary ware, porcelain, medical porcelain, and glass.

As an evidence to Gizem Frit's leadership in the industry, the company's R&D and quality control laboratories are equipped with state-of-the-art technology and these laboratories possess the technical competence required to test and analyze every mineral and both inorganic and organic structures. They are open to all academics as well as to suppliers, customers, and industry representatives that adopt the principle of high quality [3].

1.3 Hypothesis

Lithium has become the most expensive raw material of recent years with the start of its use in the energy sector. In parallel with this, the ceramic and glass sector used to be the leader in its field of use and now it has taken the lead in the energy sector. It is necessary to find new chemical components that can replace lithium, and to revise lithium-containing frit compositions.

In this study, in Gizem Frit's R & D department; enamel coating, coating of the enameled enamel, quality controls and surface tests and XRF analyzes were performed. Surface effects of lithium on enamel have been researched and tested. Apart from the flow characteristics of lithium, its effect on brightness and bond between enamel and metal is quite high.

2
Porcelain Enamel

2.1 General Information

Porcelain enamel is an inorganic coating matter which is applied to a metal substrate and fused at a high temperature to form a continuous, adherent and protective coating. Other terms which are used to define porcelain enamels include glass coatings or ground coatings, vitreous enamels or coatings, high temperature coatings, ceramic coatings or just enamels. Some of these conditions may be easily confused with other materials, such as organic paints, or are too restrictive and include only amorphous coatings [3].

A glassy coating applied to various metal surfaces by fusion process at high temperatures is called porcelain enamel. The chemical, physical, electrical and aesthetic properties of the glass reflect the strength, manufacturing and durability of the chemically bonded glass-metal compound obtained. The formulas of porcelain enamels have been modified to develop specific properties on metals and alloys.

The structure consisting of various inorganic metal oxides which dissolve between 1100^{o}C and 1400^{o}C to form an alkali borosilicate glass is called porcelain enamel. There are two different cooling processes. One of them; The glassy structure is formed by quickly passing through the rolls which are cooled by cold water. The other method is; the melt is possible by mixing the glass with water. As the product of the cooling process, two different frit structures, dry and wet, occur. In order to obtain the desired product's surface quality and properties, the frit pieces are mixed in different combinations and then fired [1].

Porcelain enamels usually contain more than an amorphous phase, hence they have been classed as solutions [4].

Porcelain (Vitreous) Enamels provides an actual and thorough compilation of materials, methods of smelting, application, firing and testing while providing fundamental understanding of the processes involved with better and larger details of porcelain enamel chemical and physical properties to improve the value for many applications such

as drinking water, solar energy and coatings on different metals and alloys. Key information on current steels is supplied as well as welding which is important for many sheet steel products. Over the last several decades, the continuous casting has revolutionized to the manufacture of steel which has changed the chemistry of steel and improved their quality [1].

2.2 The History of Enameling

It is probably that the Egyptians were the first to make enamels, but it is not likely to happen that, for many centuries; they got beyond the beginning of enameling on metals. In their jewelry they used glass in the form of a cloisonné, and from the time of the beginning of the Christian age there are many examples of Egyptian enamels on jewelry, which treasures can be seen now in the large museums; throughout the world. The Egyptians possessed the only vitreous colors for a long period of time such as, blue and white; the blue itself being lost color because of the decomposition of the enamel surface. It now becomes visible as a light dust blue instead of the dark blue, which is still obvious when scratching removed the weathered surface [2].

This method concerned a ground coat or first coat of various composition from the cover or finish coat of enamel. In fact, it was often necessary to make a series of enamel applications, heating before each separate coat, to acquire a layer thick enough to give the desired effect. The enamel had to be easily fusible, and the operations were very expensive. The muffle furnaces were not working very well, and many pieces were damaged because of the fuel gases, which turned the enamels black or reasoned them to blister. Although many difficulties were encountered, this method has, with many modifications and improvements, survived time, and is at the current being used for enamelling great quantities of our modern ware. It is particularly suitable to the enamelling of large cast iron pieces such as sanitary ware and barber chairs. Enamel was first applied to sheet iron and steel in Austria and Germany in the period following 1850 [5].



Figure 2. 1 Cast Iron Bath [2]

One of the most significant obstruction to quick improvement in enameling in this period was the lack of good, pure, and cheap raw materials. The technology of iron was not expanded and the many chemical industries appliance the raw materials for the enamels were in the process of development [6].

Undoubtedly one of the greatest benefactions to the enameling industry was the exploration of the pun into clay to keep the powdered enamel in suspension in water and make it bond to the metal before firing. This suspension of enamel and clay in water was called a slip, and was coated or with metal dipping, dried, and then fired in a furnace. At later times, the spray gun was advanced, greatly simplifying the uniform application, especially on large pieces of ware [7].



Figure 2. 2 Enamelled Built in Oven [1]

The biggest advances, nevertheless, have taken place since the beginning of the twentieth century, when enameling progressed rapidly in USA. The first few years of this century

presented a rising from a few small factories to thirty-five or forty in the United States and Canada. The factories enlarged rapidly in size and number, some employing as many as one thousand persons in 1910. In 1925 the product output numbered to six hundred and seventy-five million dollars. Such an increase naturally fascinated not only capital but also the best ceramists, chemists, and engineers of the country. The market the enameller offered and catered to his requirements were begun to appreciate by chemical industry. The steel industry made great progresses in the improvement of better enameling irons. From the last years of World War I until 1930, it was exploded. The old type of agate or granite enamel no longer met the demand and new developments in formulae and processes were made. The technique of shot blasting, cleaning, pickling, application, and firing was greatly developed. The continuous enameling furnace, automatic control, continuous conveyors, and mass production resulted from the increased order. The amount of scrap and defective ware was significantly reduced, although the specifications for quality were accomplished more acute [8].



Figure 2. 3 The Shah Alam Mosque, Malaysia. Designed by Dato H. J. Baharuddin, architect. 21,000 panels of more than 3,000 different dimensions [1]

The launch of automatic conveyor conveying systems and equipment, including cleaning and pickling, spraying, dipping, drying, electrostatic powder application, firing and inspection, resulted in smoother and more efficient production and higher quality. A continuous growth has been settled down nowadays, with a research and development program which guarantees their future [9].

2.3 Enamel Coating Application Areas

It is one of the tasks of glassy enamels that provide protection against corrosion, which is used for decorative purposes and also reduces the effect of acid, alkali and different chemicals. Therefore, the use of enamels is common in many kitchens, bathroom tools and appliances. They are also used in architectural panel applications. It has been used in the dairy, pharmaceutical, brewing and other chemical industries [10]. In the above industries used vessels made of heavy gauge steel or cast iron are widely. The broad use of enamel coatings on iron and steel was announced firing utensils, architectural panels, signs, silos, storage tanks, roofing tiles, gasoline service stations, guard rails, chalkboard and many other products of marketing where is among the most desirable of the composite system of materials [11]. Some of the common areas of application of enamel coatings are shown in Figure 2.4 below.

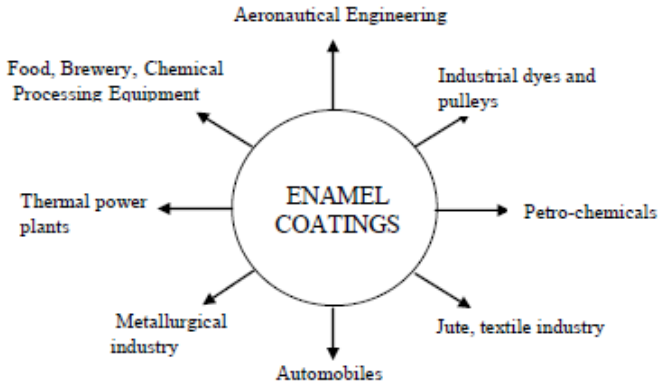


Figure 2. 4 Enamel Coating Application Areas [12]

2.4 Chemical Composition of Enamel

A material composed of oxidized compounds are called enamel. Furthermore, in this structure can be existed the oxidative bonds, oxygen and fluorine compounds. The Si^{+4}, Al^{+3}, B^{+3}, P^{+5} ions are being in the structure of enamel the and the single and bivalent cations that support to the structure [13].

Many various diversities of clay are used, but a plastic clay quite free from impurities is most common the following classification of more common enamel materials are shown in Table 2.1.

Table 2. 1 Classification of Porcelain (Vitreous) Enamel Materials [1]

Electrolytes	**Fluxes**	**Floating (Suspension) Agents**
Borax	Borax	Clay
Soda ash	Soda Ash	Gum tragacanth
Sodium aluminate	Soda Nitrite	Gum Arabic
Magnesium carbonate Magnesium sulphate Sodium nitrite	Barium carbonate Magnesium Carbonate Litharge	Ammonium alginate Bentonite Colloidal silica
Colors	Opacifiers	Refractories
Cobalt oxide Copper oxide Iron oxide Nickel oxide	Titanium oxide Tin oxide Antimonium oxide Zirconium oxide Sodium antimonate	Quartz Feldspar Clay

The six different groups; refractories, fluxes, opacifier, colors, floating (or suspension) agents and electrolytes may divide into raw materials used in enamels.

Refractories contain materials such as quartz, feldspar and clay, which lend to the acidic part of the melt and give body a glass.

Materials that make the glass structure fluid; borax, soda and fluorspar show basic properties when reacting with acidic reflectors to form a glass structure. The melting of metals such as silicon lithium into the glass structure is possible thanks to this group. However, if it is added to the glass structure too much, it forms a slag structure, which is undesirable.

Opacifiers are compounds added to the glass to give a white opaque appearance and gloss, which are characteristic of glassy enamels. Opacifiers are in general quite refractory, but the real opacifiers such as tin oxide (SnO_2), antimony oxide (Sb_2O_3), sodium antimonite,

titanium oxide (TiO_2), zirconium silicate ($ZrSiO_4$), and zirconium oxide (ZrO_2) are often assisted by accessory opacifiers, such as cryolite and fluorspar, which make the enamel much more fusible.

The color materials may be oxides, elements, salts, or frits, and may act either as refractories or fluxes. The enamel composition and the processing may influence the color contributed to an enamel [1].

The floating (or suspension) agents are mill additions, such as clay and gums, which are used to suspend the enamel in water or in some other liquids. A range of capabilities of raw materials summary is reported at Table 2.2.

Table 2. 2 Porcelain (Vitreous) Enamel Typical Composition [1]

Component	**Mineral**	**Functions**
SiO_2	Quartz Feldspar	Refractory component, glass forming oxide, hardens the vitreous system, adds chemical resistance and increases viscosity.
B_2O_3	Borates	Flux that produces the vitreous matrix, reduces viscosity and increases surface hardness.
Na_2O K_2O Li_2O	Albite Feldspar Microcline Spodumene Petalite Lepidolite	Alkaline components that lower the temperature at which glass softens, reduce its elasticity and increase its brilliance.
Al_2O_3	Feldspar Corundum	Increases viscosity and chemical, mechanical and thermal resistance, reduces the expansion coefficient and favours an opaque finish.
ZrO_2	Zirconium	Improves resistance to acids, to knocks and to shocks, acts as an opacifier.

Table 2. 3 Porcelain (Vitreous) Enamel Typical Composition [1] (continue)

ZnO	Zincite, Blende, Wurzite	Excellent flux, lowers the expansion coefficient and improves brilliance and surface quality.
CoO	Cobaltite	A very strong adherence agent, it produces a structure with lots of small, well distributed bubbles.
NiO	Niccolite	A second adherence agent, it produces a structure with a small number of large bubbles.
CuO	Copper	When combined with primary bonds, it triggers the adherence reaction at lower temperatures.
MnO_2	Manganese dioxide	Produces brown-coloured frits, intensifies dark colours and acts as an oxidant and as a weak bonding agent.
Sb_2O_3	Antimonite	Produces a high degree of opacity and improves resistance to acids.
TiO_2	Rutile, Anatase, Brookite	The epitome of opacifiers, it increases whiteness, brilliance and resistance to acids and heat.
BaO	Baryte Whiterite Calcite	Alkaline-earthy components that integrate anti- acid enamels, increasing their resistance, their smelting facility and their viscosity.
CaO MgO	Dolomite-Limestone Periclase	
P_2O_5	Apatite	Alters the opacity of the finish, improves colour stability and reduces chemical resistance.
F_2	Fluorite	Softens glass and influences the opacity.

2.5 Enamel - Metal Interface Relationship

Good adhesion between metal and enamel is the main purpose of enamel coating method. To achieve this adhesion, it is required to acquire a continuous electronic structure or a chemical bond between the two surfaces. The area in which the metal contacts the enamel relates continuously. An oxide-like transition layer occurs in the contact region [14].

The adhesion of the enameled material with the metal surface due to the oxidized components is different from the other coatings. The adhesion mechanism of enamel coating is examined in three parts as chemical, mechanical and diffusion theory.

2.5.1 Mechanical bond theory

Mechanical bond theory, the substrate is related to the surface area in contact with the enamel. The contact area increases in direct proportion to the surface roughness of the substrate.

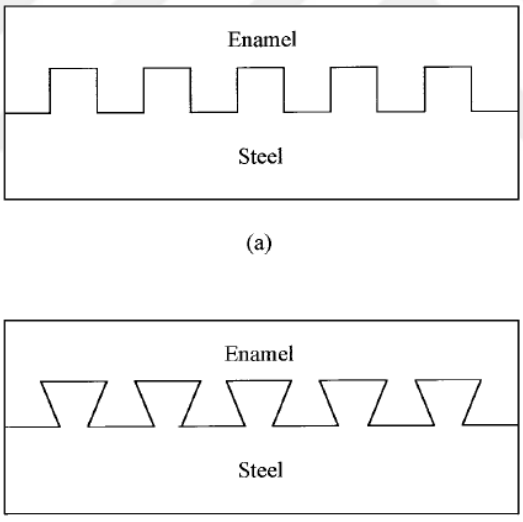


Figure 2. 5 Surface Roughness in Enamel Surface Adhesion Relationship [15]

The enamel base material contact area is increased by the chemical or mechanical roughening of the substrate surface prior to the coating process.

When the enamel coating reaches the firing temperature, the base material is oxidized and diffused into the enamel. During this event, it forms the iron projections that leave the surface; this is called the formation of the dendritic structure. Figure 2.5 shows the formation of the dendritic structure [15].

It is known that the dendritic structure formed in the base material enamel coating interface has a positive effect on the adhesion mechanism due to the increase in the holding area [16].

2.5.2 Chemical bond theory

Chemical reactions in the interface according to the chemical or oxide layer theory; It consists of dissolution, redox, precipitation and interface diffusion which form a transition layer between metal and enamel.

Metal reactions between the metal base material and the metal oxides in the enamel result in adhesion. These reactions which occur in the interface have different parameters that affect the attachment. Chemical reactions occur as the metal oxides in the base material and the enamel reach equilibrium in terms of chemical potential and activity [17].

According to the theory, the primer enamel melts during firing and dissolves the oxidized iron layer on the surface. The iron from the base material is oxidized at the firing temperature of the enamel to form the FeO compound. The cobalt oxide and nickel oxide compounds in the enamel are reduced by iron. Chemical theory is based on these reactions [18]

An iron oxide layer is required for good adherence of the enamel to the base material [19]. The oxide forms of iron are magnetite and hematite.

While magnetite improves adhesion, hematite acts to reduce adhesion. At the same time the thickness of this oxide layer at the interface is also important [20].

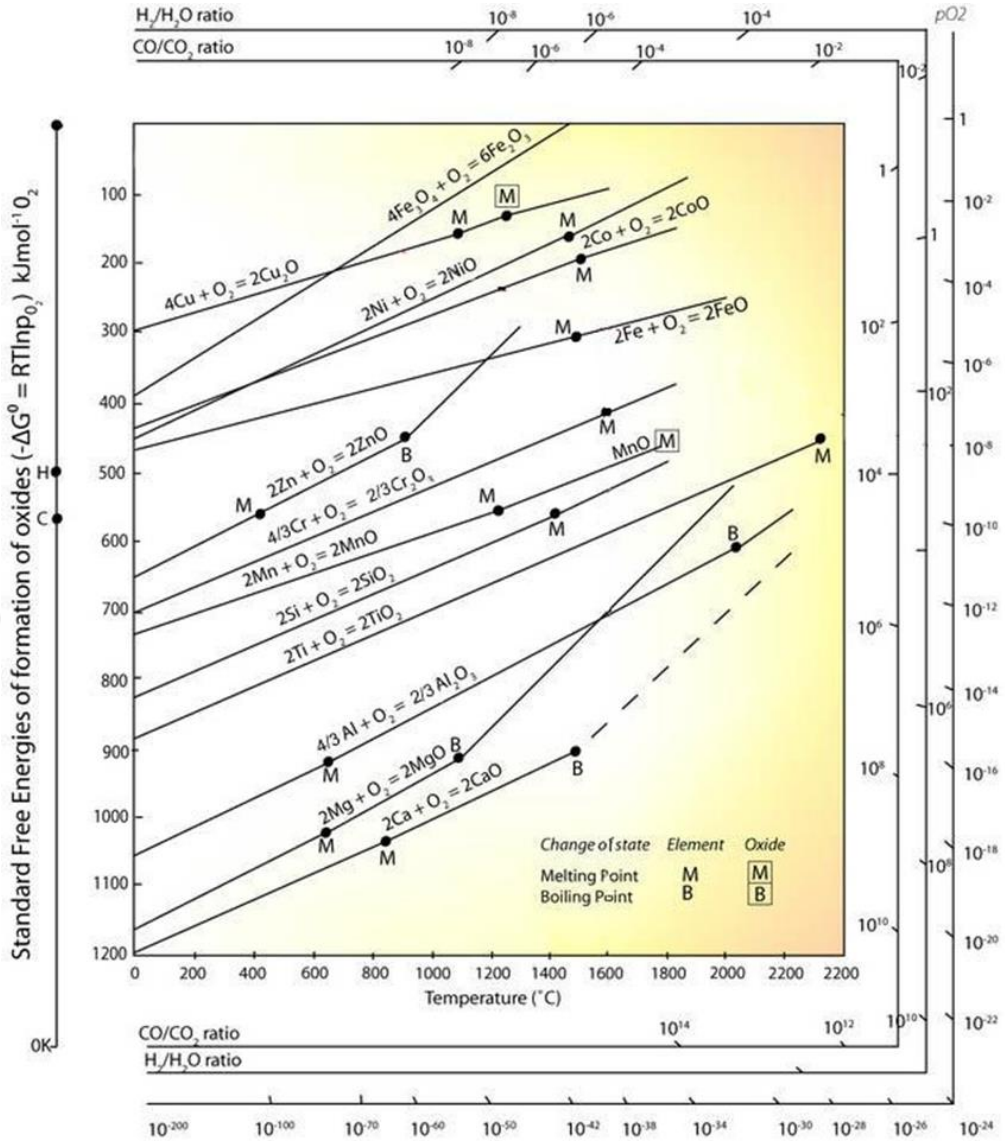


Figure 2. 6 Ellingham Diagram [13]

When the Ellingham diagram given in Figure 2.6 is examined, it is seen that the oxygen affinity of iron is higher than cobalt and nickel at the firing temperature of enamel. This supports the chemical theory of the adhesion mechanism. The iron element, which has a higher oxygen affinity for the temperature of the enamel, reduces the cobalt and metallic nickel to the redox reaction by cobalt oxide and nickel oxide [13]. The reason for the active role of cobalt and nickel in the adhesion mechanism Ellingham diagram the following (2.1) and (2.2) reactions in the base material during the firing of the enamel reaction. Iron forms the Fe^{2+} by passing to the oxidic form.

$$Fe_3O_4 \rightarrow Fe^{2+} + 2\,Fe^{3+} + 4O^{2-} \qquad (2.1)$$

$$Fe^{3+} + Fe \rightarrow 3\,Fe^{2+} \qquad (2.2)$$

The reaction of metallic iron in the base material with cobalt oxide and nickel oxide in metallic cobalt and iron is shown by reactions as (2.3) and (2.4) follows [19].

$$Fe + CoO \rightarrow FeO + Co \qquad \Delta G = -36893\ J \qquad (2.3)$$

$$Fe + NiO \rightarrow FeO + Ni \qquad \Delta G = -52988\ J \qquad (2.4)$$

One of the oldest theories of adhesion is Dietzel's theory. According to this theory, cobalt oxide and nickel oxide element are components that adhere to the enamel substrate. In order to explain this phenomenon, it has been observed that it has been baked with an oxide-free enamel coating and no adhesion. It has been observed that the increase in firing time increases with the burning enamel. However, it has been observed that the base material has become slag and has a negative effect on the adhesion. As a result of this study, it was seen that one of the parameters affecting the adhesion mechanism was the ratio of cobalt oxide and nickel oxide in the enamel composition [13].

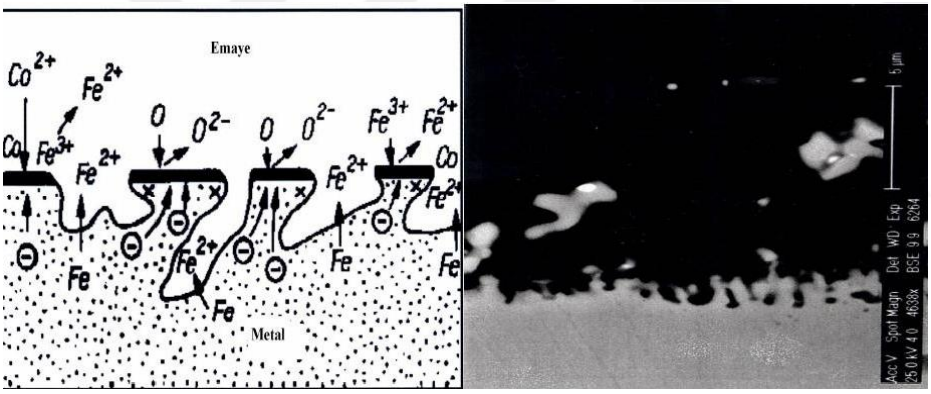


Figure 2. 7(A) Schematic View of The Interface Between Enamel Coating and Steel (B) SEM Image [21]

The parameters affecting the adherence of the enamel base material are listed as firing time, firing temperature and enamel composition.

2.5.3 Diffusion theory

In the interface studies between enamel coating and base material; It is concluded that the diffusion process contributes to the adhesion mechanism of the diffusion process from the base material to the enamel [13]. Figure 2.8 shows the iron element which diffuses into the enamel from the base material during firing.

In order to explain the diffusion theorem between enamel base material, linear analysis of iron and silicon element was performed in the interface studies. The iron concentration, which is high in the base material, decreases as it approaches enamel. The silicon element, which has a high concentration in enamel, is present at decreasing concentrations in the interface.

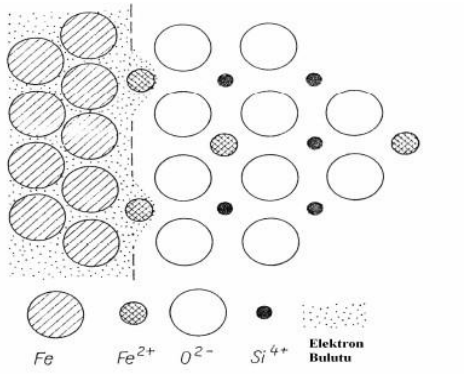


Figure 2. 8 Schematic Representation of The Diffusion Event in Metal Enamel Coating Interface [22]

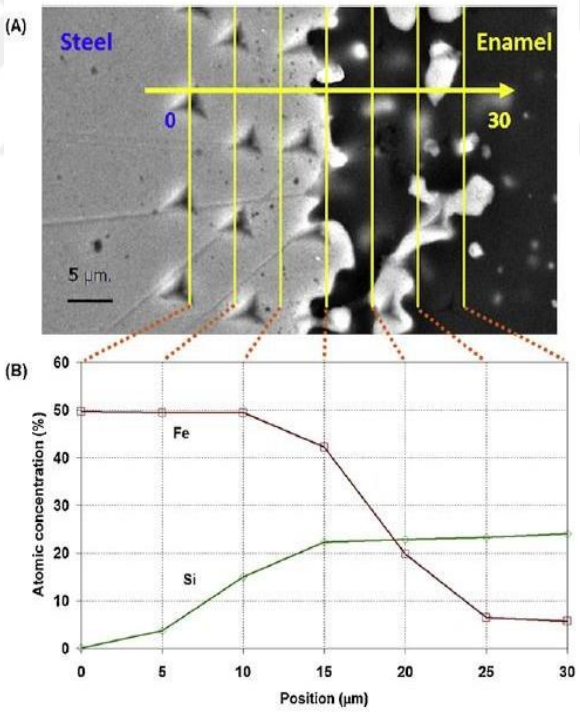


Figure 2. 9 SEM Image of The Element Diffusion on The Metal Enamel Interface [22]

3
Enamel Properties

3.1 Physical and Chemical Properties of Enamel

The mechanical and physical properties of the porcelain enamel are contributed to the metal substrate and the design of the part to be coated. Nevertheless, glass-like properties of porcelain enamel are effective in glass. Regardless of its thickness, porcelain enamels contribute to the strength of the metal substrate and also provide exceptional abrasion resistance [23].

3.1.1 Hardness

The hardness of porcelain enamels varies from 3.5 to 7 on the Mohr's mineral hardness scale due to the different enamel composition. The hardness of enameled steel surfaces falls down the range of 4 to 5.5. It refers to organic mercury with a hardness of 2-3. As a rough approach, the enamel applied to the plate with the plate glass has the same hardness. In short, the hardness of the enamel cannot be higher than the steel surface. Pen hardness scratch tests are commonly used to estimate organic varnishes on porcelain enamel surfaces. Values between 149 and 560 on the Knoop scale are comparable. The Sward rocker rating is the same as the plate glass and is 100. The surface hardness of the enamel is important for the durability quality required for a wide range of durable products [24].

3.1.2 Abrasion

Porcelain enamel coatings have excellent abrasion resistance and are even more resistant to abrasion than organic coating in different formulations. Porcelain enamels, which provide better wear and abrasion resistance than metals, are important in many industrial areas. For example; Bunker and silo discharge chutes, coal troughs, water-lubricated bearings, screw conveyors and blackboards are important areas where the resistance to abrasion is important and must be considered in terms of health. Sinks,

toilets, bathtubs and tops are the areas where human usage is intense and as important as the industry [23].

3.1.3 Adherence

Drop weight tests [9] and hydraulic deformation tests include adhesion of porcelain enamels. For heavy-scale enameled panels, a hydraulic deformation test, a drop test for open-quality metals (18-22 ga) is used. An impact energy of 0.9 kg.cm (80 inch) with a 0.27 kg (0.50 inch) hemispheric insert and a 1.9 cm (0.75 inch) diameter non-plate mold is used in the fall-weight test. Evaluating the construction with a visual grading ranging from 1 (excellent adhesion, almost no visual change on the surface) to 5 (a weak bond in which there is no visual link between metal and enamel), which typically evaluates the amount of glass retained in the impact area. it is made [9].

3.1.4 Impact resistance

Falling weight tests such as a free-falling ball or a pendulum that hits a hard-holding sample are used to measure the impact strength of vitreous enamels. In such tests, this test can be repeated over and over until there is a noticeable failure. Factors affecting impact strength of porcelain enamels:

• The low modulus of elasticity of the metal contributes to higher impact resistance;
• The curvature of the material to be applied enamel increases the impact resistance.
• As the thickness of enamel application increases with metal, the impact resistance increases.
• For example, excessive bubble content, large crystal inclusions and other discontinuities, usually changes in the physical structure of the enamel, contribute to low impact resistance.

The weak bond between the enamel and the metal reduces the impact resistance [25].

3.1.5 Thickness

0.25 mm or less thick stainless steel or aluminum surface, cast iron or 0.5 mm or more thickness on the heavy steel or enamel plate is appropriate. The optimum thickness, enamel thickness of the enamel should be determined according to the properties of the

final product. Generally, thinner porcelain enamel coatings are thinner and more resistant to breakage. In addition to having better electrical properties in the parts where the enamel thickness between metal and enamel is high, they can also withstand long-term chemical attacks [23].

For the steel applications, there are different application thicknesses such as 0.2 mm thick porcelain enamel primer coat and top coat. However, a single-ply porcelain enamel of 0.3 to 0.5 mm can be applied directly onto the steel with the modified pretreatment of the steel substrates and the decarburized steel quality. Multiple coating layers, each having a thickness of 0.2 to 1.0 mm, may be applied. Mixing multiple layers can be applied to form a single heavy layer. Normally, a white coating coat (titanium opacified) should be at least 0.3 mm thick to provide enough opacity to hide light scratches on the metal. Some colors are obtained together with thick applications [25].

3.1.6 Acid resistance

The acid resistance of porcelain enamels can vary widely depending on composition and, to some extent, the processing used. Special formulations can provide porcelain enamels with excellent corrosion protection against aqueous solutions of alkalis, salts and most acids except hydrofluoric. Even such corrosive media as molten metals and vapor phases present in hot gases have been confined within porcelain enameled structures. The degree of attack by acid solution on porcelain enamels appears to depend less on the type of solution than on its pH.

3.1.7 Corrosion resistance

Porcelain enamels which have excellent corrosion resistance in various corrosive environments are more useful and healthier than many coating products. The long-term decomposition test, porcelain enamels, resistance to various atmospheric conditions, including exposure to corrosive industrial atmospheres, gases, smoke, sea spray and sea cost has been verified by the National Standards Bureau and Porcelain Enamel Institute. The degree to which the coating retains its original glass and color is generally proportional to the air capability of the porcelain enamel. In general, acid-resistant

enamels are more durable than those without. Porcelain enamel coated items are still known to be in good condition after 50 years [2]

3.2 Thermal Properties

3.2.1 Thermal shock resistance

Inverse proportionality with the thickness of enamel the thermal shock resistance of a porcelain enamel is changing. Thermal shock is caused by rapid cooling on the enamel surface. The bond between the metal and the enamel is formed by the cracking of the bubbles on the surface, and generally the surface is seen as throwing. The thickness and thermal expansion coefficient of porcelain enamel are important. Thermal shock resistance is affected by the design and thickness of the part. Flexing the metal from its local parts with temperature causes stresses or stretching on the surface of the coating. This varies in proportion to the expansion coefficient. The coefficient of expansion of iron is expressed as 300. Enamel expansion coefficient is expected to be close to 300 in applications on iron metal. Therefore, the resistance of the coatings to thermal shock occurs with any increase in the strength or stiffness of a part. Most porcelain enamel applied in conventional thickness can be expected to receive sudden temperature drops between 400^{o}C and 149^{o}C without being damaged. Thinner coatings have a relatively high thermal shock resistance [23].

3.2.2 Thermal expansion

Thermal expansion coefficient measurements are made on the dilatometry device consisting of a fused quartz push rod in a tube of the same material. The preparation of a sample of the frit is achieved by weighing, sizing and molding, tempering and baking the powder sample. The pipe containing the frit bar sample is heated to a predetermined temperature in a small furnace with a programmed temperature rise or is automatically switched off when the dilatometer softening point is reached. Appropriate reference standards are used to calibrate the test unit [26]

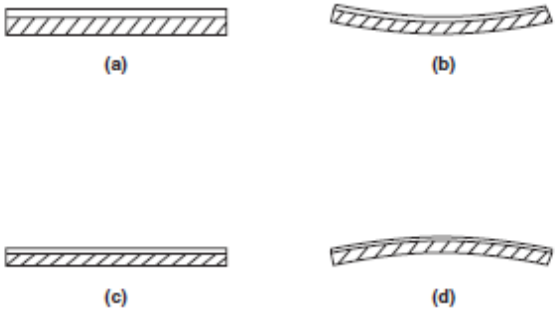


Figure 3. 1 Cooling Cycles of the Enamel Layer with Steel [26]

Residual-stress analysis must consider the cooling rates, the viscosity characteristics of the glass, the relative thickness of the metal and coating, and the modulus of elasticity of the coating and metal throughout the temperature range in which stress is developed. At high temperatures, glass behaves as a viscous material, exhibiting viscous–elastic and then primarily elastic properties as the temperature decreases [1].

3.2.3 Fluidity and fusibility

The fusibility and fluidity of enamels are essentially controlled by the compositions. However, the compositions of enamels are so complicated that any method for calculating the fluidity or fusibility is empirical. Many attempts have been made to discover satisfactory for calculating the fusibilities of glasses. Some of the proposed formulae have been applied to enamels, but the results are of limited value, and are applicable only to glasses lying within a narrow range of composition. Since enamels are glassed and do not have definite melting temperature but go through a slow transformation from a solid to a liquid over a broad temperature range, softening determinations under controlled rates and conditions of heating are used to study their fusion properties scraping [2].

3.3 Optical Properties

3.3.1 Appearance, color and gloss

Porcelain enamel allows the designer great variety about color, texture, and aesthetic appeal. The enamels exhibit exceptional color stability whether used in domestic interiors or architectural exteriors. Colors should be grouped according to the type and the usage of enamel. Categories are;

1. Ground coats, which can generally be used by themselves as a finish coat or a base coat;
2. Cover coats that are self-opacified;
3. Clear and semi-opaque enamels used for developing a wide range of colors.

Transition-metal oxides used principally to develop a bond between the glass and the substrate metal also produce specific colors. Those range in shades of grays from blue to yellow and red to green. Combinations of each are also possible. Cobalt oxide is the principal colorant for blue, nickel oxide, and iron oxide, Fe_2O_3, for green, manganese dioxide for red, and nickel oxide with other oxides for yellow [1].

Textures in enamels are developed using semi crystalline glasses or by the addition of refractory materials such as quartz, alumina, zirconia and zircon, feldspar, various clays, and titanium. More refractory glasses are also added to impart a lower gloss and a texture. Combinations of glasses such a s ground coats and small amounts of self-opacifying cover coat are used to produce speckled finishes such as those found in some oven interiors and cookware utensils. A typical mill batch of colored enamels contains 100 parts by weight frit (clear alkali borosilicate-type glass); 4 parts clay for producing a stable suspension; 1/4-part bentonite for supporting suspension; part sodium nitrite (to disperse flocs); 3 parts oxide pigment colorants; and 45 parts water [27].

Gloss is the shine or luster of porcelain enamel. A wide range of gloss I usually desirable for appliances and plumbing ware surfaces. Lower gloss is often specified for architectural and decorative applications where less reflection of distant images is sought. Gloss can be scientifically scaled in tests such as the 45-degree specular gloss test. On this scale, a polished black porcelain enamel has a value of 55. Most glossy porcelain enamels on steel will be in the 50–60 range [27].

Colored enamels are produced by tinting the titanium enamels during the smelting operation through the addition of colorant oxides. Control of enamel color is most popularly done using computer-controlled color measuring systems consisting of spectrophotometric detectors (380–720 nm) and hardware to measure, integrate, evaluate, report, and store the color data. The most common systems in use are the Commission Internationale de l'Eclairage (CIE) L*a*b* and Rd,a,b color scales and various illuminates [28].

3.4 Process of Enameling

The application of the coating process to the metal interface of the enamel consists of the following steps:

- Preparation of coated enamel
- Selection of suitable metal surface
- Metal surface cleaning
- Application of coating material
- Drying of enamel applied to metal surface if wet enamel
- Firing of coated material.

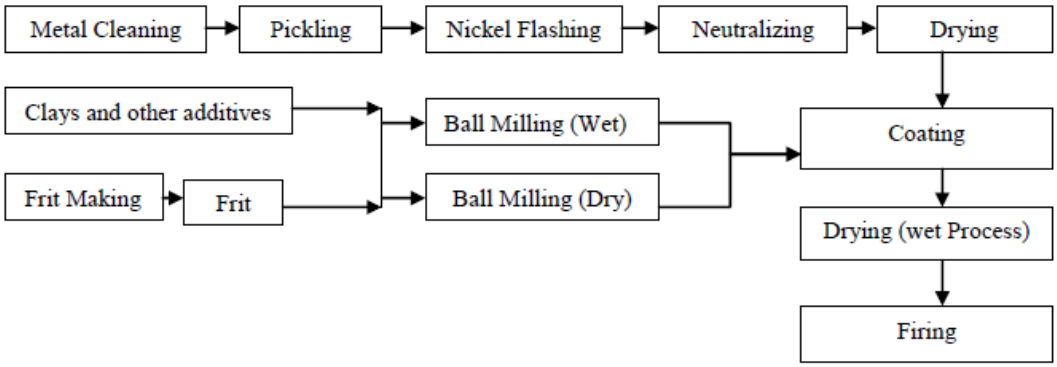


Figure 3. 2 Flow Diagram of Enamel Coating Process on Metallic Substrate [12]

3.4.1 Making glazes and smelting

Melting is defined as the melting of raw materials entering the enamel composition until a structure like glass structure is obtained. In order to obtain a uniform glass structure, it is necessary to accurately weigh and mix predetermined mineral and chemical raw materials, and to determine the appropriate heating rates and heat distribution in the melting unit. The melt processing is carried out in batches or continuously in the melt at temperatures between 1150°C and 1350°C, followed by quenching. Molten glass cooled with water or cylinder to facilitate milling [29].

The frit-making process involves all the technology ranging from proper selection of raw materials through mixing and smelting to uniform production of frit. Box smelters, predating continuous smelters, are used for small quantity production. Electric smelting of porcelain enamel glasses has been carried out in the United States and abroad. The most prevalent method of making porcelain enamel glass is in continuous smelters. Continuous

smelters may produce from 700 to 1200 kilograms of frit per hour. In a continuous furnace the thoroughly mixed raw batch is fed in at one end and molten glass flows out at the other end. Decomposition, gas evolution, reaction, and dissolution occur during smelting. Modern smelters, which are fired by natural gas and often pure oxygen, are equipped with pollution control equipment on the smelter exhaust system [28].

After the molten glass has become a homogeneous liquid, it is poured in a thin stream into water or between closely spaced, water-cooled rotating metal rollers. This quenched glass, termed frit, is a friable material easily reduced to small-sized particles by a ball-milling operation. Ball-milling the glass frit into small-sized particles can be carried out whether the frit is to be used wet or dry [29].

3.4.2 Grinding

Porcelain or alumina balls varying in size from 1.5 to 5 cm. mill size, speed and charge and ball size and charge, determination of required grinding time are the important parameters in order to achieve optimum size distribution. Milled enamels are ground milled with a fineness of 95% of solids less than 74 mm (<20 mesh). Cover coat enamels are more easily ground and less time is spent. Powder enamel is used in dry iron cast iron enamel and electrostatic application on steel sheet. Dry powders may be added to different proportions of chemicals (e.g. clay, quartz or salts) for the preparation of slurries and slippages used in wet process application techniques [22].

3.4.3 Metals for enameling

Steel sheets are then purchased in pre-cut sheets or rolls for stamping and stamping. Steel sheets to be used in enamel coating are chemically different formulated in order to be suitable for manufacturing and porcelain enameling operations. ASTM A424 coded sheet steel sheet. In order to avoid carbon output during enamel firing, the amount of carbon is continuously controlled.

Carbon content ranging from 2.8 to 3.7% by weight is used for cast iron; the carbon content of normal steels is between 3.25 and 3.6%. Carbon is generally found in two forms, namely graphite carbon and combined carbon. Cast iron contains different elements in different proportions according to the steels. Cast iron used for enamel and

known as gray cast iron is one of the most widely used. The surface of the cast iron must be thoroughly cleaned and sand blasting should be performed if possible [2].

3.4.4 Metal preparation

Steel sheets are formed by stamping, bending and cutting. Many of the welds are expected to be properly welded so that most of the welds can be enameled. Cast iron parts are formed by cast iron casting methods; However, the surface is lubricated to prevent contamination of the surface. Surface pollution causes acne and puffiness on the enamel surface. Extrusions and castings become aluminum metal sheets [30].

Since the metal surface is not thoroughly cleaned and the area applied to the emulsion is dirty, the time from enamel to curing is important. Touching the enameled surface by hand can even disrupt the surface. Cast iron, thick steel parts and aluminum castings must be blasted, otherwise they may cause unwanted defects on the surface. The thickness of enamel application prevents deformation caused by metal loss. Blasting is the most commonly used surface cleaner. In the most satisfactory and most economical way, the materials produced from the thin sheet metal are removed with chemical methods that require acid and soap solutions to remove grease and dirt and acid solutions to remove oxidized metals.

Continuous cleaning and pickling equipment and industrial products are cleaned. The second is used for smaller sized surfaces. Manufactured sheet steel products are supported on movable shelves or hangers passing through the first cleaning stage. For clean systems only, this is what you need [30].

Cast iron is ready to be enameled by sand blasting process. In order to obtain good enamel surface quality, the surface where the cast iron comes from the foundry must have a thin hard skin. Spraying also smooths the surface, edges and gates. Spraying is used to obtain a smoother surface on the metal surface of abrasive grains.

3.4.5 Application

Ground coat enamels cover coat provides continuous and good adhesion of enamel to the lower metal. In addition to this adherence, the cover coat enamels protect from the effect

of the lower plate or the casting. Ground coat enamels can be brown, black, dark blue and partly green. The most important feature of the primer enamels is adhesion. The adhesion mechanism of the primer enamels to the sheet has not been fully proven chemically. However, Dietzel's has been the most widely accepted theory [31].

Cover coat enamels are coatings that provide aesthetic appearance and also provide chemical and mechanical resistances. cover coat enamels are divided into various groups according to their intended use. Most commonly used cover coat enamels are Opaque Titan White enamels. In these enamels, there are no enamels which are used as white, without any pigment.

For enamel enamel applications, the enamel must be prepared using slip grinding technology. Alternatively, the enamel supplier grinds the enamel dry and makes the user ready for use only by mixing with water. The wet milling system is an economical method for preparing large quantities of enamel, but it is more advantageous to use RTU to prepare special applications and small amounts of enamel [31].

Frit, water, set-up salts, quartz and other additives are milled in mills and prepared to slip into the appropriate thickness (according to customer requirements). When the mill rotates around its axis, the balls fall on each other and grind the enamel.

In mills, knitting stones and balls should be of the same material. The density and hardness of each material are different. Therefore, in the case of knitting stones and balls of different materials, stones and balls will abrade each other more easily.

Spraying Technique; It has a very wide usage area. It can also be used for coating flat and perforated parts. In the enamel industry, it is a method used for coating flat parts such as side panels of the stove, covering the inner and outer surfaces of the kitchenware such as pots and pans, coating of architectural panels, coating of kitchen ovens such as trays, doors, hulls, grills, hobs and burners [11].

Enamel coating with dipping method is a preferred method for coating complex parts and rounded parts. This method is usually used for coating of stove pipes, in the primer

coating of kitchenware such as pot pans, in some kitchen kiln producing factories, in coating of parts such as inner body and tray, door, in the coating of small parts.

Electrostatic spraying has become a worldwide recognized technology. The effective use of dust enamel and the reduction of total costs have made great progress over the past 40 years. Electrostatic powder enameling is a new process. The first industrial line in France was established in 1976 [2].

The enamel powder is fluidized in a fluid bed powder chamber by adding compressed air from a porous plate. This fluidization gives the rheological properties of the dust of a fluid. In industrial, Enamel will be connected to parts on the conveyor and passes through the spray booth. In the spray booth, the gun is fixed or transported by a robot and enamel powder from the main hopper is applied.

The non-collapsing powder falls directly onto the over-spraying tanks and the finest particles are absorbed from a filter in another. These two recycled powders are continuously transferred to the main hopper by means of venturi pumps: the principle of dust recycling. The main feed hopper is always the same and is arranged with dust. After this application, the parts are transferred to the firing conveyor [32].

3.4.6 Firing of enamels

Intermittent box type furnaces or continuous furnaces can be used for firing. The dryer and the furnace form one continuous unit or function as separate units in the continuous firing process. Most industrial furnaces are fiber-lined (low thermal mass), which lowers cost and downtime between firing schedules. In a continuous tunnel-type furnace, each piece progresses through the furnace on a conveyer supported on alloy firing racks designed to withstand the repeated thermal cycles. Very efficient U-type furnaces, in which the outgoing ware preheats the incoming ware, have been built [33]. Gas-fired furnaces have alloy muffles to separate the combustion gases from the furnace atmosphere. Electrically fired furnaces have special alloy resistance-heating elements on the surface of the refractory lining. Gradual heating and cooling of the ware is more easily achieved using continuous firing than by using intermittent firing. In the latter process, a batch of ware is loaded on a large rack of special support tools and is introduced into the

box furnace. Enamels are fired to mature coatings in a matter of minutes. The firing time in the hot zone of a continuous furnace is about 3–6 minutes at 750–850^{o}C [33].

The upper layer of the enamel is usually used at similar temperatures, two coats of one-fire application. For two coats, it is expected that the ground coat will be less thick than the cover coat. It is also recommended that the cover coat enamel should be cooked at a temperature of at least 30 degrees more than the ground enamel.

The enamel firing temperature depends on the type of enamel to be coated, the type of metal and the thickness. While aluminum coatings are fired at 500 degrees Celsius, the high enameling temperature is approximately 830.

4
Lithium

4.1 General Information

Lithium is the metal with the lowest density and comes after hydrogen and helium in the periodic table. The atomic number is 3 and the atomic weight is 6.941. The name lithium comes from the name lithos, meaning stone in Greek. The reason for this name is the discovery of lithium in a mineral source, but the discovery of other important IA group elements, sodium and potassium, in plant sources [34].

The element lithium, the lightest metal in its elemental form, was discovered in 1817 by a Swedish geologist, Arfvedson, but was actually first isolated in 1855. The first commercial production was by Metallgesellschaft in Langelsheim, Germany about 1925 and soon thereafter by Maywood Chemical Company in New Jersey about 1927. Foote Mineral Company began commercial production in the late 1930s, Kerr-McGee and Lithium Corporation of America during World War II. The first significant use was for lithium hydroxide monohydrate for $C0_2$ absorption in submarines and for lithium-based lubricants beginning during World War II. Ceramic applications followed and then a major use between 1955 and 1960 by the U.S. Government and the Russian Government to produce hydrogen bombs. About the same time, in the late 1950s and beginning in the early 1960s, lithium bromide in the air-conditioning industry and normal-butyl lithium in the synthetic rubber industry. The history of the commercial development of lithium has been a fascinating unfolding of somewhat serendipitous events marked with somewhat erratic surges in new uses and demands for increased quantities. While the total commercial market for lithium products in all forms is still a small industry, the versatility of this unique element continues to stimulate man's creative interests and probably the most fascinating applications for lithium still lie in the future, rather than in the past [11].

4.2 Properties of Lithium

4.2.1 Chemical properties of lithium

Lithium (Li) is a member of the chemical group known as the alkali metals. It is the least reactive of this group. Its binary compounds are more stable than those of the other alkali metals. ICs" electron in the outer shell of a lithium atom is easily removed to form a positive ion. Removal of remaining electrons is difficult. lithium is exclusively monovalent and forms compounds with all anions, organic and inorganic [34].

In its crystalline form, pure lithium is silver white and soft. In a vacuum lithium starts to evaporate above 600^{o}C. Solid lithium at room temperature is not as dangerous as other alkali metals, since it does not burn spontaneously in water or air. Molten lithium is extremely reactive. It burns when it contacts moist skin. Its combustion products are irritating to the respiratory system. Lithium imparts a crimson color to a flame. When the metal burns strongly, the flame is dazzling white. Special handling is required because of lithium's corrosive properties [35].

Table 4. 1 Chemical Properties of Lithium [35]

Property	**Value**
Symbol	Li
Atomic Number	3
Atomic weight	6.941 a.m.u
Isotopes	Li-6, Li-7

4.2.2 Physical properties of lithium

Lithium metal is soft enough to be cut with a knife. When cut, it possesses a silvery-white color that quickly changes to gray as it oxidizes to lithium oxide. While it has one of the points among all metals (180°C), it has the highest melting and boiling points of the alkali metals [36].

Lithium has a very low density (0.534 g/cm^3) show in Table 5.2, comparable with pine wood. It is the least dense of all elements that are solids at room temperature; the next lightest solid element (potassium, at 0.862 g/cm^3) is more than 60% denser. Furthermore, apart from helium and hydrogen, it is less dense than any liquid element, being only two thirds as dense as liquid nitrogen (0.808 g/cm^3). Lithium can float on the lightest hydrocarbon oils and is one of only three metals that can float on water, the other two being sodium and potassium [37].

Table 4. 2 Physical Properties of Lithium [35]

Property	Value
Density	0,534 g/cm^3
Boiling points	1347^{o}C
Melting points	180.54^{o}C
Heat of Vaporization	4680 cal/g

4.3 Lithium Compounds

Lithium has been found in more than one hundred and fifty different minerals, only three of which occur in enough quantity and contain a high enough percentage of lithium for consideration amblygonite, spodumene, and lepidolite. all of which occur in pegmatite dikes.

The most important mineral for the industrial extraction of lithium is spodumene ($LiAlSi_2O_6$), which is found together contents of 4 to 7%) and in salt lakes. The largest known reserves are in Chile (largest known deposit), Australia, USA and Canada. The main producer countries are the USA (North Carolina), Chile, Australia, Russia, Zimbabwe, Brazil and China. The worldwide reserves including the lithium content in salt lakes is estimated to be 7.3x10^6 (as lithium), of which 60% is in salt lakes [38].

Lithium carbonate is industrially the most important lithium compound and the starting material for most of the other lithium salts. It is formed in the processing of

lithium minerals and brines. Enriched and calcined lithium ore (spodumene) is digested e.g. with concentrated sulfuric acid at is bigger than 250°C, leached with water and finally reacted with sodium carbonate. Lithium-containing brines are evaporated, the lithium chloride purified and converted with sodium carbonate into lithium carbonate [38].

Lithium carbonate is utilized as a starting material for the manufacture of all other lithium compounds and in large quantities in manufacture of by melt electrolysis. Lithium carbonate is also used as a flux in the glass, enamel and ceramic industries, which accounts for a further 25% of lithium consumption. Glasses with high lithium content (on the basis of lithium aluminosilicate) are as a result of their low thermal expansion coefficients virtually fireproof. In psychiatry high purity lithium carbonate is utilized for the treatment of manic-depressive complaints [39].

Lithium hydroxide: Lithium hydroxide is produced by the reaction of lithium carbonate with calcium hydroxide:

$$Li_2CO_3 + Ca(OH)_2 \rightarrow CaC0_3 + 2\ LiOH \qquad (4.1)$$

Lithium hydroxide monohydrate is industrially important in the manufacture of greases e.g. on the basis of lithium stearate. In the USA more than 60% of all greases are produced with the help of lithium soaps.

Lithium hydride: Lithium hydride is manufactured from metallic lithium and hydrogen. It is industrially important as a source of hydrogen and as a reducing agent in organic synthesis, particularly in the form of its derivatives: lithium aluminum hydride and lithium borohydride [39].

$$2Li + H_2 \rightarrow 2\ LiH \qquad (4.2)$$

4.4 Lithium Reserves and Distribution in the World

Lithium consumption for batteries has increased significantly in recent years because rechargeable lithium batteries are used extensively in the growing market for portable electronic devices and increasingly are used in electric tools, electric vehicles, and grid storage applications. Lithium minerals were used directly as ore concentrates in ceramics and glass applications.

Spot lithium carbonate prices in China ranged from $15,000 to $24,000 per ton throughout the year owing to tight supply of imported spodumene from Australia. The rest of the world experienced more modest price increases owing to supplies available from more diversified sources of lithium. For large fixed contracts, Industrial Minerals reported an annual average U.S. lithium carbonate price of $13,900 per metric ton in 2017, a 61% increase from that of 2016 [40].

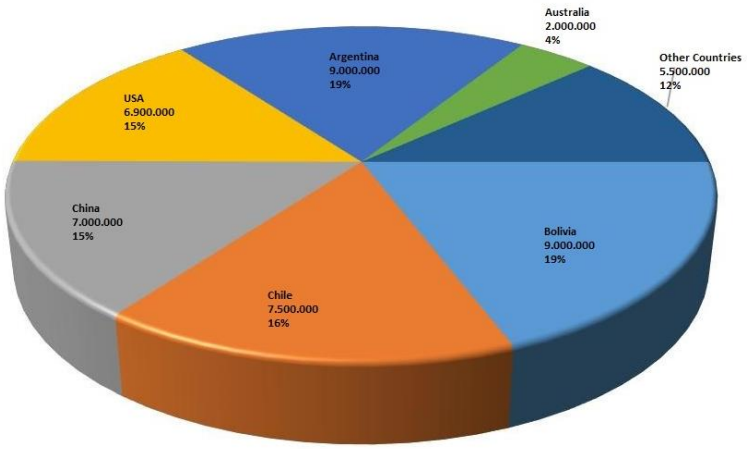


Figure 4. 1 Distribution of World Lithium Reserves by Country and Percentage [40]

Lithium supply security has become a top priority for technology companies in the United States and Asia. Strategic alliances and joint ventures among technology companies and exploration companies continued to be established to ensure a reliable, diversified supply of lithium for battery suppliers and vehicle manufacturers. Brine operations were under development in Argentina, Bolivia, Chile, China, and the United States; spodumene mining operations were under development in Australia, Austria, Canada, China, Czech, Finland, Mali, Portugal, and Spain; a jadeite mining operation was under development in Serbia; and lithium-clay mining operations were under development in Mexico and the United States. Additional exploration for lithium continued, with numerous claims having been leased or staked worldwide [40].

In our country, there is no lithium source with economic value. However, although the presence of lepidolide in pegmatite in the Yozgat-Sorgun region was known, significant results could not be obtained from the studies. In some of the lakes in our

country, lithium content did not exceed 40 ppm and 325 ppm lithium was detected in Tuz Lake. However, the magnesium content of Tuz Lake is 38.000 ppm. Again, various researches have shown lithium content in clays approaching 2000 ppm in clays. As a result of the studies carried out in the Kestelek, Emet, Kırka and Bigadic fields, the lithium content in the Bigadic and Kırka region was found to be higher than the Kestelek and Emet regions. In these areas, there was an inverse relationship between boron content and lithium content and it was determined that lithium content increased as the particle size decreased [41].

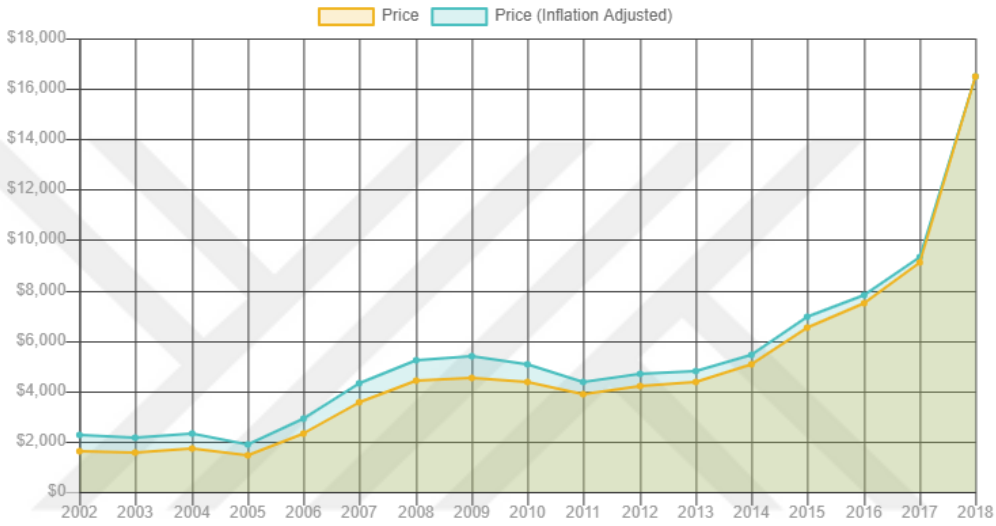


Figure 4. 2 The Historical Lithium Price Per Metric Ton [41]

Lithium Market; The main uses of lithium and its derivatives are; ceramic - glass, electronic - electrical, industrial greases, metallurgy (continuous casting), silicon, nano - welding, air filters, optics and rocket launchers. Chemical plants in China consume a large part of the world lithium concentrate.

It is projected that the lithium market will increase by 81% by 2020, to grow by 347 thousand tons of lithium carbonate equivalent (LCE), and that in the next decade, Li-ion battery-based electric vehicles will be the primary demand. Tesla Motors Inc. (Tesla) has produced less than 50,000 cars in 2015 and plans to increase the production of Model 3, which already has 400,000 pre-orders [34].

In 2014, Tesla, Nevada, has the capacity to process 25,000 tons of lithium hydroxide, while Gig factory continues to invest in the lithium plant, which is expected to be operational in 2017. For now, the cathode for Tesla's batteries are manufactured in

Japan. In September 2015, Tesla signed a discounted agreement with Pure Energy Minerals Ltd to supply lithium hydroxide from the Clayton Valley South project, approximately 418 km from Glue factory. Following this, lithium exploration activities in Nevada were accelerated [34].

Turkey in 2016 to 93.5 million lithium-containing products were imported. The 65 million-dollar portion of this area, which holds 69.5%, is lithium-ion electric accumulators. 12.8 million-dollar portion was imported as lithium carbonates which holds 12%. The kind of battery imports $ 13 million was realized.

5
Experimental

In this master's thesis, enamel coatings with a coating thickness of 120 $\pm$ 10 μm were formed on the surfaces of normal carbon steel sheets of EK04 with enamel coating methods (dipping) and dry (electrostatic powder spraying) enamel coating. All enamel coatings were prepared as a single primer coat for one-time firing.

With wet grinding, it is ensured that the slurry is of a certain fineness and in a certain flow. On the other hand, the steel plates to be enameled have been prepared by various surface preparation processes and made ready for enameling. The dipping method was used to apply the enamel layers to the steel. First enamel is applied directly on the steel. After the primer is immersed in the enamel, it is installed in the drying oven. If they are coated with the appropriate thickness, they are cooked in the baking oven.

Adhesion strengths of the enamel coatings, thermal shock resistances and their resistance to sulfuric acid corrosion were examined according to the coating thickness and coating method and compared according to the coating method for the same coating thickness. In the scope of the thesis study, enamel coating processes were performed and characterization studies of produced enamel coatings and citric acid corrosion resistance, adherence tests made at Gizem Seramik Frit Inc. SEM analyzes were performed in YTU Chemical Engineering laboratories.

5.1 Selection of the Frits/ Glazes

Different frit ratios ranging from 1-10 percent of Li_2O in Frit prescription were shown by Seger ratios. The novel compositions were labeled in a similar manner to that used for the standard frit composition; New combinations have been renamed (e.g. AME01-AME20). The content of frit used in wet and powder enamel coating is shown in Table 5.1 without giving chemical composition ratios. In addition, the Seger table is arranged by grouping oxides R_2O (Na_2O, K_2O), RO (CaO, MgO, ZnO),

R_2O_3 (B_2O_3, Al_2O_3, Fe_2O_3), RO_2 (ZrO_2, SiO_2). These frits were supplied from Gizem Frit ve Seramik A.Ş.

Table 5. 1 The Content of Frits

Name	Chemical Formula	Name	Chemical Formula
Silicon Dioxide	SiO_2	Zinc Oxide	ZnO
Boron Oxide	B_2O_3	Cobalt Oxide	CoO
Calcium Oxide	CaO	Nickel Oxide	NiO
Magnesium Oxide	MgO	Sodium Oxide	Na_2O
Titanium Oxide	TiO_2	Potassium Oxide	K_2O
Barium Oxide	BaO	Lithium Oxide	Li_2O
Copper Oxide	CuO	Alumina	Al_2O_3
Mangenese Oxide	MnO_2	Zirconium Oxide	ZrO_2
Antimony Trioxide	Sb_2O_3	Flor	F_2

5.2 Preparation of Steel Plate

EK04 low carbon steel plates used as backing material were supplied from Gizem Seramik Frit A.Ş. The dimensions of all steel plates are 150X120 mm. It is lubricated by the steel manufacturer to prevent corrosion of the steel plates. For this reason, the surface of the steel plates before the enamel coating was removed was removed from the oil by washing with detergent water before wet applications. Then the steel plates were dried so that there was no water layer. For powder applications, the oil layer on the steel plates was wiped off with alcohol.

5.3 Preparation of Enamel

5.3.1 Preparation of wet enamel

In order to obtain the enamel sludge required for application, the frits and additional additions should be grinding to the desired particle size after the mixing process.

The grinding process was carried out using a ball mill. The fryers, hand additions and water were weighed into the ball mill by weighing in the sensitive scale. In the ball mill, there are 30, 40, 50 mm alumina balls. The reason for the different sizes of these balls is to achieve a homogenous grain size after milling.

After mixing, grinding was started. The prepared mixture was milled in the ball mill approximately 13 minutes. At the end of the milling process, the enamel slurry was sieved, the grinding fineness was adjusted. The grain size was then checked using Bayer sieve. The enamel mud and Bayer sieve are shown in Figure 4.1.



Figure 5. 1 The Prepared Enamel Slurry and Bayer Sieve

At the end of the grinding, the paste was poured into 3600 mesh and the volume of the particles that could not be sieved was observed. If the ratio of those who pass through the sieve easily is less than 1/3600, then the particle size is suitable for application. If not, the milling process is repeated until the particle size is appropriate.

After the grinding process, the obtained wet primer paste was poured into pycnometer having a volume of 100 ml. The pycnometer was weighed and thus the density of the primer was determined.

The wet paste density of the primer should be in the range of 1.70-1.72 g/ml. It has been showed at Figure 5.2 This interval was determined for spray application of the sludge on the metal base. A little amount of water was added until the density of the primer enamel sludge reached the reference concentration. In order to obtain the correct values for each measurement, the pycnometer is clean and dry.

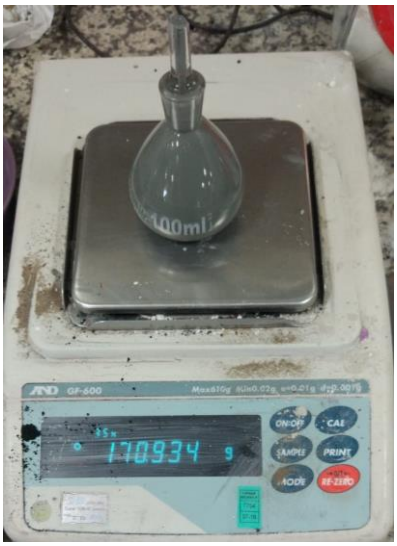


Figure 5. 2 The Enamel Suspension and Weighed to Measure The Density

5.3.2 Preparation of powder enamel

In order to obtain the enamel required for electrostatic application, the frits and DC1107 should be grind to the desired particle size after the mixing process.

In the dry process, no additional additives or water are added to the mixture of frit and silicone oil. Silicone oil increases the electrical resistance of enamel powders and prevents enamel dust from agglomerating.

The grinding process was carried out using a ball mill. The frits were weighed into the ball mill by weighing in the sensitive scale. In the ball mill, there are 30, 40, 50 mm alumina balls. The reason for the different sizes of these balls is to achieve a homogenous grain size after milling.

After mixing, grinding was started. The enamel was milled in the ball mill approximately 20 minutes. At the end of the milling process, the enamel was sieved by 80 mesh sieves.

5.4 Applications

5.4.1 Wet application

In the application of wet enamel on steel sheet, dipping method is used. In this method, the enamel suspension of 2-3 Bayer was poured into a rectangular

container is shown in Figure 5.3. Then the enamel on the sheet was enameled all over the same way. Care was taken to avoid bubbles or contamination on the surface during the coating sequence. Due to such errors, the coating process was repeated several times.



Figure 5. 3 The Device and The Process for Measuring Particle Size

The piece of enamel coated sheet was left in the oven at 180-degree for 1 min. The surface thickness of the drying plate was measured. The thickness of the enamel applied to the steel sheet was approximately 120-140 microns.

5.4.2 Powder application

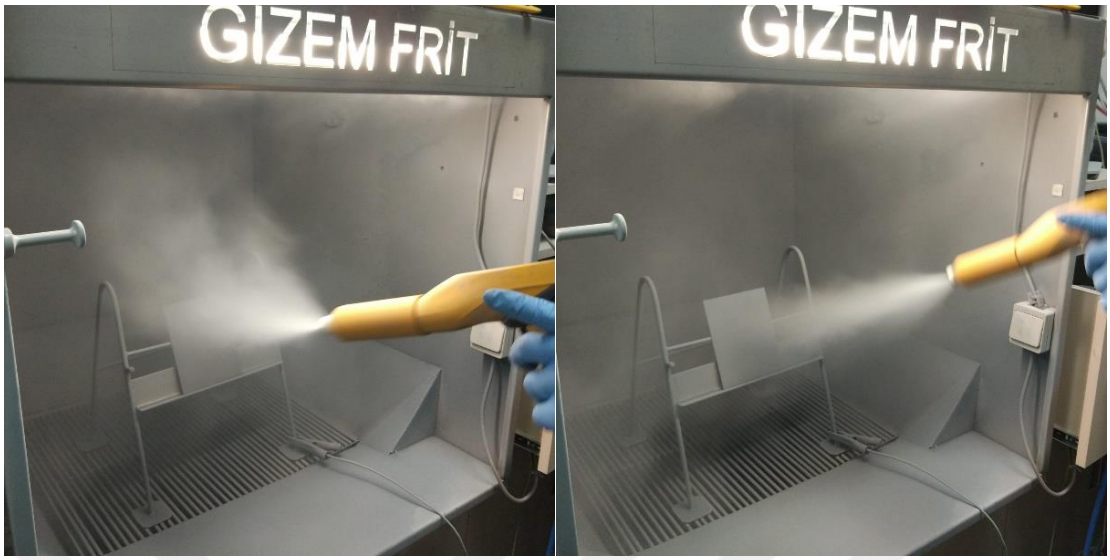


Figure 5. 4 The Application of Powder Enamel Coating

Electrostatic powder spraying method was used in the application of powder enamel to steel sheet. In this method, frits were milled by mixing silicone oil. After milling, enamel powders were electrostatically prepared as described in the previous section. Figure 5.4 shows enamel coating of steel plates by electrostatic powder spraying.

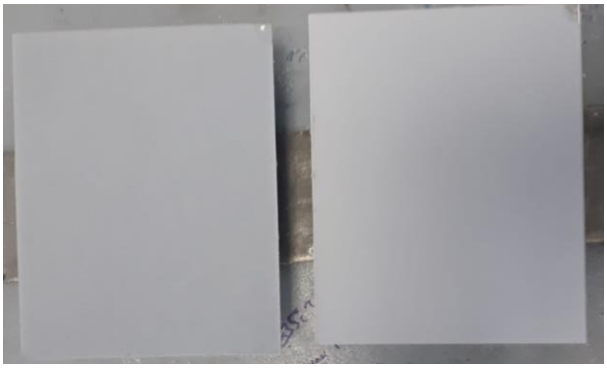


Figure 5. 5 The Preparation of Sheet Steel With Electrostatic Powder Enamel

The enamel powders which do not adhere to the enamel will be filtered by the help of a fan and deposited in the warehouse under the cabin. Thus, in the electrostatic powder spraying method, the over-sprayed enamel can be recovered.

5.5 Firing

The final treatment in the enamel coating process is the firing of the enamel coating. In both electrostatic powders spraying and dipping method, the firing process was carried out in an electric oven (Protherm) preheated at 820°C for 4 minutes. In order to prevent heat loss in the firing process, opening and closing of the oven must be carried out in series. Samples are allowed to cool after firing.

After the firing process, the coating thickness of the samples was measured by the coating thickness measuring device (elcometer). It is accepted that 120 $\pm$ 20 μm coating thickness is ready for the tests.

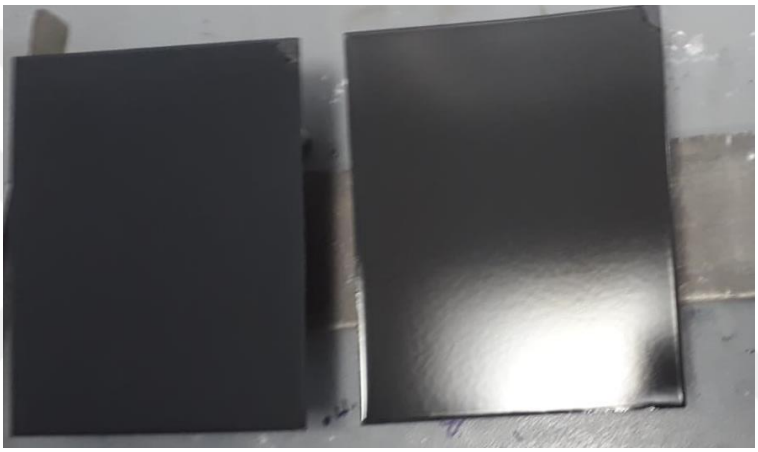


Figure 5. 6 Coated and Fired Plates

5.6 Characterization of the Samples

Properties such as surface roughness, microstructure, hardness, adhesion strength and thermal shock resistance of enamel coatings have been characterized.

5.6.1 Thickness measurement

Elcometer is used to measure the thickness of enamel coated on metal parts. The device used in thickness measurement is the Positest DFT thickness measuring device which is shown in Figure 5.7 in Gizem Frit and Seramik A.Ş. Using the elcometer; keep the electrometer upright and press the button that releases the indicator. The button is still pressed until the display remains still. The button is released after the indicator is stationary. The thickness of the enamel is read through the ruler.



Figure 5. 7 The Device of Thickness Measurement – Positest DFT

5.6.2 Color measurement

Color measurement analysis is aimed to investigate the color changes of enamel coatings in different composition. The device used in color measurement is the Minolta Spectrometer CM 700d color measuring device which is shown in Figure 5.8 in Gizem Frit and Seramik A.Ş.

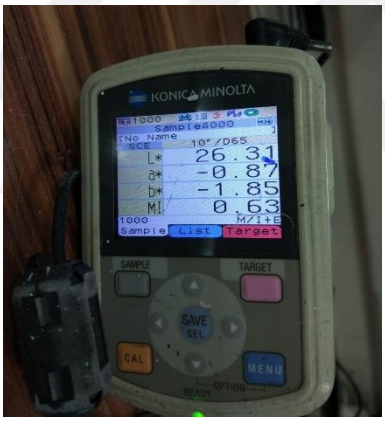


Figure 5. 8 The Device of Color Measurement – Minolta Spectrometer

L * a * b * method is the most widely used and most common color measurement methods. + a * direction is red, -a * direction is green, + b * direction is yellow and -b * direction is blue which are shown in Figure 5.9. The center is achromatic; When a * and b * values increase and move away from the center, the vividness of the color increases.

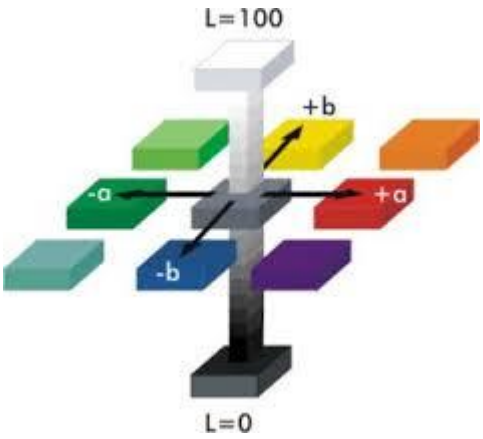


Figure 5. 9 CIE L * a * b * Color Plane

5.6.3 Citric acid test

The simplest acid test for enamels is the spot test (citric acid). It consists of placing a drop of acid solution on the ware for a given period of time, washing and observing the effect. This test is very sensitive, enamels being generally attacked in five minutes, if they are at all soluble in the solution. These bond tests are made in accordance with the ISO 28706-1:2008 standard.

Before starting the test, the surface to be tested was thoroughly cleaned with soap and dried. The citric acid and the part to be tested should be at a temperature of +/- 5 20°C. A 10% drop of 10% citric acid was added dropwise to cover the 25 mm diameter site by means of a pipette or dripper to the cleaned enamel surface. It was immediately closed with a clock glass. It was expected for 15 minutes and at the end of this period the clock glass was removed and the enamel surface was cleaned with water. Drying was done with filter paper. To understand and grade the specimen, using the procedure outlined in flowsheet in Figure 5.10.

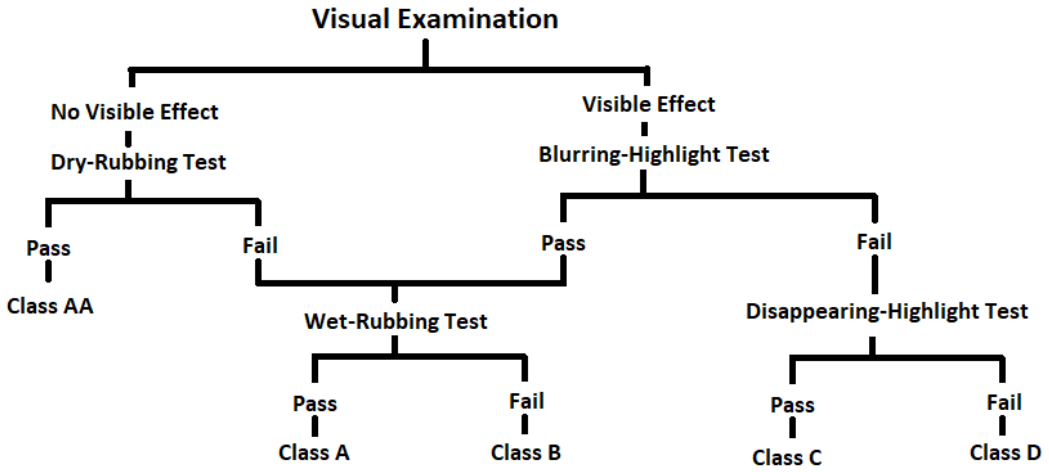


Figure 5. 10 Flow Sheet of Test Procedure For Classification of Treated Specimen [42]

a) Visual Examination: As it can be seen in the figure, visual inspection should be done first. View the specimen at various angles with respect from the protected area. During observation, hold the specimen no nearer to the light source.

b) Dry-Rubbing Test: Rub the marks with a clean, dry, soft cloth and inspect the specimen. If the marks are retained more tenaciously on the treated area than on the protected area, the specimen fails the test; otherwise, it passes.

c) Blurring-Highlight Test: Focus the eyes on the image of the light source, not on the enamel surface. Ignore any color difference in the enamel due to staining. If a definite blurring of the image is observed as it passes from the protected to treated area, the specimen fails the test; otherwise, it passes.

d) Wet-Rubbing Test: Do not use any soap, abrasive, or similar cleaning materials on this test. If the mark over the treated area, the specimen fails this test; otherwise, it passes.

e) Disappearing-Highlight Test: This test is similar in all respect to the blurring-highlight test, except that the criterion in this case is the complete disappearance of the light highlight in the treated area. If the highlight disappears in the treated area, specimen fails this test; otherwise, it passes.

Table 5. 2 Requirements for Respective Classes of Acid Resistance [42]

Classification	Requirements
Class AA	No visible stain, and pass dry-rubbing test
Class A	Pass blurring-highlight test, and pass wet-rubbing test
Class B	Pass blurring-highlight test, and fail wet-rubbing test
Class C	Fail blurring-highlight test, and pass disappearing-highlight test
Class D	Fail disappearing-highlight test

5.6.4 Bond – adherence test

The evaluation of the results is based upon inspection to determine whether the enamel breaks within the coating or is removed at the metal enamel surface. With sheet steel metal which can be deformed by impact, various adherence test has been devised to provide reproducible methods of testing. The deformation area is examined visually and a determination is made regarding the quality of the bonding of the glass to the metal.

There are two different types of adherence- bond test. One of these is those involving a minimum of deformation of the metal, such as the ASTM falling ball test. Second one is involving a definite deformation such as the falling weight test.

In this study, adherence-bond tests are made in accordance with the TS EN 10209 standard. By lowering the weight of 4.5 kg from a height of 20 cm to the spherical end, the spherical end strikes the surface of the enamel coated sample on the table and forms a circular track. Adhesion strength of the enamel is determined by comparing the circular trace formed on the enamel coating to the reference photographs in TS EN 10209 standard.



Figure 5. 11 The Device of Falling Weight Test

Table 5. 3 Adhesion Strength Levels of Enamel Coating [43]

Level	Description	View of Sample Surface
1	Excellent Adhesion	Circular trail fully enamels coated
2	Very Good Adhesion	Circular trail almost covered with enamel
3	Medium Adhesion	Circular allow large section enamel covered However some areas have been voided
4	Poor Adhesion	Circumference allowed enamel in the large section. But some regions are covered with enamel
5	Bad Adhesion	No circular trail on enamel

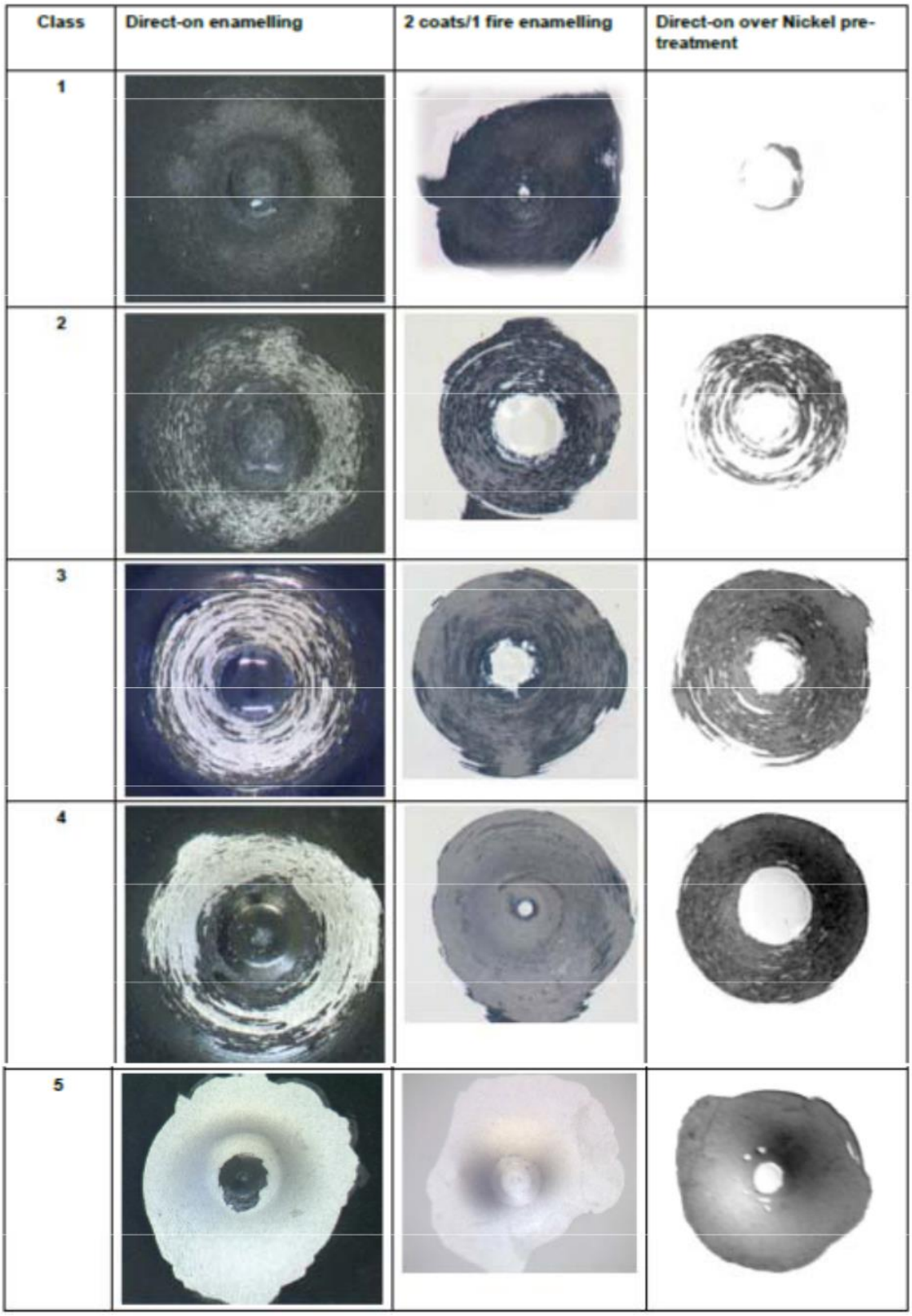


Figure 5. 12 The Adherence Test Results According to TS EN 10209

5.6.5 Scratch test

In order to examine the adhesion strength of the enamel coating, the coating was further scratched. Scratch test was performed by using Nanovea Scratch Tester. In this study, the enamel coated sample surface was drawn by applying a constant 50 N load with a length of 8 mm and a longitudinal length of 6 mm.

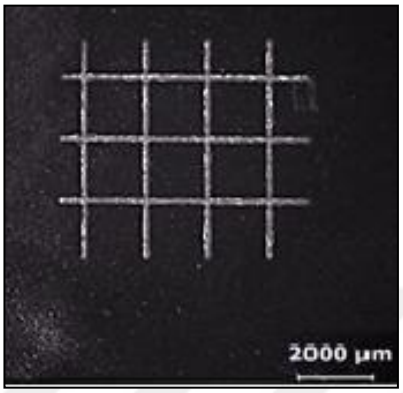


Figure 5. 13 Square Shaped Scratch Marks Created on Enamel Coating [29]

5.6.6 Gloss test



Figure 5. 14 The Device of Gloss Measurement

Gloss is the shine or luster of porcelain enamel-its specular reflectance. A wide range of glossiness is available in porcelain enamel. Gloss can be scientifically scaled in tests such as the 45-degree specular gloss test. On this scale, a polished black porcelain enamel has a value of about 55. Most glossy porcelain enamels on steel will be in the 50 to 60 span. The device used in gloss measurement is the Gloss Meter gloss measuring device which is shown in Figure 5.14 in Gizem Frit and Seramik A.Ş.

5.6.7 Easy-to-Clean test

The so called easy-to-clean (ETC) enamels are enamels optimized to achieve as low as possible levels of chemical bond between food and enamel surface and to allow for a drastically reduced stick effect. Empirical test with a multitude of foodstuff have been exercised to define a proper test for ETC-enamel. Unfortunately, the various foodstuff reacts very differently, that is why the selection is difficult and everyone has own foodstuff and own parameters [44].

The test is based on the fact that a mixture of 5 different type foods (ground beef, cheese, homogenized whole milk, ketchup, tomato sauce) is baked onto an enameled surface. This mixture can be removed more or less residue-free through defined cleaning processes.



Figure 5. 15 Five Different Type of Foods for Easy-To-Clean Test

The enameled plate of 120x150mm size is cleaned. The lithium nitrate test is performed before the ETC test. In lithium nitrate test 0.5 g of Lithium carbonate is placed on the plate and placed in a preheated oven for 15 minutes. At the end of the period, the lithium nitrate residue is removed from the enamel surface. This process is also included in the ETC test. Gizem Frit ve Seramik R & D department makes the ETC test in this way.

Sauce consisting of 5 different foods prepared for the ETC test is poured to a point of the plate. The plate is supplied to a preheated 320-degree Celsius oven and allowed to stand for 30 minutes. At the end of the period, the plate is removed from the oven and allowed to cool to room temperature. After cooling, the surface is cleaned with the help of a sponge with water. It is then cleaned with the help of a tissue.

Table 5. 4 Evaluation of The Cleaning Grade for ETC Test

Level	Description	View of Sample Surface
0	No Residue	%0
1	A small amount of Residue	%10
2	A few Residue	%25
3	An average amount of Residue	%50
4	A lot of Residue	%75
5	All Residue	%100

5.6.8 X-Ray fluorescence spectroscopy



Figure 5. 16 The XRF Device for Analyses

XRF is an analytical method to determine the chemical compositions of the frits, X-ray fluorescence (XRF) measurements were performed. The voltage and current values for Ca and K were 40 kV and 75 mA, respectively, while those for Cl, S, P, Si, Al, Mg, Na, F, and B were 30 kV and 100 mA. The materials can be in solid, liquid, powder, filtered or other form. XRF can also sometimes be used to determine the thickness and composition of layers and coatings. The elements that can be analyzed and their detection levels mainly depend on the spectrometer system used.

The elements present in the sample will emit fluorescent X-ray radiation with discrete energies (equivalent to colors in optical light) that are characteristic for these elements. A different energy is equivalent to a different color. By measuring the energies (determining the colors) of the radiation emitted by the sample it is possible to determine which elements are present. This step is called qualitative analysis. By measuring the intensities of the emitted energies (colors) it is possible to determine how much of each element is present in the sample. This step is called quantitative analysis. The wavelengths of X-rays are in the range from 0.01 to 10 nm, which corresponds to energies in the range from 0.125 to 125 KeV (Brouwer,2010).

5.6.9 Scanning electron microscopy- SEM

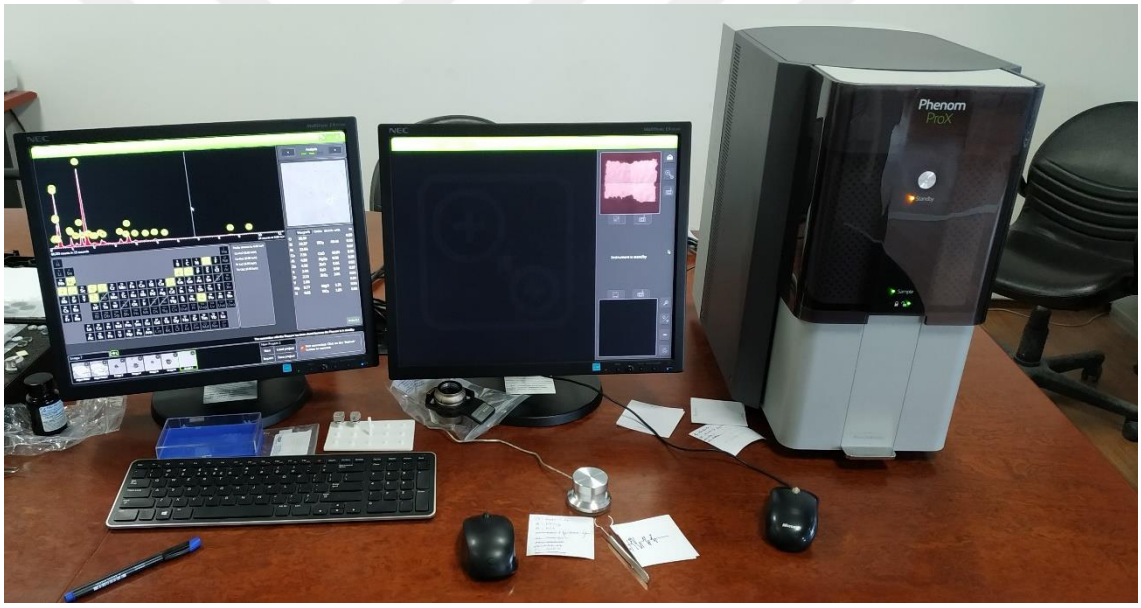


Figure 5. 17 The SEM Device for Analyses

Finally, the surface morphologies of the raw materials were determined in SEM device. The analyzes performed with the SEM Phenom Prox field-emission scanning electron microscope (SEM-EDS) Figure 4.12 were performed at 15 kV.

6
Results

In this study, the effect of frit containing different amounts of lithium on enamel surface was investigated in enamels used in health and kitchenware.

The frits produced were coated with two different coating methods according to different compositions, the same temperature values and frit type. Furthermore, coating performances are examined with various tests, such as acid resistance, adherence- bond and easy-to-clean test. The test results obtained in this part of the study were interpreted and the effects of applied methods on enamel were investigated. Afterwards, the tests carried out according to TSE standards have been interpreted in order to determine the chemical corrosion resistance of the enamels.

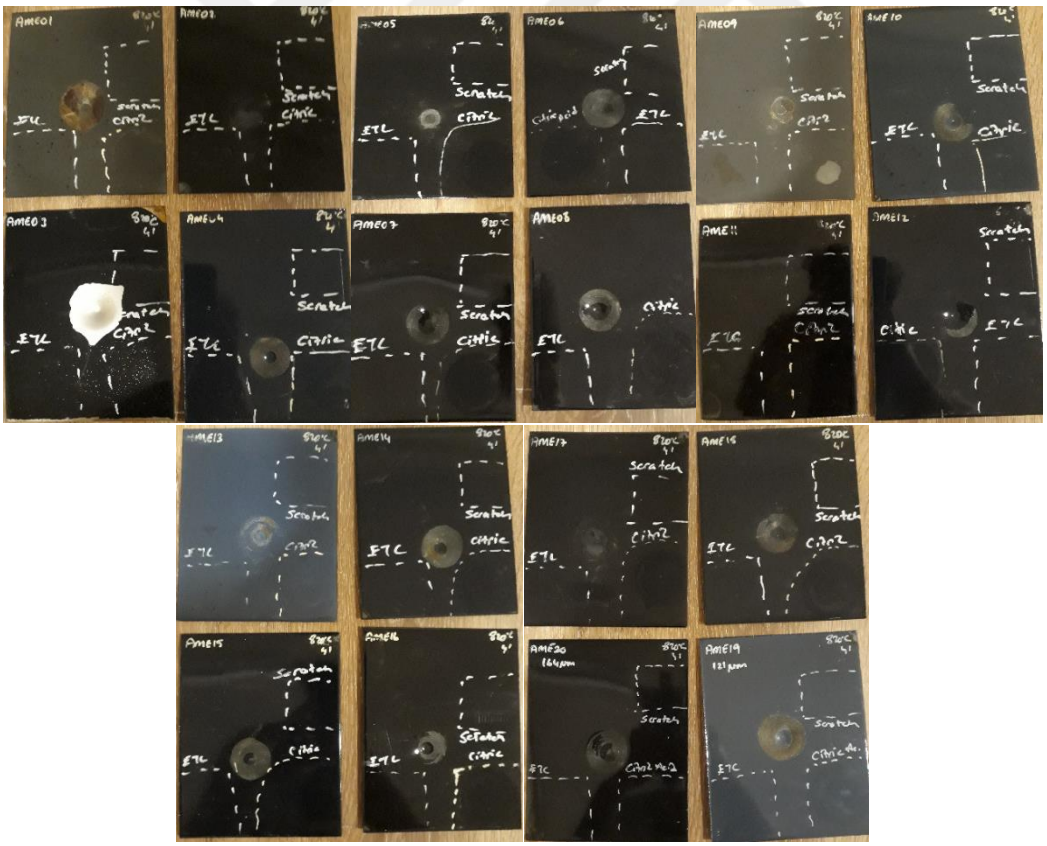


Figure 6. 1 Enamel coated and tested samples

6.1 Results of Thickness Measurement

Thickness measurements of the enamel mixtures were made with lithium oxide composition of different concentrations. The surface thickness of the enamel coating applied on the plate differs in every region. The main reason for this difference is; The thickness of the enamel coatings applied manually was not homogeneous. The thickness of the coating depends on the density of the enamel applied as a liquid.

The thickness measurements of the coatings are shown in Figure 6.2 The coating thickness varies between 110 and 150 microns.



Figure 6. 2 The images The thickness of measurements of the coatings

6.2 Results of Color Measurement

Color measurements of enamel samples given in Seger ratios in Table 6.5 are shown in Table 6.1.

Table 6. 1 The color values of the specimen

Specimen Name	L (D65)	a (D65)	b (D65)
AME01	24.97	-1.32	1.59
AME02	2.39	-0.1	0.59
AME03	7.5	-1.1	-2.26
AME04	16.83	-0.01	-8.41
AME05	7.48	0.2	-1.54
AME06	8.14	0.8	-4.41
AME07	3.03	0.25	-0.05
AME08	9.41	2.71	-4.49
AME09	27.15	-0.1	-1.93
AME10	20.67	-1.81	-7.69
AME11	4.19	0.63	0.13
AME12	8.75	1.22	-7.92
AME13	24.08	0.19	-14.42
AME14	8.67	2.14	-8.36
AME15	9.14	2.22	-7.77
AME16	4.95	1.56	-1.94
AME17	6.98	1.98	-4.59
AME18	13.29	1.67	-6.46
AME19	25.18	0.24	-15.62
AME20	4.14	0.41	0.23

6.3 Results of Citric Acid Corrosion Test

The results of the citric acid test are shown in the Table 6.2. If the classification is AA, there is no visible stain and that means it has perfect surface and chemical resistant. Specimen AME 03 is one of these. AME 01 – AME 11 are also passed the blurring-highlight test. These are also in acceptable limits. AME 02 is rarely acceptable. Because this specimen passed to first individual test but failed wet-rubbing test.

Table 6. 2 The results of the citric acid

Specimen	Classification		Specimen	Classification
AME 01	A		AME 11	A
AME 02	B		AME 12	A
AME 03	AA		AME 13	A
AME 04	A		AME 14	A
AME 05	B		AME 15	C
AME 06	B		AME 16	B
AME 07	A		AME 17	B
AME 08	B		AME 18	A
AME 09	B		AME 19	A
AME 10	A		AME 20	AA

6.4 The results of Bond-Adherence Test

After the impact test, the circular marks formed on the coating surface are shown in Figure 6.3. The circular marks formed on the surface of the enamel coating were compared with the reference photographs mentioned in Section 5.5.4 and the adhesion strength levels with details in the same section were determined. Adhesion strength levels of enamel coating are given in Table 6.3.

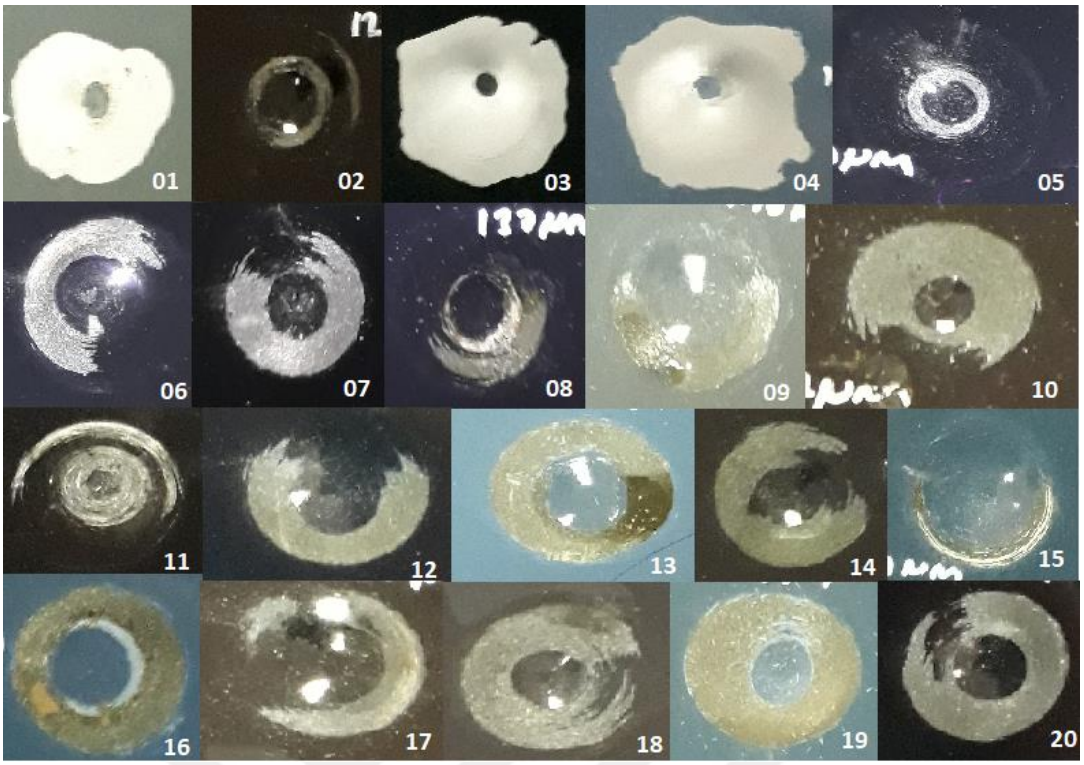


Figure 6. 3 The results of impact test

As a result of the impact tests, it is seen that the cohesion properties of the metal oxides which provide the adhesion in the enamel chemical composition decrease as the ratio of cobalt oxide and nickel oxide decreases. These results explain the chemical theorem of the enamel base material retention mechanism; The importance of cobalt oxide and nickel oxide components in the metal-interfaced with metal oxide is observed.

In the reactions with the metal interface in question, it can be thought that lithium contributes to the adhesion due to the flux property. Furthermore, the amount of R_2O was kept constant in order to reduce the amount of lithium and to avoid loss of structure. This means that; the compounds of the same group are useful, even if they do not fully replace lithium. Furthermore, due to its ability to promote lithium, the effect of lithium oxide on adhesion cannot be denied.

Table 6. 3 Adhesion strength levels of enamel coatings

Specimen	Classification		Specimen	Classification
AME01	5		AME11	2
AME02	1		AME12	2
AME03	5		AME13	2
AME04	5		AME14	2
AME05	2		AME15	3
AME06	3		AME16	2
AME07	2		AME17	1
AME08	2		AME18	2
AME09	2		AME19	2
AME10	2		AME20	2

6.5 The Results of Scratch Test

Scratch test results were evaluated with microstructure and steel / enamel interface results is shown in Figure 6.4.

As a result, a very small amount of damage was detected in the enamels covered with dry method in which the highest micron thickness of metallic structures with the highest gas content in the structure was applied. Previously, these tests have been done and have been reached the same results by Gungor et al. The scratch test on the enamel surface is not clearly visible. This is because the chemical structure of the enamel is like glass. No scratches can be seen due to glass construction.

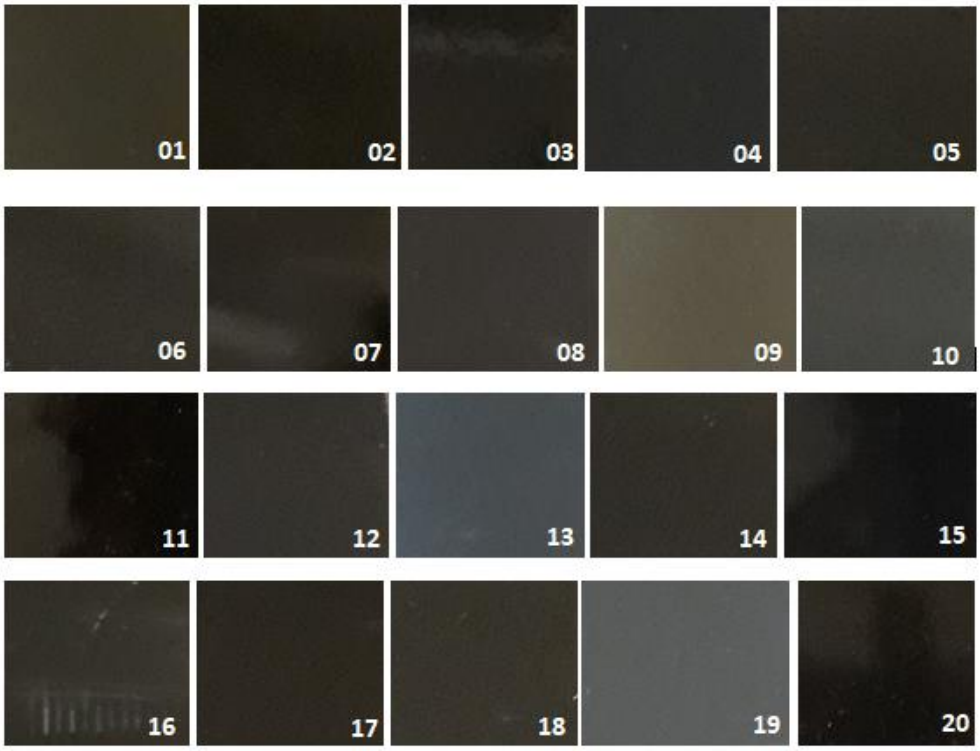


Figure 6. 4 The views of enamelled steel with scratch test

6.6 The Results of Gloss Test

The results of the measurements made with the gloss meter are as shown in the Table 6.4. As shown in the Table 6.4, the gloss values differ on all selected plates. The reason for this is the chemical formula of frit used in enamel making. The brightness of ZrO_2, ZnO elements is known to be increased. In addition, Li_2O influences brightness. It was determined that the brightness of samples such as AME11 and AME13, where lithium is higher, is higher than that of other samples.

Table 6. 4 The result values of Gloss meter

Specimen	Values		Specimen	Values
AME01	80		AME11	99
AME02	54		AME12	87
AME03	86		AME13	100
AME04	97		AME14	83
AME05	84		AME15	23

Table 6. 5 The result values of Gloss meter (continue)

AME06	96		AME16	65
AME07	42		AME17	71
AME08	98		AME18	96
AME09	64		AME19	91
AME10	97		AME20	94

6.7 The Results of Easy-to-Clean Test

The results of the ETC test are as follows. As shown in the Figure 6.5, there are black spots on some of the plates. The ETC test is described in Section 5.6.8. The lithium carbonate was completely removed from the surface in the first stage. But when 5 different sauces are poured on top, some frit doesn't have ETC properties.

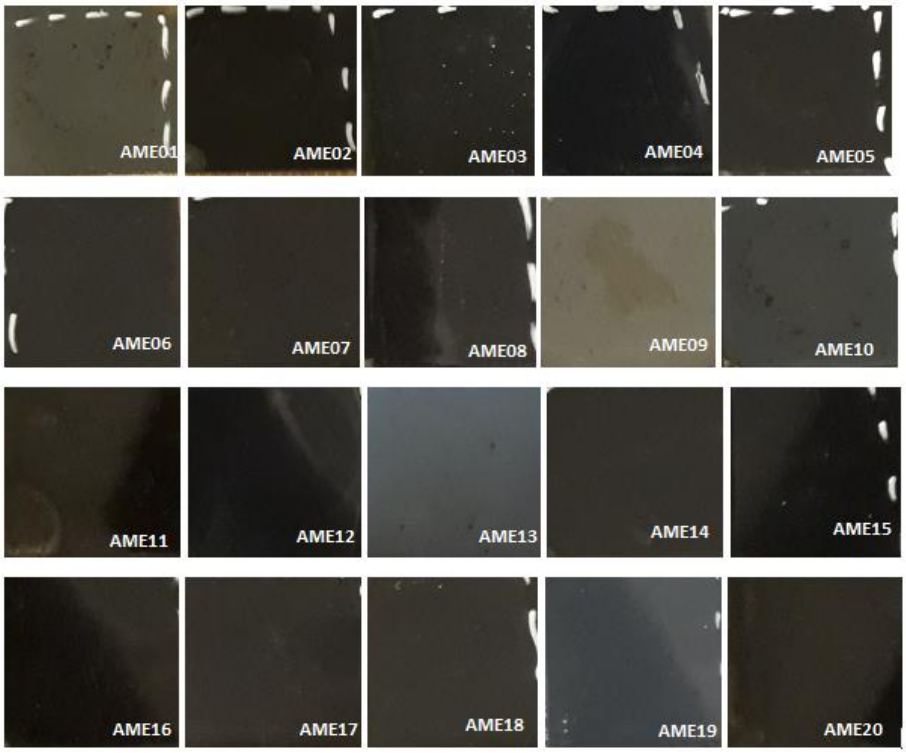


Figure 6. 5 The results of ETC test of samples

As seen in the picture, black dots are seen on some enamel surfaces. This is called lithium spitting. This is due to the formation of black spots or dots in different parts of the lithium

enamel surface with temperature. AME01, AME10 and AME13 samples are representative of these problems.

The samples AME09 and AME11 failed the ETC test. Because the food is left on the surface of the food sauce is left out of the trail. AME06 and AME14 passed the test successfully.

6.8 The Results of XRF

The results of the XRF device are as shown in the Table 6.5. As can be seen in the Table 6,5, the chemical compositions are not the same. It is possible to say that the RO_2 group forming the cage structure is high, the ratio of the R_2O group which we call the smelters is low together with the weak bond between the enamel and the metal surface. A correlation between them can be considered.

In addition, the frit, which is named AME17, and the bond test and the XRF result together, can be said to have the appropriate chemical content. There is also a correlation between R_2O and RO.

Table 6. 6 The results of XRF of the samples

	R_2O	RO	R_2O_3	R_2O_5	RO_2	R	Total
AME01	14.115	2.768	22.001	0.000	59.250	0.914	100.00
AME02	19.508	9.375	12.915	0.007	55.129	3.065	100.00
AME03	16.089	8.722	18.957	0.005	56.101	1.449	100.00
AME04	7.649	28.730	1.240	0.006	59.741	1.408	100.00
AME05	14.915	6.470	20.616	0.717	55.875	0.697	100.00
AME06	16.882	9.943	19.926	0.009	52.483	0.574	100.00
AME07	16.888	9.782	19.559	0.000	52.769	0.125	100.00
AME08	16.843	10.086	19.630	0.009	52.678	2.635	100.00
AME09	18.724	6.018	19.029	0.008	55.648	2.780	100.00
AME10	16.933	6.228	17.786	0.007	56.762	0.756	100.00
AME11	17.099	7.883	20.465	0.000	53.890	0.755	100.00
AME12	16.620	2.471	21.928	0.500	57.131	0.578	100.00

Table 6. 7 The results of XRF of the samples (continue)

AME13	15.538	10.116	20.239	0.000	53.411	1.100	100.00
AME14	17.340	8.333	18.235	0.000	54.739	0.754	100.00
AME15	10.209	10.012	15.007	0.006	63.317	0.756	100.00
AME16	15.720	8.720	27.015	0.001	47.630	1.381	100.00
AME17	23.079	11.348	23.523	0.558	38.713	0.900	100.00
AME18	18.485	3.488	13.926	0.000	63.347	1.884	100.00
AME19	14.126	3.402	21.324	0.002	59.282	1.884	100.00
AME20	17.010	8.086	17.965	0.008	56.932	1.884	100.00

6.9 The Results of SEM

The results of SEM analysis are as in the pictures. All SEM analyzes were examined one by one. Interpreting SEM analysis of samples; more efficient results are obtained by comparing the results with the adhesion properties.

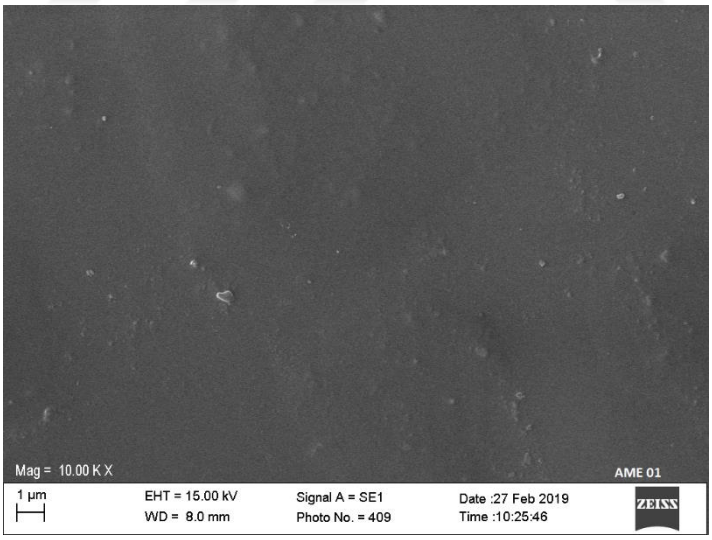


Figure 6. 6 The SEM result of AME 01

The results of the fiction code AME 01 are shown in the Figure 6.6. AME 01 has remained in the class in terms of its adhesion properties; The results of SEM analysis show no amorphous structure.

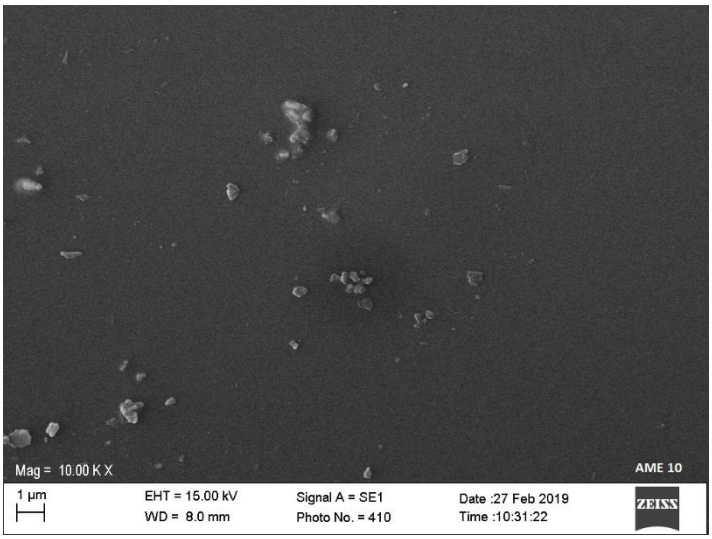


Figure 6. 7 The results of AME 10

The results of the fiction code AME 10 are shown in the Figure 6.7. The AME 10 has twice the lithium content compared to AME 01, so the number of amorphous structures is higher. The reason of this; lithium is the other elements to make it remote.



Figure 6. 8 The SEM results of AME 13

The results of the fiction code AME 13 are shown in the Figure 6.8. The AME 13 has more lithium ratios compared to AME 01, so the number of amorphous structures is higher. As a result, it was seen in the previous section that it is better to adherence.

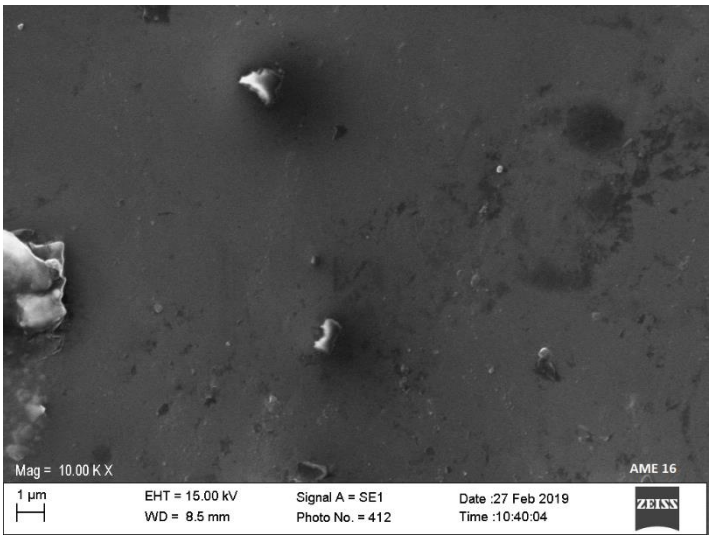


Figure 6. 9 The SEM results of AME 16

The results of the fiction code AME 16 are shown in the Figure 6.9. The AME 16 has more lithium ratios compared to AME 01, so the number of amorphous structures is higher. As a result, it was seen in the previous section that it is better to adherence. Gas outlets were also observed on the right side of the image.

7

Discussion and Recommendations

In this study, to understand the effect of lithium element on enamel surface twenty different enamel coatings were formulated with various amount of lithium. The coatings were successfully applied as a slip or powder onto already prepared steel surfaces. The coated plates were then fired at temperatures of 820^{o}C at 4 minutes. The coatings after fusion were tested for some physical properties and protection against corrosion.

Enameled boron is defined as a silica structured glassy compound. Chemical compounds in enamel affect the physical and chemical resistance of enamel. In cases where nickel oxide or cobalt oxide is high, it can be said that the bond between enamel and metal is strong, and when the amount of titanium oxide is high, the surface is white. The structure of these and such features is constantly examined.

In this study, we compared different lithium ratios of frit in different Seger ratios. In the Seger formulation, it is impossible to create a control group by keeping a value constant or changing other elements. Because the Seger should be a total hundred percent in the formulation. In making changes to the formulation, elements generally in the same group as lithium were preferred. In addition, the proportions of elements such as Ni and Co showing the same characteristics as lithium were increased.

Different surface effects in lithium enamel are given in the test analysis results. The substances contained in the enamel have separate functions. Lithium is used as an important melting material. It is one of the raw materials used to reduce the temperature of SiO_2 around 1200-degrees Celsius at high temperature.

When placed in a lithium frit enamel recipe, it contributes to the adhesion reactions with the sheet. Lithium shows a fluid property compared to other raw materials. As seen in the impact test, with the increase in the amount of lithium, the adhesion on the surface (the formation of chemical and mechanical bonds between the enamel and the sheet) increases.

Examining the color of enameled sheets, it is possible to say that the lithium-containing frit compositions have a high gloss and hence their color is opaquer.

Lithium has become the most expensive raw material of recent years with the start of its use in the energy sector. In parallel with this, the ceramic and glass sector used to be the leader in its field of use and now it has taken the lead in the energy sector. It is necessary to find new chemical components that can replace lithium, and to revise lithium-containing frit compositions.

However, with the increase in lithium values, lithium is no longer just an important component in glass, ceramics and enamel. With the development of Li-batteries, lithium has become more of an energy field. In order to increase the cost of lithium replacement of the component should be entered. It is transferred to this area of R & D investment in Turkey is of great importance. In addition, other ways to obtain the lithium mineral can also be tried.

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Contact Information: ahmet51077@gmail.com

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[1] A. M. Erayvaz ve E. Moroydor Derun, «The Research of The Enamel Frits with Lithium Efefcts on Surface Characteristics of Vitreous Enamel Coatings,*4th Internatıonal Conference On Advances In Mechanıcal Engıneerıng*, İstanbul, 2018.