Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi

Afyon Kocatepe University Journal of Science and Engineering

AKÜ FEMÜBİD **19** (2019) Özel Sayı (162-170) AKU J. Sci. Eng. **19** (2019) Special Issue (162-170)

Inkjet Applications on Vitreous Enamel Coatings

Nurullah ÇÖPOĞLU[1,2], Tamer CENGİZ[2], Buğra ÇİÇEK[1,3]

[1] *Department of Metallurgy and Materials Science Engineering, Yıldız Technical University, 34210 Istanbul / Turkey*

[2] *Gizem Frit Research and Development Center, Enamel Solutions, Sakarya 2nd Organized Industrial Zone, 54300 Sakarya/Turkey*

[3] *Koç University Akkim Boron Based Materials and High Technology Chemicals Research and Application Center, Rumelifeneri Yolu, 34450 Istanbul/Turkey*

nurullah.copoglu@gizemfrit.com / ORCID ID: 0000-0001-9328-7511
tamercengiz@gizemfrit.com / ORCID ID: 0000-0002-3642-1064
bugracicek@gmail.com / ORCID ID: 0000-0001-8195-4153

Geliş Tarihi: 26.08.2019; Kabul Tarihi: 12.09.2019

Anahtar kelimeler
Vitreous enamel, Pigment technology, Inkjet, Aesthetic surface

Abstract

Vitreous enamel coatings are inorganic coatings that are commonly used in industrial applications owing to their temperature resistance, chemical resistance, wear resistance, hardness and aesthetical properties which are derived from the glass-ceramic structure. Such advanced properties with aesthetical appearance make enamel coatings desired in washing machines, dishwashers, heaters, fire places, gas and electric cookers, BBQs, clock faces, cookware, hot water services, storage tanks, car exhaust systems, street signs, railway signs and interior and exterior architectural panels applications. The ink-jet technology is an increasingly preferred technology in the industry day by day since it has the ability to provide high resolution and numerous pattern options with the base substrate's properties in the ceramic and glass sectors. In this study, it is aimed to investigate the feasibility and structural effects of inkjet applications on the vitreous enamel surfaces with metallic substrates. In this regard, standard ground coat and different colored cover coat enamels has been applied to the low-carbon steel plates and it has seen that only white cover coat exposed the aimed color values while the other colored cover coats changed the color values with their tones. Then, a transparent enamel powder has been applied to the cover coat on the purpose of applying the inkjet homogeneously and obtaining desired visual gloss while obtaining desired color values, hence the powder has not been fired and has stayed in the biscuit form. With the inkjet application on this surface and final firing process, the desired color contrast, values and density were obtained with the beneficial effect of white cover coat and transparent coat.

Vitröz Emaye Kaplamalarda Inkjet Uygulamaları

Keywords
Vitröz emaye, pigment teknolojisi, inkjet, estetik yüzey

Öz

Vitröz emaye kaplamalar, endüstriyel uygulamalarda cam-seramik yapısından elde edilen sıcaklık direnci, kimyasal direnç, aşınma direnci, sertlik ve estetik özellikler nedeniyle yaygın olarak kullanılan inorganik kaplamalardır. Estetik görünüme sahip bu gelişmiş özellikler emaye kaplamaları, çamaşır makinelerinde, bulaşık makinelerinde, ısıtıcılarda, şöminelerde, gaz ve elektrikli ocaklarda, barbekülerde, saat yüzeylerinde, pişirme kaplarında, sıcak su hizmetlerinde, depolama tanklarında, araba egzoz sistemlerinde, sokak tabelalarında, demiryolu tabelalarında ve iç ve dış mimari panel uygulamalarında çekici hale getirmiştir. İnkjet teknolojisi, temel substratın özellikleri koruması, yüksek çözünürlük ve sayısız desen seçeneği sunma yeteneğine sahip olması sebebiyle seramik ve cam sektörlerinde gün geçtikçe daha fazla tercih edilen bir teknolojidir. Bu çalışmada inkjet uygulamalarının metal üzerine kaplanmış vitröz emaye yüzeylere uygulanabilirliği ve yapısal etkilerinin araştırılması amaçlanmıştır. Bu bağlamda, düşük karbonlu çelik levhalara standart astar kat ve farklı renkli üst kat emayeleri uygulanmış ve renkli üst katların renk değerlerini kendi tonlarıyla değiştirdiği, sadece beyaz üst katın hedeflenen renk değerlerine ulaştığı görülmüştür. Ardından, inkjet teknolojisini homojen bir şekilde uygulamak ve istenen renk değerlerini elde ederken istenen görsel parlaklığı elde etmek amacıyla üst kata transparan emaye tozu uygulanmıştır, dolayısıyla kaplama pişirilmemiş ve bisküvi biçiminde kalmıştır. Bu yüzeydeki inkjet uygulama ve son pişirme işlemi ile, beyaz üst katın ve transparan katın faydalı etkisiyle istenen renk kontrastı, değerler ve yoğunluk elde edilmiştir.

1. Introduction

Porcelain (vitreous) enamel coatings have been used for aesthetic purposes since ancient times (Andrews, 1961). Combined with the superior technical features and aesthetic properties discovered in the 18th century and later, it has become a widely encountered coating material in many areas today (Pagliuca & Faust, 2011).

Vitreous enamel coatings are a preferred type of inorganic glass-ceramic coating due to their high thermal resistance, chemical resistance and mechanical resistance properties as well as their aesthetic properties such as brightness, different color options and low roughness. The frit compositions obtained by rapid cooling after melting of quartz, borax, feldspar and metal oxides in certain ratios are the raw materials of enamel coatings. The frits are ground and powdered and combined with different mill additives (quartz, sodium nitrite, bentonite, etc.) in aqueous or powder form and applied to the metal surface (steel, aluminum, copper, etc.) by immersion, spraying, electrostatic and electrophoretic methods at temperatures of 550-850 ° C. The structure formed as a result of cooking is called enamel. Owing to the superior engineering properties mentioned above, enamel coatings are used in many areas (Andrews, 1961) (Pagliuca & Faust, 2011) (MILLAR & WILSON, 1994).

Ink-jet technology is described as non-impact dot-matrix printing technology where droplets of ink are jetted from a small opening straight to a specified location on a media to create an image (Le, 1999).

Ink-jet technology is divided into two: continuous and drop-on-demand. Continuous systems are examined in four main headings: Binary deflection, Multiple deflection, Hertz and Microdot. However, these systems are less preferred because of their high cost, low contrast and not being environmentally friendly (Hutchings & Martin, 2012). Drop-on-demand (DOD) systems are divided into four main headings: Thermal, Piezo, Electrostatic and Acoustic. In the DOD systems the ink drops are ejected according to the requirement and ejection of drops process is achieved via creation of a pressure pulse (YOSHIMURA, KISHIMOTO, & SU, 1998).

The thermal inkjet technology (TIJ-DOD) was found in the 1980s by Canon and Hewlett-Packard . In this technology the ink droplets are formed by rapidly heating element in a chamber which contains ink. The temperature of the element rises about 400 °C very fast and causes rapid vaporization of the thin film of ink. This vaporization forms a bubble which causes a pressure pulse that forces the ink droplet straight to the nozzle. After the ejection a void is formed, and this void immediately filled by another ink for creation of the next drop. This technology is widely used because of the small drop size, high nozzle density and low-cost properties (USA Patent No. US4723129A, 1988) (USA Patent No. US4490728A, 1984) (Yeates, ve diğerleri, 2014) .

Nowadays Ink-jet technology has started to take place in many areas of our lives, especially ceramic tiles owing to its aesthetic appearance and different color options. However, in vitreous enamel coating's case the color of the ground coat and glassy nature do not allow the ink-jet coating application.

In this study, it is aimed to investigate the feasibility and surface effects, and to find appropriate frit compositions for the ink-jet applications on vitreous enamel coatings.

2. Materials and Methods

All the frit compositions used during the study was produced in Gizem Frit R&D Center. The inkjet machine (KeraJET) which is the fundamental for this study, was also a property of Gizem Frit R&D Center. Within the scope of the study, frit prescriptions were prepared in order to ensure adhesion with the base metal surface and to provide a good relationship with the frit composition to be used in the cover coat and designated as G. The oxidic composition range of the prepared frit composition is given in Table 1. The frit composition given in Table 1 was used in all experimental studies for the ground coat applications.

Table 1 Prepared oxidic composition for ground coat applications (G).

Compound	Percentage (%)
RO Group (CaO, MgO, BaO, NiO, CoO, CuO, MnO)	9,81
R_2O Group (Na_2O, K_2O, Li_2O)	14,84
RO_2 Group (SiO_2, TiO_2, ZrO_2)	56,67
R_2O_3 Group (Fe_2O_3, Cr_2O_3, Sb_2O_3, Al_2O_3, B_2O_3)	17,77
F	0,88

2.1 First Experimental Procedure

The study was started at two stages. In the first step, only two layers of ground and cover coats were studies. Two different frit compositions were prepared and designated as C1 and C2. C1 composition was selected with the concerns of opacity so that the composition consists of high amount of TiO_2 and low amount of metal oxides (El-Sherbiny, Morsy, Samir, & Fouad, 2014).

The C2 composition was selected with the concerns of low opacity with high transparency so that the composition consists of low TiO_2 with high amount of metal oxides. The frit compositions prepared in this context are given in Table 2.

Wet spraying deposition method was used in this application with 2c2f (two-coat two-fire) method. The prepared frit compositions were applied to a low carbon steel and fired 100 °C in order to eliminate water evaporation defects. After thermal treatment of the specimens the ink-jet application was made while the enamel coatings were in the biscuit form. Details about the experiment procedure is described in Table 3.

2.2 Second Experimental Procedure

Table 2 Studied frit compositions

	C1	C2	C3	C4
Compound	Percentage (%)	Percentage (%)	Percentage (%)	Percentage (%)
Na_2O	11 – 13	7,5 – 10,5	9,5 – 12,5	10,5 – 12,5
K_2O	3 – 4	6,5 – 8,5	4,1 – 6,2	8,5 – 10,5
Li_2O	0	0,1 – 0,5	0	0
CaO	0,04 – 0,12	0,04 – 0,12	0,01 – 1,1	0
MgO	1,1 – 1,7	0	0	0
ZnO	0	2,2 – 2,8	0	9,5 – 11,5
CoO	0,01 – 0,05	0	0	0
Fe_2O_3	0,01 – 0,05	0,01 – 0,05	0 – 0,5	0,01 – 0,05
P_2O_5	3,1 – 3,9	0,2 – 0,8	0	0
Al_2O_3	3,4 – 4,2	0,14 – 0,42	0,7 – 1,7	0,1 – 0,4
B_2O_3	12,5 – 14,5	13,5 – 15,5	15 – 22	12,5 – 15,5
SiO_2	40,5 – 55,5	45,5 – 65,5	45 – 70	45 – 60
TiO_2	11,4 – 16,4	5,5 – 7,1	0	1,5 – 3,5
F	1,5 – 3,5	1,5 – 3,5	0,9 – 1,8	0,9 – 1,8

In the second step, it is aimed to make two cover coats in order not to affect the color values of the inkjet coating from the ground coat. The frit composition containing high titanium dioxide (TiO_2), designated as C1, was selected for the first cover coat. The second cover coat was prepared with the transparency concerns so firstly the C2 composition was applied as second cover coat. In order to increase glassy structure with the concerns of transparency C3 composition was prepared and applied. Also it’s a known fact that the ZnO amount in the composition has a positive effect on transparency so that C4 composition was prepared (Lee, Ko, & Park, 2003).

Table 3 *Detailed description of experimental procedure.*

	Designation	Ground Coat	Cover Coat(s)		Coating Method	Firing Temperature	Firing Time
First Experimental Procedure	A1	G	C1		3C2F	820 °C	10 min.
	A2	G	C2		3C2F	820 °C	10 min.
			First	Second			
Second Experimental Procedure	A3	G	C1	C2	4C3F	820 °C	10 min.
	A4	G	C1	C3	4C3F	820 °C	10 min.
	A5	G	C1	C4	4C3F	820 °C	10 min.

Wet spraying deposition was used in the all the application processes according to optimization and comparison standards with clay as floating agent to keep the particles suspended in the slip mixture. The samples are dried in a tunnel kiln 100 °C for 15 minutes. This thermal treatment is necessary in the case of wet application process to limit the formation of cracks and surface pores which occurs because of the rapid evaporation of water and hydrogen formation at high temperatures. The second cover coats in all experimental conditions were applied before firing process. After the thermal treatment of water evaporation, the inkjet was applied. Then the specimens were fired in a box furnace. The firing temperature was 820 °C and the firing process was 10 minutes.

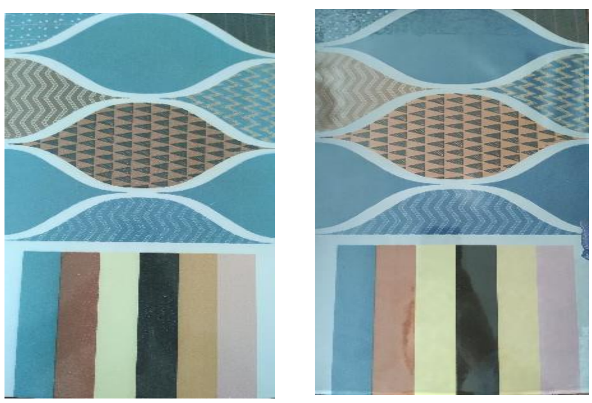
3. Results

3.1 First Experimental Procedure

The image of the sample obtained in the A1 experiment is shown in Figure 1a. It is observed that the relatively dark color of the ground coat comes out after inkjet application. The frit composition with high opacity shows that the opaque color effected by the black ground coat. The color stability has not been observed but colored areas can be observed so the ink-jet application in the technical meaning is successful.

The image of the sample obtained in the A2 experiment is shown in Figure 1b. It is observed that the dark color of the ground coat comes out after inkjet application. The frit composition with high dyeability and transparency used in the study could not give the desired colors exactly in ink-jet application. Although the desired frit composition can be applied ink-jet application, the color values shifted towards the dark color of the ground coat and the study did not result in a positive result.

Figure 1: *Image of the sample obtained in the first experimental procedure: left) A1 and right) A2*



3.1 Second Experimental Procedure

The image of the A3 sample is shown in Figure 3. The green-like colors were meant to be blue colors however the appearance is shifted. The cover coats of the A3 sample were studied in the separately for the first experimental procedure. The opacity of the C1 composition satisfied the required opaqueness however the C2 composition has not showed the required transparency which is probably related to the low zinc content or the reactions of the pigments during firing process.

Figure 2: *Image of the sample obtained in the A3 sample*

Figure 3: *Image of the sample obtained in the A4 sample*

The A4 experiment aims to investigate the TiO_2 effect for the ink-jet application. The image of the A4 sample is shown in Figure 3. It can be seen that with the increase in amount of TiO_2 in the second cover coat increases opacity and color intensity. However, the desired color hue has not been achieved.

Figure 4 shows the image of A5 sample. The A5 experiment aims to investigate the effect of zinc oxide (ZnO) for the dyeability and transparency.

Figure 4: *Image of the sample obtained in the A5 sample.*

The color hue and color intensity is perfect for the A5 sample. The color values and lines were ontained according to the standards. The first cover coat's opacity has not been disturbed and the tranparency is achieved perfectly.

SEM and EDS analyses were made, in order to investigate the surface and metal-enamel adhesion properties and to A5 sample which has shown the best results. Figure 5 shows the SEM images of the A5 sample. Fig. 5a shows brown and black triangle areas with different coloured areas. Fig. 5b shows the blue area with consistent surface pattern. Fig. C shows the are between the yellow and black rectangle area. Both areas show the similar pattern however the black area can be seen tinted. The reason is probably the titanium presence in the yellow pigments.

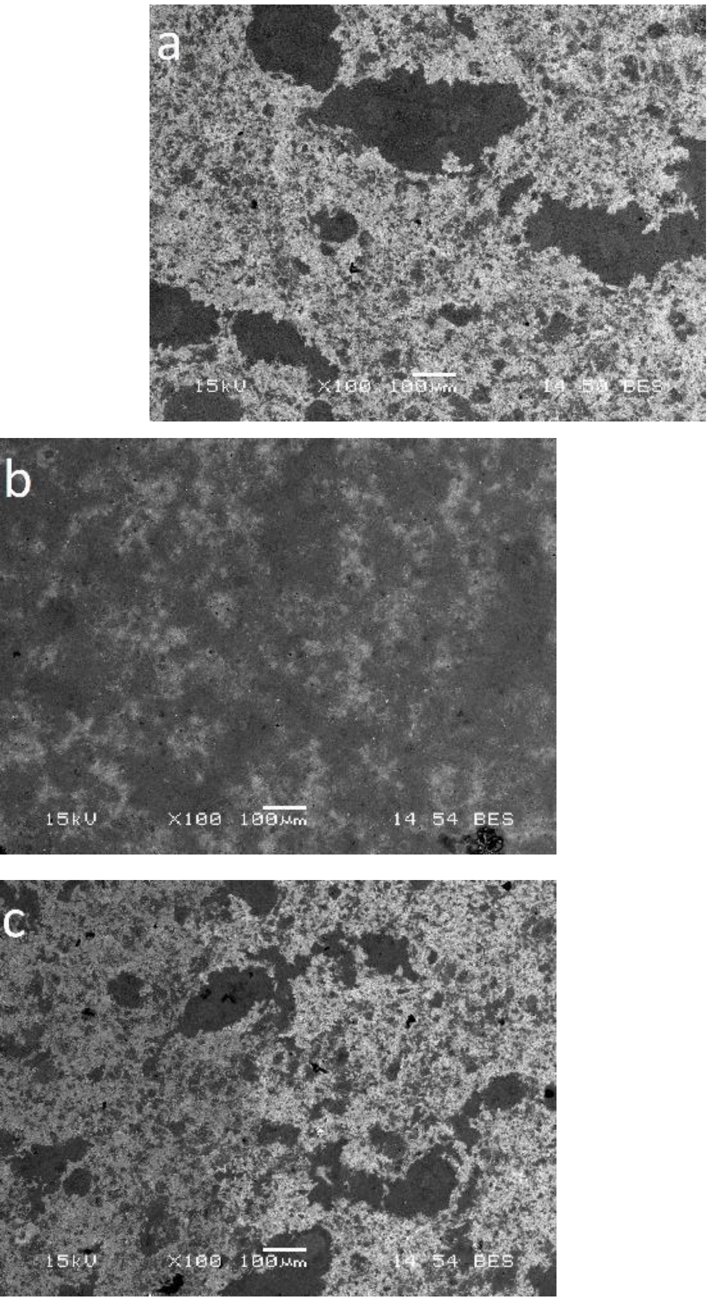
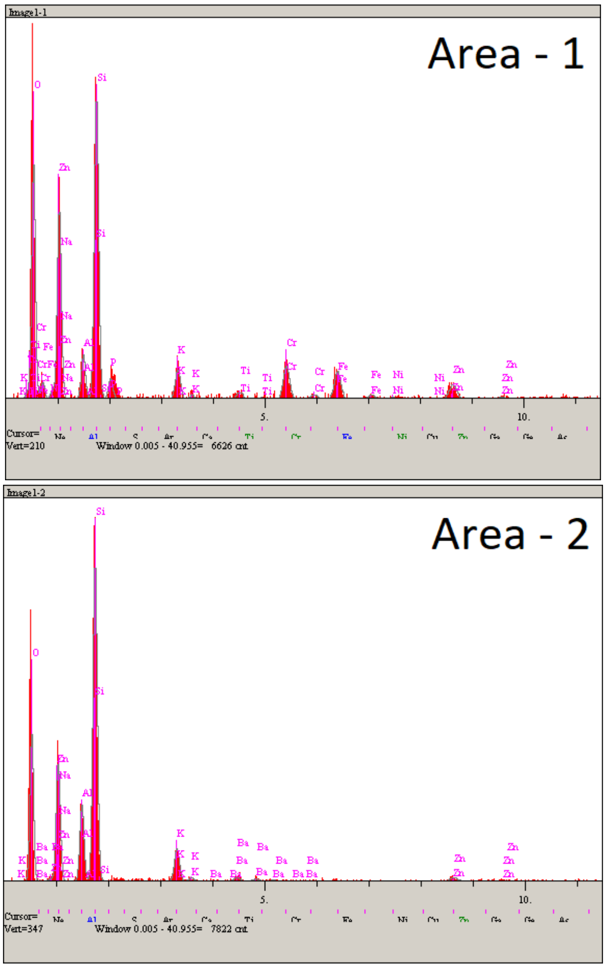


Figure 5: SEM images of the A5 sample in three different areas.



EDS analyzes were also made to investigate the color difference and pigment concentration in the close areas. Fig.6 shows EDS analyses of the A5 sample. The analysis was made as same in the Fig. 5a. It can be seen that high amount of Cr is the main reason of the difference. The brown and black pigments have Cr in their structure and Fig. 6 Area 2 shows the typical enamel structure.

Figure 7 shows the EDS analyses of the same area as Fig. 5b. In the Fig. 7 Area 1 the high amount of Co content is responsible for the blue color while the Area 2 shows the enamel structure with the

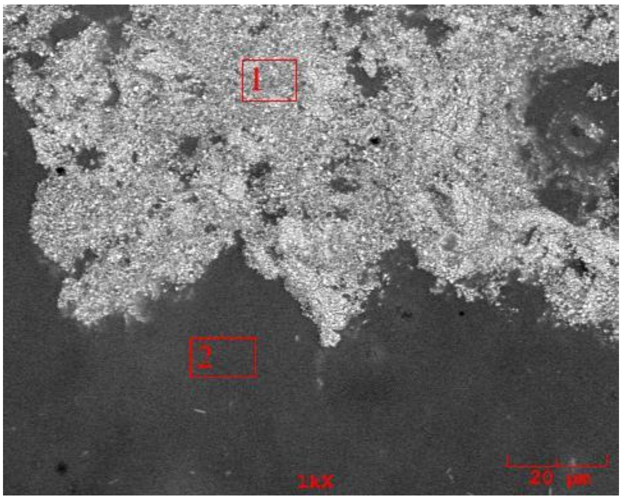
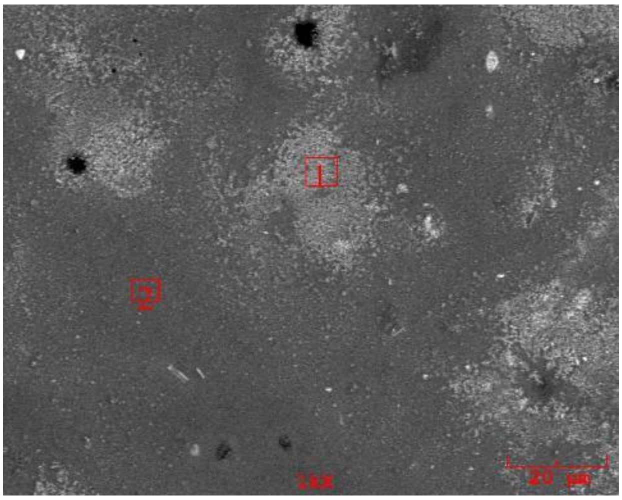


Figure 6: EDS analyses of the black-brown area of the A5 sample

high amount of SiO_2 and little amount of other RO and RO_2 groups without colouring pigments.

Figure 8 shows the EDS analyses of the same area as Fig. 5c. In the Fig. 8 Area 1 the tinted area shows the black colored area with high amount of Cr and Fe content. Area 2 shows the light area with high amount of Zr.



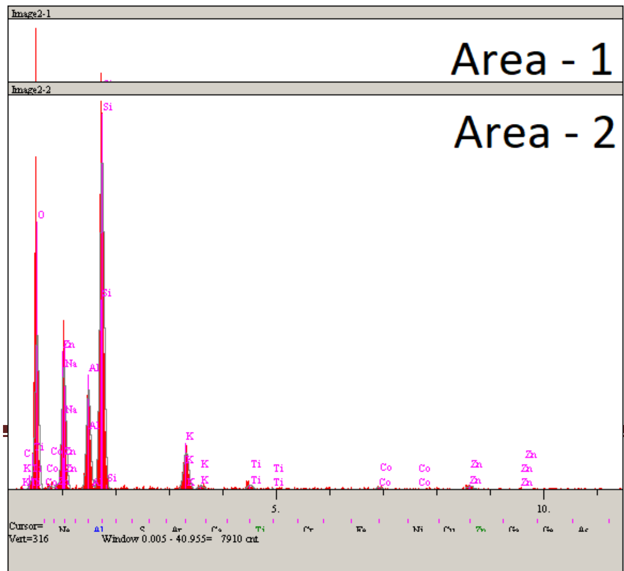
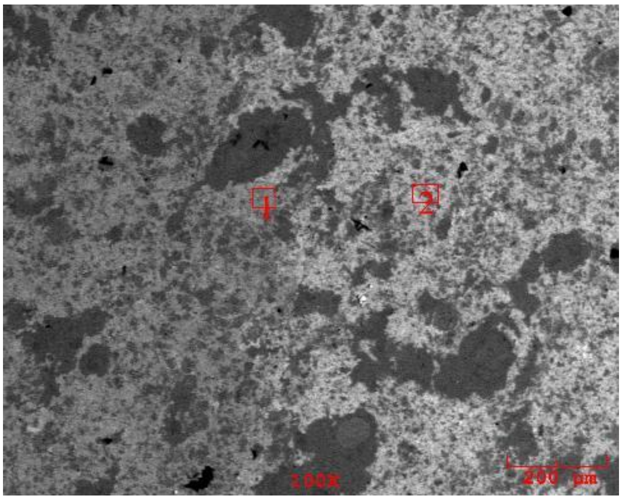
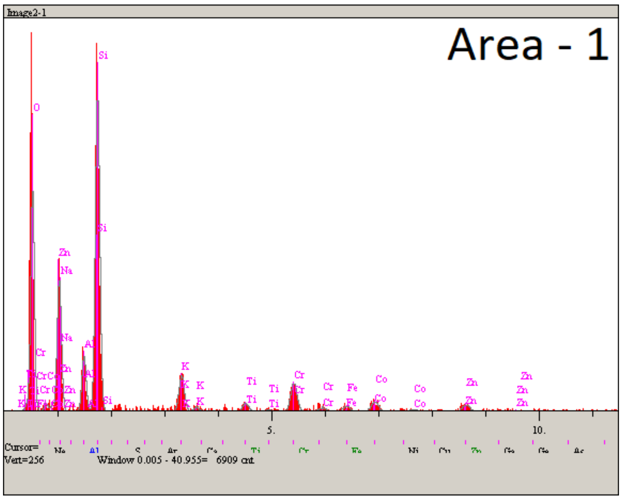


Figure 7: EDS analyses of the blue-white area of the A5 sample

Cross sections of the A5 sample in three different areas as in Fig. 5 is shown in Fig. 8. For all the three areas the adhesion between metal and enamel is perfect since the images provide mechanical, chemical, dendritic and electrolytic adhesion requirements.





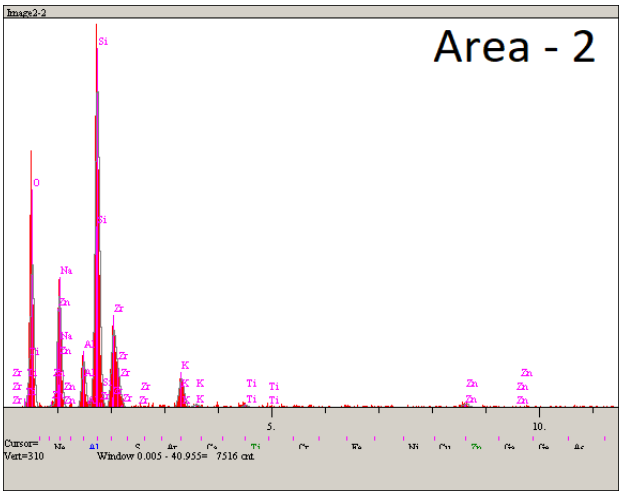


Figure 8: EDS analyses of the yellow-black area of the A5 sample

Coating thickness of the four coating was measured 500 ± 25 µm approximately. The measurement was made with three different points and the results are the mean of the five measurements. Three layers of the coating can be seen easily from the images.

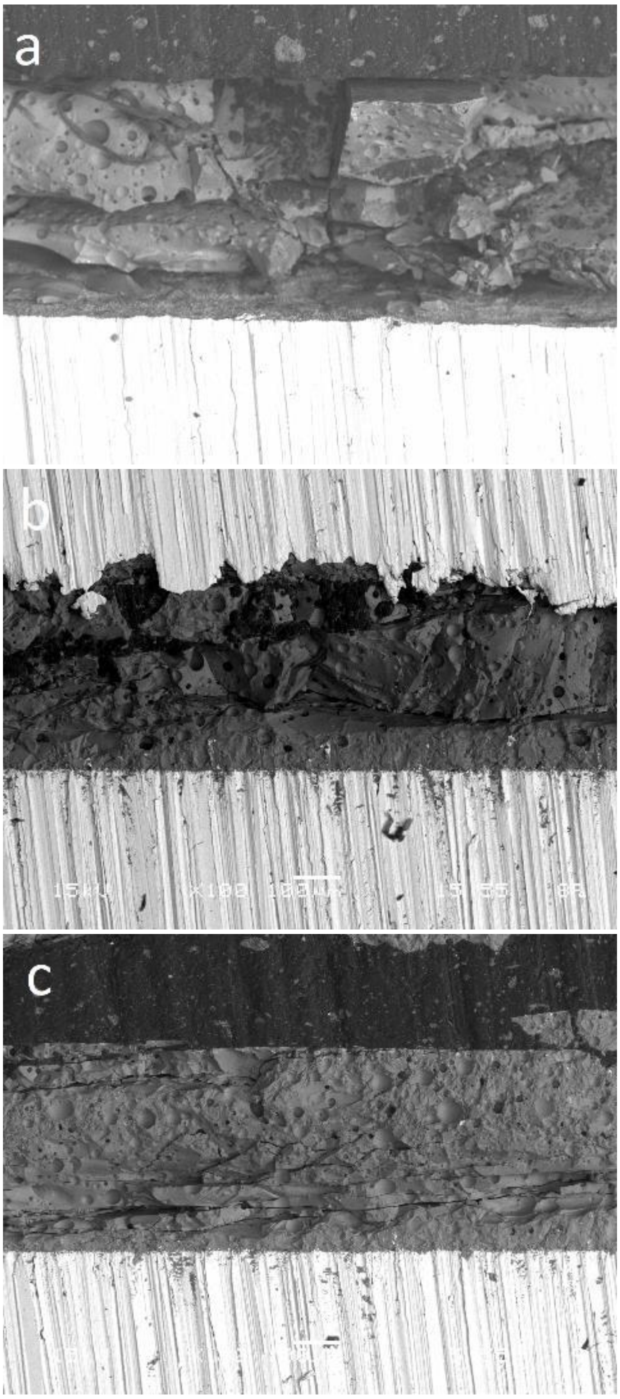


Figure 9: SEM images of the cross section of the A5 sample in three different areas.

4. Discussion and Conclusions

The feasibility and surface effects of the ink-jet application on vitreous enamel coatings were investigated in this study. Different frit compositions were prepared with the concerns of opacity and transparency. The ink-jet application was made in the biscuit form which is the state before the firing process of the second cover coat. It was stated that the high amount of TiO_2 in the composition of the first cover coat has a beneficial effect for the ink-jet application of the second cover coat. Also, second cover coat's ZnO content increases the transparency of the coating. Therefore, with the high opacity of the first cover coat and high transparency of the second cover coat the ink-jet systems can be applied to the vitreous enamel coatings.

Acknowledgements

The authors acknowledge Gizem Frit Enamel R&D Laboratory and Mr. Murat Kaya for their consistent support for this study.

5. References

Andrews, A. A. (1961). *Porcelain Enamels: The Preparation, Application and Properties of Enamels.* Champaign: Gerrard Press.

El-Sherbiny, S., Morsy, F., Samir, M., & Fouad, O. A. (2014). Synthesis, characterization and application of TiO2 nanopowders as special paper coating pigment. *Applied Nanoscience*, 305-313.

Endo, I., Sato, Y., Saito, S., Nakagiri, T., & Ohno, S. (1988). *USA Patent No. US4723129A.*

Hutchings, I., & Martin, G. D. (2012). *Inkjet Technology for Digital Fabrication.* Cambridge: Wiley.

Le, H. P. (1999). Progress and Trends in Ink-jet Printing Technology. In E. Hanson, *Recent Progress in Ink Jet Technologies II* (pp. 1-

14). Springfield: Society for Imaging Science and Technology (IS&T).

Lee, J., Ko, K., & Park, B. (2003). Journal of Crystal Growth. *Electrical and optical properties of ZnO transparent conducting films by the sol–gel method*, 119-125.

MILLAR, N., & WILSON, C. (1994). Vitreous Enamel Coatings. In L. L. Shreir, R. A. Jarman, & G. T. Burstein, *Corrosion* (pp. 16:3 - 16:12). Oxford: Butterworth-Heinemann.

Pagliuca, S., & Faust, W. (2011). *Procelain (Vitreous) Enamels and Industrial Enamelling Processes .* Mantıva: The International Enamellers Institue.

Vaught, J. L., Cloutier, F. L., Doanld, D. K., Meyer, J. D., Tacklind, C. A., & Taub, H. H. (1984). *USA Patent No. US4490728A.*

Yeates, S. G., Xy, D., Madex, M., Caras-Quintero, D., Alamry, K. A., & Sachez-Romaguera, V. (2014). Fluids for Inkjet Printing. In I. M. Hutchings, & G. D. Martin, *Inkjet Technology for Digital Fabrication* (pp. 87-112). Cambridge: Wiley.

YOSHIMURA, K., KISHIMOTO, M., & SU, T. (1998). *Inkjet Printing Technology. Technical Report.* Tokyo: OKI.