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Effect of Cr_2O_3 on Abrasion Resistance of Na_2O-B_2O_3-SiO_2 Enamel Coatings for Use in Architectural Panels

Şemsi Melih Gülen[1,2], İremnur Ceylan[1,3], Nurullah Çöpoğlu[1,3], Murat Kaya[1,2], Tamer Cengiz[1,3] and Buğra Çiçek[3]

[1] *Akcoat R&D Center, Enamel Coatings Division, 2nd IZ, 54300 Hendek, Sakarya/Turkey*

[2] *Sakarya University of Applied Sciences, Department of Metallurgy and Materials Science Engineering, 54050 Serdivan, Sakarya/Turkey*

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

Sorumlu Yazar / Corresponding Author
Şemsi Melih Gülen
melih.gulen@akcoat.com

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ORCID
Şemsi Melih Gülen
https://orcid.org/0000-0002-5533-9680
İremnur Ceylan
https://orcid.org/0000-0002-1346-3544
Nurullah Çöpoğlu
https://orcid.org/0000-0001-9328-7511
Murat Kaya
https://orcid.org/0000-0001-9455-0166
Tamer Cengiz
https://orcid.org/0000-0002-3642-1064
Buğra Çiçek
https://orcid.org/0000-0001-8195-4153

Abstract

Enamel coatings (ECs) are an ideal choice for external panel coating because they provide a multitude of artistic merits such as color and gloss, as well as physical and chemical resistance. The visual characteristics as well as the wear resistance of an enamel coating on decarburized steel panels intended for use in architectural panels were studied. An EC formulation that contains transparent parent glass and mill additives were fabricated in four steps: i) batch preparation, ii) grinding, iii) electrostatic spraying application on steel substrate, and iv) firing at 820°C for 4 min. To evaluate the influence of Cr_2O_3 on color values and wear resistance of the ECs, Cr_2O_3 was added to the EC formulation as a mill additive. Abrasion resistance was evaluated with Taber Abrasion device up to 1000 cycles. The ECs' wear resistance was assessed by determining the weight loss at pre- and post-Taber Abrasion tests. The optimum wear resistance was found in a sample containing 2 wt.% Cr_2O_3. Cr_2O_3 addition only modestly improved the wear resistance, since excess Cr_2O_3 does not incorporate into the structure and increases the stress fields.

Cr_2O_3'ün Mimari Panellerde Kullanılan Na_2O-B_2O_3-SiO_2 Emaye Kaplamaların Aşınma Direncine Etkisi

Özet

Emaye kaplamalar (EK), renk ve parlaklık gibi çok sayıda estetik özelliklerinin yanı sıra fiziksel ve kimyasal direnç sağladıkları için dış panel kaplaması için ideal bir seçimdir. Çalışmada, mimari panellerde kullanılması amaçlanan dekarbürize çelik paneller üzerindeki bir emaye kaplamanın görsel özellikleri ve aşınma direnci incelenmiştir. Şeffaf frit ve katkı maddeleri içeren bir EK formülasyonu dört adımda üretildi: i) harman hazırlama, ii) öğütme, iii) çelik substrat üzerine elektrostatik sprey uygulaması ve iv) 820°C'de 4 dakika pişirme. Cr_2O_3'ün EK'lerin renk değerleri ve aşınma direnci üzerindeki etkisini değerlendirmek için, EK formülasyonuna değirmen katkısı olarak Cr_2O_3 eklenmiştir. Aşınma direnci Taber Abrasion cihazı ile 1000 devire kadar test edilmiştir. EK'lerin aşınma direnci, Taber Aşınma testleri öncesi ve sonrası ağırlık kaybı belirlenerek hesaplanmıştır. Optimum aşınma direnci, ağırlıkça %2 Cr_2O_3 içeren numunede bulunmuştur. Cr_2O_3 ilavesi, aşırı Cr_2O_3 yapıya dahil edilmediğinden ve stres alanlarını artırdığından, aşınma direncini yalnızca orta derecede iyileştirmiştir.

1. INTRODUCTION

Architecture has become an important field of study for humanity in the long run. Buildings, which were used to protect against adverse natural conditions and attacks in the early days, have become an indispensable part of our daily life. Over time, the buildings ceased to be safe and sheltered spaces and turned into living spaces where visual pleasures come to the fore. With the effect of industrialization, architectural practices have changed, and it has become mandatory for building exteriors to meet the aesthetic point of view and to meet the necessary criteria in terms of performance. With this point of view, panels have taken the place of reinforced concrete walls.

In architecture, exterior panels have been a constant practice throughout history. Panels are preferred in many building types such as houses, offices, hospitals. Panels are used for many different purposes such as providing aesthetic features, saving energy and protecting the main structure from external influences, and different color options. Also, panels provide easy repair, low investment cost, and surface properties, chemical and graffiti resistance. Architectural panels are produced from wood, polymeric, ceramic-based, metallic, or composite materials. [1-6]

Material selection in architectural panels varies according to the features expected from the panel. Features such as formability, aesthetic appearance, acid resistance, heat permeability, impact resistance, unit weight are the most important parameters in panel selection. Polymeric panels, called siding, are often preferred due to various color alternatives and shaped parts. However, polymeric materials have a low lifespan due to their low temperature and UV resistance. Ceramic panels have low fracture toughness despite improved surface properties due to their glassy glaze. Glass panels have superior mechanical properties and aesthetic appearance, similar to ceramic tiles, but have low mechanical properties such as easy breaking and cracking. Aluminum panels are the most preferred metallic panels due to their low density and easy formability. However, its low corrosion resistance compared to other panel types and the need for an extra coating or paint to provide the desired aesthetic appearance are its negative features. Enamel coated steel plates are an important panel candidate in terms of property performance in exterior applications, as they are composite materials with advanced mechanical properties of metals and superior surface properties of ceramics. [5-7]

The application of enamel coatings dates back to BC. Enamels first used in jewelry were later used on mummies and pyramids in ancient Egypt. With industrialization, it has been used in many areas of industry such as kitchen utensils, heat exchangers, water heaters, and whiteboards. Enamel coatings improve the surface properties of the surface on which they are coated, increase chemical and physical wear resistance, and provide aesthetic properties such as desired color and gloss. It can be applied to different metals such as steel, cast iron, aluminum, and copper. [8,9]

Frit compounds obtained by quenching after melting the quartz, borax, feldspar, and metal oxides which are raw materials in enamel coatings. Frits are ground and pulverized and mixed in aqueous or powder form with various grinding additives (quartz, sodium nitrite, bentonite, etc.) and applied to the metal surface (steel, aluminum, copper, etc.) by dipping, spraying, electrostatic and electrophoretic methods, subsequently fired between 710 - 850°C. [8]

The desired color, brightness, light transmittance values, frit structure, and pigment can be easily obtained. Enamel coatings can be opaque, translucent, and transparent depending on the frit structure. Titanium oxide (TiO_2) in the frit structure is the oxide that regulates the opacity.[8,10-13]

Studies on the use of enamel coatings in architectural applications are limited in the literature. In a study investigating the effect of surface properties on strength, two different enamel application methods, wet and dry, were preferred. As a result of the studies, it has been observed that all enamel types have good UV and acid resistance due to their inorganic structure but have degradation and aesthetic properties against alkaline solutions.[14] In a study evaluating the application of stainless steel and vitreous enamel coated steel in architecture, it was stated that enameled panels have superior visual properties and low cost.[15]

Wear is defined as the "weight loss of materials from the surface by the mechanical removal of the wear particle". When two materials rub against one other at different speeds, the energy of the moving item is dissipated at the rubbing interface and is generally used in loosening the surface particles, resulting in wear debris that separates off the surface. For instance, in a coastal setting, high-speed winds during storms force sand particles towards the façade, producing wear of the surface finishing layer and tiles.[16]

In this study, the determination of the color properties of chromium oxide (Cr_2O_3) in enamels used in architectural coatings and its effect on wear resistance were investigated. Ground coat is suitable for low carbon steel surfaces was coated with electrostatic powder method. On the cover coat, 0 wt.% (Y00), 0.5 wt.% (Y05), 2 wt.% (Y20) and 4 wt.% (Y40) chromium oxides were added to the transparent frit respectively and applied on the surface with the wet spraying method. Color and wear values of the prepared samples were investigated.

2. EXPERIMENTAL DETAILS

All frit compositions used in the study were obtained from Akcoat Co. Enamel coated metal samples were prepared as a coating layer applied on the ground coat, which is defined as a two-coat two-fire (2C2F) coating process. The purpose of the ground coat application is to provide adhesion between the enamel and the metal. The adhesion phenomenon between enamel and metal is an indispensable property for enamels, and cobalt oxide (CoO) and nickel oxide (NiO) are the most important adhesion agents. The oxide composition of the ground coat enamel used is given in Table 1.

Low carbon steel in accordance with EN 10209 standards is used as a substrate for coating application with 1.5 mm thickness (according to EN 14127 standard) and 12 cm x 15 cm dimensions. The composition of the steel substrate is given in Table 2.

The cover coat was applied on both sides of the steel surface by the electrostatic spraying method. Organosilicon oil was used to provide the electrostatic property of the powder. After application, the samples were fired in a box furnace (Protherm PLC 130) at 830 °C for 4 minutes and 30 seconds. After firing, a coating thickness of 80 microns was obtained.

Table 1. Cover coat chemical composition (%).

Oxide Group	Amount (%)
R_2O (Na_2O, K_2O, Li_2O)	16.59
RO (CaO, MgO, BaO, NiO, CoO, CuO, MnO)	6.39
RO_2 (SiO_2, TiO_2, ZrO_2)	54.78
R_2O_3 (Fe_2O_3, Cr_2O_3, Sb_2O_3, B_2O_3, Al_2O_3)	19.69
Others (P_2O_5, MoO_3, F_2)	2.55

Table 2. Chemical composition of steel substrate

Element	Percentage (%)
C	<0.005
Mn	<0.4
P	<0.02
S	<0.03
Fe	> 99

In this study, the composition of the transparent frit used on the cover coat is given in Table 3. The codes of the prepared samples and the mill additives are given in Table 4.

Table 3. Transparent frit chemical composition (%)

Oxide Group	Composition (%)
RO (CaO, MgO, ZnO, CoO)	6.23
R_2O (Na_2O, K_2O, Li_2O)	16.97
RO_2 (SiO_2, TiO_2, ZrO_2)	49.89
R_2O_3 (Fe_2O_3, B_2O_3, Al_2O_3)	20.91
R_2O_5 (P_2O_5)	0
R (F)	6.00
Total	100

Table 4. Sample codes and mill additives

Sample Code	Transparent Frit	Cr_2O_3	K_2CO_3	Na_2AlO_4	Clay
Y00	100	0	0.2	0.3	5
Y05	100	0.5	0.2	0.3	5
Y20	100	2	0.2	0.3	5
Y40	100	4	0.2	0.3	5

The coating application was conducted by the wet spraying method. In wet applications, additives such as water, clay, potassium carbonate, and sodium aluminate were added depending on the suspension conditions before the application. Frit and mill additives were ground in a ball mill at 60 rpm for 17.5 minutes. After grinding, water was added to provide the enamel density of 1.7 g/mL for all coating coat applications.

The samples were kept in a drying oven for 15 min. to prevent rapid evaporation of the water in the firing process. Then the samples fired at 550 °C in a box furnace for 4 min and subsequently fired at 820 °C for 4 min. The enamel-coated samples were removed from the furnace and allowed to cool down to room temperature. After the process, a total coating thickness of 250 µm was obtained. Thus, the preparation phase of the enamel-coated steel samples to be used in the study was completed.

Chemical composition analysis of the prepared compositions was analyzed with the Bruker S8 Tiger X-ray fluorescent (XRF) device. The oxide percentages of the frits were observed to see if the desired composition was achieved and to give a more accurate interpretation of the work.

Crystal phase analysis was performed to examine the chromium oxide used. X-ray diffraction (XRD) analysis with Cu K radiation was performed on the pellet powders in the 2θ scanning range of 15°–70° (Bruker 2D Phaser).

Color measurements (L, a, b) of the plates of 4 samples were analyzed with a spectrophotometer (Konica Minolta CM-700d) in SCI D65 index according to EN ISO 28722:2011 standard.

Abrasion resistance was evaluated by a two-body wear process with Taber test according to ASTM D4060-19 standard. The samples were placed in the test device and 2 wheels with abrasive wheels were provided to rotate under constant load at a constant speed of 60 rpm. The abrasive wheels move in different directions as the samples begin to spin in the tester. At the end of the wear process, a circular wear mark is formed on the surface. Since the tester has its vacuum system, particle losses during wear are drawn directly from the system. During the wear test, the Taber S-33 strip, closed ply abrasive paper composed of extra-fine aluminum oxide grit rated 360 FEPA (P360) with an average particle size of approximately 40.5 µm, was used as an abrasive. It is glued around the CS-0 Rubber Wheel with a constant load of 500 grams.

3. RESULTS AND DISCUSSION

3.1. Chemical Structure

The XRD analysis of the studied chromium oxide additive is shown in Figure 1. According to the XRD analysis, it was observed that the structure is the eskolaite phase. Eskolaite is an oxide with a chemical formula of Cr_2O_3, soluble in all glazes except glazes with high alkali and boron oxide content, providing opacity in additions of 2-5 wt. %, and a green color. It was found to be suitable for use in this study as well. XRF analysis of chromium oxide used in the study is given in Table 5. It contains a high amount of Cr_2O_3 as desired and contains a low amount of impurities that will not harm the enamel structure. The final product images of the studied samples are shown in Figure 2.

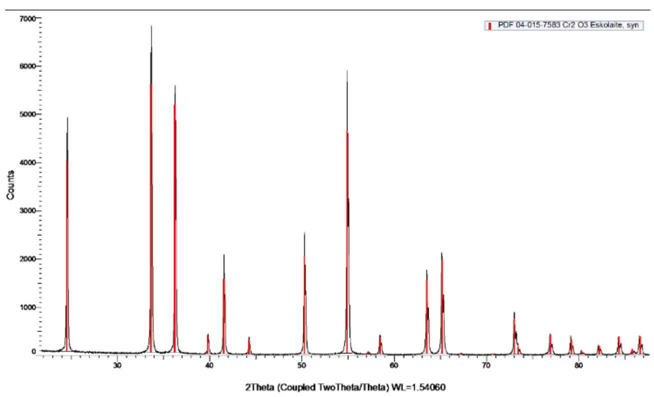

Figure 1: XRD analysis of chromium oxide particles used in the study

Table 5. XRF analysis of the chromium oxide used

Oxide	%
Cr_2O_3	99.76
SiO_2	0.13
Fe_2O_3	0.061
CaO	0.042
ZnO	0.007

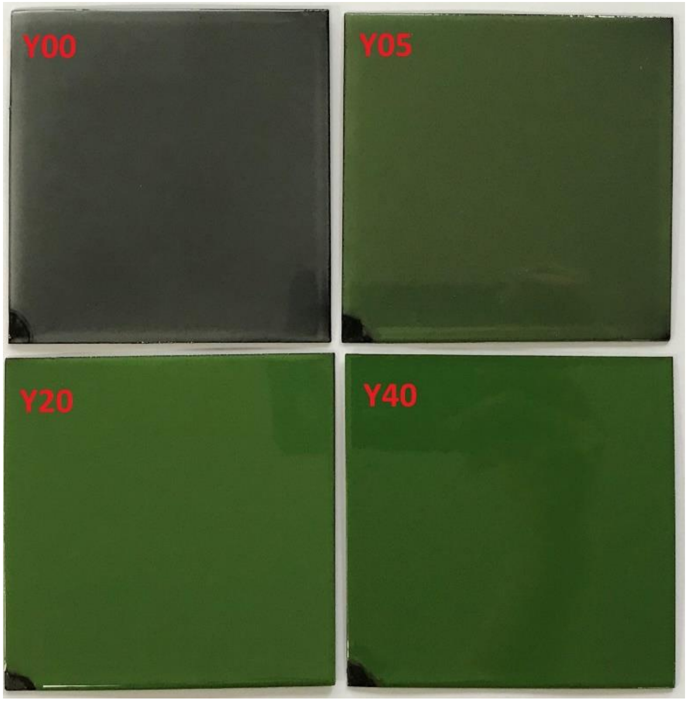

Figure 2: Final product images of the prepared samples

3.2. Color Change

Color measurements (L, *a*, *b*) of the plates of 4 samples were analyzed with a spectrophotometer. In order to ensure that there is no difference in the results and continuous measurement from the same area, the areas where the measurement was made were fixed with the help of a mold. The measured values are given in Table 6.

According to the values given in Table 6, L opacity (0 black and 100 white), *a* red-green variation (positive values red, negative values green and 0 neutral), and *b* yellow-blue variation (positive values yellow, negative values blue, and 0 neutral) values. As the chromium oxide ratio increased, as expected, an increase in L value, an increase in *a* value in the direction of green, and an increase in *b* value in the direction of yellow were observed.

Table 6. Spectrophotometer results of the prepared samples

Sample Codes	SCI D65		
	L	*a*	*b*
Y00	40.32	-0.2	-0.99
Y05	41.53	-4.79	4.83
Y20	42.16	-11.95	12.98
Y40	43.15	-13.07	13.7

3.4. Microstructural Analysis

In order to investigate the morphology of the studied samples, SEM analysis was conducted, and the images are shown in Fig. 3. Y00 shows the SEM image of the reference sample without Cr_2O_3 addition. The surface is defect-free, and no crystal formation is observed. The whitish dots are arising from the mill additives that are not completely dissolved in the vitreous structure. The first edition of the Cr_2O_3 is shown in the Y05 sample. The web-like appearance is coming from the Cr_2O_3 particles. It can be seen that the incorporation of the particles is successful. In the SEM image of the Y20 sample with 2 wt. % Cr_2O_3 addition, the Cr_2O_3 particles increased in the amount. Also, the greenish appearance is increased due to the Cr_2O_3 addition (Fig. 2). In the SEM image of the Y40 sample with 4 wt. % Cr_2O_3 addition, the whitish particles are increased tremendously due to the addition. Yet the vitreous matrix can be hardly seen.

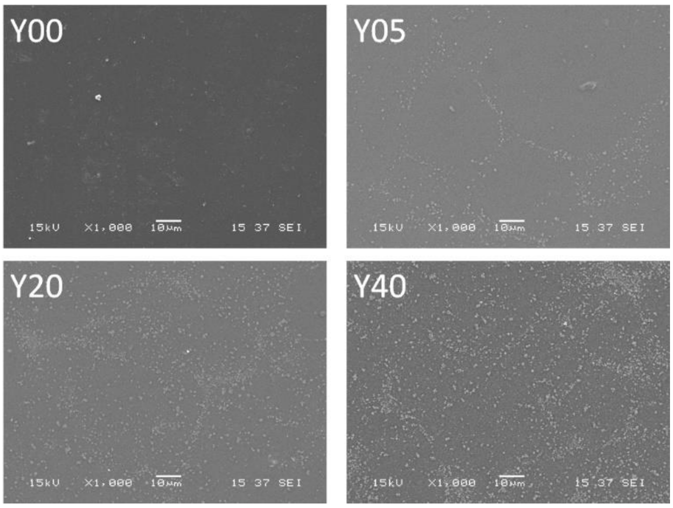

Figure 3. SEM images of the studied samples

Figure 4 shows the mapping EDS analysis of the studied samples for the element of Cr. As can be seen in the figure, with the increasing amount of Cr_2O_3 the count of atoms increases through the surface. The EDS analysis results support the SEM analysis results. The increasing amount distorts the web-like appearance of Cr_2O_3 in the surface and cannot be embedded in the vitreous matrix. The particles that are not incorporated in the matrix create stress points and stress areas in the wear mechanism. Since the enamel coatings deform with the brittle fracture mechanism, the stress points have importance due to the crack initiation and propagation. Yet, as a result of the EDS analysis results, it can be considered that the homogeneous distribution of Cr_2O_3 particles through the surface is seen in Y05 and Y20 samples. However, the Y40 sample shows a distorted surface with non-homogeneously distributed Cr_2O_3 particles.

3.5. Wear Resistance

Figure 5 shows the masses of the samples before and after the wear test. As expected, mass loss is observed in all samples. However, in order to show the most accurate form of the mass loss, the mass loss after the abrasion test is shown in Table 7 in unit of gram.

As can be seen from the values shown in Table 7, the chromium oxide additive has the most positive effect on the wear resistance of enamel coatings. It can be said that the chromium oxide ratio increases the wear resistance for each sample in comparison with the reference sample. The optimum value was observed in the Y20 sample, in which chromium oxide was added as 2 wt. % by weight mill additives. A relative decrease in wear resistance was observed with an increasing chromium oxide ratio in the Y40 sample.

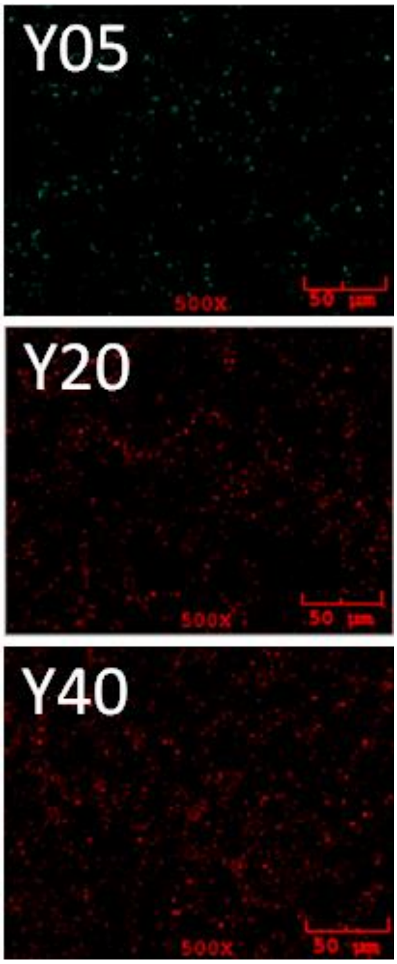

Figure 4. Cr mapping EDS results of the studied samples

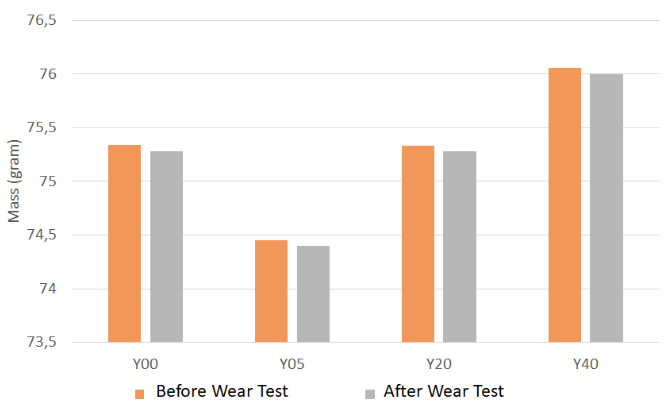

Figure 5. Masses of the prepared samples before and after the abrasion test.

Table 7. Mass loss after wear test

Sample Code	Mass Loss (gram)
Y00	0.078
Y05	0.065
Y20	0.054
Y40	0.062

4. CONCLUSIONS

In this study, the effect of chromium oxide ratio on the wear resistance of enamel coatings used in architectural applications was investigated. Chromium oxide was added to the structure as a mill additive. The color change was an expected phenomenon in terms of greenish and yellowish scales. Mass loss of the samples showed beneficial results in order to better understand the wear resistance of the enamel coatings. It has been observed that the amount of Cr_2O_3 in the enamel structure as a mill additive, is an important issue in determining the abrasion behavior due to the crystals that are not embedded in the enamel matrix can cause stress points and areas. These stress areas initiate the crack propagation and hence lower the wear resistance of the studied surfaces.

The study contributed by adding a comparative review on the state of the literature. In further studies, the external panel performances of wet and powder enamel applications and the effect of different coloring oxides can be examined.

- In all samples, the color change was mostly on green and yellow.
- Although the wear resistance showed an increase up to the Y20 sample, the increase stopped in the Y40 sample.
- It has been observed that the addition of a high amount of chromium oxide provides a relative increase in the wear resistance of the enamel surfaces.

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