

# POLITEKNIK DERGISI JOURNAL of POLYTECHNIC

ISSN: 1302-0900 (PRINT), ISSN: 2147-9429 (ONLINE)

URL: http://dergipark.org.tr/politeknik



Enhancement of coating features by supporting zinc-based coating with cataphoresis process: effect of acidity and coating thickness on the coating quality

Çinko-esaslı kaplamanın kataforez prosesi ile desteklenerek kaplama özelliklerinin geliştirilmesi: asitlik ve kaplama kalınlığının kaplama kalitesine etkisi

Yazar(lar) (Author(s)): Adife Şeyda YARGIÇ<sup>1\*</sup>, Bünyamin EREN<sup>2</sup>, Nurgül ÖZBAY<sup>1</sup>

ORCID<sup>1</sup>: 0000-0002-8671-5896 ORCID<sup>2</sup>: 0000-0002-5109-1462 ORCID<sup>3</sup>: 0000-0002-0666-3417

<u>To cite to this article</u>: Yargıç A. Ş., Eren B. and Özbay N., "Enhancement of coating features by supporting zinc-based coating with cataphoresis process: effect of acidity and coating thickness on the coating quality", *Journal of Polytechnic*, 27(5): 1761-1772, (2024).

<u>Bu makaleye şu şekilde atıfta bulunabilirsiniz:</u> Yargıç A. Ş., Eren B. ve Özbay N., "Enhancement of coating features by supporting zinc-based coating with cataphoresis process: effect of acidity and coating thickness on the coating quality", *Politeknik Dergisi*, 27(5): 1761-1772, (2024).

<u>Erişim linki (To link to this article):</u> <a href="http://dergipark.org.tr/politeknik/archive">http://dergipark.org.tr/politeknik/archive</a>

**DOI:** 10.2339/politeknik.1199586

# Enhancement of Coating Features by Supporting Zinc-Based Coating with Cataphoresis Process: Effect of Acidity and Coating Thickness on the Coating Quality

# Highlights

- The effective coating method was developed by combining the properties of the cataphoresis coating and the zinc alloy coating.
- The acidity and coating thickness effects on the coating quality of casting materials were investigated.
- Coatings with optimum performance properties were achieved under acidic conditions.

# Graphical Abstrac

The tree diagram of the integration conditions of zinc and cataphoresis coatings and the results of the performance tests for casting materials were displayed in the graphical abstract.

# Combination of Zinc and Cataphoresis Coatings

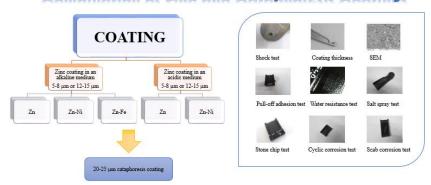


Figure. Conditions of Zinc and Cataphoresis Coatings and Characterization Techniques

#### Aim

In the present study, zinc coatings were applied using various metal additives (nickel or iron) in different environments (acidic/basic), and then cataphoresis coating was implemented over this coating to increase the corrosion resistance of the parts frequently utilized in the automobile sector.

#### Design & Methodology

In the context of the research,, firstly 5-8 µm or 12-15 µm zinc-coating in an alkaline (Zn, Zn-Fe, Zn-Ni) or an acidic (Zn, Zn-Ni) environment, followed by 20-25 µm cataphoresis-coating were implemented on GGG40 casting elements and coating qualities were investigated by various characterization methods. In addition, the zinc-coating thickness and the phosphate-crystal appearance were evaluated in the x-ray diffraction laminography equipment and the scanning electron microscope.

# **Originality**

In this work, a cast material that is often used in the automobile sector was employed to produce cast elements with enhanced corrosion performance at low microns by combining two forms of cost-effective coatings (zinc + cataphoresis).

# **Findings**

According to the characterization data, the tensile strengths were determined by the pull-off adhesion test between 171 and 433 psi. Zinc-coated items' coating levels in alkaline and acidic conditions were found to be between 5.88 and 7.18 µm and 12.10 and 12.96 µm, respectively. It was concluded that the corrosion resistances of the cast parts applied with acid-based zinc and zinc-nickel-cataphoresis coating processes were improved.

#### Conclusion

An industry-guiding study (supported by TUBİTAK-1501 program) was carried out for the coating process of cast materials with high corrosion resistance and adjustable properties for the automotive industry.

# Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

# Enhancement of Coating Features by Supporting Zinc-Based Coating with Cataphoresis Process: Effect of Acidity and Coating Thickness on the Coating Quality

Araştırma Makalesi / Research Article

Adife Şeyda YARGIÇ<sup>1\*</sup>, Bünyamin EREN<sup>2</sup>, Nurgül ÖZBAY<sup>1</sup>

<sup>1</sup>Chemical Engineering Department, Engineering Faculty, Bilecik Seyh Edebali University, Bilecik, Turkey
 <sup>2</sup>Uzman Cataphoresis Surface Coating Industry Trade Inc. NOSAB N.318. St. No:2, Bursa, Turkey
 (Geliş/Received: 04.11.2022; Kabul/Accepted: 12.09.2023; Erken Görünüm/Early View: 06.11.2023)

#### **ABSTRACT**

In this work, a cast material that is often used in the automobile sector was employed to produce cast elements with enhanced corrosion performance at low microns by combining two forms of cost-effective coatings (zinc + cataphoresis). In the context of the investigation, firstly 5-8  $\mu$ m or 12-15  $\mu$ m zinc-coating in an alkaline (Zn, Zn-Fe, Zn-Ni) or an acidic (Zn, Zn-Ni) environment, followed by 20-25  $\mu$ m cataphoresis-coating were performed on GGG40 cast-parts. Ink, hogaboom, shock, pull-off adhesion, water resistance, salt spray, stone impact, cyclic-corrosion, and scab-corrosion performance tests were implemented for characterization. In addition, the zinc-coating thickness and the phosphate-crystal appearance were evaluated in the x-ray diffraction laminography instrument and the scanning electron microscope. The tensile strengths were determined by the pull-off adhesion test between 171 and 433 psi. The coating thicknesses of zinc-coated parts in alkaline and acidic environments were assigned in the range of 5.88-7.18  $\mu$ m and 12.10-12.96  $\mu$ m. Due to the characterization results; it was deduced that the cataphoresis-coating after all zinc-based-coatings under alkaline medium did not afford the required quality and corrosion protection, while cast parts coated under acidic medium before cataphoresis-coating gave appropriate corrosion performance, thus the low-cost coatings could be performed with the eligible properties.

Keywords: Cast materials, cataphoresis coating, corrosion performance, acidic/alkaline zinc-based coatings.

# Çinko-Esaslı Kaplamanın Kataforez Prosesi ile Desteklenerek Kaplama Özelliklerinin Geliştirilmesi: Asitlik ve Kaplama Kalınlığının Kaplama Kalitesine Etkisi

ÖΖ

Bu çalışmada, otomobil sektöründe sıklıkla kullanılan döküm malzeme, uygun maliyetli iki kaplama formunun (çinko + kataforez) birleştirilmesiyle düşük mikronlarda geliştirilmiş korozyon performansına sahip döküm elemanı üretmek için kullanılmıştır. Araştırma kapsamında, GGG40 döküm malzemeleri üzerine önce alkalı (Zn, Zn-Fe, Zn-Ni) veya asidik (Zn, Zn-Ni) ortamda 5-8 μm veya 12-15 μm çinko-kaplama, ardından 20- 25 μm kataforez-kaplama uygulanmıştır. Karakterizasyon için mürekkep, hogaboom, şok, pull-off adhezyon, su direnci, tuz sisi, taş çarpma, çevrimsel-korozyon ve scab-korozyonu performans testleri yapılmıştır. Ayrıca çinko-kaplama kalınlığı ve fosfat-kristal görünümü, x-ışını kırınım laminografi cihazında ve taramalı elektron mikroskobunda değerlendirilmiştir. Çekme dayanımları, 171 ve 433 psi arasında çekme yapışma testi ile belirlenmiştir. Alkali ve asidik ortamlarda çinko-kaplı parçaların kaplama kalınlıkları 5,88-7,18 μm ve 12,10-12,96 μm aralığında ölçülmüştür. Karakterizasyon sonuçlarına göre; alkalı ortam altında tüm çinko-esaslı-kaplamalardan sonra uygulanan kataforez-kaplamanın gerekli kaliteyi ve korozyon korumasını sağlamadığı, buna karşılık kataforez-kaplamadan önce asidik ortam altında kaplanan döküm parçaların uygun korozyon performansı gösterdiği sonucuna varılmış, dolayısıyla istenilen özelliklere sahip düşük-maliyetli kaplamaların yapılabileceği belirlenmiştir.

Anahtar Kelimeler: Döküm malzemeler, kataforez kaplama, korozvon performansı, asidik/alkali cinko-esaslı kaplamalar.

#### 1. INTRODUCTION

In the automotive industry, acidic zinc/zinc-nickel and alkaline zinc/zinc-iron/zinc-nickel procedures are independent processes. The coatings performed with

these processes have positive and negative aspects compared to each other. Therefore, the motivation in the realization of these coatings creates a more economical and new coating process that can be applied to parts of all shapes and sizes, resulting in coatings with good

\*Sorumlu Yazar (Corresponding Author) e-posta: seyda.guler@bilecik.edu.tr properties. Zinc coatings are frequently used for corrosion protection of materials in many structural and broad engineering purposes. These coatings allow for welding and painting, exhibit excellent mechanical qualities on the material, and demonstrate strong corrosion resistance. On the other hand, the usage of zinc coatings is constrained by the rapid rate of dissolution. Passivation techniques including phosphating, trivalent chromium passivation, and silicification can prolong the useful life of zinc coatings. Alloying transition metals like Ni, Co, Sn, and Cr can dramatically increase the qualities of zinc's corrosion resistance [1]. In addition to zinc, magnesium and its alloys are widely used in the automotive and aerospace industries due to their high specific strength and low densities, but their low wear and corrosion resistance limits the industrial use of this material. The corrosion and wear resistance of magnesium alloys can be improved by surface modifications. Gül et al. [2] investigated the Al/Zn/Al<sub>2</sub>O<sub>3</sub> and Zn/Al<sub>2</sub>O<sub>3</sub> coating of WE43 magnesium alloy by cold spray coating method, and as a result, they reported that the wear loss of WE43 alloys decreased by 40% with cold spray coatings compared to the uncoated condition. Due to their outstanding qualities, such as low density, high specific strength, and good deformation ability, aluminum alloys are employed in various industries, the construction, automotive, including aerospace, and defense sectors. When Karacif and Candemir [3] examined the corrosion behavior of the aluminum alloy coated with graphene oxide, they noticed that when the ambient temperature rose, the rate of corrosion of the graphene oxide-coated samples increased and the corrosion resistance declined.

A surface treatment called electrochemical coating involves submerging the material to be coated as an electrode in an electrolysis cell, which is used for the coating process. It is attainable to produce a metal, alloy, cermet, or composite coating on the material surface according to the potential difference utilizing materials transferred from the electrolyte and the counter electrode [4]. In the main automotive industry, a cataphoresis coating is applied to the metal surface as the first coat (primer), as well, the widespread use of cataphoresis coating increases with the development of automotive sub-industries, and different volume sizes (1 ton - 500 tons) are processed as contract manufacturing. After the 2000s, cataphoresis coating has been actively used in industries such as household appliances, furniture, defense, general industry, and agricultural equipment, as well as increasing the capacity day by day. This coating method is the most effective system for protecting metal parts against corrosion as well as extends the life of the

part. Today, approximately 70% of the cataphoresis coating volume used in the world is cathodic cataphoresis coating and this volume is generally used by the automotive industry. The cathodic cataphoresis coating technology has increased the life of the parts used in the automotive industry. There are thousands of patents related to the various cataphoresis coating compositions, processes, and goods coated with cataphoresis coating [5, 6].

Investigations were done on the connections between cataphoresis coating and solvent-based and water-based lamellar coatings, also topcoat coatings used over lamellar coating. Kılınç (2019) evaluated the performance parameters of the coating operation and assessed visually which coating procedures were best. It was observed that the water-based zinc lamellar coating for all the coating tests did not comply with the cataphoresis coating due to the visual appropriateness evaluations and the test results. It was reported that the reason for this performance was the hydrophobic nature of the cataphoresis coating, and the inability to react with the zinc lamellar coating, the solvent of which was water, and could not adhere to the surface covered with cataphoresis [7].

Solvent-based lamellar coating and top coating applications have been applied on alkaline zinc, zinciron, and zinc-nickel coated materials. The desired adhesion (adhesion and tensile adhesion) values of solvent-based lamellar coating applications with Deltaprotekt KL 100 on alkaline zinc, zinc-iron, and zinc-nickel were not achieved. It was determined that this problem could be overcome by increasing the surface roughness and by conducting studies on the wetting angle and contact angle of Deltaprotekt KL 100, which could be applied on alkali zinc/zinc-iron/zinc-nickel [8].

Today, manufacturing high-micron powder paints involves a costly coating procedure and takes a lot of effort during production. The requisite corrosion performance, however, cannot be attained when the zinclamellar, phosphate, zinc, and cataphoresis coatings are performed separately. Cataphoresis coating has been used in various sectors because it can coat extremely complicated objects. After 2010, the acceleration of research on the development of a new coating method that provides high corrosion resistance and high chemical resistance in parts such as key hinge groups, fasteners, and battery fasteners in the automotive sector has been effective for the transfer of this study into the practice. The superiority of this study compared to other studies in the literature was that an effective coating method was developed by combining the properties of cataphoresis coating such as high corrosion, adhesion,

penetration, and the properties of the zinc alloy coating such as chemical resistance, friction coefficient, thin and homogeneous coating thickness. As a consequence of applying cataphoresis coating on acidic Zn/Zn-Ni coatings, it was found in our earlier work that the F899 and F990 hot-forged casting materials had sufficiently strong corrosion performance [9]. Hot-forged casting materials coded F889 and F990 are two distinct materials that generally have different technical properties and application areas. The high mechanical strength, chemical resistance, and electrical characteristics of F889 material are well recognized. In applications requiring high-temperature resistance in the automotive, aerospace, and energy sectors, F889 is a material that is frequently utilized. The F990, on the other hand, draws attention with its electrical conductivity, thermal conductivity, and magnetic properties. Thermal management systems used in electronic circuits and electrical components frequently include the F990 material. Hot-forged casting and regular casting offer special advantages over metalworking needs. Hot-forged casting procedure uses metal that has been heated to a high temperature before it is poured into a mold. High temperatures cause the metal to soften without melting it, allowing forging to shape it. Hot-forged casting often results in more durable, strong, and dense parts. In the standard casting process, metal is heated and liquefied before being poured into molds. Standard casting produces parts that are typically weaker and less dense. Large manufacturing quantities and complicated shapes are better suited for this technology. In the present research, in contrast to studies in the literature, a zinc and cataphoresis coating combination was applied to ductile cast iron type (Spheroidal Graphite Cast Iron), whose code is GGG in the Turkish Standards. GGG is a special kind of iron that receives a special treatment (grafting) with magnesium before casting to give it a particularly strong structure against impact and long life. The ductile iron material grade GGG40 is great, having excellent tensile and yield strength as well as a very high elongation rate. GGG40 has the highest elongation rate among all ductile iron grades since a higher grade will result in a lower elongation. Due to their durability, products made using GGG40 ductile iron are preferred in various industries in the global industrial markets. It is widely utilized in levers, fasteners, brake systems, and connecting rods. The main purpose of the study was that coating the casting material (GGG40) used in the automotive industry with zinc, zinc-iron or zinc-nickel in different thicknesses (5-8 µm or 12-15 µm) under acidic or alkaline environments, followed by the application of cataphoresis coating (20-25 µm), and finally comparing

the durability and corrosion performance behavior of coatings.

# 2. MATERIAL AND METHOD

The zinc and cataphoresis coating processes of the GGG40 cast material widely used in the automotive industry and the characterization methods of the materials were explained in this section. Zinc coatings applied to the samples were coded as alkaline zinc (BZ), alkaline zinc-iron (BZF), alkaline zinc-nickel (BZN), acidic zinc (AZ), and acidic zinc-nickel (AZN).

#### 2.1. Surface Cleaning and Preparation

The degreasing process before the coating was performed to remove the oil on the parts to be sandblasted and to allow better sandblasting. Sandblasting, which was a mechanical cleaning method; was used to make the surface suitable for coating by removing all chemicals that may remain on the metal surface, metal burrs, and rust that may occur before the coating. The samples were degreased and sandblasted before 5-8 µm and 12-15 µm BZ, BZF, BZN, AZ, and AZN coatings. The theoretical and measured parameters of these processes were given in Table 1 [10, 11].

Table 1. Degreasing and sandblasting process parameters

Process	Parameters	Theoretical	Measured
Hot degreasing	Time (min)	1-30	20
	Temperature (°C)	50-85	53
	Concentration (%mL)	3-10	5
Sandblasted	Time (min)	≥10	10

#### 2.2. Zinc and Cataphoresis Coating Processes

BZ, BZF, BZN, AZ, and AZN coatings in the range of 5-8 μm and 12 -15 μm were applied to the parts that were subjected to degreasing and sandblasting processes. In the last step, 20-25 µm cataphoresis coating was applied to the materials that were coated by the zinc-based processes. The letter -C was added to the codes of the casting parts on which cataphoresis coating was applied on zinc-based coatings. The theoretical and measured values of the parameters to be used for zinc-based coating and cataphoresis coating processes were shown in Table 2-4 [11-23]. Table 2 gave general parameters of the preliminary stages of the electrical-ultrasonic-acidic degreasing and neutralization processes with the neutralization, blowing air, and drying oven processes of the zinc based coating process. Table 3 showed the details of several zinc-based coatings, while Table 4 provided the parameters of the cataphoresis coating. The theoretical values in these tables represented the

Table 2. The general parameters for theoretical and measured analysis for zinc coating processes

10 min. 53 °C 5 mL 4.5 A/dm <sup>2</sup>
5 mL 4.5 A/dm <sup>2</sup>
4.5 A/dm <sup>2</sup>
10 min
10 1111111
55 °C
4 mL
8 min.
18 mL
30 sec.
4.7
-
30 sec.
2
2 min.
10 min.
98 °C

Table 3. Theoretical and measured analysis of 5-8  $\mu m$  and 12-15  $\mu m$  coating processes

Process	Parameters	Theoretical	Measured	
riocess	rarameters	i neoi eucai	5-8 µm	12-15 μm
	Time	>3 min for 1 μm	21 min.	45 min.
	Temperature	20-40 °C	2	8 °C
BZ Coating	Zinc	8-15 g/L	9	g/L
	Caustic	110-150 g/L	13	0 g/L
	Current	$1-5 \text{ A/dm}^2$	4 /	A/dm <sup>2</sup>
	Time	>3 min. for 1 μm	21 min	45 min.
	Temperature	20-30 °C	2	8 °C
BZF Coating	Zinc	8-12 g/L	9	g/L
BZI Coating	Iron	50-150 ppm	90	ppm
	Caustic	110-140 g/L	13	0 g/L
	Current	$1-5 \text{ A/dm}^2$	4 /	A/dm <sup>2</sup>
	Time	>3 min. for 1 μm	21 min	45 min.
	Temperature	22-30 °C	2	9 °C
BZN Coating	Zinc	5.5-6.2 g/L	6	g/L
BZN Coating	Nickel	0.7-2  g/L		9 g/L
	Caustic	110-140 g/L	13	8 g/L
	Current	1-3 A/dm <sup>2</sup>	2.5	A/dm <sup>2</sup>
	Time	>3 min. for 1 μm	21 min	45 min.
	Temperature	18-32 °C	30	°C
	pН	4.5-5.5		5
AZ Coating	Total Zinc	30-35 g/L	32	g/L
	Total Chloride	130-170 g/L	150	) g/L
	NH <sub>4</sub> Cl	150-200 g/L	190	g/L
	Current	$4-6 \text{ A/dm}^2$	5 A	/dm <sup>2</sup>
	Time	>3 min. for 1 μm	21 min	45 min.
	Temperature	18-32 °C	31	°C
	pН	4.5-5.5	5	.2
AZN Coating	Total Zinc	30-35 g/L	31	g/L
AZIV Coating	Total Chloride	130-170 g/L	155	g/L
	NH <sub>4</sub> Cl	150-200 g/L	165	g/L
	Total Nickel	1-5 g/L		g/L
	Current	4-6 A/dm <sup>2</sup>	6 A	/dm <sup>2</sup>

conditions to be followed in the processes, and the measured values expressed the actual conditions in the

applied process.

Table 4. Theoretical and measured analysis of cataphoresis coating process

Process	Parameter		Theoretical	Measured
	Time	Time		7 min.
Hot Alkaline Degreasing	Temperature	Temperature		52 °C
	Concentration		3-10 % mL	4 %mL
Activation	Time	Time		45 min.
Activation	pН		8.5-10	9.5
	Time		2-5 min.	3 min.
	Total Acid		17-25 %mL	23 %mL
	Free Acid		0.6-1.1 %mL	1 %mL
	Accelerator		1.5-3 % mL	2.7 %mL
DI 1 C C	Total Fluorine		550-850 ppm	770 ppm
Phosphate Coating	Free Fluorine		50-150 ppm	85 ppm
	Nickel Rate		0.6-1.1 g/L	0.82 g/L
	Zinc Rate		0.6-1.2 g/L	1.1 g/L
	Manganese Ra	Manganese Rate		0.42 g/L
	Iron Rate	Iron Rate		0
	Time	Time		30 min.
Passivation	Titration Point	Titration Point		3.5 %mL
	Conductivity		Max. 900 μS	700 μS
	Time		3-5 min.	3.05 min.
	Solid Amount		14-20 %	16 %
	Ash Amount		1.2-2.5 %	1.7 %
	P/L Rate		0.11-0.16	0.14
0 . 1	Temperature		29-35 °C	32 °C
Cataphoresis		Cataphoresis	5.6-6.1	6
	pН	DI Water Tank	5.5-7.5	6.5
		Cataphoresis	1000-2000 μS	1300 μS
	Conductivity	Anolyte Tank	4000-6000 μS	700 μS
	•	DI Water Tank	10-250 μS	650 μS
Ultrafiltration	Time		1-10 min.	1 min.
	Conductivity		400-1200 μS	1000 μS
	рН		5.6-6	5.8
Curing Orion	Time		>15 min.	62 min.
Curing Oven	Temperature		>155 °C	200 °C

# 2.3. Characterization of Coatings

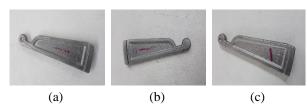
Various characterization processes were carried out to determine the quality and corrosion resistance of the coating processes applied to the cast parts. For this purpose, the results of ink, hogobom, and shock tests were evaluated visually and remarked about the suitability of the coating. Also, the measurements performed by using x-ray diffraction laminography (Helmut Fischer XDL-B XYmZ), scanning electron microscope (SEM, Hitachi TM-1000), pull-off adhesion (DeFelsko), water resistance (Nüve BM 402), salt spray (Vötsch SC1000), cyclic corrosion (Ascott CC1000IP), and scab corrosion (Angelantoni DCTC 1200P) devices were examined.

#### 3. RESULTS AND DISCUSSION

Test results of 5-8  $\mu$ m and 12-15  $\mu$ m *BZ*, *BZF*, *BZN*, *AZ*, and *AZN* coating and cataphoresis coating samples after surface cleaning were examined in detail in this section.

#### 3.1. Ink Test

The suitability of the degreasing process before zincbased coatings was determined by ink test, and test results were shown in Fig. 1. To confirm that the degreasing process is performed effectively, the ink drawn on the part surface must remain in a straight line at the end of the test [24]. It was determined that the 5 min and 15 min degreasing processes applied to the cast material were insufficient, but the 20 min degreasing process passed the test (Fig. 1).



**Figure 1.** Ink test results: (a) 5 min., (b) 15 min., and (c) 20 min. degreasing

#### 3.2. Hogaboom Test

The convenience of the sandblasting process before 5-8  $\mu m$  or 12-15  $\mu m$  zinc-based coatings was controlled by the hogaboom test (Fig. 2). In case the copper in the prepared solution adheres to the metal part surface homogeneously, the sandblasting process is considered to have been performed properly [25]. According to the hogaboom test results, it was specified that while a homogeneous coating could not be obtained in the 5-min. blasting process, the copper ions adhered to the metal surface uniformly due to the smooth surface of the material that was blasted for 10 min. (Fig. 2).



Figure 2. Hogaboom test results: (a) 5 min., and (b) 10 min. blasting process

#### 3.3. Shock Test

With the shock test, the adequacy of the ultrasonic degreasing process applied before 5-8  $\mu$ m or 12-15  $\mu$ m the zinc-based coatings (*BZ*, *BZF*, *BZN*, *AZ*, and *AZN*) was investigated (Fig. 3). The surface of the part should not be swelled and flaking due to adhesion as a result of

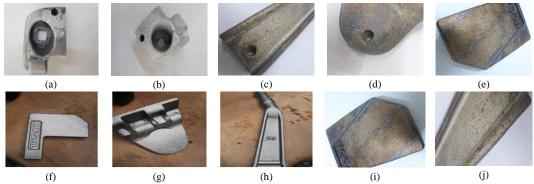
the shock test so that the ultrasonic degreasing process can be accepted [26]. According to the shock test results, it was found that parts that were not subjected to ultrasonic degreasing could not pass the test, conversely, no swelling was observed on the metal surface after 10 minutes of ultrasonic degreasing.

# 3.4. Coating Thickness Measurement on X-Ray Diffraction Laminography Device

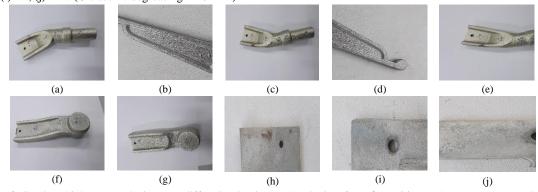
The images obtained during the determination of the zinc coating thickness with the x-ray diffraction laminography device were presented in Fig. 4 and the measurement results were given in Table 5. The coating thickness (coded as "CT") should be between 5-8  $\mu$ m and 12-15  $\mu$ m as desired for the applied zinc-based coating process to be accepted [27].

# 3.5. Phosphate Coating Appearance and Crystal Measurement with SEM

The hiding capability and crystal sizes of phosphate coatings on cast materials to be coated with different thicknesses of *BZ*, *BZF*, *BZN*, *AZ*, and *AZN* techniques were examined by SEM. SEM images were shown in Fig. 5 and measured phosphate crystal sizes were listed in Table 6. In SEM images, the hiding capability was evaluated at a magnification of 1000x, and the size of the phosphate crystals was measured at a magnification of



**Figure 3.** Shock test results: for 5-8  $\mu$ m (a) BZ, (b) BZF, (c) BZN, (d) AZ, (e) AZN, and for 12-15  $\mu$ m (f) BZ, (g) BZF, (h) BZN, (i) AZ, (j) AZN (Ultrasonic degreesing = 10 min.)



**Figure 4.** Coating thickness results in x-ray diffraction laminography device: for 5-8 μm (a) BZ, (b) BZF, (c) BZN, (d) AZ, (e) AZN, and for 12-15 μm (f) BZ, (g) BZF, (h) BZN, (i) AZ, (j) AZN

3000x. The phosphate must cover the entire surface and the phosphate crystals must be 3-6  $\mu$ m in size for a phosphate coating to be accepted [28]. According to the SEM images, the whole surface was covered by the phosphate coatings, and the phosphate crystals were 3.19-5.89  $\mu$ m in size. Therefore, it was concluded that the phosphate coating process was successfully applied to all samples.

#### 3.6. Pull-off Adhesion Test

20-25 µm cataphoresis coating was performed after zincbased coatings were applied to cast materials in five different mediums and two different thicknesses. For these samples, the adhesion of the cataphoresis coating to the zinc coating was examined by pull-off adhesion test (Fig. 6). The cohesion value should not be below 100 psi for cataphoresis coatings to adhere to the zinc coating [29]. According to the pull-off adhesion test results, the adhesion values were between 171-433 psi proved that the adhesion was successfully achieved (Table 7).

#### 3.7. Water Resistance Test

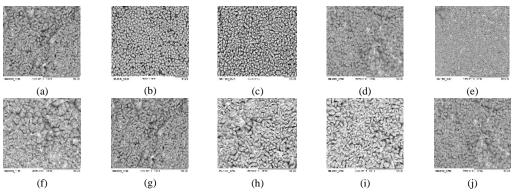
After the cataphoresis coating was applied on zinc-based coatings, a water-resistance test was carried out by following Fiat's specification no 50470 (Fig. 7). According to the water-resistance test, it was specified that the coatings had different adhesion resistance values such as Ad0, Ad1, and Ad2 (Table 8). To approve that the coating has a good quality, the result of the adhesion resistance test should be Ad0 and Ad1 and the coating color should not be changed [30]. Hereunder, most of the

**Table 5.** Coating thickness measurement results (desired coating thickness: 5-8 μm and 12-15 μm, coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coating Type				
	BZ	BZF	BZN	AZ	AZN
5-8 μm	7.18 µm / P	6.17 µm / P	5.98 µm / P	$5.88~\mu m/P$	5.91 µm/P
12-15 μm	$12.77~\mu m/P$	$12.51~\mu m/P$	$12.10~\mu m/~P$	$12.73~\mu m$ / P	$12.96~\mu m/P$

Table 6. Phosphate coating crystal size results (desired crystal size: 3-6 μm, coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coating type (phosphate coating after zinc-based process)						
_	BZ	BZF	BZN	AZ	AZN		
5-8 μm	3.81 µm / P	3.19 µm / P	4.90 μm / P	4.13 μm / P	4.57 μm / P		
12-15 μm	$5.55~\mu m/P$	$5.89~\mu m/P$	$5.10~\mu m/P$	$5.63~\mu m/P$	$5.26~\mu m$ / $P$		



**Figure 5.** SEM analysis results for phosphate crystal appearance (phosphate coatings applied after zinc-based coatings): for 5-8 µm (a) *BZ*, (b) *BZF*, (c) *BZN*, (d) *AZ*, (e) *AZN*, and for 12-15 µm (f) *BZ*, (g) *BZF*, (h) *BZN*, (i) *AZ*, (j) *AZN* 

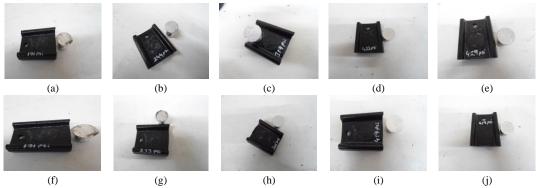
Table 7. Pull-off adhesion test results (desired adhesion> 100 psi, coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coating Type (20-25 µm cataphoresis coating after zinc-based process)				
	BZ-C	BZF-C	BZN-C	AZ-C	AZN-C
5-8 μm	171 psi / P	244 psi / P	317 psi / P	433 psi / P	429 psi / P
12-15 μm	171 psi / P	233 psi / P	305 psi / P	417 psi / P	419 psi / P

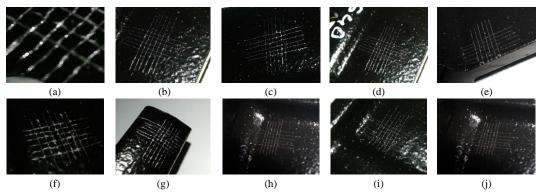
cast samples passed the test, except materials coated with 12-15 µm thickness in *BZ-C* and *BZF-C* techniques.

# 3.8. Salt Spray Test

After the cataphoresis coating was implemented on zincbased coatings, the results of the salt spray test performed by following the specifications numbered ASTM B117 and DIN EN ISO 9227 were shown in Fig. 8. Salt spray test evaluation results were summarized in Table 9. To accept the coatings, there should be no surface defects such as staining, deterioration, cracking, breakage, swelling, flaking, delamination, a rupture in paint adhesion after 500 hours of salt spray test, and also there should be red rust on a maximum 5% of the material's surface [31, 32]. According to the test results, 5-8 µm BZN-C, AZ-C, AZN-C coated cast samples (Fig. 8.c, d, and e) and 12-15 µm AZ-C, AZN-C coated parts (Fig. 8i and j) passed the test. Research in the literature determined that nickel can be utilized as an alternative instead of cadmium [33, 34]. The investigations found that zinc-nickel alloy coatings performed better in terms of quality, and they compared the characteristics of



**Figure 6.** Pull-off adhesion test results: for 5-8  $\mu$ m (a) BZ-C, (b) BZF-C, (c) BZN-C, (d) AZ-C, (e) AZN-C, and for 12-15  $\mu$ m (f) BZ-C, (g) BZF-C, (h) BZN-C, (i) AZ-C, (j) AZN-C



**Figure 7.** Water resistance test results: for 5-8 μm (a) *BZ-C*, (b) *BZF-C*, (c) *BZN-C*, (d) *AZ-C*, (e) *AZN-C*, and for 12-15 μm (f) *BZ-C*, (g) *BZF-C*, (h) *BZN-C*, (i) *AZ-C*, (j) *AZN-C* 

**Table 8.** Water resistance test results (coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coat	Coating Type (20-25 µm cataphoresis coating after zinc-based process)				
	BZ-C	BZF-C	BZN-C	AZ-C	AZN-C	
5-8 μm	Ad1 / P	Ad0 / P	Ad1 / P	Ad0 / P	Ad0 / P	
12-15 μm	Ad2 / F	Ad2 / F	Ad0 / P	Ad0 / P	Ad0 / P	

Table 9. Salt spray test results (coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coating Type (20-25 µm cataphoresis coating after zinc-based process)				
-	BZ-C	BZF-C	BZN-C	AZ-C	AZN-C
5-8 μm	F	F	P	P	P
12-15 μm	F	F	F	P	P

coatings produced using both acidic and basic methods [35, 36].

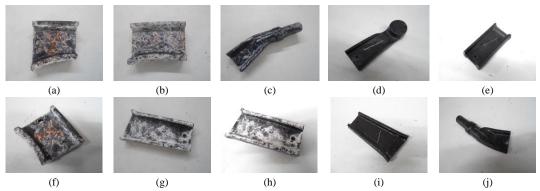
# 3.9. Stone Chip Test

Stone chip test was handled through the specification numbered SAE J400 on cast materials that were coated with cataphoresis method on zinc-based coatings (Fig. 9). According to the stone chip test results given in Table 10, it was determined that the coatings had various surface resistance values as 5B, 5C, 6A, 6B, 6C, 7A, and 7B. The surface resistance must be 6A, 7A, or 7B to pass the stone

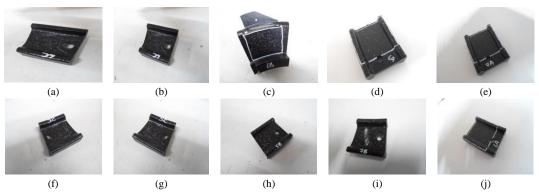
chip test [37]. As a result, 5-8  $\mu$ m *AZ-C*, *AZN-C*, and 12-15  $\mu$ m *AZ-C*, *AZN-C* coated cast specimens (Fig. 9d, e, i, and j) were found to pass the test.

# 3.10. Cyclic Corrosion Test

Cyclic corrosion test was carried out after cataphoresis coating following the specification numbered PV1200 and the results were presented in Fig. 10 and Table 11. After 8 cycles, there should be no surface defects such as swelling, base metal corrosion, a rupture in paint adhesion as a result of the cyclic corrosion test, and the



**Figure 8.** Salt spray test results: for 5-8  $\mu$ m (a) BZ-C, (b) BZF-C, (c) BZN-C, (d) AZ-C, (e) AZN-C, and for 12-15  $\mu$ m (f) BZ-C, (g) BZF-C, (h) BZN-C, (i) AZ-C, (j) AZN-C



**Figure 9.** Stone chip test results: for 5-8  $\mu$ m (a) BZ-C, (b) BZF-C, (c) BZN-C, (d) AZ-C, (e) AZN-C, and for 12-15  $\mu$ m (f) BZ-C, (g) BZF-C, (h) BZN-C, (i) AZ-C, (j) AZN-C

Table 10. Stone chip results (coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coating Type (20-25 µm cataphoresis coating after zinc-based process)				
	BZ-C	BZF-C	BZN-C	AZ-C	AZN-C
5-8 μm	6C / F	6C / F	6B / F	6A / P	7A / P
12-15 μm	5C / F	5C / F	5B / F	7B / P	6A / P

Table 11. Cyclic corrosion test results (coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coating Type (20-25 µm cataphoresis coating after zinc-based process)				
•	BZ-C	BZF-C	BZN-C	AZ-C	AZN-C
5-8 μm	F	F	P	P	P
12-15 μm	F	F	F	P	P

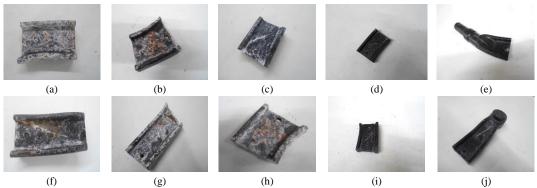
adhesion loss should be d $\leq$ 1.5 mm [38]. From the test results, it was determined that 5-8  $\mu$ m *BZN-C*, *AZ-C*, *AZN-C* coated cast samples (Fig. 10.c, d and e) and 12-15  $\mu$ m *AZ-C*, *AZN-C* coated parts (Fig. 10i and j) passed the test.

#### 3.11. Scab Corrosion Test

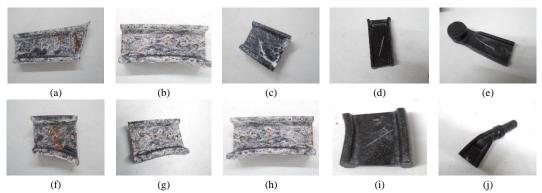
Zinc-based and cataphoresis coated cast materials were subjected to scab corrosion test according to the specification numbered 50488/01 (Table 12). To establish the suitability of the coating, the number of oxidized points is determined as a result of 500 hours scab corrosion test, and the magnitude of the spread corrosion is measured [39]. The test results showed that 5-8 μm *BZN-C*, *AZ-C*, *AZN-C* coated cast samples (Fig. 11.c, d and e) and 12-15 μm *AZ-C*, *AZN-C* coated cast samples (Fig. 11.i and j) were successfully passed the test.

#### 4. CONCLUSIONS

The process of protecting the surfaces of metal and metal alloys against corrosion is of great importance, the aforementioned protection process is carried out with the help of coatings. In the first part of this study, the suitability of degreasing applied to cast parts before sandblasting was examined by ink test. Accordingly, it was revealed that cast parts degreased for 5 and 10 minutes failed the test, whereas all elements degreased for 20 minutes achieved the ink test. The hogaboom test was used to analyze the convenience of the sandblasting process and that 10 minutes of sandblasted cast materials passed the test. The availability of the ultrasonic degreasing process performed before zinc-based coatings was analyzed by shock test and 10 minutes was found to be sufficient. X-ray diffraction laminography device was used to prove that the zinc-based coating thickness of the samples was between 5-8  $\mu m$  and 12-15  $\mu m$ . The cast



**Figure 10.** Cyclic corrosion test results: for 5-8  $\mu$ m (a) *BZ-C*, (b) *BZF-C*, (c) *BZN-C*, (d) *AZ-C*, (e) *AZN-C*, and for 12-15  $\mu$ m (f) *BZ-C*, (g) *BZF-C*, (h) *BZN-C*, (i) *AZ-C*, (j) *AZN-C* 



**Figure 11.** Scab corrosion test results: for 5-8 μm (a) *BZ-C*, (b) *BZF-C*, (c) *BZN-C*, (d) *AZ-C*, (e) *AZN-C*, and for 12-15 μm (f) *BZ-C*, (g) *BZF-C*, (h) *BZN-C*, (i) *AZ-C*, (j) *AZN-C* 

Table 12. Scab corrosion test results (coded as "P" for passed and "F" for failed)

CT of Zn-based process	Coating Type (20-25 µm cataphoresis coating after zinc-based process)				
	BZ-C	BZF-C	BZN-C	AZ-C	AZN-C
5-8 μm	F	F	P	P	P
12-15 μm	F	F	F	P	P

parts coated with phosphate on the zinc-based coatings were analyzed by SEM and it was observed that the coating had the desired appearance and phosphate crystal size were 3-6 µm. In addition, it was determined that phosphate crystals, which allowed the zinc coating and cataphoresis coating to adhere to each other, were horizontal on BZ-coated surfaces and vertical on AZcoated surfaces. In the last stage, cataphoresis coating was implemented on the phosphate coating. According to the pull-off adhesion test results, the adhesion of the cataphoresis coating to the zinc coatings was reasonable for all parts. It was determined that only 12-15µm BZ-C and BZF-C samples under basic environment coatings could not pass the water resistance test. In contrast, all basic environment coatings remained from the stone chip test; all acidic environment coatings and only 5-8 µm BZN-C material passed the cyclic/scab corrosion and salt spray tests. The desired adhesion, impact, and corrosion resistance could not be achieved due to the roughness of the surfaces of the casting parts, the inhomogeneity of the crystals in the alkaline zinc and phosphate coating deposited on these surfaces, and the crystal coverage not being at the desired level. On AZ-coated surfaces, it was observed that performance qualities deteriorated as coating thickness increased, and the required performance tests were only successful when 5-8 µm of nickel-added coating were applied in an alkaline environment. In conclusion, the most practicable coatings to increase the corrosion resistance of casting parts were 5-8 µm and 12-15µm AZ and AZN-C processes. Since the AZN process is a more compelling coating than AZ in terms of cost, cataphoresis coating on AZ can be preferred for the corrosion resistance of cast parts.

# **ACKNOWLEDGEMENTS**

This study was supported as part of the TÜBİTAK 3180632 project carried out by Uzman Cataphoresis Surface Coating Industry Trade Inc., and the authors would like to thank TÜBİTAK and Uzman Cataphoresis Surface Coating Industry Trade Inc.

# DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

#### **AUTHOR CONTRIBUTIONS**

**Bunyamin EREN:** Material preparation and characterization processes were performed. The first draft of the manuscript was written

Nurgul OZBAY: The study was supervised

**Adife Seyda YARGIÇ:** The first draft of the manuscript was written. The study was supervised. All authors contributed to the study conception and design.

#### CONFLICT OF INTEREST

The authors declare no financial or commercial conflict of interest.

#### REFERENCES

- [1] Ganesan S., Prabhu G. and Popov B. N., "Electrodeposition and characterization of Zn-Mn coatings for corrosion protection", *Surface and Coatings Technology*, 238: 143-151, (2014).
- [2] Gül C., Albayrak S.,Çömez N. and Durmuş H., "Al/Zn/Al<sub>2</sub>O<sub>3</sub> and Zn/Al<sub>2</sub>O<sub>3</sub> coatings by cold spray coating method of WE43 magnesium alloy and investigation of its wear behaviors", *Journal of Polytechnic*, 25(4): 1791-1798, (2022).
- [3] Karacif K. and Candemir D., "The effect of environment temperature on corrosion properties of aluminum alloy coated with graphene oxide", *Journal of Polytechnic*, 26(2): 787-794, (2023).
- [4] Yildiz U.T., Varol T., Purcek G., and Akcay S.B., "A Review on the Surface Treatments Used to Create Wear and Corrosion Resistant Steel Surfaces", *Journal of Polytechnic*, \*(\*): \*, (\*).
- [5] Lawrance J. D., "Electroplating Engineering Handbook", 4<sup>th</sup> ed., New York, (1963).
- [6] Zaki N., Frederick Gumm Chemical Company, Inc.; Zinc Alloy Plating, Surface Engineering (Introduction) Volume 5; ASTM.
- [7] Kılınç M., "The investigation of the effect of dublex coating on the corrosion and life test of solvent based and water based flake coating applications on cataphoresis coating", Master Thesis, Eskişehir Technical University, Institute of Science and Technology, (2019).
- [8] Can A., "Examining the effect of duplex coating on corrosion and life testing with solvent based lamelled coating on alkaline and alloy zinc coating", Master Thesis, Eskişehir Technical University, Institute of Science and Technology, (2019).
- [9] Yargıç A. Ş., Eren B., and Özbay N., "Comparison of Coating Conditions for Improving Performance Properties of Hot-Forged Casting Materials", *European Journal of Science and Technology*, (21): 506-517 (2021).
- [10] Ekinoks Kimya Cleanox 1972 TDS, "The application procedure of the strongly alkaline degreasing material used for iron, steel, aluminum, and zinc surfaces in the metal industry and

- automobile industry by dipping and spraying method", (2018).
- [11] Uzman Cataphoresis Surface Coating Industry Trade Inc., "Reports of surface cleaning, zinc and cataphoresis coating procedures", (2019).
- [12] Ekinoks Kimya Alukleen CV TDS, "Surface cleaning procedure of metals and alloys such as aluminum, copper, brass, zamak", (2017).
- [13] Ekinoks Kimya Cleanox E TDS, "Electrolytic degreasing procedure in metal and automobile industries", (2019).
- [14] Eser Kimya ES/FE 36 TDS, "Cyanide-free alkaline zinc-iron plating process", (2017).
- [15] Eser Kimya ES/F1 TDS, "Cyanide-free alkaline zinc plating process", (2017).
- [16] Eser Kimya ES/RKR TDS, "Acidic zinc plating process", (2018).
- [17] Eser Kimya ES/RKR-NI TDS, "Acidic zinc-nickel plating process", (2018).
- [18] Eser Kimya ES/ZN-NI Plus TDS, "Alkaline zinc-nickel plating process", (2017).
- [19] Chemetall Gardobond AP9809 TDS, "Liquid, phosphorous-free pre-treatment for multi-metal applications", (2017).
- [20] Chemetall Gardobond 24T TDS, "A manganese modified low zinc phosphating process for steel and galvanized steel materials", (2018).
- [21] Chemetall Gardolene V 6513 TDS, "Activating prerinsing agent for metal surfaces applied by immersion or spray prior to phosphating", (2017).
- [22] Ppg CP458A TDS, "Electrocoating Process", (2017).
- [23] Ppg Powercon P6200 TDS, "Electrocoating Process", (2018).
- [24] International Standard ISO 8296, "Plastics Film and sheeting Determination of wetting tension", Geneva, (2003).
- [25] NOF Metal Coatings Group, "GEOMET 321/500 Technical manual (EN)", (2017).
- [26] Adhesion Test 50765, "Metallic Material Surface Treatments Electrolytic Plating and Chemical Coating Heat Shock Adhesion Test", (1990).
- [27] International Standard ISO 3497, "Metallic coatings Measurement of coating thickness X-ray spectrometric methods", (2001).

- [28] Volvo car corporation test standard VCS 5740,1049, "Phosphating", (2011).
- [29] ASTM D4541 Standart test method, "Pull-Off Strength of Coating Using Portable Adhesion Testers", (2017).
- [30] Fiat Auto Normazione Material Standart 50470, "Water Resistance Test for Decorations and Paints", (2005).
- [31] ASTM B117 Standart Method, "Salt Spray (Spray) Testing", (1939).
- [32] International Standard DIN EN ISO 9227, "Corrosion tests in artificial atmospheres Salt spray tests", (2006).
- [33] Alzahrany R. A., "Corrosion fatigue behavior of AISI 4340 steel coated with cadmium and zinc-nickel with and without scribed damage in saltwater environment", Thesis, Air Force Institute of Technology, Department of Aeronautics and Astronautics, Graduate School of Engineering and Management (2017).
- [34] Dubent S., Mertens M. L., and Saurat M., "Electrodeposition, characterization and corrosion behaviour of tin–20 wt.% zinc coatings electroplated from a non-cyanide alkaline bath", *Materials Chemistry and Physics*, 120(2-3): 371-380 (2010).
- [35] Louda P., "Applications of thin coatings in automotive industry", *Journal of Achievements in Materials and Manufacturing Engineering*, 24(1): 51-56 (2007).
- [36] Oriti T., "A comparative study of gamma-phase zinc-nickel deposits electroplated from various alkaline and acid systems", NASF Surface Technology of White Papers, 79: 1-16 (2014).
- [37] International Standard SAE J400, "Surface vehicle recommended practice", (2012).
- [38] Test standard PV1200, "Testing of resistance to environmental cycle test (+80/-40) °C" (2004).
- [39] Fiat Auto Normazione Material Standart 50493/04, "Determination of the resistance of organic coatings to the propagation of bubble under skin corrosion (scab in door)".