

Comparison of the Surface and Physical Effects of Chromate and Chromium-Free Processes on Different Color Powder Coatings on Electrostatic Powder Coated 6063 Alloy Aluminum Profiles

Fırat Çetinkaya¹, Bahadır Karaca², Elvan Araz³,
Büşra Boşnakoğlu⁴, Emircan Gök⁵

^{1,2,3,4,5}Department of R&D Center, Zahit Alüminyum San. ve Tic. A.Ş.

ABSTRACT

In this study, the effects of chromated and chrome-free pretreatment tests on the painted profiles of aluminum alloys used in many different fields were compared on different paints. The comparison process and results of chemical, mechanical and dimensional tests applied to painted profiles are discussed. The parameters are considered as paint voltage value 100 V, oven temperature 190 °C and conveyor speed 1.3 m/1. Paint colors were determined as RAL 7016, 9005 and 9016 and were completed with different works only on the front surface treatment. As a result of the experiments, the highest paint thickness value was found to be 106 µ and the highest gloss value was 81.7 GU. The paint drying process for all processes was determined as a 190 °C for 80 minutes. In the discussion section, powder coating processes and experiments are described and compared.

Keywords: Dye process, AA6063 Alloy, Chromate, Chromium Free, Surface Treatment, Foundry

1. INTRODUCTION

Metals have been used for different purposes in many different areas for many years due to their superior metallic properties. The metals used in transportation had to be primarily durable. The impact resistance of metals was quite high, but fuel consumption was quite high due to weight. As a result of the effective material selection studies that will resist the deformations of the buildings caused by gravity, physical factors and time, the most suitable material to be used was determined to be metals [1]. Ships used in overseas transportation had to be built with metals that would resist the corrosive effects of the sea. Metals were mostly used for all structures and vehicles designed to withstand all these factors and last for many years [2]. With the development of the industry and increasing R&D studies in the last century, the physical properties of metals have been increased. Higher performance can be achieved with metals that weight less. These studies, which make metals more useful, were mostly done by combining different metallic properties.

The alloying process combines the properties of different metals in a certain proportion and enables them to be made into a new type of alloy metal. Aluminum is one of the best metals that incorporates the properties of different metals as a result of alloying metals [3]. It is one of the most used metals in industrial studies due to its high mechanical properties, low melting temperature, oxidation resistance, easy shaping and low weight [4]. Aluminum is often used as an alloy. Iron, zinc, magnesium, silicon etc. By being alloyed with elements, it becomes even stronger with the properties of other metals. The most commonly used Aluminum alloy in the construction industry can be determined as 6xxx series alloy. The weldability feature makes it possible to obtain aesthetic and different shaped structures by combining different shapes of aluminum [5]. When examined metallographically, it is known that in 6xxx series aluminum alloys, the alloying elements are distributed homogeneously, and with the mechanical properties it exhibits, undesirable formations at the grain boundaries are low and the grain boundaries become thinner with the Al–Mg–Si–Cu elements present in the alloy [6]. The effect of the elements used in the alloy on the grain structure also directly affects the surface and shaping process of the product being processed. It is known that a well-homogeneous microstructure ensures that the alloy exhibits good resistance during the shaping process and creates a profile that is more prone to the desired shape, and that surface treatments such as painting and anodizing coating to be applied after the shaping process are carried out more appropriately [7].

One of the most commonly used methods of aluminum forming is the extrusion process. The extrusion process is the shaping process of heating aluminum billets and then pushing them into a mold with pressing force. The extrusion process allows the production of different and complex shaped profiles. Thanks to the extrusion process, the production of complex shaped profiles enables the use of aluminum in a wide range of areas in industry [8].

Among the main reasons for the increased use of metal in architectural systems is that they are healthy, durable and long-lasting. Apart from the main reasons, it can be easily shaped and different surface treatments can be applied. Aluminum is a metal that is resistant to oxidation. Naturally, it has a thin oxide layer on its surface. Surface treatments ensure that aluminum increases its oxidation resistance. Anodizing and painting processes are generally applied to aluminum profiles. The anodizing process is done by first etching the surface of the aluminum using chemicals and electric current and then covering the surface with an oxide layer [9].

In the electrostatic powder coating process, the surface is coated with chrome-free or chromate treatment and then coated with the desired painting method and color. Chromium free process is a metal passivation that does not contain the element chromium. Since chromium is a heavy metal, it must be reduced during the process [10]. Profiles coated with Cr^{+6} must be reduced to Cr^{+3} during refining. This reduction process is done during a kind of purification bath [11]. Chromium free process is a passivation that does not contain chromium, unlike chromate. Since it does not contain chromium, it seems to be more environmentally friendly and healthy. For both processes, the surfaces of the profiles can be coated with the bath system and become ready for use, or they can be used for the packaging or painting process.

2. EXPERIMENTAL STUDY

This study includes the examination and evaluation of chromate-free and chrome-free process parameters of RAL 7016, 9005 and 9016 paints after the casting, extrusion and aging processes of 6063 alloy aluminum billet.

2.1 Casting and Homogenization Process

DC casting technique is a type of aluminum casting that includes a direct cooling system. Molten metal flows through a casting path towards a mold table containing different shapes [12]. The casting form for the extrusion process generally takes place in a long cylindrical structure to create billet. Billet formation is achieved by rapidly cooling the molten aluminum shaped under the casting table with water [13].

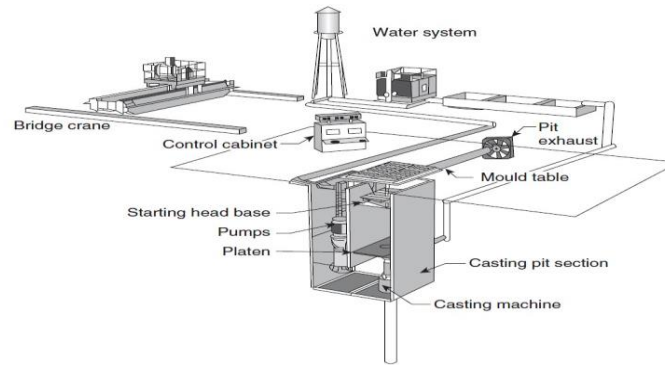


Figure 1. Schematic representation of DC casting

During the billet casting to be examined, the casting process is carried out at 685 °C and 118 mm/s. The aluminum solidification process takes place in 3 stages depending on cooling. During slow cooling, which is the second stage of the process, the billet separates from the mold wall and takes its shape. Titanium doped wires are added to the casting path to ensure that the phase structures are well formed and the grain structure becomes more homogeneous during aluminum casting [14]. The refining effect of elements such as titanium and boron on the grain boundaries of aluminum enables the dendrite structures extending from the center to the grain boundaries to reach the grain quickly and crystallize, resulting in a smaller grain structure. The strength created by billets with small grain structure during the tensile test creates a visible effect [15]. The homogenization process takes place in 4 steps; Heating, holding, annealing and cooling. The time for the billet placed in the oven to reach 590 °C during the heating process was determined as 3.5 hours. After the heating process was completed, the billets were kept at 590 °C for 30 minutes to get used to the upper temperature and prevent recrystallization. The annealing process takes 8 hours. For the cooling process, which is the last stage of the homogenization process, the samples taken from the oven were kept in the cooling cabinet for 3 hours and brought to the appropriate temperature and the homogenization process was completed.

Table 1. EN 573-3 Standard and Sample Analysis Result

EN 573-3	Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
Basic Value	AA6063	0,2-0,6	0,35	0,1	0,1	0,45-0,90	0,1	0,1	Remainder
S-1	AA6063	0,35	018	0,02	0,01	0,58	0,02	0,01	98,65

2.2 Extrusion and Aging Process

The extrusion process carries out the shaping process by passing aluminum billets through steel molds containing a prepared shape by applying force. The extrusion process performs very complex shaping operations [16]. After the foundry and homogenization processes, the sample billet is first heated in billet furnaces up to 550 °C. The mold selected for the sample was heated to 450 °C and then the sample billet

mold was shaped. After the extrusion process, a stretching process was performed to ensure linearity and the sample was cut into 3-meter pieces after providing the appropriate linearity.



Figure 2. Aluminum Profile Sample

As a result of thermal heat treatment, the hardness of the profiles increases. After the heat treatment, the tensile strength, yield strength and hardness values (Hardness Brinell) of aluminum alloys are increased by the aging process [17]. The aluminum profiles, sized after the extrusion process, were then sent to the thermal furnace for aging, including T6 heat treatment. After the heat treatment applied to AA6063 alloys, the values in Table 2 were reached.

Table 2. Mechanical Properties of Sample

EN 755-2	Temper	Rm MPa (Least)	Rp0,2 MPa (Least)	A% (Least)	A50mm % (Least)	HBW (Least)
Basic Value	T6	215	170	8	6	75
S-1	T6	224	188	8	7	78

2.3 Surface Treatments

Another factor that adds value to aluminum profiles is surface treatment. The surface treatments provided protect the aluminum against surface effects that may occur due to atmospheric gases. The surface treatment applied in this study is Electrostatic powder coating. Pre-treatments before painting, which is also the subject of the research article, are chromate and chrome-free treatments [18].

2.3.1 Chromate and Chormium Free Processes

The chromating process is to ensure that the surface of aluminum, which does not have any layer on its surface, reacts in the chromating bath to form a protective layer. The chromating process consists of several different steps [19]. As a first step, the metal surface is cleaned of dirt and other parts before starting the process. It is then placed in a chromate bath, where a reaction occurs on the metal surface and the coating process is expected to be completed. During this process, the concentration of the solution, waiting time and temperature values during the process are very important. After the surface coating process is completed, the aluminum is rinsed again. After the conditioning process, a drying process is

carried out to completely evaporate the water on the piece. The same processes apply to chrome-free surface treatment. A different situation is the content of the passivation solution used [20].

Table 3. Chemical ratio and measurement table used in chromate

1. NaOH (mL)	2. NaOH (mL)	AC 20 (g/L)	AL (max. 5 g/l)	Temperature °C
25	32,4	25	0,6	26

Table 4. Chemical ratio and measurement table used in chrome-free

1. H ₂ SO ₄ (mL)	2. H ₂ SO ₄ (mL)	AlFINAL 275/1	AL (max. 5 g/l)	Temperature °C
7,3	13,2	25,5	0,6	61

With the measurements made, the ideal parameters of the front surface treatments were determined and the percentages used were recorded. The acidic etching pH measurement of the chromate pool was 1.7, and the acidic etching degree of the chrome-free pool was measured as 1.9 pH. In the passivation pool in the chrome-free process, the ALIFICOAT 748/3 value was measured as 5.7 g/L, and the chemical rate of Na₂S₂O₃ in the chromate pool was measured as 10.5 g/L. 10 profiles were used in each front surface treatment process.

2.3.2 Electrostatic Powder Coating

Electrostatic powder coating process is a painting method that involves charging the previously surface-treated profiles with determined electric current levels in a magnetic environment and coating the aluminum surfaces with powder paint with this magnetic effect. The electrostatic powder coating process ensures that the surfaces are resistant to external factors and provides long-lasting permanence [21].

This surface treatment consists of 3 basic parts; Chemical front surface treatment, Powder coating and drying processes. Chemical pre-treatment is a passivation process performed to increase paint adhesion and to protect it from atmospheric gases such as oxygen and hydrogen that can damage the metal surface. After pre-treatment, the profile surface is coated with powder paint. As a final process, the powder paint applied is dried in drying ovens and ensures complete adhesion to the surface [22].

Profiles with and without chrome treated front surfaces were processed with the same parameters. The powder coating process was carried out at 190°C with an electric current of 100 V to electrically charge the profiles and the conveyor speed was 1.3 m/1'.

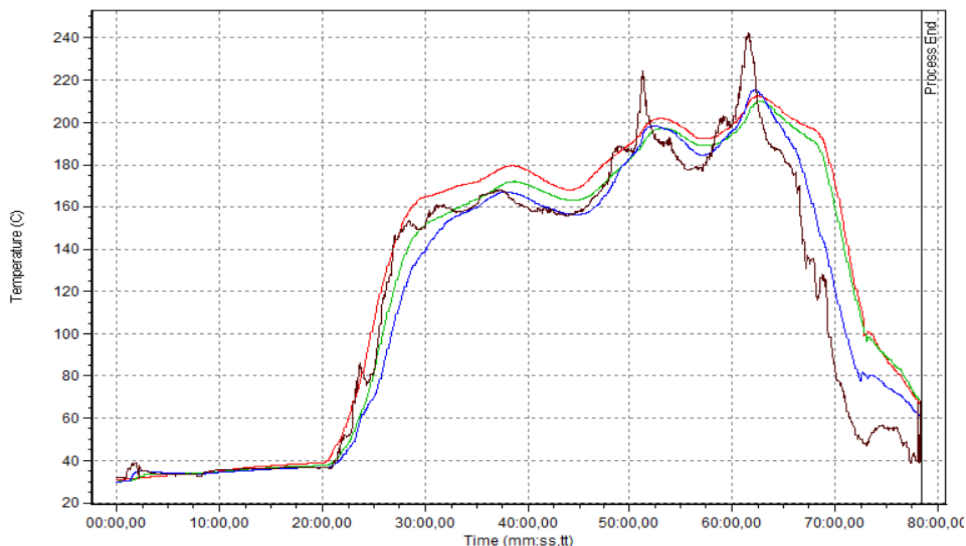


Figure 3. Paint Drying Oven Heat Distribution Chart

Ten samples were painted in one process using a single type of powder paint coating with the same parameters. After the paint coating process, the paint drying process started. It started at room temperature and reached up to 190°C and then dropped back to room temperature. This process took 80 minutes. The use of the paint drying oven and heat distribution were carried out in a regular process, and the heat balance was determined according to periods.

3. RESULTS AND DISCUSSION

In the conclusion part, in order to determine the main purpose of the study and make comparisons, mechanical, paint thickness, gloss, corrosion resistance and physical strength tests were carried out to ensure that the surface treated and painted profiles comply with standard values and to compare chromate and chrome free processes. The test results give us information about the results of chromate and chrome-free processes when the same dye stuff is used.

3.1 Dye Thickness

The painted sample profiles have been completed in accordance with the standard values. The lower thickness value of the profiles was determined as 60 microns. In measuring paint thickness, measurement is made by taking the thickness of the pediment between the upper beginning of the paint layer and the metal layer on which the process is applied [23]. Thickness measurement was made at 32 °C with a device that can measure between 150 - 1000 mm at a speed of 2500/s. Thickness values as a result of the painting process has given on the table 3.

Table 3. Dye thickness values of chromate and chrome free samples

Sample	Chromate (μ)	Chrome-Free (μ)
RAL 9005	96,5	64,4
RAL 9005	94,9	78,9
RAL 9005	95,0	91,4
RAL 9016	75,6	74,9
RAL 9016	85,1	87,2
RAL 9016	97,8	84,8
RAL 7016	77,7	74,1
RAL 7016	74,8	106
RAL 7016	71,4	85,3

3.2 Gloss Values

The gloss value is determined as the reflection rate of the paint process outside the permeable surface of the light hitting the surface. Measuring the amount of light reflected by the surface as a result of the painting process on metals is very important for visible surfaces used in architectural systems [24]. The D65 light source and light with a wavelength of 400 to 700 nm are used in brightness measurement. The paint gloss measurement values made on the samples used in this study are given in table 4.

Table 4. Gloss values of chromate and chrome free samples

Sample	Chromate (Gloss Unit)	Chrome-Free (Gloss Unit)
RAL 9005	25,5	27,4

RAL 9005	21,4	26,9
RAL 9005	27,8	26,6
RAL 9016	75,6	73,4
RAL 9016	72,8	70,5
RAL 9016	75,8	81,7
RAL 7016	27,7	24,4
RAL 7016	25,8	24,1
RAL 7016	24,7	23,7

3.3 Bending Test

One of the biggest reasons why aluminum profiles are used in different sectors is their ability to shape differently. After the surface treatment of the alloys, bending is applied to aluminum profiles to bring them into a different shape. It is expected that the surface treatment applied as a result of the bending process will not be damaged [25]. It is expected that the bending tested profiles will not have any paint breakage or metal surface observed in the bending area. Bending test made by folding aluminum profiles, to which physical force is applied, by 180° using a mechanic.

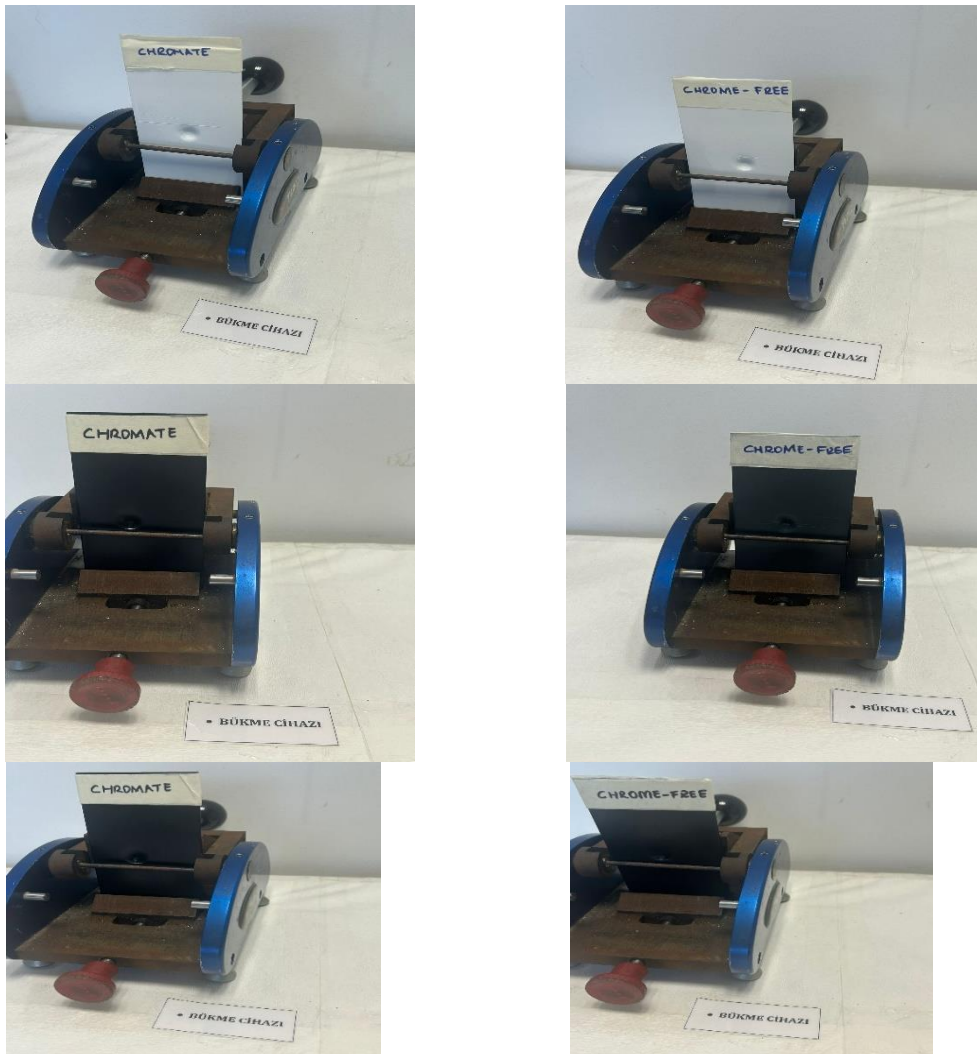


Figure 4. Bending test process

3.4 Crosscut Test

The cross-cut test is measured by the adhesion strength to the surface of the metals to which paint is applied. As a result of this test, a special adhesive tape is placed on the painted profile whose surface is cut diagonally, pressed for a while, and then the tape is pulled from the surface at a 45° angle [26]. After the tape is removed, it is checked whether there is any paint removal from the surface. As a result of the cross-cutting test, it was determined that there was no paint peeling on chrome-free and chromated surfaces.

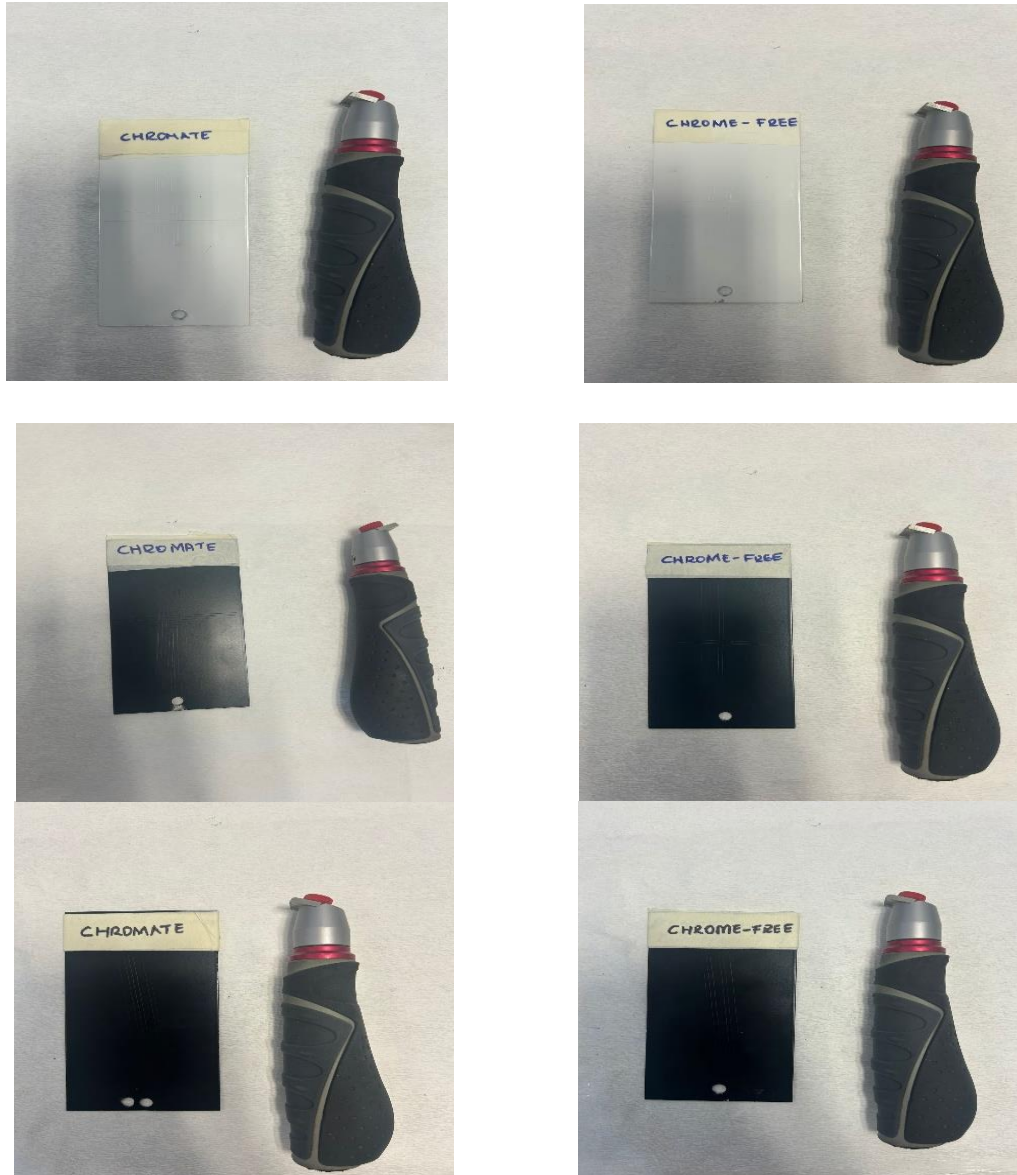


Figure 5. Crosscut Test Results

3.5 Impact Resistance Test

Impact test is very important for metals that are being painted. While physically durable metals can withstand external impacts, the same cannot be said for surface treatments. This situation is measured visually in the paint impact resistance test [27]. Impact resistance test is a destructive test method created

by the free fall of 1 kg weight from a height of 1 meter onto the plates that have been pre-treated and painted. As a result of this test, no separation should be observed in the painted part.

During the testing phase, the weight for the force applied to the painted plate is calculated as the free fall weight. The damage caused by the force must be visible. The test results are shown below.



Figure 6. Impact Resistance Test Process and Results

3.6 Corrosion Test

Corrosion testing is an important factor affecting the service life of the metal. Corrosion can be defined as the effect of metals and alloys on atmospheric gases (oxygen, hydrogen, etc.) and chemicals [28]. In the corrosion test, the surfaces of the painted aluminum profiles were damaged and exposed to aqueous solution containing 5% salt with a pH value of 3.0 - 3.3 Acetic acid solution for 48 hours.





Figure 7. Corrosion Test Results

4. CONCLUSION

In this study, a study was conducted on how chrome-free and chromate coating processes would affect the different powder coating process. By using powder paints of different colors, the paint process parameters, sample alloy and all other processes were kept the same, and the results were examined by making differences only in the front surface treatments. As a result of the tests, the following results were obtained;

1- In paint thickness measurements; It was observed that the highest value in RAL 7016 coded powder paint was 106μ in the profile with chrome-free front surface treatment, 97.8μ in the RAL 9016 chrome front surface treated profile and 96.5μ in the RAL 9005 chromate front surface treated profile. As a result of the thickness examinations, it was determined that the thickness value depends on the powder coating application parameters and the paint, not the preliminary surface treatment.

2- In gloss measurements, it was observed that the profile with the highest gloss in RAL 7016 powder coating was 27.7 GU in the chromate front surface treated profile, 81.7 GU in the RAL 9016 chrome-free front surface treated profile and 27.8 GU in the RAL 9005 chromate front surface treated profile. When the results were examined, it was observed that the difference in the chemicals used in the powder paint, apart from the front surface treatment, affected the gloss level.

3- When the Impact Resistance, Crosscut and Bending tests were examined, no deviation or wear was found on the plates coated with different powder paints and with different front surface treatments. In this case, it has been observed that the chemicals and paint parameters used in the paint increase the paint wear resistance.

4- In accordance with QUALICOAT standards, corrosion should not be observed in the materials painted. When the corrosion test results were examined, no corrosion was observed in the paint process based on chromated and chrome-free pretreatments. It has been determined that the alloy metal and paint chemicals, not the front surface treatment used, affect the corrosion resistance. It is thought that the corrosion resistance of aluminum increases due to the presence of trace amounts of copper elements in the 6xxx series alloy used in the experiments.

5- In wet adhesion tests carried out in accordance with ISO 2409 standard, it was observed that the processes performed on chromate and chrome-free front surface treated profiles affected the adhesion test and ensured that powder coatings did not peel off.

In summary, as a result of the tests performed with the same parameters on the profiles powder coated with chromate-free and chrome-free processes, it was seen that the pre-treatment did not have much effect on the paint distribution and the powder paints used had an effect. It has been observed that the distribution of the applied powder paint on the surface directly affects the paint thickness and gloss values, but does

not affect the mechanical tests and chemical tests. The chemicals present as binders in the paint were thought to be effective for mechanical tests. Chemical tests showed that both the chemicals in the paint and the metallic properties of the elements in the alloy metal were effective.

REFERENCES

1. BARTZ W J. Aluminium materials technology for automobile construction [M]. London: Mech Eng Publ, 1993:1
2. Sielski, R.A., 2008. Research needs in aluminum structure. *Ships Offshore Struct.* 3 (1), 57–65. <https://doi.org/10.1080/17445300701797111>.
3. Das S., Mondal D.P., Sawla S., Ramkrishnan N.; Synergic effect of reinforcement and heat treatment on the two body abrasive wear of an Al–Si alloy under varying loads and abrasive sizes, *Wear*, Vol. 264 (2008): pp. 47–59.)
4. Otarawanna, S., & Dahle, A. K. (2011). Casting of aluminium alloys. *Fundamentals of Aluminium Metallurgy*, 141–154. doi:10.1533/9780857090256.1.14
5. Troeger, L. P., & Starke, E. A. (2000). Microstructural and mechanical characterization of a superplastic 6xxx aluminum alloy. *Materials Science and Engineering: A*, 277(1-2), 102–113. doi:10.1016/s0921-5093(99)00543-2
6. L.P. Troeger 1, E.A. Starke Jr *Materials Science and Engineering: A Volume 277, Issues 1–2*, 31 January 2000, Pages 102-113
7. R. S. Rana, Rajesh Purohit, and S Das (2012). Reviews on the Influences of Alloying elements on the Microstructure and Mechanical Properties of Aluminum Alloys and Aluminum Alloy Composites - Department of Mechanical Engineering, Maulana Azad National Institute of Technology, Bhoapl-462051, India, *International Journal of Scientific and Research Publications*, Volume 2, Issue 6, June 2012 1 ISSN 2250-3153
8. Eraslan Y. (1999) Etial-60 Alaşımında Döküm ve Homojenizasyon Uygulamalarının Ekstrüzyon Kabiliyetine Etkileri, Yıldız Teknik Üniversitesi, Fen Bilimleri Enstitüsü, Doktora Tezi, İstanbul.
9. The oxidation resistance of copper-aluminum alloys at temperatures up to 1,000°C - Research Summary Failure in Structural Materials Published: January 2005 Volume 57, pages 80–84, (2005) - Gabriel Plascencia, Torstein Utigard & Tanai Marín Doi: 10.1007/s11837-005-0068-3
10. Álvarez-Ayuso, E., García-Sánchez, A., & Querol, X. (2007). Adsorption of Cr(VI) from synthetic solutions and electroplating wastewaters on amorphous aluminium oxide. *Journal of Hazardous Materials*, 142(1-2), 191–198. doi:10.1016/j.jhazmat.2006.08.004
11. Becker, M. (2019). Chromate-free chemical conversion coatings for aluminum alloys. *Corrosion Reviews*, 0(0). doi:10.1515/correv-2019-0032
12. As-Cast Residual Stresses in an Aluminum Alloy AA6063 Billet: Neutron Diffraction Measurements and Finite Element Modeling Published: 05 October 2010 - Volume 41, pages 3396–3404, (2010)
13. Toptan, F., Kilicarslan, A., Karaaslan, A., Cigdem, M., & Kerti, I. (2010). Processing and microstructural characterisation of AA 1070 and AA 6063 matrix B4Cp reinforced composites. *Materials & Design*, 31, S87–S91. doi:10.1016/j.matdes.2009.11.064
14. AA6063 and AA6951 Aluminum Alloy Billet Casting Parameter and Heat Treatment Optimization, Firat Cetinkaya, Bilgehan Tunca, Bahadır Karaca, Anıl Demirci, DOI: 10.36948/ijfmr.2023.v05i04.5865

15. Tunca B., Yüksek Lisans Tezi, “8 inch AA6063 Billet for DC Casting Process with Simulation Program Casting Billet Mold Design and Production”, Adana Alparslan Türkeş Bilim ve Teknoloji Üniversitesi, Fen Bilimleri Enstitüsü, Nanoteknoloji ve Mühendislik Bilimleri Ana Bilim Dalı, 2020
16. A Review on Recycling Aluminum Chips by Hot Extrusion Process - Ab Rahim , M.A. Lajis , S. Ariffin - DOI: 10.1016/j.procir.2015.01.013
17. Chen, J., Zhen, L., Yang, S., Shao, W., & Dai, S. (2009). Investigation of precipitation behavior and related hardening in AA 7055 aluminum alloy. *Materials Science and Engineering: A*, 500(1-2), 34-42.
18. Innovative Method to Reduce Process Costs in the Field of Electrostatic Powder Painting Doi: 10.1016/j.promfg.2020.03.008 - Boer Jozsef , Petruta Blaga
19. Corrosion Inhibition of Aluminum and Aluminum Alloys by Soluble Chromates, Chromate Coatings, and Chromate-Free Coatings - M. W. Kendig; R. G. Buchheit – DOI: 10.5006/1.3277570
20. Formation and characterisation of a chromate conversion coating on AA6060 aluminium - O. Lunder , J.C. Walmsley , P. Mack , K. Nisancioglu Received 15 August 2003; accepted 24 August 2004 Available online 22 October 2004 - doi:10.1016/j.corsci.2004.08.012
21. Improving an Electrostatic Powder Coating Process via Signal to Noise Response Surface - Pongchanun Luangpaiboon Department of Industrial Engineering, Faculty of Engineering, Industrial Statistics and Operational Research Unit, Thammasat University, Pathumthani, 12120 Thailand - *American Journal of Applied Sciences* 7 (11): 1521-1527, 2010 ISSN 1546-9239
22. Investigation of the trivalent-chrome coating on 6063 aluminum alloy - Hui-cheng Yu, Bai-zhen Chen, Xichang Shi, Xiliang Sun, Bin Li School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China (2007)
23. Application of experimental design for AA6351 aluminum alloy anodization and coloring - Guilherme José Turcatel Alves DOI 10.1088/2053-1591/aae347
24. Aluminum Structures: A Guide to Their Specifications and Design - J. Randolph Kissell, Robert L. Ferry (2002)
25. Tensile and bending properties of AA5754 aluminum alloys - J. Sarkar , T.R.G. Kutty [https://doi.org/10.1016/S0921-5093\(01\)01226-6](https://doi.org/10.1016/S0921-5093(01)01226-6)
26. Direct metallization of PMMA with aluminum films using HIPIMS - R. Bandorf , S. Waschke <https://doi.org/10.1016/j.surfcoat.2015.10.070>
27. Experimental and numerical investigation of impact resistance of aluminum–copper clad sheets using an energy-based damage model - M. R. Saeedi, M. R. Morovvati & B. Mollaei-Dariani (2020)
28. Role of Chemical Composition in Corrosion of Aluminum Alloys - Lenka Kuchariková ,Tatiana Liptáková ,Eva Tillová ,Daniel Kajánek and Eva Schmidová (2018)