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Research Article

Effect of Different Passivation Treatments on Alkaline Zn-Ni Coatings: Corrosion Resistance and Adhesion Performance of Geomet 321 and ML Black Coatings

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Abstract

This study aims to improve the corrosion properties of (AISI 1040) materials used in the automotive industry. For this purpose, two different coating techniques were applied to the same surface. As part of the research, different passivation processes (transparent, blue, yellow, and black) were applied to alkaline Zn-Ni coatings. Geomet 321 and Geomet ML Black coatings were deposited on the passivation layer to form a double-layer coating. In order to investigate the adhesion and corrosion effects of these coatings, a dry adhesion test, a water test, a humidity test, and a salt spray test were carried out, and cross-cut adhesion tests were carried out after each corrosion test. After all these tests, rust formation was analysed by visual analysis, and atomic weight percentages and coating thicknesses were examined by X-ray. The transparent passivation after the Zn-Ni coating fully satisfied both adhesion and corrosion protection requirements for 321 and ML Black coatings. No red rust formation was observed on the coating samples after the test; only partial white rust formation was observed, and no peeling of the coating layer was detected in the adhesion tests. As a result, the optimum result of the passivation processes used for Geomet 321+ML Black coatings applied after the Zn-Ni + passivation process was obtained with transparent passivated Zn-Ni coatings. Even after 1200 hours, no red rust was observed in passivated Zn-Ni coating+ Geomet 321+ Geomet ML Black.

Keywords: Zinc-Nickel, Passivation, Geomet, Zink Flake, Corrosion

Farklı Pasivasyon İşlemlerinin Alkali Zn-Ni Kaplamalara Etkisi: Geomet 321 ve ML Black Kaplamaların Korozyon Direnci ve Yapışma Performansı

Özet

Bu çalışma, otomotiv endüstrisinde kullanılan malzemelerin (AISI 1040) korozyon özelliklerinin iyileştirilmesi amaçlanmıştır. Bu amaçla aynı yüzeye iki farklı kaplama tekniği uygulanmıştır. Araştırma kapsamında Alkali Zn-Ni kaplamalara farklı pasivasyon işlemleri (şeffaf, mavi, sarı ve siyah) uygulanmıştır. Pasivasyon tabakası üzerine Geomet 321 ve Geomet ML Black kaplamalar ile kaplanarak; çift katmanlı bir kaplama tabakası oluşturulmuştur. Bu kaplamaların yapışma ve korozyon etkilerini incelemek için kuru yapışma, su, nem ve tuz püskürtme testleri gerçekleştirilmiş ve her bir korozyon testinden sonra Cross Cut Çapraz kesme testleri yapılmıştır. Tüm bu testlerden sonra kırmızı ve beyaz pas oluşumu görsel analiz ile, atomik ağırlık yüzdeleri ve kaplama kalınlıkları ise X-ray ile incelenmiştir. Zn-Ni kaplamada uygulanan şeffaf pasivasyon, 321 ve ML Black sonraki uygulanan kaplamalar için hem yapışma hem de korozyon koruma gereksinimlerini tam olarak karşılamıştır. Testten sonra kaplama numunelerinde kırmızı pas oluşumu gözlenmedi; sadece kısmi beyaz pas oluşumu gözlendi ve yapışma testlerinde kaplama katmanında sıyrılma tespit edilmemiştir. Sonuç olarak, Zn-Ni + Pasivasyon işlemi sonrası uygulanan Geomet 321+ML Black kaplamaları için kullanılan pasivasyon

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işlemlerinden optimum sonuç; şeffaf pasifleştirilmiş Zn-Ni kaplamalar ile elde edilmiştir. 1200 saat sonunda bile kırmızı pas gözlenmemiştir.

Anahtar kelimeler: Çinko-Nikel, Pasivasyon, Geomet, Çinko Flake, Korozyon,

1. Introduction

The most common metals used in the automobile industry include steel, iron, and aluminium. Each metal has unique properties that make it ideal for different automotive parts. Their low resistance to corrosive environments limits some of their uses. Corrosion that starts at a tiny point on the surface of the metal progresses to the inner parts of the metal over time, and rusting occurs. This reduces the service life of the metal. Corrosive wear resistance can be increased by coating the metal with different techniques (galvanizing [1], hot dip [2], electrodeposition [3], electroless [4]).

Zinc plating is widely used to protect materials used in structural and engineering applications. These coatings provide good corrosion resistance as well as good mechanical properties for the material. On the other hand, a high dissolution rate limits the applications of zinc coatings. The life of zinc coatings can be extended by phosphating and passivating with trivalent chromium (Cr^{+3}). The corrosion resistance of zinc can be significantly improved by alloying with transition metals such as Ni, Co, Sn and Cr [5].

Zinc is a silver-white metal that is soluble in acid and alkaline solutions and is brittle at room temperature. Zinc carbonate may form on the zinc surface with humid air and this slowing down corrosion [6], [7]. The standard electrode potential of zinc is -0.762 V, which is more negative than iron (-0.447 V) [6]. Therefore, zinc is used as anode dissolution to protect the steel substrate from corrosion [8] [9]. Zinc coating thicknesses of 6-12 µm are sufficient in dry weather conditions, whereas zinc coating thicknesses of 15-20 µm are required in humid conditions [10]. Zinc plating baths can be basically divided into two categories as cyanide and non-cyanide baths. Cyanide zinc solutions have a faster and better dispersion capacity on the surface. However, cyanide is toxic and dangerous for human health [11]. Therefore, cyanide-free baths are preferred for obtaining zinc thin films. Chloride zinc technology is a typical type of cyanide-free zinc coating with many advantages [12]. Some researchers have investigated using chloride zinc technology to make zinc thin films [13]. Weak acid electrolytes give deposits with the desired nickel content (about 12-17% Ni) with high current efficiency, but the dispersion of the plated metal is poor. In contrast, alkaline processes are less efficient but give more uniform plating, and the baths are non-corrosive [14]. Essential alkali baths usually contain Zn and Ni ions, an alkali metal hydroxide, and a complexing agent for nickel. In addition, brighteners and carrier chemicals are also used.

Zinc coatings are subjected to passivation treatment after coating because of their poor corrosion resistance in aggressive environments such as acid and alkaline. The chromate passivation process is widely used to further improve the corrosion resistance of zinc coatings. After passivating, an intensive film can be formed on the surface of the zinc plating to improve its corrosion resistance. The zinc surface has been passivated to prevent fingerprints and to enhance the surface. McLaren et al. reported in detail the passivation technology of +6 valence chromium for zinc [15]. However, due to its toxicity, hexavalent chromium used in passivation is restricted in many industrial sectors. Trivalent chromium is like hexavalent chromium in many ways, but its toxicity is only 1% of that of hexavalent chromium [14]. During the passivation process, zinc begins to dissolve by anodic dissolution, and a reaction occurs between zinc and chromate ions. During the passivation process, zinc begins to dissolve by anodic dissolution and a reaction occurs between zinc and chromate ions. As a result of this reaction, zinc forms a barrier layer called zinc chromate, which is resistant to moisture and air [16]. Water is absorbed when the passivation layer is scratched or mechanically damaged, and the damaged area is repaired [17]. The zinc chromate layer prevents anionic oxidation of the substrate surface by preventing interaction with oxygen, thus supporting the durability and longevity of the zinc coating. Zn^{2+} and Cr^{3+} hydroxide precipitates can be obtained at higher interfacial pH, which directly contributes to forming the dense passivating layer. The trivalent chromium passivation of zinc can be broadly categorized into transparent, blue, yellow, black. The trivalent chromium passivation of zinc can be broadly categorized into transparent, blue, yellow, black. There is a great demand for the development of trivalent chromium passivation technology for zinc coating with the development of environmental protection. However, the component of trivalent chromium passivation solution is more complex and less stable compared to hexavalent chromium passivation solution [18]. Cr^{+3} passivation baths are organic (resin), or inorganic (silicate) based.

This study investigated trivalent chromium transparent, blue, yellow, and black passivation technology to improve the corrosion resistance of Zn-Ni coatings. In addition, non-passivated Zn-Ni coating samples were produced for comparison. Then, organic lamellar zinc coatings were made on passivated and non-passivated coatings. Alkaline zinc-nickel alloy coating, Geomet 321 and ML Black processes are applications to improve corrosion performance. This study will test Alkali Zn-Ni alloy coating + Geomet 321, and Alkali Zn-Ni alloy coating + ML Black, and their effects on corrosion resistance will be investigated. For this research, five different tests were carried out: Crosscut (dry adhesion), moisture resistance, water resistance and salt spray.

2. Materials and Methods

Zinc alloy coating produced were carried out to investigate the effect of different passivation applications on the corrosion resistance of zinc alloy coatings. Geomet 321 and Geomet ML Black coatings were produced after the passivation process was applied on the zinc coating surface, aiming to improve the tribological properties. This study used 10x15 cm sheet plates (AISI 1040) as coating substrate. Coating bath and parameters are presented in Table 1. After the coating baths were prepared, analyses were performed, and the coating procedure was started according to the positive analysis results. The analyses are presented in Table 3. A model of the coating layers is presented in Figure 1 and the process flow in Figure 2. Each of the coatings was carried out in 100 L baths.

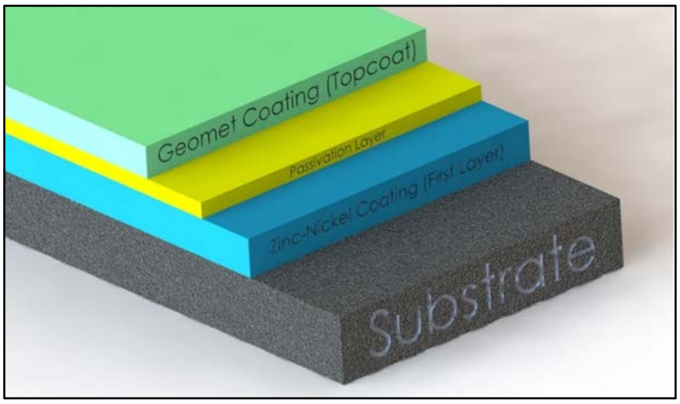

Figure 1. Coating layer model.

Firstly, metal materials were subjected to pre-treatment procedure and Zn-Ni alloy coatings were applied on them. Twenty-five pieces of Zn-Ni were coated with a 5-10 µm coating thickness. After coating, five pieces each of non-passivated, transparent, blue, yellow, and black passivated coatings were produced and the effects of passivation on the adhesion strength and corrosion properties of Geomet 321 and Geomet ML Black coatings were investigated in detail.

Table 1. Concentration of Zn-Ni coating bath.

BATH VOLUME	**BATH CHEMICALS CONCENTRATION**				
	Potassium Hydroxide (caustic)	ZnO (Zinc Oxide)	A Plus (Support)	B Plus (Nickel Feed)	C Plus (Polisher)
100 L	17 kg	1 kg	8 L	1,2 L	0,5 L
BATH PARAMETERS					
Temperature (℃)			25-35 **(Should not exceed 35 ℃)**		
Time (min.)			20		
Current (A/dm^2)			6		

In general, zinc coatings produced in high temperature baths were operated at room temperature (maximum 35 ℃) since some problems such as surface roughness were encountered. The type of passivation processes applied after coating and the number of samples produced are presented in detail in Table 2. Geomet 321 and ML Black coatings were applied to the Zn-Ni coating surfaces after passivation process.

Table 2. Counts of passivation and samples performed after Zn-Ni coating.

PASSIVATION	**SAMPLE QUANTITY (Zn-Ni)**
Non-Passivation	5
Transparent Passivation	5
Blue Passivation	5
Yellow Passivation	5
Black Passivation	5
	TOTAL **25**

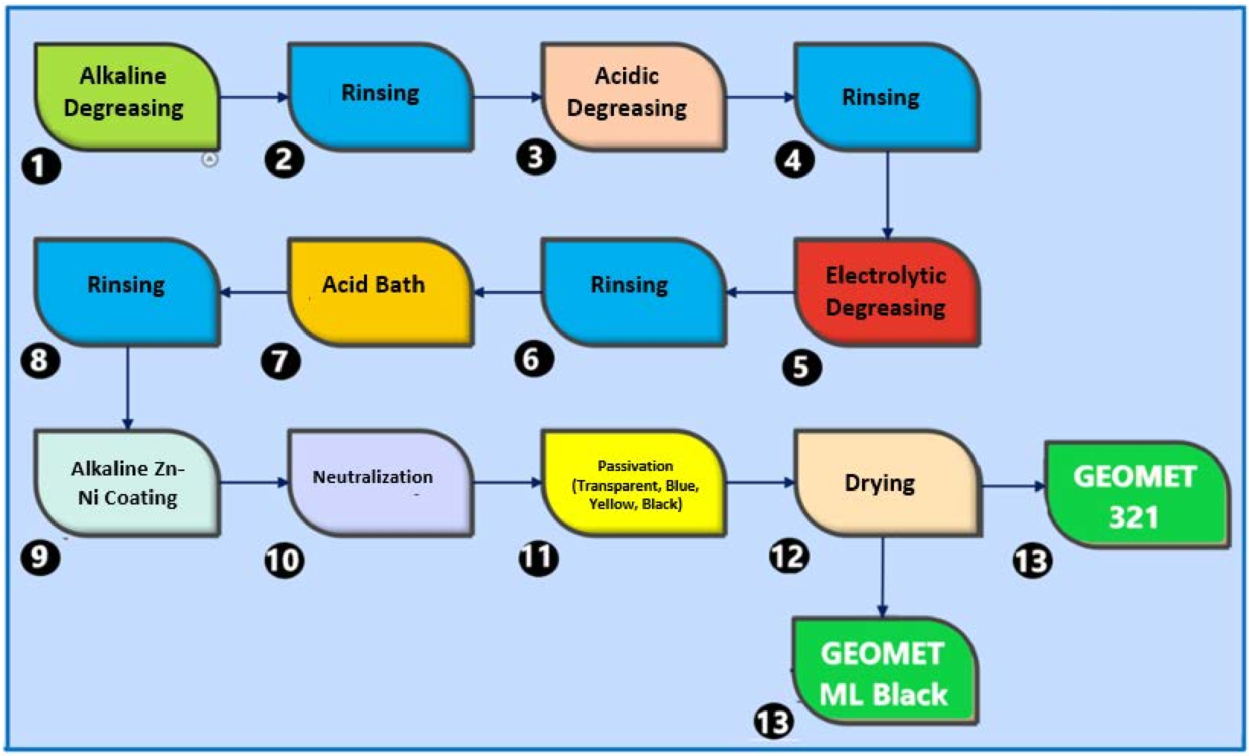

Figure 2. Production flow card.

Alkaline, acidic, and electrical degreasing processes were carried out to remove impurities on the sample surface before coating. The alkaline degreasing bath consisted of chemicals containing powder caustic and surfactant, and the procedure was carried out at 60 °C for 15 minutes. After rinsing, acidic degreasing was used to remove rust from the metal surface. The acidic degreasing bath consisted of sulphuric, hydrofluoric, and nitric acid. Acidic degreasing was carried out for 15 seconds at room temperature. The samples were rinsed again, and the electrical degreasing (alkaline) procedure with surfactant was started. In cathodic cleaning, the sample to be cleaned is connected as a cathode and current is passed in the electrolyte. The hydrogen gas generated by the current is scrubbed and stirred, and the sample surface is cleaned in detail. The samples were rinsed again and immersed in a hydrochloric solution at 31% concentration. At this point, dilute acid was used to neutralize the surface of the substrate. After final rinsing, alkaline Zn-Ni plating was started, which concentration and parameters are given in Table 1. After coating, the neutralization process was carried out. This process is applied to reduce the effect of chemicals remaining from the coating bath on the surface of the material, to clean the residues, to prevent oxidation and to maintain the pH balance on the surface. After rinsing, it was neutralized with a 5-6% weak acid to neutralize the alkalinity completely.

Once the concentration and convenience of the contents were achieved, the coating processes were carried out by pre-treating the sample in Figure 2. The baths prepared before coating were analysed using the methods given in Table 3. The amount of caustic must always be much higher than the amount of ZnO. Because this caustic content, which is more than the amount required to react with zinc oxide, prevents zinc oxide from precipitating. In the cyanide-free method, the reduction of Zn^{+2} ions occurs after this reaction chain. The amount of zinc and caustic is determined according to the bath volume. The amount of zinc oxide (ZnO) should be between 5 and 10 g/L, while the amount of sodium hydroxide (NaOH, caustic) should be between 120 and 140 g/L. The zinc oxide is dissolved by the heat given off by the caustic. This solution is added to the bath after cooling. Organic substances are added during the cooling phase and the bath volume is completed. At this stage the presence of free Zn^{+2} ions in the solution are important for the plating process. Especially in a cyanide-free process, the reduction of Zn^{+2} ions takes place in the last step of this reaction chain.

Table 3. Analyses performed in the baths prepared before coating.

ALKALINE Zn-Ni BATH ANALYSIS	**1.)** Add 5 mL zinc bath solution to 100 mL distilled water. **2.)** Add 35 mL of pH 4,2 buffer solution. **3.)** Add 3-5 drops of Xylenol orange indicator. **4.)** Titrated with 0,1 M EDTA until the color changed from red to yellow. **5.)** The consumption is obtained by multiplying by 1,31.
ALKALINE Zn-Ni CAUSTIC ANALYSIS	**1.)** Add 5 mL zinc bath solution to 100 mL distilled water. **2.)** 20 mL $BaCl_2$ solution is added in solution. **3.)** 3-5 drops of phenolphthalein indicator are added. **4.)** Titrate with 1 N HCl until the pink colour disappears. **5.)** The consumption is obtained by multiplying by 8.
ZINC ALKALINE DEGREASING BATH ANALYSIS	**1.)** Add 2 mL of electrolyte from zinc bath to 50 mL of distilled water. **2.)** Add 2-3 drops of methyl rhodamine indicator. **3.)** Titrate with 0,1 N HCl. The colour changes from orange to red. **4.)** The consumption is obtained by multiplying by 0,27.

Passivation has been applied to prevent fingerprints and improve properties on zinc coated surfaces, to give the surfaces a decorative appearance and to increase the corrosion resistance of the coating. Passivation is the process of depositing a protective chromate layer on metal. Zinc chromate layer is formed by anodic dissolution of zinc and reaction of zinc and chromate ions. The conversion of oxygen to anion oxide inhibits electrochemical phenomena and increases corrosion protection [19]. Passivation baths are chromium based and Cr^{+3} ions are used in the baths. The use of Cr^{+6} ions is banned in many industries due to their toxicity to nature. [20]. The passivation layer has decorative colours according to the applied formulation. In addition, transparent, blue, yellow, and black colored protection layer can be applied to this layer to increase corrosion resistance. These protection baths are organic (resin) or inorganic (silicate) based. During this process, the metal surface is made in an acidic or basic solution. This solution dissolves the oxide layer on the surface and forms a more durable passivation layer. The bath parameters of all passivation processes are presented in Table 4. As a final process after passivation, drying was carried out for 10 minutes at 80 °C.

Table 4. Passivation types and applied parameters.

PASSIVATION TYPE	TEMPERATURE (°C)	TIME (Sec.)	PH	Cr CONCENTRATION (g/L)
Transparent	28	30	1,5-2	0,80 - 1,01
Blue	28	60	1,5-2	1,1-3
Yellow	Room Temperature	60	1,8-2	9-11
Black	28	40	1,8-2	1,2-1,4

Carbonates, which cause a decrease in the conductivity of the solution, increase in the solution with the temperature of the solution and the stirring of the solution, which causes an inhibition of the electroplating process. The acceptable amount of carbonates in the solution varies between 50 and 100 g/L, which is the usual range of the amount of CO_2 absorbed from the air. There are many methods of precipitating and removing carbonates from the solution. The first technique is to cool the solution down to 5 - 10 °C until the carbonates freeze and then to filter the carbonates out of the solution. A less commonly used method is to precipitate the carbonates with calcium hydroxide [19]. The effect on the corrosion resistance of Geomet 321 and ML Black coatings produced after different passivation treatments for Zn-Ni coatings was investigated.

3. Results and Discussions

All the passivation types described were applied after Zn-Ni plating and the surface images are shown in Figure 3. When the surface images are examined, the presence of passivation formed after Zn-Ni coating can be clearly observed on the surface. The layer thicknesses and atomic distributions (%) obtained by X-ray after passivation are given in Table 5. Considering the atomic weights and layer thicknesses, the %Ni ratio of the non-passivated layers is lower compared to the passivated layers. It can be said that the %Ni ratio is maintained after passivation. While the thickness of the non-passivated layer was 6.7 µm, the thickness of the transparent, the blue and the yellow passivated layers increased, respectively. For the black passivation, the film thicknesses decreased again. When Table 4 is analysed can be said that the amount of Cr in the bath and the passivation times are effective.

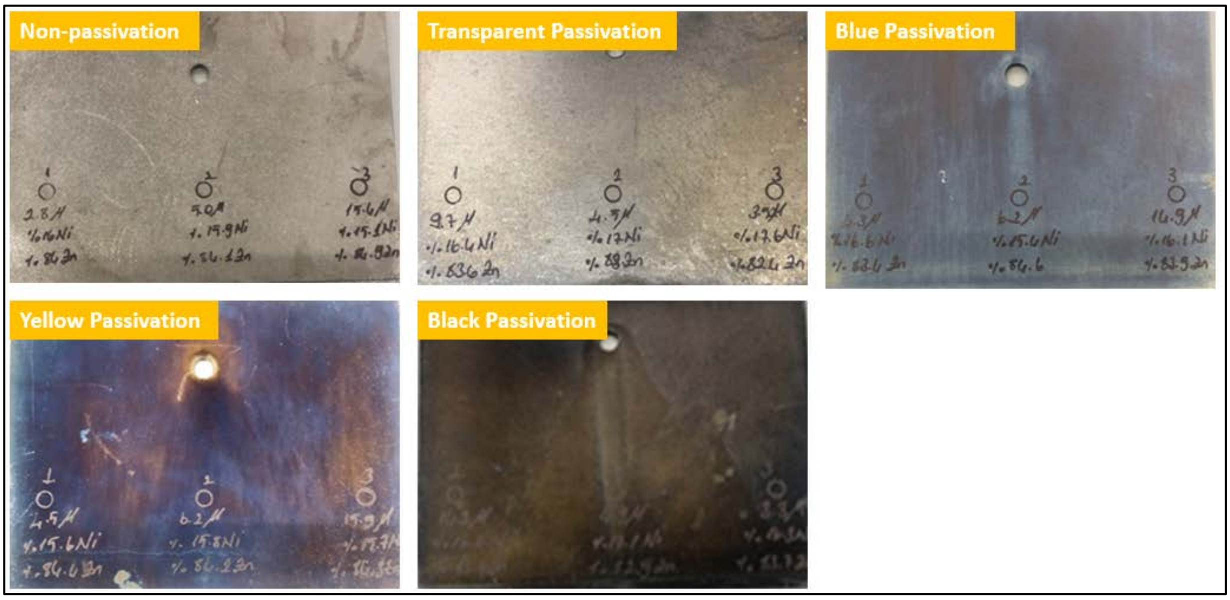
Non-passivation
Transparent Passivation
Blue Passivation
Yellow Passivation
Black Passivation

Figure 3. Surface images of different passivation layers applied after coating.

Table 5. Coating thickness and (%) atomic weight obtained after passivation with X Ray device.

PASSIVATION TYPE	% Ni	% Zn	COATING THICKNESS (μm)
Non-passivation	15,7	84,3	6,7
Transparent	15,8	84,2	7,8
Blue	16	84	8,5
Yellow	17,1	82,9	8,9
Black	16,6	83,4	7,6

For zinc-nickel alloy coatings, the nickel ratio in the alloy should be between 15-16%, above 16% the cathodic protection effect is reversed, and an anodic corrosion effect is caused. In other words, an alloy ratio greater than 16% will cause the coated part to show red rust in a much shorter time than expected [21]. The following coding system has been used to facilitate understanding of the coatings in the text and images.

Table 6. Coding system of produced coatings.

CODE		CODE	
Zn-Ni-321	Zinc Nickel + Geomet 321 (non-passivation)	**Zn-Ni-ML**	Zinc Nickel + ML Black (non-passivation)
Zn-Ni-Transparent-321	Zinc Nickel + Transparent Passivation + Geomet 321	**Zn-Ni-Transparent-ML**	Zinc Nickel + Transparent Passivation + ML Black
Zn-Ni-Blue-321	Zinc Nickel + Blue Passivation + Geomet 321	**Zn-Ni-Blue-ML**	Zinc Nickel + Blue Passivation + ML Black
Zn-Ni-Yellow-321	Zinc Nickel + Yellow Passivation + Geomet 321	**Zn-Ni-Yellow-ML**	Zinc Nickel + Yellow Passivation + ML Black
Zn-Ni-Black-321	Zinc Nickel + Black Passivation + Geomet 321	**Zn-Ni-Black-ML**	Zinc Nickel + Black Passivation + ML Black

When a zinc-coated part starts to oxidize, it is first covered with a white layer for when consist of white zinc oxide (ZnO) [22]. After all the zinc has been oxidized, the iron begins to oxidize, and its color becomes red [23]. Therefore, the white rust resistance defines the performance of the passivation layer, and the red rust value defines the performance of the zinc layer. Most red rust metals (Fe_2O_3) occur as compounds in nature. Metals or alloys are formed by adding materials to these compounds. These formed metals or alloys tend to return to their stable state, the compound state.

After the preparation of the organic zinc lamellar coatings, the weights of the coatings were measured with an X-ray and the results of the weights of the coatings with different passivation processes are given in Table 6. Since the lamellar coating is not a homogeneous coating, a wide shear gap is observed. It was observed that the parts which were expected 24 g/m^2 in a 2-layer zinc flake coating had very high coating weights. The measurements were evaluated as Zn-Ni + Geomet coating weight, as both types of coating used to coat the substrates are zinc containing. Table 7 shows the weights of the coatings in g/m^2 according to the passivation type.

Geomet 321; The lowest weight of 59.2 g/m^2 was obtained with Zn-Ni+ Geomet 321 coating non-passivation. This value increased to 76.3 g/m^2 with transparent passivation. The highest film thickness was obtained in the transparent passivation layer. Coating weights of 65.5, 69.3 and 60.8 g/m^2 were obtained with blue, yellow, and black passivation respectively.

Geomet ML Black; While 35.1 g/m^2 was observed for the non-passivated Zn-Ni+ Geomet ML Black coating, this value increased to 48.7 g/m^2 for the transparent passivation, the highest observed. For the other types of passivation, coating weights of 44.4, 47.8 and 36.2 g/m^2 were observed for blue, yellow, and black respectively. The highest value was again observed for the transparent passivation when comparing the thickness of Geomet 321 and ML Black.

Table 7. [Zn-Ni Coating+ Geomet Coating] weight obtain by X Ray.

PASSIVATION TYPE	 **ALKALINE Zn-Ni + GEOMET 321**	 **ALKALINE Zn-Ni + GEOMET ML BLACK**
Non-passivation	59,20 g/m^2	35,10 g/m^2
Transparent	76,30 g/m^2	48,70 g/m^2
Blue	65,50 g/m^2	44,40 g/m^2
Yellow	69,30 g/m^2	47,80 g/m^2
Black	60,80 g/m^2	36,20 g/m^2

3.1 Cross-Cut/ Dry Adhesion Test

Before and after corrosion, good adhesion of coatings with different passivation processes to the substrate surface is essential. The reason for this is that the mechanical and tribological properties of the material can be adversely affected if a coating is easily detached from the surface of the substrate. Cross-cut (dry adhesion) tests were performed on coatings with different passivation processes to assess this adhesion resistance. Figure 4 compares the surface images of the coatings with different passivation processes after the cross-cut test. Table 8 also shows the test results of Zn-Ni+ Geomet coatings with different passivation treatments after dry bonding. Analysis of the images shows that the Zn-Ni coating successfully passed the dry adhesion test of all Geomet 321 and Geomet ML Black coatings with no passivation, transparent, blue, and yellow passivation processes. However, the Geomet 321 coating with black passivation passed the dry adhesion test, while the Geomet ML Black coating failed due to high peeling after the test.

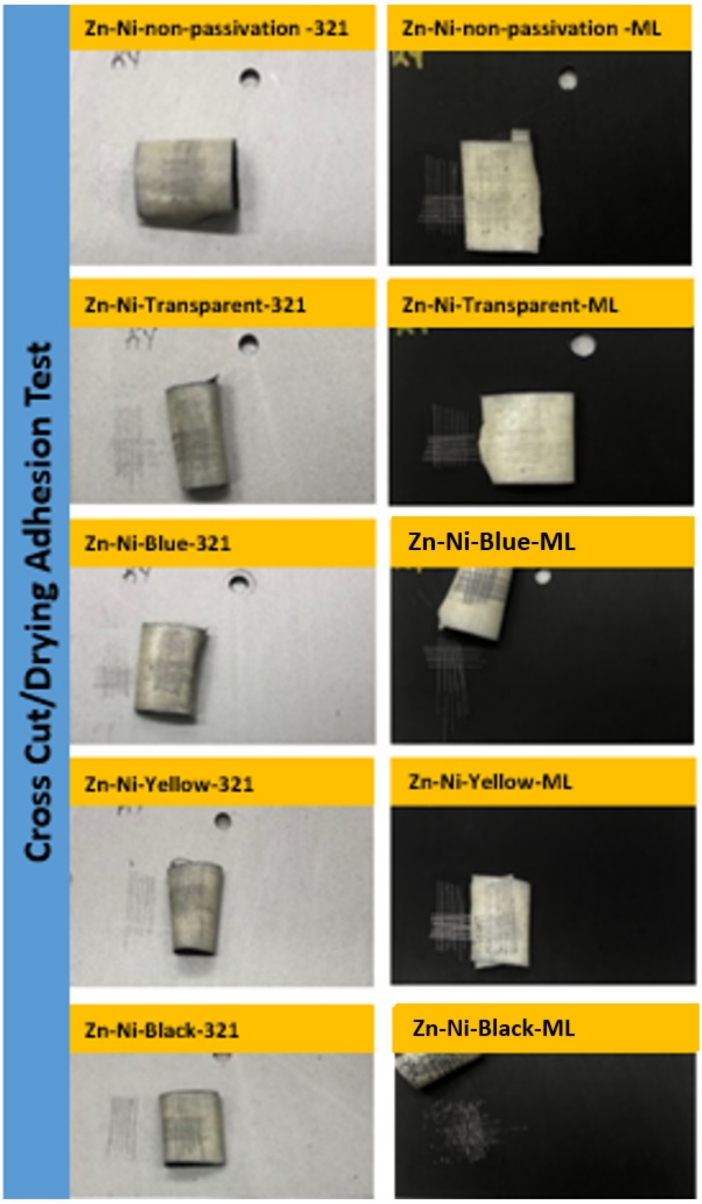

Figure 4. Dry adhesion tests of coatings produced in different passivation processes.

Water resistance, moisture resistance and salt spray resistance tests were not performed as the samples with ML Black Geomet applied over alkaline Zn-Ni + Black passivation failed the dry adhesion test.

Table 8. Dry post-adhesion test results for ML Black and 321 coatings for passivation applied to Zn-Ni coatings.

Zn-Ni (DRY ADHESION)	GEOMET 321	GEOMET ML Black
Non-passivation	✓	✓
Transparent Passivation	✓	✓
Blue Passivation	✓	✓
Yellow Passivation	✓	✓
Black Passivation	✓	X

3.2 Water Resistance Test

The water resistance test was performed according to ASTM D 870-02. All coating samples were soaked in deionised water at a constant temperature of 40°C for 48 hours. At the end of this time, the part was removed from the water, dried with blotting paper, and kept in ambient conditions for two hours. After this time, it was subjected to an adhesion resistance test. After the peel test, no change in the colour of the coating is expected. Figure 5 shows the surface image of the adhesion test results after the water resistance test. Table 9 also shows the results of the adhesion test of the coatings with different passivation treatments after the water resistance test. According to the adhesion test results, the blue passivated Geomet 321 and yellow passivated Geomet ML Black coatings failed the test.

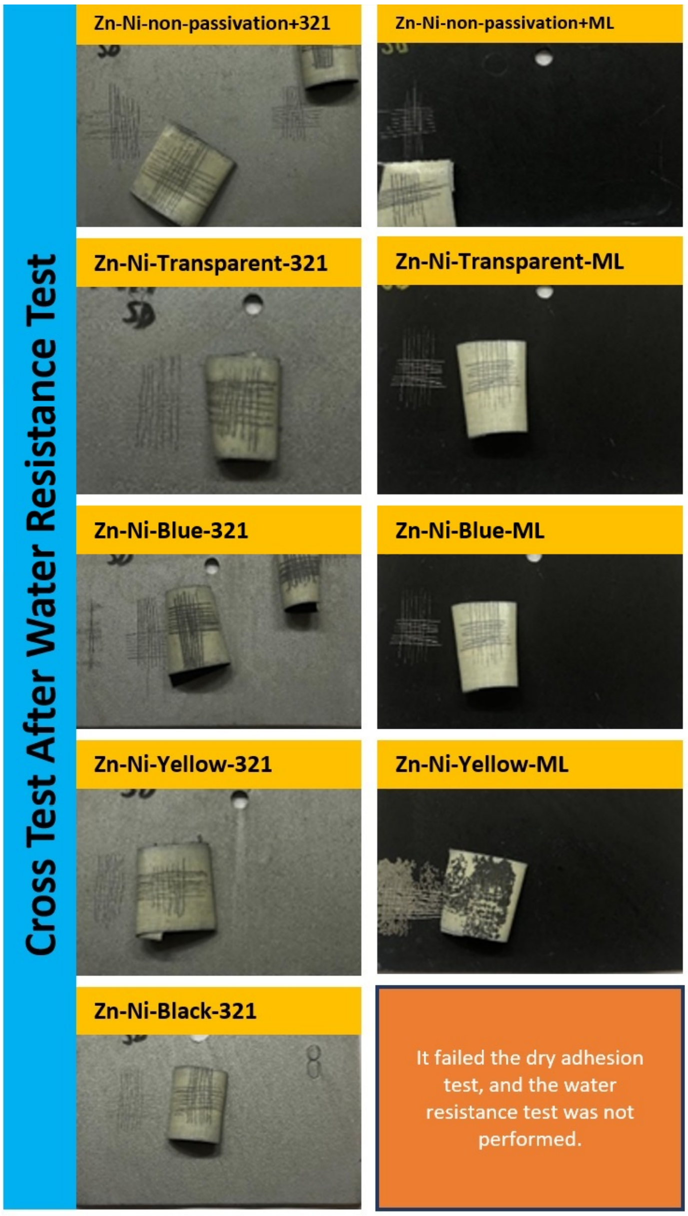

Figure 5. Surface images of adhesion test conducted after water resistance test.

The adhesion test was carried out after the water resistance test. Moisture and salt spray tests were not performed on Geomet ML Black applied over alkaline Zn-Ni + Yellow Passivation because these coatings failed the dry adhesion test.

Table 9. The results according to the adhesion test performed after the water resistance test.

Zn-Ni (WATER TEST)	GEOMET 321	GEOMET ML Black
Non-passivation	✓	✓
Transparent Passivation	✓	✓
Blue Passivation	X	✓
Yellow Passivation	✓	X
Black Passivation	✓	It failed the dry adhesion test, and the water resistance test was not performed.

3.3 Moisture Resistance Test

High humidity results in oxidation of metals, enhanced chemical reactions and chemical or electrochemical breakdown of organic and inorganic surface coatings. Humidity influences the surface properties of the material. Effects include swelling of the material due to moisture absorption, loss of physical strength of the material, loss of electrical and thermal insulation properties, change in flexibility or plasticity. MIL-STD-810G Method 507.5 described a test method for determining the resistance of a material to the effects of a hot and humid atmosphere. Hot and humid conditions are generally found year-round in tropical regions and seasonally in mid-latitude areas. In these regions, moisture damage occurs primarily in materials exposed to changes in pressure, temperature, and relative humidity [24]. Figure 6 shows the surface images of Geomet 321, and ML Black coatings applied after the different passivation processes following the moisture resistance test. Table 10 shows the test results of coatings with different passivation processes after the moisture resistance test. The coatings that were not passivated for Geomet 321 and blue passivated for ML Black failed the adhesion test after moisture resistance. They were not included in the salt spray test.

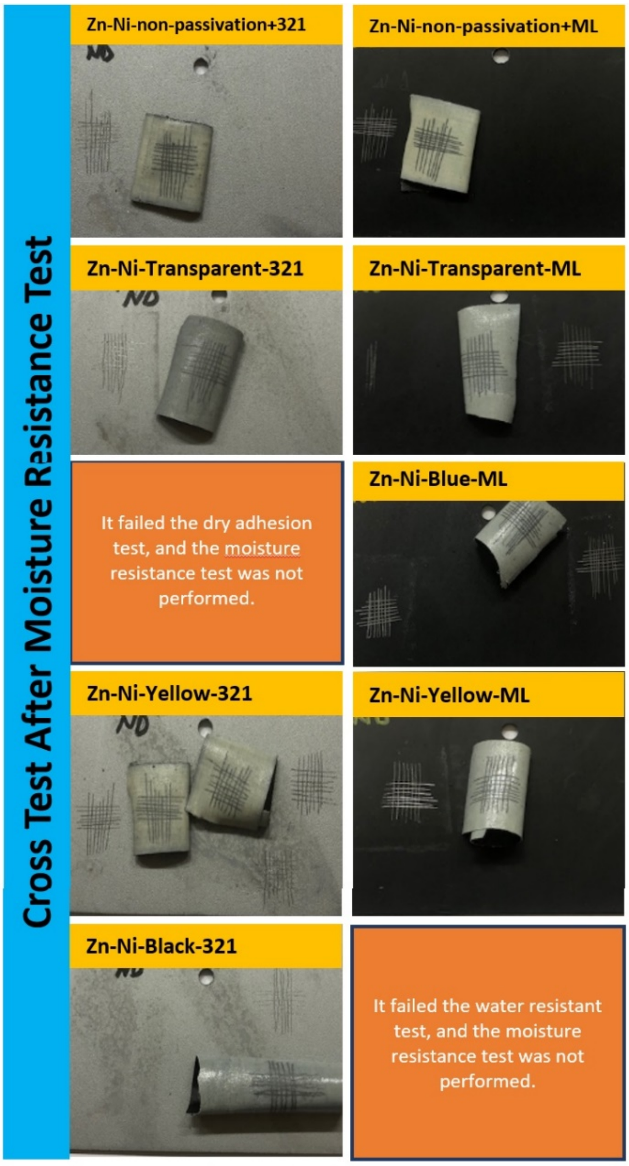

Figure 6. Surface images after coating adhesion test of different passivation treatments applied after moisture resistance test.

Moisture resistance was followed by the adhesion test. The parts with the Geomet ML Black Geomet applied over the alkaline Zn-Ni + Black passivation unsuccessful the dry adhesion test. Therefore, the salt spray was not carried out to this samples.

Table 10. Test results of coatings with different passivation treatments after moisture resistance test.

Zn-Ni (MOISTURE TEST)	GEOMET 321	GEOMET ML Black
Non-passivation	X	✓
Transparent Passivation	✓	✓
Blue Passivation	Because it failed the water resistance test, it was not subjected to the moisture resistance test.	X
Yellow Passivation	✓	Because it failed the water resistance test, it was not subjected to the moisture resistance test.
Black Passivation	✓	It failed the dry adhesion test, and the water resistance test was not performed.

3.4 Salt Spray Test

This test is used to determine the resistance of the protective coatings and surfaces of the sample to the effects of salt. The samples are placed in the test chamber and exposed to the salt spray. When the test is completed, the specimen is subjected to physical, electrical, and corrosive tests and any defects recorded [25].

Due to high white rust formation, Zn-Ni+ ML Black and Zn-Ni+ Geomet 321 coatings without passivation treatment failed the salt spray test. The other samples passed the test. Figure 7 shows the surface images of the coatings with different passivation processes after the salt spray test. The results of the salt spray test are shown in Table 11. The surface images 321 and Black coatings without passivation showed a high rate of white rust after the test and therefore failed. The transparent passivated 321 and Black coatings showed no red rust and a very low level of white rust and passed the test. The samples were not included in the salt spray test for blue passivation as they had failed in the previous tests. In the yellow passivation application, 321 coating passed the salt spray test, while ML Black coating was not included in the salt spray test because it failed the water test. 321 coating passed the salt spray test, but ML Black coating failed the salt spray test.

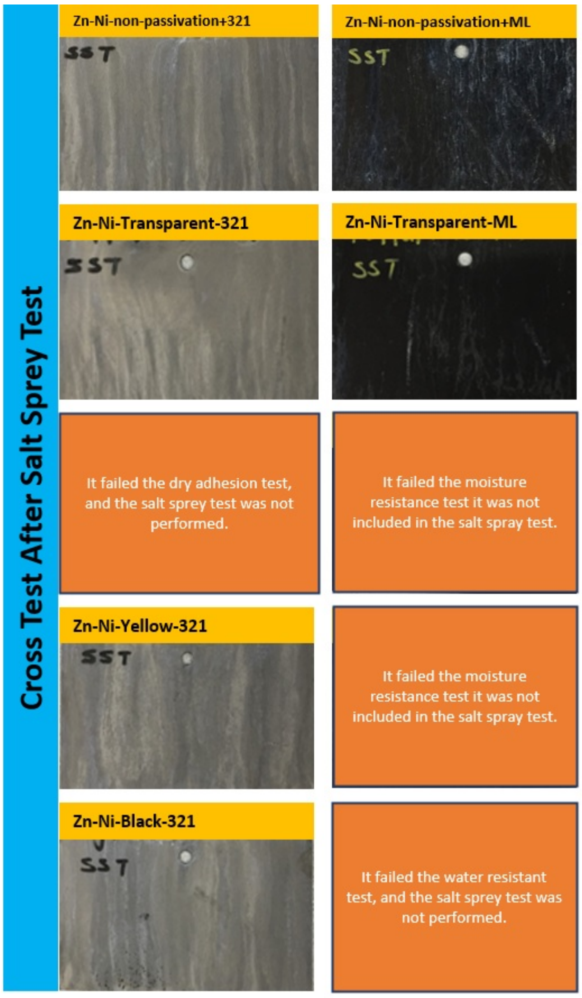

Figure 7. Surface images after salt spray test of coatings with different passivation.

Table 11. Geomet 321 and ML Black coatings salt spray test results after different passivation process.

Zn-Ni (SALT SPRAY TEST)	Geomet 321	Geomet ML Black
Non-passivation	X	X
Transparent Passivation	✓	✓
Blue Passivation	Because it failed the water resistance test, it was not subjected to the salt spray test.	Because it failed the moisture resistance test, it was not included in the salt test.
Yellow Passivation	✓	Because it failed the water resistance test, it was not subjected to the salt spray test.
Black Passivation	✓	It failed the water resistance test, and the salt spray test was performed.

Table 12 shows the corrosion resistance times after the salt spray test without red rust formation. According to these test results, Geomet 321 coatings showed corrosion resistance for 720 hours. In the same test, Zn-Ni coatings showed corrosion resistance for 1000 hours. Using these two coatings together, the combination of Zn-Ni + Geomet 321 provided 1200 hours of salt spray resistance. In addition, the combination of Zn-Ni + ML Black showed a slightly higher corrosion resistance with a salt spray resistance of 1500 hours. These results showed that the combination of the two coatings provided a higher corrosion resistance in the salt spray test.

Table 12. Durability times of different coatings after the salt spray test.

SALT SPRAY TEST (ISO 9227)	TIME (WITHOUT RED RUST)
Organic Zinc Lamellar Coating (Geomet-321) Corrosion Performance [25]	720 hours
Alkaline Zinc Nickel Coating (Zn-Ni) Corrosion Performance [26]	1000 hours
Organic Zinc Lamellar (Geomet 321) + ML Black Corrosion Performance [25]	1008 hours
Zn-Ni Coating +Geomet-321 Corrosion Performance [26]	1200 hours
Zn-Ni Coating+ ML Black Corrosion Performance [26]	1500 hours

4. Conclusions

Corrosion performance has been improved by combining organic zinc lamella plating with alkaline Zn-Ni coating. As a result, a new process with high corrosion resistance was obtained by using two different processes in a single process. Given that the corrosion resistance of the lamellar coating is high, a new process has been developed that can exceed this level. All different passivation samples passed the dry adhesion test except for ML Black coating over alkaline Zn-Ni+ black passivation.

The alkaline Zn-Ni + blue passivation + Geomet 321 and ML Black Geomet over alkaline Zn-Ni + yellow passivation sample failed the water resistance test. Except for this sample, the coated parts successfully passed the water resistance test. The samples passed the water resistance test with an alkaline Zn-Ni coating + passivation over Geomet 321 coating. The moisture resistance test was failed by the non-passivated alkaline Zn-Ni+321 coating sample and the blue passivated Zn-Ni+ ML Black coatings.

In the salt spray test, the samples that passed the test passed the test for Geomet 321 for the transparent, yellow and black passivation, while the samples with the other passivation failed the test. For ML Black only the transparent passivation passed the test. In the salt spray tests, no red rust was observed on any of the samples, only white rust caused by zinc. Therefore, white rust rates were considered for comparison. It can be said that all samples passed the test if red rust is considered. Red rust was not observed in any of the samples.

Substrates coated with 321 Geomet over alkaline zinc nickel + passivation showed no red rust even after 1200 hours. Besides, no red rust formation was observed on the parts coated with ML Black at the end of 1500 hours.

When the Zn-Ni alloy coatings with ML Black were analysed, it was found that the coatings with non-passivation, with blue passivation, with yellow passivation and with black passivation failed pass the tests. Coatings without passivation and blue passivation failed the test with 321 Geomet. The main reason for the poor adhesion of ML Black coating to the surface after Zn+ Ni passivation and the high failure rate in the corrosion tests is that ML Black coating has a lower deposition rate than Geomet 321.

Based on the tests carried out on the Geomet coating process to be carried out on Zn-Ni+ passivation, the process that should be preferred is to produce Geomet 321 coatings on Zn-Ni alloyed coating. Transparent passivation + Geomet 321 and Geomet ML Black coatings applied after Zn-Ni coating with different passivation processes passed all tests.

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