Effect of Phosphate Concentration on Anodizing Process Efficiency and Aluminium Surface Hardness in 16% Sulfuric Acid Solution

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**Abstract**

One of the problems the aircraft industry faces is equipment that has decreased performance in the period before planning. The solution to this condition is that a material that has hard properties and is corrosion-resistant is needed. Aluminium is a metal that is applied as equipment in the industry because it has the characteristics of being light, strong, corrosion resistant and easy to shape, but has properties that are easy to deform, have low hardness and wear resistance. Anodizing process has the characteristics to improve the surface properties of aluminium metal in physical and mechanical properties. The anodizing process of aluminium metal using sulfuric acid solution produces a thicker oxide layer than in other solutions, such as phosphoric acid solution. This research studied the effect of phosphoric acid concentration on process efficiency, oxide layer thickness, and the hardness of the anodized oxide layer in 16% sulfuric acid solution. Phosphoric acid solution concentration varied from 0; 0.5; 1; 2; 4; and 8% in 16% sulfuric acid solution at 5 Volts voltage or 1.12 A/dm² current density with 25 minutes processing time. The results showed that the anodizing process in 16% sulfuric acid solution had the lowest efficiency of 19.3% after adding variations in the concentration of phosphoric acid. These conditions reached the optimum in 16% sulfuric acid solution with the addition of 1% phosphoric acid; 26.6 mg oxide mass; 50.33% efficiency; 90.48 mg/dm² oxide layer thickness and 86.57 HV metal surface hardness.

**Keywords:** aluminium, anodizing efficiency, phosphoric acid hardness, thickness

**Introduction**

Aluminium has good corrosion resistance, electrical conductivity and formability, and is lighter than iron or steel. [1]. In a corrosion process, aluminum reacts with oxygen and forms a thin oxide layer which is able to improve corrosion resistance. This layer functions as a protective layer capable of blocking further reactions to oxygen. Aluminium metal is a metal that is resistant to corrosion attack under neutral conditions, such as ordinary water, sea water, and water vapor because it forms a passive oxide layer, while under alkaline conditions it forms aluminate [1].

Aluminium is a non-ferrous metal that is applied as a material for equipment in industry because it has superior properties such as being strong, light, and easy to shape. The application of this process in the process industry can be applied in plate heat exchangers, pressure vessels, pipes, and others. One of the problems faced by the aircraft industry is equipment performance decreasing in a shorter period. The solution to this condition is a material that has hard properties and corrosion resistant. The material used is an aluminium non-ferrous metal, because aluminium has some beneficial properties such as being easily deformed, hard, and low wear resistance. An anodizing process can be applied to improve the physical and mechanical properties. This study aimed to determine the effect of phosphoric acid solution in 16% sulfuric acid solution on process efficiency, oxide layer thickness, and surface hardness after anodizing.

Anodization is a controlled process of forming an oxide layer by electrolysis...
through the aeration process, so that the oxide layer is dense, and porous. This oxide layer has the characteristics of being hard, transparent, resistant to loads, wide color range, and no debris on the surface. The anodization process is influenced by the type of electrolyte solution, solution concentration, pH, current, voltage, temperature, and processing time.

The anodization process is a process that makes the surface of the aluminum metal oxidize to form an oxide layer which aims to prevent corrosion attacks and beautify the surface. This oxide layer is porous and allows coloring the aluminium in various colors, making it more attractive [2], [3]. Anodizing in sulfuric acid solution is the most common process and results in a coating of up to 1 mil (25 microns), 67% penetration into the substrate, and 33% growth occurring on it. Anodizing using sulfuric acid is very good for coloring, binding agents, organic coatings, and very long corrosion resistance and is applied to architecture, aerospace, automotive manufacturing, and computers. Anodizing using a sulfuric acid electrolyte can be carried out at higher concentrations at lower temperatures, resulting in a hard coating with excellent abrasion resistance, corrosion resistance, color fading resistance, dielectric strength, and surface hardness.

Anodization is the process of forming a thin oxide layer on the surface of aluminum metal through an electrolysis process in an electrolyte solution such as sulfuric acid at the anode. Suppose the anode (+) aluminum is immersed in a sulfuric acid solution and a direct current is applied. In that case, the aluminum anode (Al) will dissolve into aluminum ions, which react with the resulting oxygen to form a thin aluminum oxide layer. At the same time, hydrogen will be liberated at the cathode.

The anodized oxide layer has a different structure from the naturally occurring oxide layer. Namely, the layer has a porous hexagonal pillar structure. The oxide layer has characteristics that can improve the mechanical properties of the aluminum surface. The characterization of the oxide layer depends on the electrolyte solution. The oxide layer comprises a barrier layer and a thin porous layer [4].

The anodized aluminum oxide layer is affected by the process temperature, current density or voltage. Temperature aims to control the course of the reaction and protect the coating. The magnitude of the current density affects the time of formation of the oxide or the layer reaches its maximum thickness. Voltage is the potential difference between two points, is the amount of work required to transfer current from one point to another in volts (V). The magnitude of the electric voltage can affect the anodization results. The voltage affects the appearance of the oxide layer results, namely the higher the voltage, the higher the potential difference so that the ionization energy becomes greater, then the energy used to release aluminum ion bonds is also greater. The greater the ionic bonds from the aluminum that are released, the greater the aluminum ions in the electrolyte solution attached to the aluminum surface. With the increasing number of aluminum ions from the attached electrolyte and also the decay process in the aluminum oxide layer, the hardness on the surface will increase [3], [5], [6]. The degree of acidity (pH) is a factor in controlling the electrolyte solution. The time of the anodization process affects the results of the anodization process related to the efficiency, thickness, and density of the coating. The longer the anodization process is expected to increase the thickness of the layer and the hardness.

Mechanical properties and oxide layer of the aluminum surface are tested quantitatively. The oxide layer thickness test is carried out using the gravimetric method [7]. A thickness test can be done using a metallographic microscope. Hardness is a measure of a material’s resistance to localized plastic deformation. Hardness testing aims to determine the characteristics of the material and see that the quality of the material has certain quality specifications [8]. The hardness of the oxide layer on the aluminum surface was determined using the Vickers method. Process efficiency is calculated using Faraday's law, which states the relationship between the oxide layer product produced and the amount of current flowing with the following formula:

\[ W = (e.I.t / F) \]

Description:
- \( W \) = weight of the substance formed (g),
- \( I \) = amount of current flowing (A),
- \( t \) = time (s),
e = equivalent weight of the oxide layer
1F = 96,500 Coulomb.

For the efficiency of the anodization process, it can be calculated based on the formula:

$$\eta = \left( \frac{W_e}{W} \right) \times 100\% \quad \text{(2)}$$

Description:

$\eta$ = process efficiency (%),
$W_e$ = oxide layer weight (gram),
$W$ = layer weight according to Faraday's law (gram).

**METHODS**

This study uses equipment such as a rectifier as a current rectifier or battery, a container in the form of a beaker, aluminum workpieces, and aluminum electrodes which have a larger area and thickness than the workpiece. The main chemicals are 16% sulfuric acid solution with phosphoric acid solution as process solution, NaOH are 10% and nitric acid solution are 10% used as workpiece surface pretreatment solution, and phosphoric acid and chromic acid solution used to dissolve the oxide layer formed to determine process efficiency.

The experimental process stages are in accordance with the process flow diagram in Figure 1, which begins with the preparation of tools and makes a 10% NaOH solution and a 10% HNO3 solution, the anodization process solution is a sulfuric acid process solution with a concentration of 16% with variations in the addition of phosphoric acid (0; 0.5; 1; 2; and 4%) and aluminum workpieces. During the work, the surface was pretreated by mechanical cleaning using abrasive paper, pickling, and etching solution in 10% NaOH solution, rinsed with distilled water, in 10% nitric acid solution for about 3 minutes, and rinsed with distilled water, dried, and weighed. The workpiece was anodized in a 16% process solution and the addition of variations in the concentration of phosphoric acid was carried out for 25 minutes at a voltage of 5 Volts or a current density of 1.12A/dm2. The workpiece at the anode (+) and the Al electrode at the cathode (-), are connected to direct current (DC) either from the battery or PLN which has been passed through a rectifier. The anodization process products are tested for process efficiency, thickness measurements are carried out using the gravimetric method. Surface hardness of aluminum metal by the Vickers method. Experimental data were analyzed by calculating and presenting in graphical form and discussing it which was then concluded. The process flow diagram is shown in Figure 1.

**RESULTS AND DISCUSSION**

The anodization process is the process of forming an oxide layer on the surface of the aluminum metal by the electrolysis method with the workpiece at the anode. The oxide layer formed acts as a barrier and is porous. The oxide layer as a barrier is formed by the direct reaction between aluminum ions with oxygen or hydroxide ions which combine with the base metal, and subsequently forms a porous oxide layer. This porous layer is heated to close and shrink which causes the surface properties of the aluminum metal to harden. The cross-section of the aluminum metal anodization process is presented according to Figure 2.
Figure 2. Cross section of aluminium metal anodized product (20x)

Figure 2 shows that the cross-section of the aluminium metal anodization product forms an oxide layer. This oxide layer acts as a barrier that can withstand corrosion reactions and is porous. [1] which can adsorb dyes when immersed in a dye solution.

**Effect of phosphoric acid concentration on mass, process efficiency**

The anodization process was carried out in a 16% sulfuric acid solution at a voltage of 5 Volts or a current density of 1.12A/dm$^2$ for 25 minutes and 16% sulfuric acid was added into various solution of phosphoric acid (0; 0.5; 1; 2 and 4%), the results of which are presented in Figure 3.a and Figure 3.b.

Figure 3.a Effect of phosphoric acid concentration and oxide mass

Figure 3.b Effect of phosphoric acid concentration and process efficiency

Figure 3.a shows the effect of concentration 1% phosporic acid in a 16% sulfuric acid process solution to produce an oxide layer (Al$_2$O$_3$) which is fused with aluminium metal reaching a maximum yield of 26.6 mg with a process efficiency of 50.33% (Figure 3.b). This means that the process of formation of aluminium oxide on the metal surface increases until the addition of 1% phosphoric acid into a 16% sulfuric acid solution, which then decreases the rate of formation with the greater sulfuric acid concentration by 25 minutes processing time. The efficiency of the anodization process reached a maximum of 50.33%, this indicates that the rate of the aluminium dissolution process is much greater than the process of forming the oxide layer, which is shown in Figure 4 and the reaction mechanism at the anode.

Alumunium: Al $\rightarrow$ Al$^{3+}$ + 3e
Electrolite: H$_2$O $\rightarrow$ O$_2$ + 2H$^+$ + 2e
Which is the next reaction will be

Reaction 1: 2Al$^{3+}$ + 3/2O$_2$ $\rightarrow$ Al$_2$O$_3$ + 6e
or
Reaction 2: 2Al + 3H$_2$O $\rightarrow$ Al$_2$O$_3$ + 6H$^+$ + 6e

This oxide forms a thin layer on the surface of aluminium which is a barrier and has a constant thickness and resists corrosion attack, then the oxide forms a layer that is porous and initially cylindrical which finally has a hexagonal shape that has a pore in the middle. [1], [3]–[5].

**Effect of phosphoric acid concentration on the thickness of the oxide layer and the surface hardness of aluminium metal**

The thickness of the oxide layer was calculated according to the standard gravimetric method according to ISO 2106:2019 and the surface hardness of the metal was carried out by the Vikers method.
According to ASTM E384–89, the results of which are presented in Figure 5.

**Figure 5.** Phosphoric acid concentration and oxide layer thickness & surface hardness.

Figure 5 shows the results of the thickness of the oxide layer and the surface hardness of the aluminium anodized product based on variations in the addition of phosphoric acid solution to 16% sulfuric acid solution at a voltage of 5 Volts or a current density of 1.12 A/dm² during the 25 minute process. The results of the thickness of the oxide layer and the surface hardness showed the same tendency, namely reaching a maximum at the addition of 1% phosphoric acid with an oxide layer thickness of 90.48 mg/dm² and a surface hardness of 86.57 HV. This means that the oxide layer formed on the metal surface is getting thicker causing the hardness of the metal surface to increase and causing the metal material to become more resistant to corrosion processes.[6][7], but the nature of the metal becomes harder[8], [9].

Figure 5 also shows that the anodizing process of 16% sulfuric acid solution produces the thinnest oxide layer thickness and the lowest surface hardness and even lower surface hardness than the base metal. This is because the rate of dissolution of aluminium metal is faster than the rate of oxide formation on the surface, which causes the base metal to be thinner than after the anodization process.[10]–[12] and the efficiency of the anodizing process is only 19.3% (Figure 3.b).

**CONCLUSION**

Based on the experimental results and discussion, it can be concluded that the concentration of phosphoric acid added to a sulfuric acid solution of 16% in the aluminium metal anodization process at 5 Volt conditions or current density of 1.12A/dm² with a processing time of 25 minutes affects the anodization result, namely the addition of phosphoric acid concentration 1% into 16% sulfuric acid solution reached the optimum condition with an oxide layer product of 26.6 mg with an efficiency of 50.33%, and the thickness of the oxide layer reached 90.48 mg/dm² with a metal surface hardness of 86.57 HV.

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