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(71) Applicant: **Politeknik Metal Sanayi Veticaret A.I.**
Istanbul (TR)

(72) Inventors:
- **Afsin, Pinar**
  B1/B4 Istanbul (TR)
- **Akdas, Guney**
  B1/B4 Istanbul (TR)
- **Akyil, Can**
  B1/B4 Istanbul (TR)

(74) Representative: **Boult Wade Tennant LLP**
Salisbury Square House
8 Salisbury Square
London EC4Y 8AP (GB)

(54) BRIGHTENING SOLUTION FOR ALUMINIUM OR ALUMINIUM ALLOY AND PROCESS FOR BRIGHTENING ALUMINIUM OR ALUMINIUM ALLOY

(57) The present invention refers to a pretreatment bath for anodizing aluminum or aluminum alloys and a process for anodizing aluminum or aluminum alloys on a substrate.

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Description

[0001] The present invention refers to a pretreatment bath for anodizing aluminum or aluminum alloys and a process for anodizing aluminum or aluminum alloys on a substrate.

[0002] In the field of aluminum anodizing, due to the use of many different types of chemicals, and effects that other variables can have on aluminum it can still become faded and matte over time. Aluminum can be polished to a high gloss, but it must be fully decontaminated before this is possible. An aluminum brightener is a product that will remove vast amounts of contamination from aluminum and remove the outer most layer of the aluminum. As soon as it meets oxygen again, the protective layer will be re-created again. It will improve the aspect of the aluminum and shorten the amount of time needed to clean it prior to polishing.

[0003] The bright dip (Chemical Brightening) bath functions by levelling the microscopic roughness of the aluminium surface, thus reducing the amount of light that is scattered and increasing the specularity of the surface. The other two methods to obtain a bright aluminium finish are mechanical polishing and electrochemical polishing. Mechanical polishing produces a flowed amorphous surface under the influence of pressure and local high temperatures which may cause problems for sequential operation. Additionally, the labour cost of such a mechanical treatment is higher than chemical applications. By using e-brightening a high gloss mirror finish can be achieved. However, the initial investment cost of the e-brightening procedure is higher than a chemical version.

[0004] The phosphoric acid, nitric acid and sulphuric acid based chemical polishing baths (bright dip) are widely used to produce specular finishes on a variety of aluminium alloys used for the automotive, appliance, and architectural trim. The classical bright dip contains nitric acid which increases 1400-800 the surface gloss at geometric angles of 20°- 60° respectively. However, nitric acid based chemical polishing solutions produce nitrous gases which are highly carcinogenic and environmentally hazardous. Because of that, usage of nitric acid should be eliminated. The nitric acid-free version of brightening baths includes a high amount of (>50% Phosphoric acid). This kind of brightening bath is called a semi-bright chemical brightening bath and the highest gloss that can be achieved is around 500.

[0005] In the prior arts phosphoric acid, sulphuric acid, organic additives, metal salt is added to solution to increase the brightness. However, the performance of the classical nitric acid based, and nitric free chemicals are unlike. Also most of those baths contain copper metal ion that precipitates in the bath creating a pollution that requires to renew the bath quite often.

[0006] CN106521507A discloses an aluminum alloy chemical polishing additive, comprising phosphoric acid, sulphuric acid, brightener, inhibitor, complexing agent and water.

[0007] CN101476126A discloses a chemical polishing liquid composition of aluminum products, wherein said composition is free from nitric acid and takes sulphuric acid and phosphoric acid as basis solution, and additive thereof is composed of aluminum sulphate (or aluminum nitrate), potassium permanganate, sodium nitrate, diphenylamine sulphuric acid sodium salt, tartaric acid, and zinc sulphate. When polishing by using the polishing liquid, polishing temperature is 110-150 degrees centigrade, polishing time is 10-120 S. The invention can ensure free the harm of yellow fume of nitrogen oxide during the treatment process of aluminum material, and further can supply excellent polishing effect for the aluminum material, such that the aluminum material can be provided with mirror brightness and low weightlessness rate.

[0008] CN107488857A discloses a polishing solution of aluminum product, comprising the following raw materials in terms of parts by weight: 30-65 of phosphoric acid, 55-85 of sulphuric acid, 0.2-2.5 parts of aluminium salt, persulphate 0.05-0.2 parts, 0.04-0.18 parts of sodium silicate, 0.01-0.3 parts of thiourea, dithiodi-propanol 0.05-0.5 parts, ethylenediamine tetramethylene phosphonic acid 0.02-0.2 parts, 0.01-0.1 parts of oil hydroxyethyl imidazoline. The polishing step is as follows: preparing polishing liquid; the polishing liquid is heated to 75 degrees centigrade to 110 degrees centigrade; the drying product to be polished is soaked into the polishing liquid, soaking for 20S to 150S; after taking out the aluminum product, washing by de-ionized water of 50 degrees centigrade; blowing to dry. The polishing solution of the invention uses phosphoric acid, sulphuric acid, aluminum ion, strong oxidizer, corrosion inhibitor and brightener for cooperation, it can effectively avoid the problem of corrosion of aluminum material, and the polishing effect is good, and the efficiency is high.

[0009] CN108914130A discloses an environment-friendly aluminum product chemical polishing liquid and its preparation method and polishing method; the environment-friendly aluminum product chemical polishing liquid, comprising the following raw materials by weight percentage: 38-52 % of phosphoric acid, sulphuric acid, 5-13 % of aluminum salt, 0.05-0.5 % of organic acid, 3-10 % of polyethylene glycol, 5-15 % of sodium dodecyl sulphate, 1-3 % of thiourea, 0.5-1.5 % of coconut oleic acid diethanolamide 1.0-3.0 %, and the rest is water. The chemical polishing solution does not harm human body in the using process, no air pollution, good aluminum material surface brightness and surface smoothness after polishing, can be industrially produced in large scale.

[0010] CN110438508A discloses a chemical polishing liquid, wherein it comprises the following materials according to weight parts: 52-60 parts of phosphoric acid, 31-41 of sulphuric acid, 0.21-0.31 parts of copper sulphate, 0.03-0.07 parts of oxalic acid, sodium tungstate, 0.54-0.7 parts of ferric sulphate, 0.13-0.17 parts of titanium, 0.06-0.1 parts of

glycol, 1.1-1.5 parts of chemical polishing liquid of the invention is not limited by the product shape, uniformly polishing the surface of aluminum, the same; the aluminum product glossiness after chemical polishing liquid of the present invention processing is high, no flow trace, chemical polishing liquid of the invention when processing the aluminum product has enough detention time, can meet the requirement of automatic production.

[0011] CN111020590A discloses an environment-friendly aluminum alloy chemical polishing solution, the formulation comprising 25 to 40wt % of organic acid, 30 to 50 wt % of sulfuric acid, 0.15 to 0.5wt % of sulfate. 15 to 20wt % of fluorinecontaining brightener, 0.1 to 0.2wt % of polyethylene glycol 6000, 0.15 to 0.3wt % of fatty acid derivatives, 0.01 to 0.1wt % of corrosion inhibitor, and the rest of de-ionized water. the fatty acid derivative is saponification or esterification products of fatty acid with diethanolamine, triethanolamine, glycerol, isopropanol or sorbitol, and molecular carbon 12-28. The environment-friendly aluminum alloy chemical polishing solution not only environment-friendly, but also can make the plate surface with a high gloss, can solve the swash surface flower, and marks many problems.

[0012] CN111996533A discloses an environment-friendly aluminum alloy chemical polishing solution and preparation method and polishing method thereof, wherein the chemical polishing solution comprises the following parts by weight: phosphoric 85 % 40- 90 parts, 98 % acid 10-50 parts, ammonium polyphosphate 0.1- 1 parts, nitrate 0.1 ~ 2.5 parts, sulphate 0.02 ~ 0.07 parts, chloride 0.00003 ~ 0.00004 parts. The chemical polishing solution of the invention mainly uses phosphoric acid, sulphuric acid, nitrate, sulphate, chloride, ammonium polyphosphate as auxiliary, realizing the wide phosphorus-sulphur ratio, changing the traditional" three acid " chemical polishing need according to different material aluminum alloy light condition two frequently adjusting polishing liquid phosphorus-sulphur ratio mode, and completely avoiding the risk of " triacid " chemical polishing crystallization, simple operation, improved production efficiency, good polishing effect, the production cost is greatly reduced.

[0013] None of those prior art documents has focused on obtaining a more efficient bath with less pollution.

[0014] It was therefore an object of the present invention to provide a solution for improving the brightening performance of phosphoric acid/nitric acid and sulphuric acid chemical polishing baths on aluminium and/or anodized aluminium alloys with limiting the pollution of those baths.

[0015] This problem is solved by the brightening solution with the features of claim 1 and the process for brightening an aluminium or aluminium alloy substrate with the features of claim 10. The further dependent claims mention preferred embodiments.

[0016] According to the present invention, a
brightening solution for aluminium or aluminium alloys is provided comprising

- at least 50 wt.-%%wt of sulphuric acid 98% ppa,
- phosphoric acid 85% ppa,
- at least one tungsten ion salt,
- at least one metal ion selected from the group consisting of iron, nickel, zinc, molybdenum, and combinations thereof,

wherein the weight ratio between the sulphuric acid and the phosphoric acid is between 1:1 to 4:1.

[0017] Surprisingly, it has also been found that the presence of a second metal ion increases the rate of the etching solution and stabilizes the solution.

[0018] In a preferred embodiment, the brightening solution comprises at least one wetting agent.

[0019] In a preferred embodiment, the brightening solution comprises at least one corrosion inhibitor.

[0020] In a preferred embodiment, the brightening solution comprises 0,05 wt.-% to 2 wt.-%, preferably 0,1 wt.-% to 1 wt.-% of the at least one metal ion.

[0021] In a preferred embodiment, the brightening solution comprises 0,001 wt.-% to 1,2 wt.-%, preferably in an amount of 0,005 wt.-% to 0,58 wt.-% of the at least one wetting agent.

[0022] In a preferred embodiment, the brightening solution is comprised from 0,01 to 25,0 wt.-% of phosphoric acid.

[0023] In a preferred embodiment, the weight ratio between the sulphuric acid and the phosphoric acid is from 1,2:1 to 3:1, preferably from 1,5:1 to 2,5:1.

[0024] In a preferred embodiment, the at least one metal ion is iron.

[0025] In a preferred embodiment, the brightening solution comprises 0,001 wt.-% to 2 wt.-%, preferably in an amount of 0,01 wt.-% to 1 wt.-% of at least one corrosion inhibitor.

[0026] In a preferred embodiment, the brightening solution comprises less than 0,1 wt.-% of copper, and preferably the brightening solution is free of copper.

[0027] According to the present invention, a process for brightening an aluminium or aluminium alloy substrate is provided including the following steps:

a) Providing a brightening solution of any of the preceding claims,
b) Immersing a substrate in the solution and,
c) rinsing the substrate for brightening .

[0028] In a preferred embodiment, the temperature of the solution is from 50 to 150°C, preferably from 60 to 140°C, more preferably from 80 to 130°C.

[0029] In a preferred embodiment, the duration of step c) is from 1 second to 600 seconds, preferably from 5 seconds to 300 seconds, more preferably from 10 seconds to 200 seconds.

[0030] In a preferred embodiment, the step c) is followed by a deoxidizing step of the substrate.

[0031] In a preferred embodiment, the step c) is followed by a desmutting step of the substrate.

[0032] In a preferred embodiment, there is a deoxidizing step of the substrate before step c).

[0033] In a preferred embodiment, there is a desmutting step of the substrate before step c).

[0034] With reference to the following figures and examples, the subject matter according to the present invention is intended to be explained in more detail without wishing to restrict said subject matter to the specific embodiments shown here.

Fig.1 shows the ratio of specific gravity per g/cm^3 according to the dissolved aluminium for the comparative example.

Fig.2 shows the ratio of specific gravity per g/cm^3 according to the dissolved aluminium for the example.

Fig.3 shows the ratio of etching rate per g/cm^3 according to the dissolved aluminium for the comparative example.

Fig.4 shows the ratio of etching rate per g/cm^3 according to the dissolved aluminium for the example.

Fig. 5 shows the ratio of gloss according to the dissolved aluminium for the comparative example.

Fig.6 shows the ratio of gloss according to the dissolved aluminium for the example.

Examples

[0035] The gloss measurements were realized according to the norm ISO 7668.

[0036] The L*a*b* Colour measurement were realized according to the norm ISO 11664.

[0037] The Surface Roughness measurement were realized according to the norm MIL DTL 81706.

[0038] The solution for the examples was prepared using a ready to use solution of ALUMAL BRIGHT C 342.

[0039] The comparative examples were realized using a solution of 70% of H_3PO_4 and 20% of H_2SO_4.

[0040] The following sequence was used for the examples and comparative examples.

- Cleaning with soft alkaline cleaner (ALUMAL CLEAN 180) : 40g/L; 5 min; 55°C
- Rinse x 2 (demineralised water)
- Deoxidizing/Desmutting: 3 g/l ALUMAL DEOX 444 , 150 g/l Sulphuric Acid, 1 min, Room temperature
- Rinse x 2 (demineralised water)
- Chemical Brightening: solution according to the examples or comparative examples
- Rinse ED x 2 (demineralised water)
- Deoxidizing/Desmutting: 10-25% ALUMAL DEOX 409, 1-3 min, Room temperature

[0041] The following results were obtained.

Table 1: Experimental data

Brightening Solution	Process Parameters		Specific Gravity (g/cm3)	Etching Rate (g/m2)			Gloss at Geometric Angles After 1 min Treatment			
							Before Treatment		After Treatment	
	Temperature (°C)	Dissolved Aluminum (g/l)		30 sec	1 min	2 min	20°	60°	20°	60°
Comparative Solution	100	0	1,737	17,88	47,61	104,33	157	318	86	253
	100	10	1,770	15,66	42,77	96,94	160	389	70	227
	100	20	1,823	7,00	14,22	27,66	149	325	77	243
	100	30	1,865	3,33	7,61	14,94	155	320	79	265
Invention	100	0	1,715	23,00	45,77	117,05	88	214	761	685
	100	10	1,758	19,27	63,00	105,55	94	228	578	640
	100	20	1,805	14,00	36,61	77,16	86	209	505	621
	100	30	1,780	9,77	26,11	60,38	83	212	359	520

[0042] It has been found that better results with the present invention were achieved compared with the comparative examples. A superior etching rate and a better gloss after treatment were obtained. Fig. 3 and 4 show no sharp decrease of the etching rate at 20 and 30 g/l of dissolved aluminium.

Claims

1. A brightening solution for aluminium or aluminium alloys comprising

   - at least 50 wt.-% of sulphuric acid 98% ppa.
   - phosphoric acid 85% ppa,
   - at least one tungsten ion salt,
   - at least one metal ion selected from the group consisting of iron, nickel, zinc, molybdenum, and combinations thereof,

   wherein the weight ratio of the sulphuric acid and the phosphoric acid is from 1:1 to 4:1.

2. The brightening solution according to claim 1, **characterized in that** the brightening solution comprises at least one wetting agent.

3. The brightening solution according to claim 1 and 2, **characterized in that** the brightening solution comprises 0,05 wt.-% to 2 wt.-%, preferably 0,1 wt.-% to 1 wt.-% of the at least one metal ion.

4. The brightening solution according to claim 2, **characterized in that** the brightening solution comprises 0,001 wt.-% to 1,2 wt.-%, preferably in an amount of 0,005 wt.-% to 0,58 wt.-% of the at least one wetting agent.

5. The brightening solution according to any of the preceding claims, **characterized in that** the solution comprises from 0,01 to 25,0 wt.-% of phosphoric acid.

6. The brightening solution according to any of the preceding claims, **characterized in that** the weight ratio of the sulphuric acid and the phosphoric acid is from 1,2:1 to 3:1, preferably from 1,5:1 to 2,5:1.

7. The brightening solution according to any of the preceding claims, **characterized in that** at least one metal ion is iron.

8. The brightening solution according to any of the preceding claims, **characterized in that** the brightening solution comprises 0,001 wt.-% to 2 wt.-%, preferably in an amount of 0,01 wt.-% to 1 wt.-% of at least one corrosion inhibitor.

9. The brightening solution according to any of the preceding claims, **characterized in that** the brightening solution comprises less than 0,1 wt.-% of copper, and preferably the brightening solution is free of copper.

10. A process for brightening an aluminium or aluminium alloy substrate including the following steps:

    a) providing a brightening solution of any of the preceding claims,
    b) immersing a substrate in the solution and,
    c) rinsing the substrate for brightening.

11. The process according to claim 10, **characterized in that** the temperature of the solution is from 50 to 150°C, preferably from 60 to 140°C, more preferably from 80 to 130°C.

12. The process according to claim 10 and 11, **characterized in that** the duration of step c) is from 1 second to 600 seconds, preferably from 5 seconds to 300 seconds, more preferably from 10 seconds to 200 seconds.

13. The process according to any of the preceding claims, **characterized in that** the step c) is followed by a deoxidizing step of the substrate.

14. The process according to any of the preceding claims, **characterized in that** there is a deoxidizing step of the substrate before step c).

Fig. 1

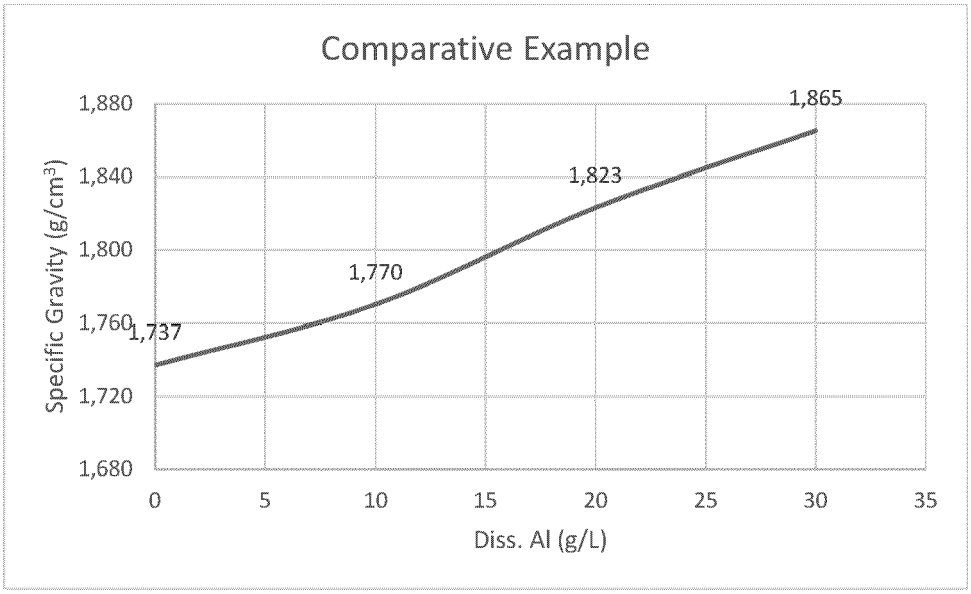

Comparative Example
Specific Gravity (g/cm³)
1,880
1,840
1,800
1,760
1,720
1,680
1,737
1,770
1,823
1,865
0
5
10
15
20
25
30
35
Diss. Al (g/L)

Fig. 2

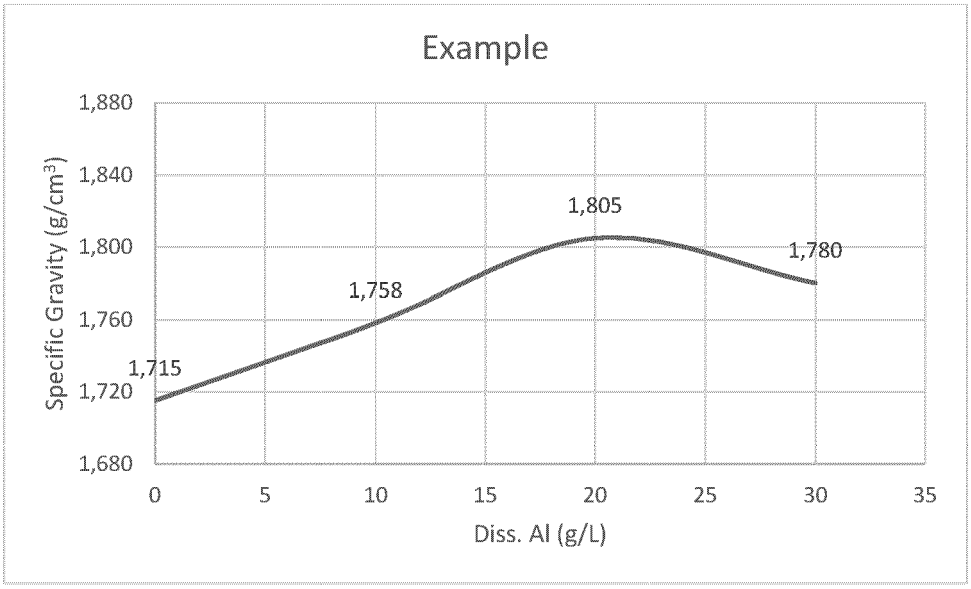

Example
Specific Gravity (g/cm³)
1,880
1,840
1,800
1,760
1,720
1,680
1,715
1,758
1,805
1,780
0
5
10
15
20
25
30
35
Diss. Al (g/L)

Fig. 3

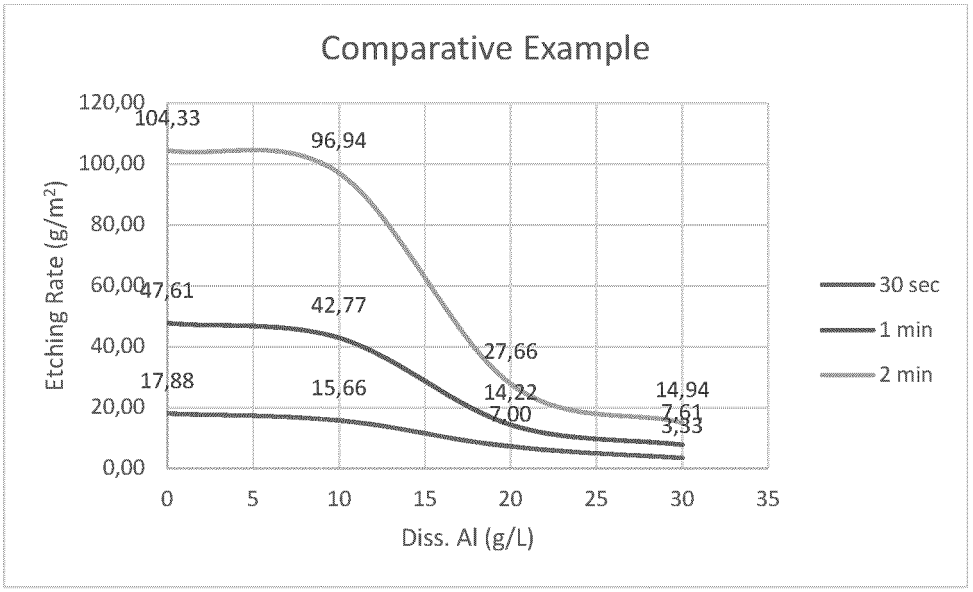

Comparative Example
Etching Rate (g/m²)
Diss. Al (g/L)
120,00
100,00
80,00
60,00
40,00
20,00
0,00
0
5
10
15
20
25
30
35
104,33
96,94
47,61
42,77
27,66
17,88
15,66
14,22
14,94
7,61
7,00
3,33
30 sec
1 min
2 min

Fig. 4

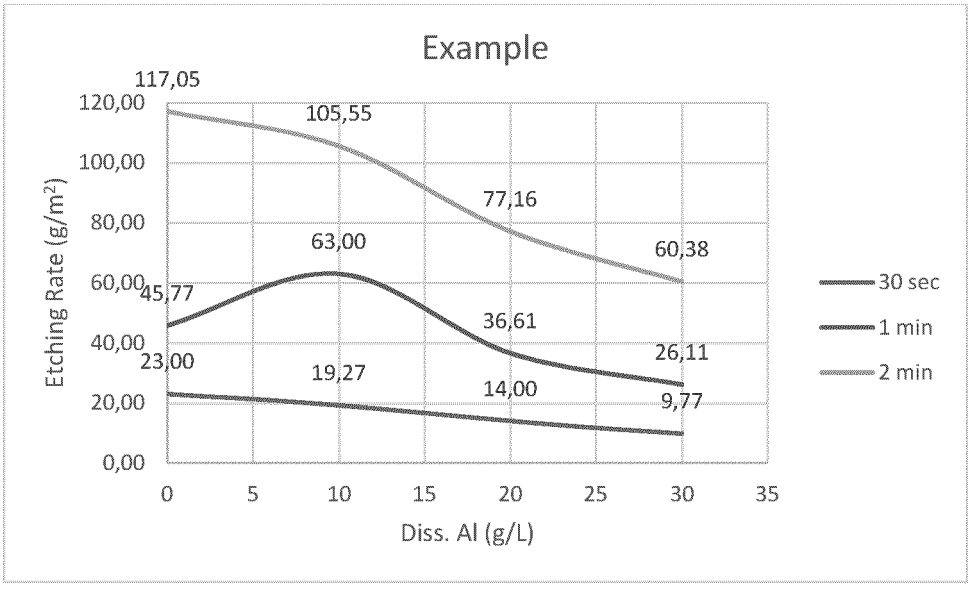

Example
Etching Rate (g/m²)
Diss. Al (g/L)
120,00
100,00
80,00
60,00
40,00
20,00
0,00
0
5
10
15
20
25
30
35
117,05
105,55
77,16
60,38
63,00
45,77
36,61
26,11
23,00
19,27
14,00
9,77
30 sec
1 min
2 min

Fig. 5

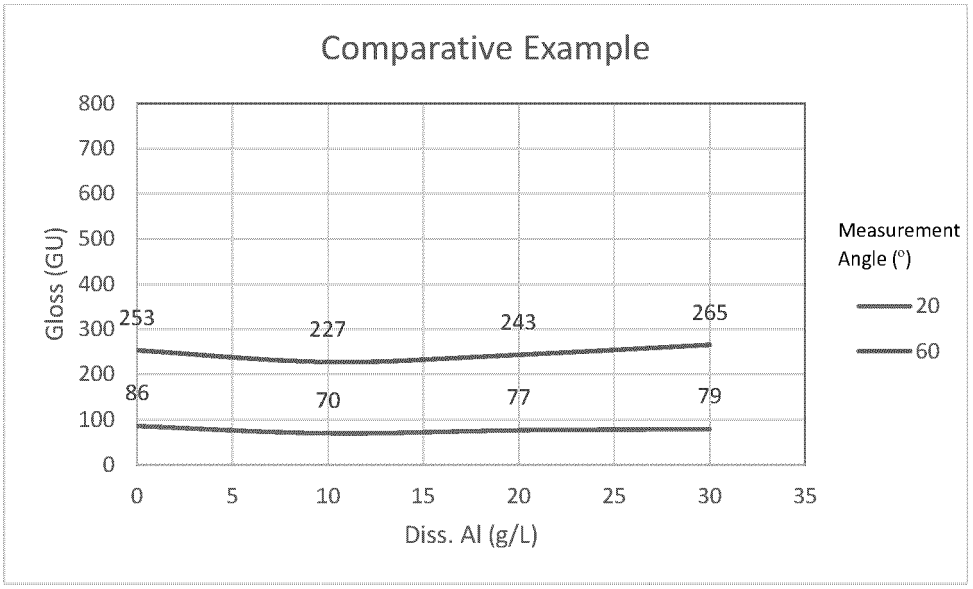
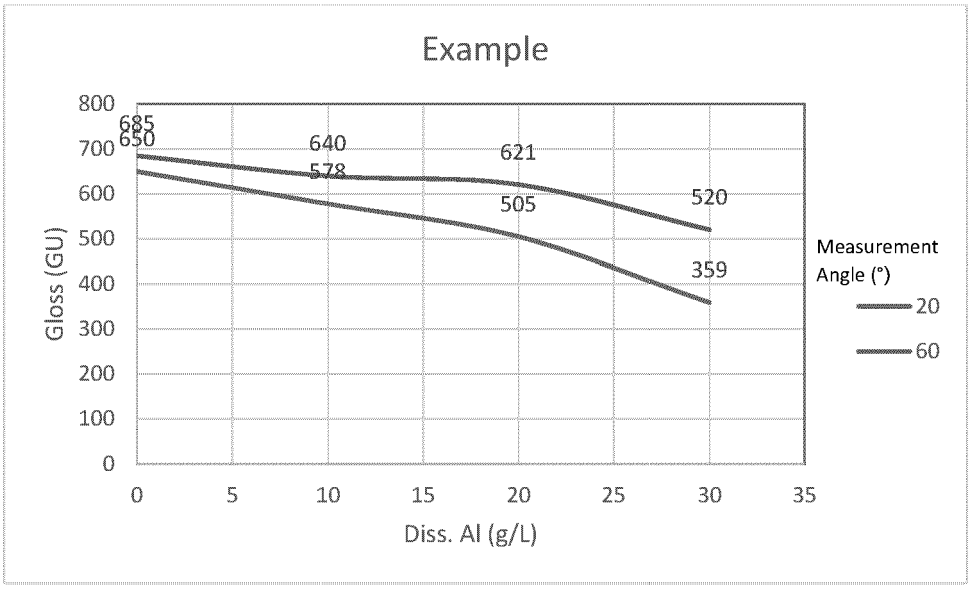

Comparative Example
Gloss (GU)
800
700
600
500
400
300
200
100
0
253
227
243
265
86
70
77
79
0
5
10
15
20
25
30
35
Diss. Al (g/L)
Measurement Angle (°)
20
60

Fig. 6


Example
Gloss (GU)
800
700
600
500
400
300
200
100
0
685
650
640
578
621
505
520
359
0
5
10
15
20
25
30
35
Diss. Al (g/L)
Measurement Angle (°)
20
60

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EUROPEAN SEARCH REPORT

Application Number
EP 22 16 1155

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	29 July 2022	Handrea-Haller, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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