United States Patent [19]

Meyer et al.

[11] **3,897,287**

[45] **July 29, 1975**

[54] **METHOD OF SEALING AND DESMUDGING OF ANODIZED ALUMINUM**

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[22] Filed: **Aug. 11, 1972**

[21] Appl. No.: **279,821**

[52] **U.S. Cl.** ..... **156/22;** 148/6.24; 148/6.27; 252/79.2; 204/35 N

[51] **Int. Cl.** **C23c 3/00;** C23f 13/00

[58] **Field of Search** 148/6.14, 6.24, 6.1, 6.27; 117/62, 63; 204/35, 33, 36; 252/79.4; 156/22; 134/41

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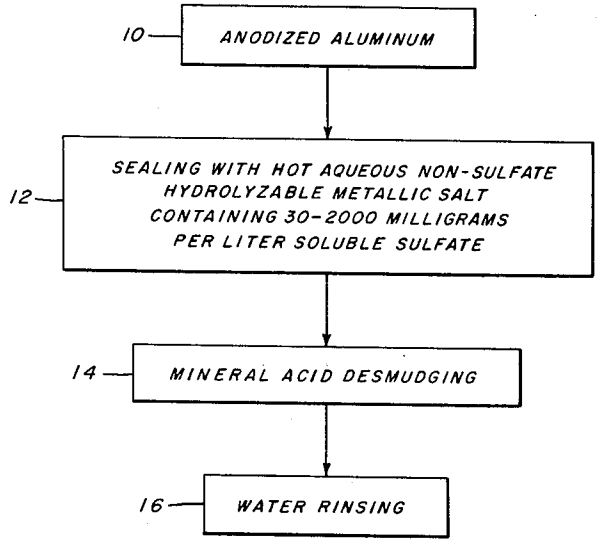
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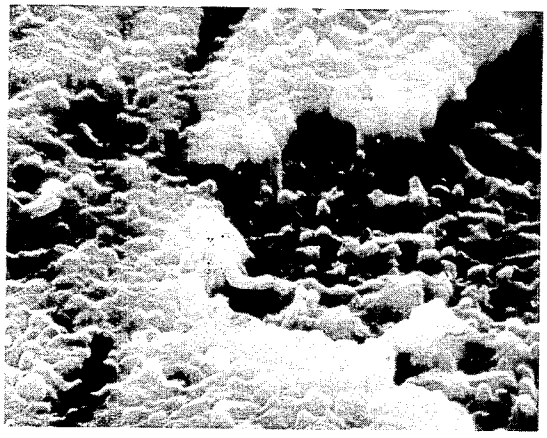
[57] **ABSTRACT**

Addition of sulfate to hydrolyzable metal salt sealing solution to promote subsequent mineral acid removal of smudge from the surface of anodized aluminum.

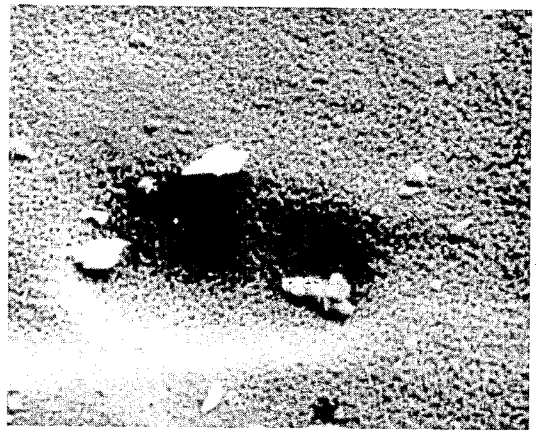
8 Claims, 2 Drawing Figures



PRIOR ART

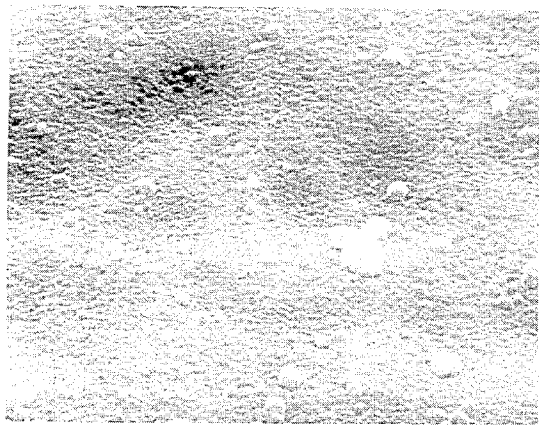


a
Smudge Formed by Non-Sulfate Hydrolyzable Metallic Salt (Nickel Acetate) By Itself

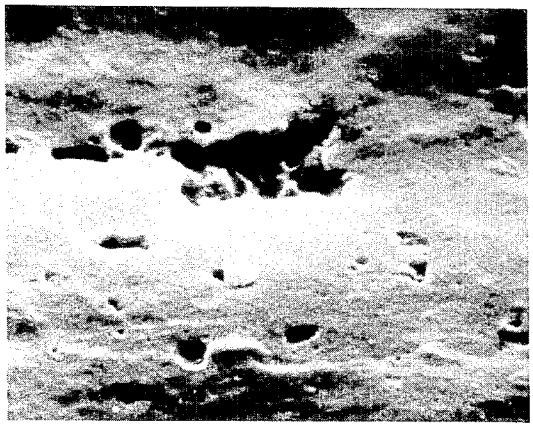


b
Surface "a" After Treatment With 41% HNO_3

THIS INVENTION



c
Smudge Formed by Non-Sulfate Hydrolyzable Metallic Salt (Nickel Acetate) Plus Soluble Sulfate (H_2SO_4)



d
Surface "c" After Treatment With 41% HNO_3

Fig. 1

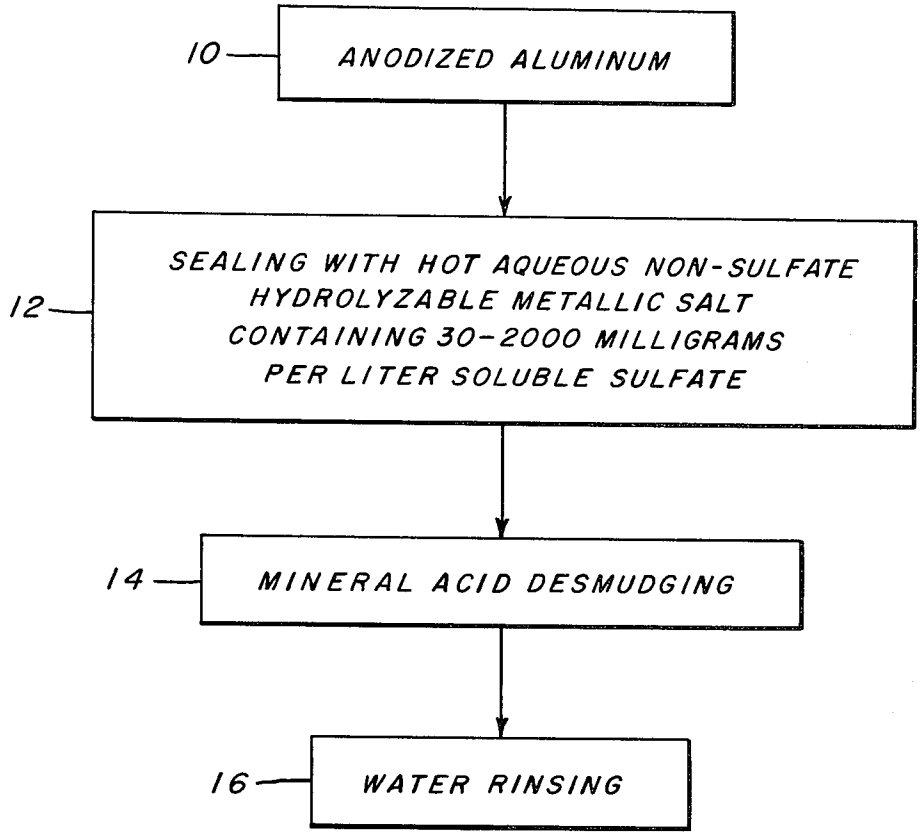

10
ANODIZED ALUMINUM
12
SEALING WITH HOT AQUEOUS NON-SULFATE HYDROLYZABLE METALLIC SALT CONTAINING 30-2000 MILLIGRAMS PER LITER SOLUBLE SULFATE
14
MINERAL ACID DESMUDGING
16
WATER RINSING

FIG. 2.

METHOD OF SEALING AND DESMUDGING OF ANODIZED ALUMINUM

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to treatment of anodized aluminum. The anodized aluminum of this specification is an aluminum or aluminum base alloy which has an anodic oxide coating thereon such as conventionally formed, for example, by electrolytic treatment with sulfuric acid or sulfuric acid/sulfophthalic acid. More particularly, it relates to improved sealing and desmudging of anodized aluminum.

2. Description of the Prior Art

Removal of unattractive multicolored smudge formed during sealing of anodized aluminum, both dyed and undyed, with a hydrolyzable metallic salt such as those employed by Tosterud in U.S. Pat. No. 2,008,733, has for some time presented a constant problem to the aluminum industry, particularly in architectural applications. Limited success in solving this problem has been achieved by treating the smudge-containing surface with mineral acids. Another approach has been to add wetting agents to the sealing bath to minimize the amount of smudge formed. This is sometimes successful. However, in many instances use of either of these procedures results in some permanent smudge. Furthermore, with the development of the acid dissolution test, which involves, after acid desmudging, checking the weight loss (mg/in^2) upon treatment with chromic/phosphoric acid, it has been found that known desmudging procedures have often been detrimental to the seal, this being shown when weight loss by the acid dissolution test exceeds 2 mg/in^2. With the benefit of the acid dissolution test, we have now found that use of a sulfate as the hydrolyzable metallic salt in the aqueous sealing bath, while providing a surface which is readily desmudged with mineral acids, is unsatisfactory because it sometimes has a tendency to cause an inferior seal.

SUMMARY OF THE INVENTION

After extended investigation we have further found that this situation can be remedied by addition of 30–2,000 ppm, preferably 200–1,000 ppm, of a soluble sulfate to a hydrolyzable metallic salt, preferably nickel acetate or cobalt acetate, sealing bath which contains substantially no sulfate and which we will refer to hereinafter as a nonsulfate hydrolyzable metallic salt. More precisely, our invention involves sealing anodized aluminum with an aqueous non-sulfate hydrolyzable metallic salt bath to which 30–2,000 ppm of a soluble sulfate have been added and thereafter desmudging the surface with a mineral acid. It is important, in other words, that the aqueous sealing bath contain both a non-sulfate hydrolyzable metallic salt and between 30 and 2,000 ppm of the added soluble sulfate. Surprisingly, this results not only in a substantially smudge-free surface but one which has a satisfactory seal. For some reason, which we are unable to explain, addition of this amount of sulfate results in formation of a smoother smudge which is both less in quantity and easier to remove in the subsequent mineral acid treatment step. Also surprisingly, sulfuric acid now becomes more efficient in smudge removal when used as the mineral acid with which the smudge-containing sealed anodized aluminum surface is treated.

While any compound which supplies the required soluble sulfate is useful according to the invention, among sulfates which we have found most suitable are sulfuric acid, nickel sulfate, sodium sulfate and aluminum sulfate.

Conventional amounts, preferably at least about 1 g/l, of the non-sulfate hydrolyzable metallic salt may be used in the sealing step of the invention.

For most efficient results the mineral acid employed in the desmudging step should be of a concentration of at least about 15% by weight, preferably at least about 20% by weight. Application of the acid may be by spraying, dipping or the like.

The sealing bath used in the sealing step of the invention should be maintained hot, preferably at a temperature of 195°–212°F. Proper sealing usually requires at least about 15 minutes.

Representative mineral acids useful in the desmudging step of the invention include nitric, hydrochloric, sulfuric, phosphoric, chromic and the like.

Representative non-sulfate hydrolyzable metallic salts useful in the sealing step of the invention include nickel acetate, cobalt acetate and the same and like or similar non-sulfate salts of aluminum, zinc, copper, lead and the alkali metals and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of our invention, reference will now be made to the drawings, which form a part hereof.

In the drawings,

FIG. **1** is a photomicrographic comparison of anodized aluminum sealed and desmudged according to the present invention with the same anodized aluminum sealed and desmudged according to the prior art.

FIG. **2** is a schematic diagram in flow-sheet form illustrating the sealing and desmudging steps of the invention.

In FIG. **1**, which comprises photomicrographic reproductions at 5,000X, the heavy smudge formed (a) by prior art hydrolyzable metallic salt sealing (here 4 g/l nickel acetate) and that left (b) after desmudging with mineral acid (here 5 minutes with 1:1 by volume HNO_3) is contrasted with the light smudge (c) formed by non-sulfate hydrolyzable metallic salt (here nickel acetate) plus added soluble sulfate (here 375 ppm $SO_4^=$) sealing and the almost smudge-free surface (d) after desmudging with the same mineral acid (5 minutes with 1:1 HNO_3).

In FIG. **2**, a specimen of anodized aluminum **10** is sealed in a hydrolyzable metal salt sealing solution containing 30–2,000 mg/l soluble sulfate at **12** and thereafter desmudged at **14** by treatment with a mineral acid. Substantially complete smudge removal is insured by subsequent rinsing with water at **16**, followed by spraying with water (not shown), if desired.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are further illustrative of the invention.

EXAMPLE 1

This example illustrates prior art.

Two specimens of aluminum base alloy sheet containing 0.5 Cu, 0.18 Fe, 0.10 Si, 0.01 Mn, 0.04 Mg, 0.18 Cr and 0.02 Ti were simultaneously anodized in a

sulfuric acid/sulfophthalic acid electrolyte at 70°F and 24 asf to a plateau voltage of 75 volts. Total anodizing time was 35 minutes. Each specimen was treated as follows:

1. sealed in 4 g/l nickel acetate at 5.6 pH and 212°F
2. desmudged for 5 minutes by immersion in 41% by weight HNO_3
3. rinsed by immersion in water, followed by spraying.

After drying, the specimens did not retain on their surface a white chalky smudge or residue that was formed by the sealing step but exhibited a yellowish hue and had a relatively textured appearance.

EXAMPLE 2

The procedure of Example 1 was followed on the same alloy except for use of 0.1 g/l H_2SO_4 (approximately 100 ppm soluble sulfate) in the nickel acetate sealing solution. After drying, the single specimen was free of surface residue and did not exhibit the yellowish hue or relatively textured appearance of the desmudged specimen of Example 1.

EXAMPLE 3

A specimen anodized as in Example 1 was immersed in an aqueous sealing solution containing 4 g/l nickel acetate and 700 mg/l (700 ppm) soluble sulfate (as sulfuric acid) for 20 minutes with air agitation. The treatment temperature was 212°F and the pH of the bath 5.7. The specimen was then rinsed by immersion in water before immersion in a static aqueous solution of 41% by weight nitric acid for 5 minutes at 75°F. It was then rinsed by immersion in water prior to spraying with water and drying in air. There was an absence of sealing residue or smudge on the specimen after the drying. Excellent seal quality was indicated by an acid dissolution value of less than 2 mg/in^2 as measured by the acid dissolution test.

EXAMPLE 4

Equally good results were obtained by following the procedure of Example 3 except for substituting use of 20% by weight HNO_3 in the desmudging step for the 41% HNO_3.

EXAMPLE 5

15% by weight H_2SO_4 was employed in the desmudging step in place of the 41% HNO_3 of Example 3 with successful desmudging.

EXAMPLE 6

The procedure of Example 3 was employed except for use of 50% by weight H_2SO_4 in place of the 41% by weight HNO_3 used in the smudge removal step. Smudge was again successfully removed without adversely affecting the quality of the nickel acetate seal.

EXAMPLE 7

The procedure of Example 3 was followed except that the final water-spraying step was not used. There was substantially complete removal of the smudge formed by the sealing step as a result of the mineral acid (HNO_3 here) treatment step which followed.

EXAMPLE 8

The following table shows the sealing results (acid dissolution test in two successive 15-minute intervals) for four samples of an anodized aluminum base alloy sheet containing 0.5 Cu, 0.18 Fe, 0.10 Si, 0.01 Mn, 0.04 Mg, 0.18 Cr and 0.02 Ti sealed for 20 minutes with 4 g/l nickel acetate solution containing 758 mg/l (758 ppm) soluble sulfate ($SO_4^=$) supplied by H_2SO_4 and then desmudged by a 5-minute 41% HNO_3 dip. In each instance desmudging was sufficiently satisfactory to pass commercial architectural use requirements.

Table I

Sample No.	Temp. (°F)	pH	Acid Dissolution (mg/in^2) 1st Interval	2nd Interval
1	205	5.95	0.79	1.36
2	205	5.55	1.11	1.86
3	205	5.25	1.24	2.37
4	195	5.55	1.97	4.80

EXAMPLE 9

Sulfuric acid, sodium sulfate and nickelous sulfate were used in separate instances to supply the soluble sulfate in a 30–2,000 ppm non-sulfate (here nickel acetate) hydrolyzable metallic salt sealing step according to the invention. In all cases subsequent acid desmudging produced sealed anodized aluminum surfaces meeting commercial architectural requirements.

EXAMPLE 10

The following table records visual observation desmudging results and acid dissolution values for a series of anodized aluminum samples sealed and desmudged according to the invention. Results are compared with those obtained by use of a non-sulfate hydrolyzable metal salt bath to which soluble sulfate was not added. Various concentrations of nitric and sulfuric acids were employed in the desmudging step as indicated in the table. Sealing prior to desmudging was accomplished by using an aqueous bath containing 4 g/l nickel acetate and 721 mg/l soluble sulfate coming from sulfuric acid except for, for comparison of prior art, the samples shown as being sealed in a bath containing nickel acetate only, upon which no acid dissolution tests were run. Sealing was at 208°F and at a pH of 5.8 for 20 minutes. Where run, acid dissolution was in two successive steps of 15 minutes each.

Table III

Specimen	Desmudging Acid	Desmudging Concentration (% by weight)	Desmudging Time 2 min.	5 min.	Visual Appearance	Acid Dissolution 1st 15 min. mg/in^2	2nd 15 Min. mg/in^2
1	HNO_3	41	X		Clean	0.48	0.98
2	H_2SO_4	15	X		Clean	0.48	1.01
3	"	25	X		Clean	0.51	0.87
4	"	35	X		Residue	0.56	1.01
5	"	50	X		Residue	0.59	1.23
6	HNO_3	41		X	Clean	0.56	1.02
7	H_2SO_4	15		X	Clean	0.46	0.91
8	"	25		X	Clean	0.56	0.97
9	"	35		X	Residue	0.69	1.29

Table III – Continued

Specimen	Acid	Desmudging Concentration (% by weight)	Desmudging Time 2 min.	Desmudging Time 5 min.	Visual Appearance	Acid Dissolution 1st 15 min. mg/in²	Acid Dissolution 2nd 15 Min. mg/in²
10	"	50		X	Residue	1.03	1.17
11	HNO_3	41	X		Clean	0.41	0.79
12	H_2SO_4	15	X		Clean	0.39	0.68
13	"	25	X		Clean	0.35	0.80
14	"	35	X		Clean	0.37	0.68
15	H_2SO_4	50	X		Clean	0.39	0.65
16	HNO_3	41		X	Clean	0.40	0.68
17	H_2SO_4	15		X	Clean	0.33	0.53
18	"	25		X	Clean	0.38	0.63
19	"	35		X	Residue	0.52	0.79
20	"	50		X	Residue	0.56	0.78
21	HNO_3	41	X		Clean	0.22	0.21
22	H_2SO_4	15	X		Clean	0.19	0.23
23	"	25	X		Clean	0.22	0.20
24	"	35	X		Clean	0.22	0.23
25	"	50	X		Clean	0.26	0.22
26	HNO_3	41		X	Clean	0.27	0.22
27	H_2SO_4	15		X	Clean	0.25	0.22
28	"	25		X	Clean	0.28	0.21
29	H_2SO_4	35		X	Residue	0.43	0.24
30	"	50		X	Residue	0.39	0.25
31	HNO_3	41	X		Clean	0.24	0.20
32	H_2SO_4	15	X		Clean	0.23	0.19
33	"	25	X		Clean	0.23	0.19
34	"	35	X		Clean	0.25	0.17
35	"	50	X		Clean	0.24	0.19
36	HNO_3	41		X	Clean	0.25	0.21
37	H_2SO_4	15		X	Clean	0.25	0.21
38	"	25		X	Clean	0.27	0.21
39	"	35		X	Clean	0.33	0.32
40	"	50		X	Clean	0.36	0.35
41[1]	HNO_3	41	X		Iridescence & Residue		
42[1]	H_2SO_4	15	X		Iridescence & Residue		
43[1]	H_2SO_4	25	X		Iridescence & Residue		
44[1]	"	35	X		Residue		
45[1]	"	50	X		Residue		
46[1]	HNO_3	41		X	Iridescence & Residue		
47[1]	H_2SO_4	15		X	Iridescence & Residue		
48[1]	"	25		X	Iridescence & Residue		
49[1]	"	35		X	Residue		
50[1]	"	50		X	Residue		
51	HNO_3	41	X		Clean	0.96	1.32
52	H_2SO_4	15	X		Clean	0.89	1.81
53	"	25	X		Clean	0.96	1.89
54	"	35	X		Clean	1.06	2.02
55	"	50	X		Clean	1.31	2.67
56	HNO_3	41		X	Clean	1.00	2.02
57	H_2SO_4	15		X	Clean	1.01	2.27
58	"	25		X	Clean	1.04	2.10
59	"	35		X	Clean	1.64	2.55
60	"	50		X	Clean	1.99	2.69

[1]Sealed in sulfate-free nickel acetate solution

EXAMPLE 11

This example illustrates the range of soluble sulfate concentration in the sealing step that can be tolerated according to the invention without adversely affecting the quality of the seal. A microscopic study of samples sealed and desmudged under varying conditions was made. An anodized aluminum alloy containing 0.5 Cu, 0.18 Fe, 0.10 Si, 0.01 Mn, 0.04 Mg, 0.18 Cr and 0.02 Ti was sealed in boiling water containing 4 g/l nickel acetate plus 0, 75, 375, 750, 1,500 and 2,000 ppm soluble sulfate supplied by H_2SO_4. The amount of smudge formed decreased in proportion to the concentration of sulfate in the sealing bath. The surface of the sample sealed at a level of 200 ppm sulfate resembled that of an imperfectly sealed film. Transmission electron micrographs taken of a magnification of 50,000X revealed that this surface was basically the same as that produced without sulfate or with less sulfate, respectively. The smudge formed by the baths employing soluble sulfate was considerably more compact and of a substantially finer structure than the deposit formed in pure nickel acetate solution.

Desmudging was accomplished in 1:1 (by volume) or 41% by weight HNO_3 for from 3 to 60 minutes. A nitric acid treatment of 5 minutes left considerable surface roughness on the sample sealed in an aqueous solution containing 4 g/l nickel acetate and no sulfate. The samples sealed in baths with 375 ppm and 750 ppm sulfate showed a smooth surface after immersion in nitric acid. Holes in the surface resulted from dissolved intermetallic constituents.

According to the transmission micrographs the acid removed an outer layer of smudge which resembled crinkled tissue paper. It then partially dissolved the intermediate, optically structureless layer that covered the pore mouths. Rather severe attack occurred on layers formed in baths containing 100 and 0 ppm sulfate, respectively. The surface roughness of the 2,000 ppm sulfate sample was on the order of only a few hundred angstroms. Since the pattern was very uniform, this surface would probably appear substantially smooth in visible light.

Sealing in solutions containing sulfate not only affected the morphological structure of the surface layer, but also improved its resistance to acid. After 60 minutes of immersion in nitric acid, the sample sealed in pure nickel acetate solution showed severe attack on pores and cell boundaries of the coating. Incipient attack of this nature was visible on the sample sealed with 100 ppm sulfate. The 2,000 ppm specimen, however, showed less surface dissolution than the 100 ppm sample after 5 minutes immersion in acid.

The results of microscopic investigation indicated addition of up to 2,000 ppm soluble sulfate to non-sulfate hydrolyzable metallic salt sealing solutions reduced the volume of the outer smudge layer. The more compact layers were smoother and, therefore, scattered visible light to a lesser extent. In addition, the reduced surface area resulted in a slower rate of reaction during the acid treatment, thus increasing the chemical stability of the sealing layer.

EXAMPLE 12

In this example use of nickel sulfate as the hydrolyzable metallic salt for both sealing and supplying of a soluble sulfate was tried to demonstrate how such use does not work according to the invention but instead results in a detrimental effect on the quality of the seal, as evidenced by a greater than 2 mg/in^2 acid dissolution value except for one sample treated with a sealing bath having a 5.9 pH. For each sample of the following table, however, satisfactory desmudging was obtained by use of 41% by weight nitric acid.

Table IV

Nickelous Sulfate Concentration g/l	Solution pH	Surface Appearance As Sealed	After Desmudging	Acid Dissolution (mg/in^2)
1.48	5.0	streaked-yellowish smudge	clean — uniform	3.1
1.48	6.0	streaked velvety smudge	clean — few spots of residue	5.5
1.48	7.0	velvety iridescent smudge	clean — slight mottling	3.5
5.94	4.8	streaked iridescent smudge	clean — uniform	4.7
5.94	5.9	streaked iridescent smudge	clean — slight mottling	1.78
5.94	7.0	velvety iridescent smudge	clean — slight mottling	3.2

EXAMPLE 13

This example, in Table V below, compares desmudging of anodized aluminum after sealing with nickel sulfate as the sole hydrolyzable metallic salt (Samples I*a*, I*b*, I*c*, II*a*, II*b* and II*c*) with desmudging after sealing with only a non-sulfate hydrolyzable metallic salt (here nickel acetate) plus sulfate (Samples III*a*, III*b* and III*c*). Each sealing solution was operated at 212°F for 20 minutes. Sealing trials were conducted respectively at pH's of 5, 6 and 7. Each sample was desmudged by immersion for 3 minutes in 41% by weight nitric acid after the sealing step. Process effectiveness in terms of quality of desmudging by visual examination and quality of sealing by the acid dissolution test was determined.

The quantities of each of the sealing bath constituents, in each case, were determined on the basis of the amounts of either sulfate, nickel, or acetate present in a known effective sealing solution consisting of 4 g/l nickel acetate. Seals III*a*, III*b*, and III*c* consisted of 4.0 g/l $NiAc_2$ and the nickelous sulfate added yielded 750 ppm soluble sulfate. For Seals I*a*, I*b* and I*c* the nickelous sulfate used was such that the $SO_4^=$ is equivalent to the quantity of acetate present in a 4 g/l $NiAc_2$ solution. Seals II*a*, II*b* and II*c* were the same as Seals I*a*, I*b* and I*c* but with an additional 750 ppm of $SO_4^=$ added.

The pH of each solution as made up was adjusted with acetic acid or sodium hydroxide in each instance to bring it from the original pH's for Samples I*a*, I*b* and I*c* of 5.05, for Samples II*a*, II*b* and II*c* of 6.05 and for Samples III*a*, III*b* and III*c* of 5.10 to the values shown in the following Table V.

Table V

Sealing Solution Makeup	Sample No.	pH	Acid Dissolution (mg/in^2)	Appearance After Desmudging
$NiSO_4.6H_2O$ 7.31 g/l	Ia	5	0.68	Clean
	Ib	6	0.52	Clean
	Ic	7	1.99	Reddish iridescence
$NiSO_4.6H_2O$ 9.36 g/l	IIa	5	0.57	Yellowish iridescence
	IIb	6	0.64	Yellowish iridescence
	IIc	7	0.90	Clean
$NiAc_2.4H_2O$ 5.63 g/l	IIIa	5	2.15	Yellowish iridescence
	IIIb	6	1.60	Clean
$NiSO_4.6H_2O$ 2.05 g/l	IIIc	7	0.43	Yellowish iridescence

While the invention has been described in terms of preferred embodiments, the claims appended hereto are intended to encompass all embodiments which fall within the spirit of the invention.

Having thus described our invention and certain embodiments thereof, we claim:

1. In a process for sealing anodized aluminum in an aqueous bath containing a hydrolyzable metallic salt followed by removal of smudge with a mineral acid, the improvement which comprises:

a. sealing said anodized aluminum in an aqueous bath consisting essentially of:
   1. water,
   2. at least one non-sulfate hydrolyzable metal salt, and
   3. 375–2,000 ppm soluble sulfate ($SO_4^=$) and

b. thereafter removing smudge formed on said anodized aluminum by said sealing by treating same with a solution consisting essentially of:
   1. mineral acid, and
   2. water

without adversely affecting the seal produced by said sealing.

2. The improvement of claim **1** wherein the non-sulfate hydrolyzable metal salt comprises at least about 1 g/l of said sealing bath.

3. The improvement of claim **1** wherein the soluble sulfate is supplied by at least one sulfate selected from the group consisting of sulfuric acid, nickel sulfate, aluminum sulfate and sodium sulfate.

4. The improvement of claim **1** wherein the mineral acid comprises at least one acid selected from the

group consisting of nitric, hydrochloric, sulfuric, phosphoric and chromic.

5. The improvement of claim **1** wherein the concentration of the mineral acid is at least about 15% by weight.

6. The improvement of claim **1** wherein the concentration of the mineral acid is at least about 20% by weight.

7. The improvement of claim **1** wherein the non-sulfate hydrolyzable metallic salt is selected from the group consisting of nickel acetate and cobalt acetate.

8. In a process for sealing and desmudging anodized aluminum, the improvement which comprises:

a. sealing said anodized aluminum in a bath consisting essentially of:
   1. water,
   2. at least one non-sulfate hydrolyzable metal salt selected from the group consisting of nickel acetate and cobalt acetate comprising at least about 1 g/l of said sealing bath, and
   3. 375–2,000 ppm soluble sulfate selected from the group consisting of sulfuric acid, nickel sulfate, aluminum sulfate, and sodium sulfate, and

b. thereafter removing smudge formed on said anodized aluminum by said sealing by treating same with a solution consisting essentially of:
   1. water, and
   2. at least about 15% by weight of a mineral acid selected from the group consisting of nitric, hydrochloric, sulfuric, phosphoric, and chromic acid,

without adversely affecting the seal produced by said sealing.

* * * * *