

[54] **CORROSION AND ABRASION RESISTANT ALUMINUM AND ALUMINUM ALLOY PLATES PARTICULARLY USEFUL AS SUPPORT MEMBERS FOR PHOTOLITHOGRAPHIC PLATES AND THE LIKE**

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[58] Field of Search **204/35 N, 38 A, 17, 42, 204/28, 58, 38 E; 117/34**

[56] **References Cited**

UNITED STATES PATENTS

3,376,205	4/1968	Cohn	204/35 N
3,531,381	9/1970	Amore et al.	204/42
3,658,662	4/1972	Casson, Jr. et al.	204/58

3,775,266	11/1973	Ikeda et al.	204/38 A
3,852,124	12/1974	Fassell	204/35 N

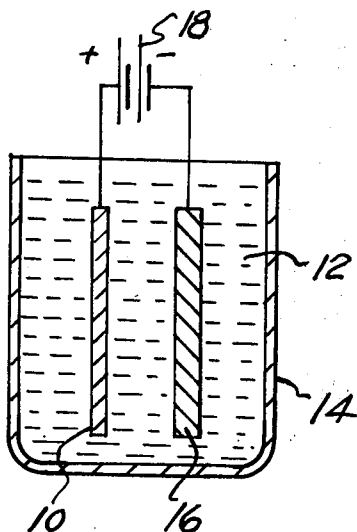
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[57] **ABSTRACT**

A process for electrolytically forming on an aluminum or aluminum alloy sheet or plate a protective layer of film which is corrosion- and abrasion-resistant and provided with a hydrophilic surface. The process consists in first anodizing the aluminum or aluminum alloy sheet or plate in an electrolyte consisting of an aqueous solution of a mineral acid such as to form on the aluminum or aluminum alloy surface an aluminum oxide film, and subsequently electrolytically treating the film in an aqueous solution of sodium silicate, such as to form a durable abrasion-resistant and corrosion-resistant barrier layer on the sheet or plate of aluminum or aluminum alloy which is hydrophilic and which prevents deterioration of a light sensitive diazo resin, or the like, placed as a photosensitive coating on the sheet or plate so as to form a presensitized lithographic plate.

14 Claims, 8 Drawing Figures



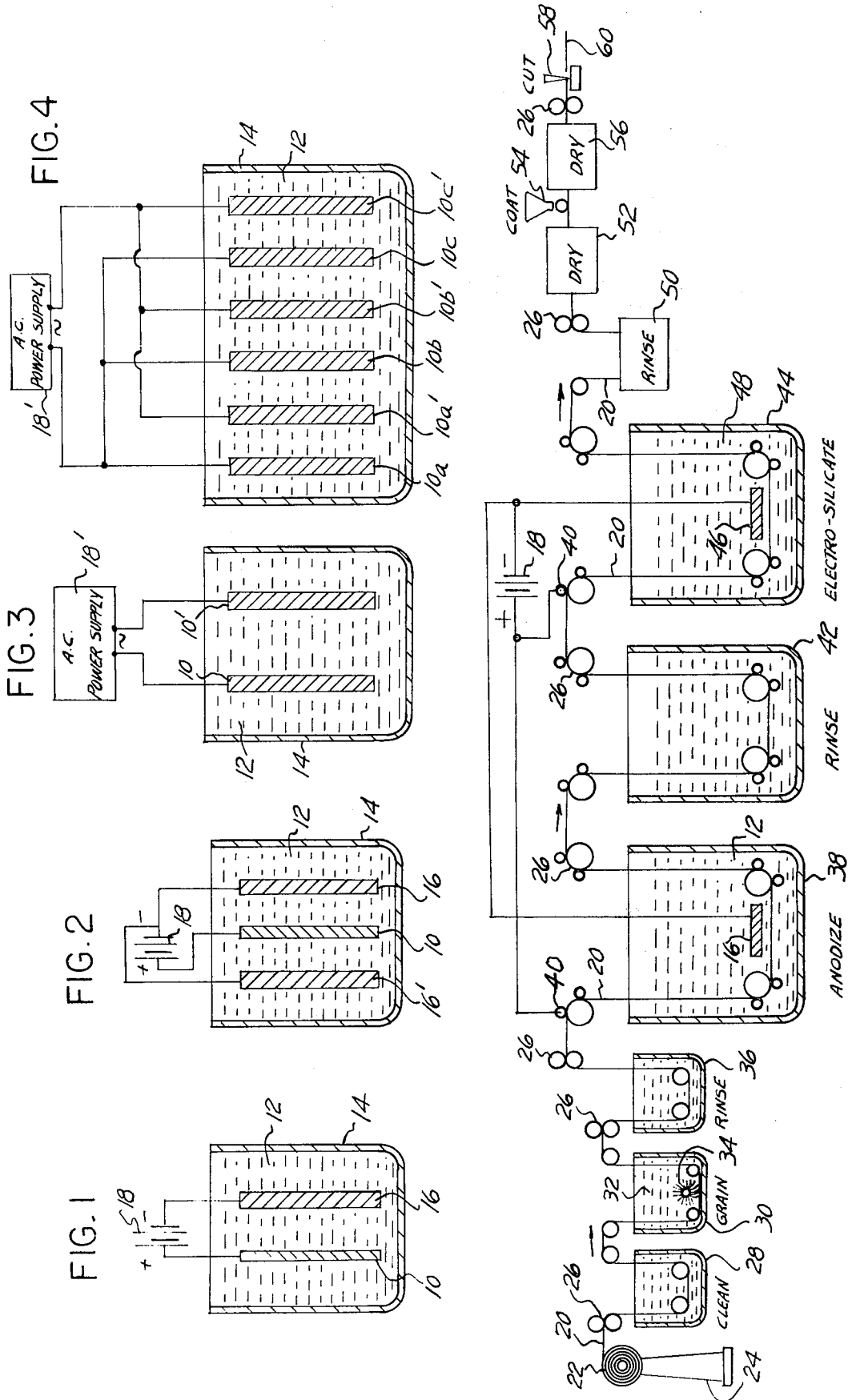


FIG. 8

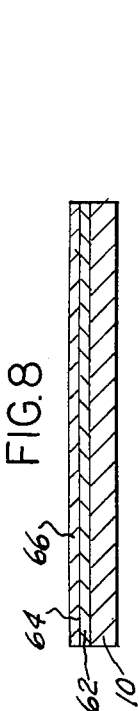
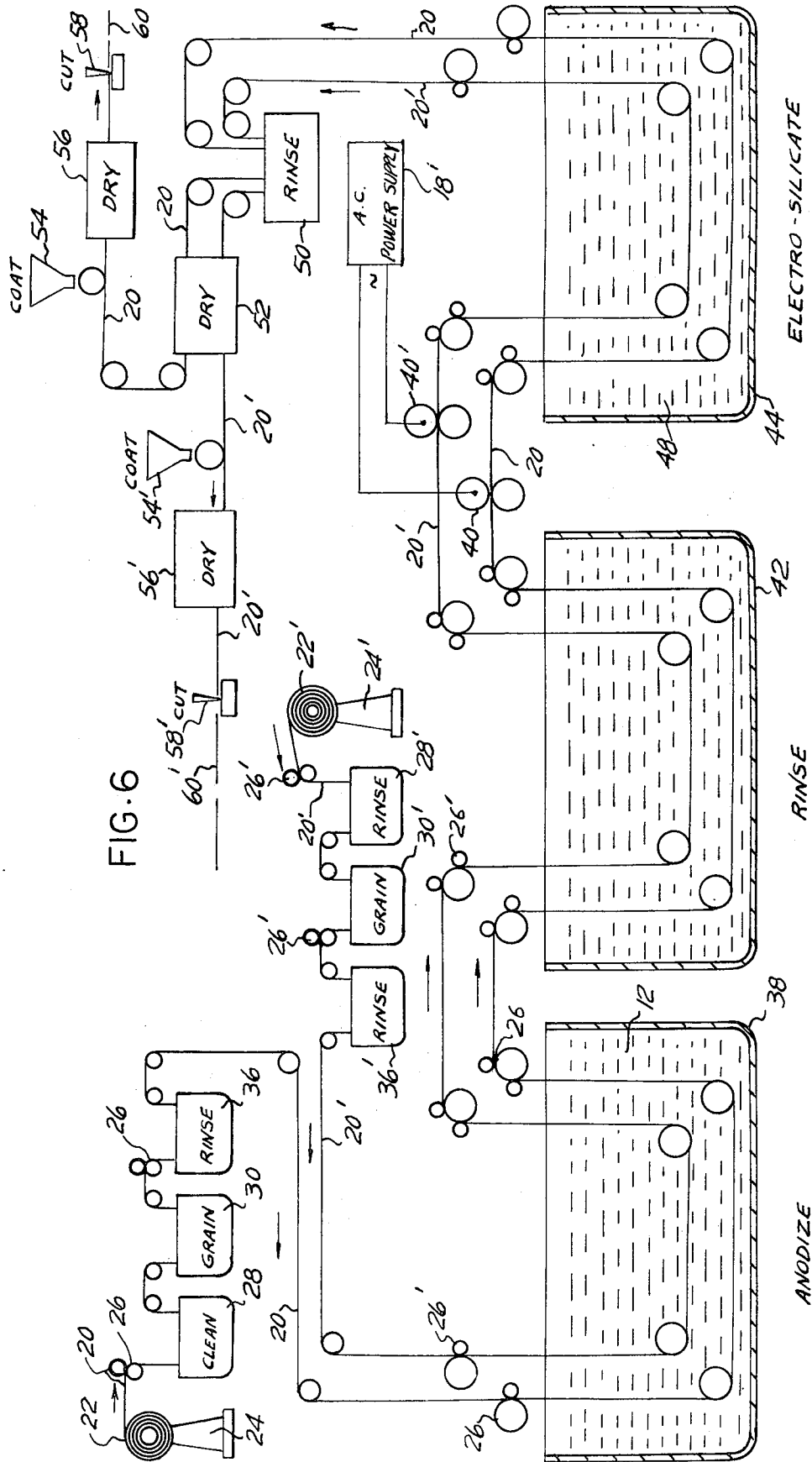


FIG. 7



FIG. 6



oleophilicity to the image areas, thus insuring long runs of the plates in the printing press. Such qualities are difficult to obtain in a repetitive manner by way of the chemical processes of the prior art.

In U.S. Pat. No. 3,658,662 issued Apr. 25, 1972 and assigned to the same assignee as the present application, there is disclosed an electrolytic process for forming an improved functional surface on aluminum and aluminum alloy plates which permits to achieve consistent and repetitive quality of the surface and permits to obtain a surface greatly enhancing the quality of photolithographic plates as compared to what is achieved by prior art methods.

The invention disclosed in said patent provides an electrolytic process for forming on the surface of a metallic plate, such as is generally used as a support member for a coating of diazonium salts or the like in photolithographic plates, a pacified, corrosion-resistant, hydrophilic surface layer greatly enhancing lithographic and printing performances as compared to the surface layer obtained by strictly chemical processes. Although silication obtained by prior art chemical methods provides a barrier layer between the metallic plate and the diazonium salt compounds or the like utilized as the photosensitive coating in photolithographic plates, electrolytically formed surface layers are much improved as far as lithographic hardness, and continuity and uniformity of the layers or films are concerned. The electrolytic process of said patent also produces surface layers which are intimately bonded to the underlying metal, which have high hydrophilic qualities and which result in an important improvement in the fine grain of the plate surface. In addition, the electrolytically formed surface layer has a much improved anchoring quality for adhesion of the diazo resin thus reducing any tendency to image failure and resulting in improved printing runs. The improved surface grain and the increase in bonding quality of the electrolytically treated surface also result in more retained diazo, more retained lacquer and a more oleophilic image, leading to longer running and higher quality press performances, as compared to conventional lithographic plates.

Although the electrosilicated surface obtained by the method of U.S. Pat. No. 3,658,662, when provided with a coating of diazonium salts or other photosensitive material, has proved to provide greatly improved photolithographic plates, such plates still require to be handled with a certain amount of caution as the surface is not entirely scratch-free.

It has now been discovered that when an aluminum or aluminum alloy surface is first anodized in an acidic electrolyte and subsequently electrosilicated according to the method of the aforementioned patent, the anodized and electrosilicated surface is scratch-resistant and at the same time all the advantageous characteristics of the electrosilicated surface are maintained in their entirety.

Among the advantages provided by the surface treatment obtained by the method of the present invention relative to photolithographic plates and printing press cylinder, rollers and other support members, are less propensity to attack from the printing press fountain solutions, a marked decrease in soluble film remaining on the lithographic plate after rinsing, improved hydrophilic quality of the plate background surface, a lithographically harder surface and a decrease in deterio-

ration of the plate as a result of wear. The hard, compact surface film or layer obtained by the present invention on the surface of aluminum or aluminum alloy elements, because of its corrosion-resistant characteristics, its bonding and anchoring qualities with respect to decorative or protective films which may subsequently be applied thereto and the increase in electrical resistivity as compared to the resistivity of the base material, presents the added advantage of providing articles having general usefulness in the industry.

SUMMARY OF THE INVENTION

The present invention therefore is an improvement upon the method disclosed in U.S. Pat. No. 3,658,662 which consists in electrolytically anodizing a sheet or plate of aluminum or aluminum alloy in an acidic electrolyte so as to provide on the surface of the sheet or plate a film of aluminum oxide which after being subjected to a further anodic treatment in an electrolyte bath of an alkaline metal salt, such as sodium silicate, provides an effective barrier film, an anchoring surface for paint, varnish and the like, or for a coating of photosensitive material when the sheet or plate is used as a support member for a lithographic plate.

These and other advantages and objects of the invention will become apparent to those skilled in the art when the accompanying description of some of the best modes contemplated for practicing the invention is read in conjunction with the accompanying drawing wherein like reference numerals refer to like or equivalent parts.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic representation of an example of arrangement for practicing the electrolytic process of the present invention;

FIG. 2 is a schematic representation of a modification thereof;

FIG. 3 is a schematic representation of a further modification thereof;

FIG. 4 is a schematic representation of a further modification thereof;

FIG. 5 is a schematic representation of a continuous line process for manufacturing a photolithographic plate according to the present invention;

FIG. 6 is a view similar to FIG. 5 but showing a modification of the method for manufacturing photolithographic plates according to the present invention;

FIG. 7 is a schematic sectional view of an aluminum or aluminum alloy plate having been subjected to the process of the invention; and

FIG. 8 is a schematic sectional view of the plate of FIG. 7 provided with a coating or photosensitive material such as a diazo resin or the like.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to practice the present invention, a cleaned aluminum or aluminum alloy element such as a plate 10, as shown at FIG. 1, is dipped in an appropriate electrolyte 12, contained in a tank 14, the plate 10 being disposed in proximity to an electrically conductive electrode 16. The plate 10 is connected to the positive terminal of a DC power supply 18, and the electrode 16 is connected to the negative terminal of the power supply, such that the plate 10 is electrolytically anodic and the conductive electrode 16 is electrolytically cathodic.

The conductive electrode 16 may be in the form of a solid metallic plate, or in the shape of a grid or mesh made of the same material as the metallic plate 10, or made of a dissimilar material.

The DC power supply 18 may be a bank of storage batteries, an AC-DC dynamo-electric or a static converter, an AC-DC rectifier or any other convenient source of DC power. A pulsed DC current power supply may be used, and it does not seem material whether the DC voltage across the terminals of the power supply is constant and steady or includes an AC ripple. An AC power supply may be also used, which is arranged to operate on that portion of the cycle when the metallic element 10 is substantially anodic.

EXAMPLE 1

Plates of 1100 aluminum, having an area of 25 sq. in. and .009 in. thick were prepared by having a surface of a continuous web of the aluminum material grained at a line speed of 12 feet per minute using a sand slurry. The web was then cut so as to provide plates of the indicated area.

The plates were electrolytically anodized according to the arrangement of FIG. 1, by dipping each plate in the electrolyte at a predetermined distance from a cathode 16 consisting of a stainless steel grid, having an area matching that of the plate 10, the grained surface of the plate 10 being disposed opposite the cathode 16. The spacing between the plate and the cathode was three inches. The electrolyte 12 used was an aqueous solution of 8% sulfuric acid. A DC power supply 18 of 18 volts at 50 amps was used.

After each anodizing operation, the plates 10 were rinsed with water and dried.

In order to test the degree to which the plates were anodized, a saturated solution of stannous chloride (SnCl_2) was poured on the surface of the plates on the anodized side. The better the barrier formed by the anodization step the longer it took for the stannous chloride to break through the barrier film and react with the subjacent aluminum, the reaction being according to the following formula:



The penetration of the stannous chloride through the pores of the aluminum oxide layer obtained by anodization is noticeable as a plurality of dark points, and the reaction is complete when the plate ceases to darken.

In order to determine the influence of temperature of the anodizing bath and the influence of the duration of treatment of the plates in the anodizing bath, a first series of runs were made while maintaining the temperature of the electrolyte at 40°C and a second series of runs were made while maintaining the temperature of the electrolyte at room temperature (25°C). The results achieved are tabulated in Tables 1 and 2:

TABLE 1

TEMPERATURE OF ELECTROLYTE 40°C	
Duration of Anodization (sec.)	Time for SnCl_2 to break through (min.)
0 (control)	immediately
3	0.25 - 0.30 (15-20 sec.)
6	2
9	6
12	11.5
15	18.0

TABLE 2

TEMPERATURE OF ELECTROLYTE 25°C	
Duration of Anodization (sec.)	Time for SnCl_2 to break through (min.)
0 (control)	immediately
3	2
5	5
10	9
15	20
20	27

The test results tabulated in Tables 1 and 2 indicate clearly that at a given concentration of the electrode the best barrier films are provided at lower temperature of the electrolyte.

EXAMPLE 2

To further determine the influence of acid concentration in the electrolyte, a series of tests was run for different anodization durations with the arrangement of FIG. 1 and under the general conditions described with respect to Example 1, maintaining the electrolyte temperature at a constant 25°C and using a 5% solution of sulfuric acid, a 10% solution and a 15% solution. The results achieved are tabulated in Tables 3-5:

TABLE 3

5.0% solution of H_2SO_4 at 25°C	
Duration of Anodization (sec.)	Time for SnCl_2 to react (min.)
0 (control)	immediately
3	2.5
5	6.8
10	11.3
15	25.0
20	33.3

TABLE 4

10.0% solution of H_2SO_4 at 25°C	
Duration of Anodization (sec.)	Time for SnCl_2 to react (min.)
0 (control)	immediately
3	1.8
5	4.5
10	8.2
15	18.1
20	25.0

TABLE 5

15.0% solution of H_2SO_4 at 25°C	
Duration of Anodization (sec.)	Time for SnCl_2 to react (min.)
0 (control)	immediately
3	1.5
5	4.2
10	7.8
15	17.2
20	22.0

EXAMPLE 3

The tests of Example 2 were repeated, at the diverse concentrations of sulfuric acid of respectively 5%, 10% and 15%, but maintaining the electrolyte temperature at 40°C. The results of the stannous chloride attack tests are tabulated in Tables 6-8:

TABLE 6

5% solution of H ₂ SO ₄ at 40°C	
Duration of Anodization (sec.)	Time for SnCl ₂ to react (min.)
0 (control)	immediately
3	2.0
5	5.7
10	10.2
15	22.6
20	29.0

TABLE 7

10% solution of H ₂ SO ₄ at 40°C	
Duration of Anodization (sec.)	Time for SnCl ₂ to react (min.)
0 (control)	immediately
3	1.5
5	3.9
10	7.0
15	16.4
20	22.0

TABLE 8

15% solution of H ₂ SO ₄ at 40°C	
Duration of Anodization (sec.)	Time for SnCl ₂ to react (min.)
0	immediately
3	1.1
5	3.7
10	6.1
15	14.8
20	20.3

EXAMPLE 4

The tests of the preceding Examples were repeated, at the diverse concentrations of electrolyte of respectively 5%, 10% and 15% solutions of sulfuric acid, maintaining the temperature of the anodizing electrolyte at 55°C. The results achieved are tabulated in Tables 9-11:

TABLE 9

5.0% solution of H ₂ SO ₄ at 55°C	
Duration of Anodizations (sec.)	Time for SnCl ₂ to react (min.)
0 (control)	immediately
3	1.8
5	5.1
10	9.3
15	20.7
20	28.2

TABLE 10

10.0% solution of H ₂ SO ₄ at 55°C	
Duration of Anodization (sec.)	Time for SnCl ₂ to react (min.)
0 (control)	immediately
3	1.1
5	3.0
10	5.9
15	13.3
20	20.1

TABLE 11

15.0% solution of H ₂ SO ₄ at 55°C	
Duration of Anodization (sec.)	Time for SnCl ₂ to react (min.)
0 (control)	immediately
3	0.7
5	3.2
10	5.4
15	12.5
20	18.6

From the tests of Examples 1-4 it is readily apparent that the best quality anodized plates, as far as the stannous chloride test hereinbefore explained is concerned, are obtained for a duration of anodization of about 20 seconds, with a relatively low concentration of acid in the electrolyte (5%), and while operating at room temperature, 25°C.

Decreasing the concentration of acid in the electrolyte below 5% was found not to provide sensible improvement in quality of the surface barrier film obtained, although concentrations as small as 0.7% were found to be quite effective. Lower concentrations, however, require slightly longer anodization durations, and if the duration of operation is shortened by way of increasing the voltage, and thus the current density, there results a proportional requirement for increasing the flow of the cooling fluid, such as water, through the cooling coils disposed in the electrolyte tank. Although decreasing the temperature of the electrolyte below 25°C permits to improve the quality of the barrier film formed by anodization of the plate surface, such increase in quality does not warrant the expenditure in refrigeration equipment and in energy used to control the temperature of the electrolyte.

The stannous chloride test, hereinbefore referred to, provides a good indication of the amount of porosity of the anodized surface and of the thickness of the anodized oxide layer. The time taken for the stannous chloride solution to reach the aluminum surface is directly proportional to the thickness of the layer, and for layers of equal thickness, the time is inversely proportional to the porosity of the oxide layer. Such test does not provide any information about the hardness of the oxide layer or, in other words, its resistance to abrasion.

Two additional tests were developed which although incapable of providing an absolute quantitative determination of the resistance to abrasion of the oxide layer were capable of providing a good comparison between the quality of a plate and the quality of another plate.

The first test consists in stroking a soft, non-metallic ordinary eraser across the surface of the plates, the eraser being applied to the surface of the plates with an even pressure. The resistance to abrasion of the plate surface is determined by counting the number of strokes required to break through the surface layer. The strokes are applied repetitively to the same area of the plates and the moment at which the anodized layer is broken through is recognized by the surface of the craser turning black.

The other comparative test consists of pouring a saturated solution of stannous chloride over the surface of the plates and, with an even pressure, in stroking an ordinary bristle brush across the surface of the plates. The bristles of the brush abrade the anodized oxide film on the surface of the plates, and the reaction of the

stannous chloride with the aluminum indicates to what extent the surface is damaged.

Both tests may be effected by means of an appropriate fixture for the purpose of removing human error in applying the eraser or the brush with an even pressure over the surface of the plates. The plates are placed on the table of a machine tool such as a milling machine, and the eraser or the brush is mounted on the tool holder. The table is reciprocated by way of the table slides, the eraser end or the brush bristles being engaged with the surface of the plates being tested. A spring loaded holder is preferably used for mounting the eraser and applying the eraser with a constant pressure to the plate surfaces.

Using both the eraser test and the brush test, a direct correlation was established between the resistance of the anodized plates to penetration by the stannous chloride solution of Examples 1-4, and the relative time that it took to break through the anodized surface layer by means of the eraser test and the brush test.

The stannous chloride test, the eraser test and the brush test are indicative of the mechanical quality of the plate anodized surface, namely the degree of porosity of the anodized barrier film, its hardness, and its resistance to abrasion. They are not indicative of a further desirable quality for lithographic plates, namely the hydrophilic quality of the plate surface.

The hydrophilicity of the plate surface is tested by means of a dry ink test and by means of a wet ink test. The dry ink test consists in rubbing the surface of the plate with a rag impregnated with printer's ink which has been allowed to dry. The wet ink test consists in rubbing the surface of the plate with wet printer's ink. To be acceptable for use as a lithographic plate, the surface should not smudge when subjected to the wet ink test, and it should not ink readily when subjected to the more stringent dry ink test.

It will be appreciated that anodized aluminum or aluminum alloy plates have commonly been used for lithographic plate support members, after coating the anodized surface with an appropriate light-sensitive material such as water soluble diazo resins or the like. However, the lithographic quality of such plates leaves much to be desired, as the hydrophilicity of the surface in somewhat on the weak side. Plates anodized according to the procedure described at Examples 1-4 were subjected to the wet and dry ink tests and failed to pass the test satisfactorily, especially the dry ink test.

EXAMPLE 5

Plates of 1100 aluminum were prepared by being cut from a web of aluminum material grained at a line speed of 12 feet per minute using a sand slurry. After rinsing, the plates were electrolytically anodized according to the arrangement of FIG. 1, by dipping each plate in the electrolyte at a distance of 3 inches from the cathode 16 consisting of a stainless steel plate having the same area as that of the plate 10. The grained surface of the plate 10 was disposed opposite the cathode 16. For the purpose of determining the effect of using an acidic electrolyte containing an acid other than sulfuric acid, diverse electrolytes at concentrations of 5%, 10% and 15% of an organic or inorganic acid were used, repeating the runs of Examples 1-4, and subjecting the anodized plates to the diverse tests hereinbefore mentioned. The results achieved were as follows:

The anodized oxide layer obtained with nitric acid electrolytes was thin, non-resistant to any of the mechanical tests and accepted ink readily in the course of the wet ink test as well as the dry ink test.

5 The anodized layer obtained by anodizing with a hydrochloric acid electrolyte was also relatively thin and not very resistant to the abrasion tests. The sample plates did not pass the dry ink test, but were found to be acceptable when subjected to the wet ink test.

10 Plates anodized with acetic acid electrolytes were provided with a surface anodized film which was fairly resistant to abrasion. The film was not at all dark in appearance, contrary to the surface film obtained by anodization with other electrolytes. The anodized surface 15 was not receptive to ink when subjected to the dry ink test.

The anodized surface layers obtained by using electrolytes of chromic acid and of boric acid were comparable in lack of resistance to the abrasion test, and therefore were considered unacceptable for the purpose intended as a support member for a lithographic plate.

20 The anodized surface layers obtained by electrolytes of phosphoric acid were in all points comparable with those obtained with the sulfuric acid electrolytes of Examples 1-4, from the point of view of lithographic quality, and they even appeared to be slightly superior when subjected to the stannous chloride penetration test and the diverse abrasion tests. The quality of the surface layers obtained with phosphoric acid electrolytes is apparently not as affected by the temperature of the electrolytes as is the case when using sulfuric acid electrolytes. Phosphoric acid electrolytes would therefore be quite acceptable for anodizing aluminum and aluminum alloy plates for support members for lithographic plates, if the price of phosphoric acid was not two times the price of sulfuric acid.

The arrangement of FIG. 1 for batch anodizing of aluminum or aluminum alloy plates or sheets may be modified to anodize a pair of plates 10 by placing a second plate 10 a predetermined distance from the cathode 16 in the tank 14, such as three inches away from the cathode, on the other side of the cathode and connecting both plates 10 to the negative terminal of the power supply 18. If it is desired to anodize both surfaces of a plate 10, the arrangement of FIG. 2 is used, 45 a pair of cathodes 16 and 16' being disposed each on one side of the plate 10 and connected to the negative terminal of the power supply 18.

50 Instead of using a DC power supply, an AC power supply may be used, as shown at 18 at FIG. 3, each terminal of the power supply being connected to one of the two aluminum or aluminum alloy plates 10 and 10'. When it is desired to anodize both sides of the plate, the arrangement of FIG. 4 may be used, utilizing an AC power supply 18', and the diverse plates being connected electrically as shown, with the results that plates 10a', 10b, 10b' and 10c are anodized on both surfaces, and the plates 10a and 10c' are anodized on the surface disposed respectively towards plates 10a' and 10c. 60

The present invention contemplates manufacturing presensitized lithographic plates by a method which includes as one of its steps an anodization step prior to subjecting the aluminum or aluminum alloy plate member to electrosilication according to the method disclosed in said U.S. Pat. No. 3,658,662, thus obtaining a support member which, once coated with a photosensitive material, provides a presensitized lithographic

plate of high quality, not subject to the formation of "black spots," and provided with an effective barrier layer between the subjacent metal of the support member and the photosensitive coating preventing spontaneous reaction between the two until the photolithographic plate is removed from its wrapper, exposed and developed.

The conditions of operation for the electrosilication step in the method may be any one of those disclosed in the aforesaid U.S. Patent and consist generally in anodically treating the anodized plates by means of DC, AC or pulse current in an alkaline electrolyte made of an aqueous solution of sodium silicate containing from about 0.5% to about 37% by weight of sodium silicate, the electrolyte being maintained at a temperature between 20°C and the boiling temperature of the electrolyte, the plate to be treated and the other electrode in the electrolytic bath being in close proximity to each other, the voltage being anywhere between 6 and 220, or more, volts, and the duration of the electrosilication step being only a few seconds.

EXAMPLE 6

A plurality of plates of 1100 aluminum were grained in a sand slurry and anodized in an electrolyte made of a 5% aqueous solution of sulfuric acid, using 18 volts DC, passing the current for 15 seconds and maintaining the temperature of the electrolyte at 25°C.

The plates were then rinsed and placed in a tank containing an aqueous solution of 17% sodium silicate by weight. The plates were connected to the positive terminal of a 36 volt DC power supply, and the temperature of the electrolyte was maintained at 70°C. The period of time during which the current was turned on was varied from plate to plate, the minimum duration being 2 seconds and the maximum duration being 60 seconds.

The plates were then submitted to the diverse tests described hereinbefore, and no significant difference in quality was found between plates having been subjected to electrosilication for a short period of time and those having been subjected to electrosilication for a long period of time. For that reason, a duration of electrosilication of 15 seconds was arbitrarily selected as a practical duration of the electrosilication step in a continuous web process wherein the duration of the anodization step is also arbitrarily selected to be 15 seconds, such that identical tanks may be used in the process for the anodization step and for the electrosilication step.

When subjected to the stannous chloride penetration test, the diverse plates having been subjected to an anodization step followed by an electrosilication step showed no attack by the test solution in a duration of more than an hour. Plates having been subjected to anodization alone were used as control plates in the eraser comparison test with plates having been subjected to the electrosilication step following the anodization step. The number of eraser strokes necessary to break through the layer of film formed on the plates having been subjected to both the anodizing the electrosilication steps were between 2.7 and 3.1 times greater than the number of strokes required to break through the surface layer film of the plates having been only anodized.

The comparative brush test yielded the same results. Repetitively, the plates provided with an anodized sur-

face were affected by the brush test, while the plates anodized and electrosilicated remained unaffected.

Plates which had been anodized only and plates which had received the anodizing and electrosilication treatments were subjected to the dry ink test, side by side. The plates which had only been anodized readily accepted the ink and toned. The plates which had been electrosilicated in addition to having been anodized did not accept ink, when subjected to the dry ink test as well as the wet ink test.

EXAMPLE 7

Plates which had been anodized and electrosilicated according to the process disclosed relative to Example 6 were coated, on their face provided with a barrier film, with a conventional diazo resin according to conventional methods in the lithographic plate manufacturing industry. A 6% solution of type "L" diazo manufactured by Fairmount Chemical Company was used for coating the plates. Control plates subjected only to anodizing were coated in the same manner. After drying of the coating, both types of plates were exposed to a mercury vapor light source for 30 seconds and developed with a subtractive developer, such as the subtractive developer in copending application Ser. No. 500,475. After development, the image area of both types of plates was subjected to the eraser test. The plates having received only the anodizing treatment were abraded at the image area in half as many strokes as were required to abrade the image area of the plates which had received both the anodizing and the electrosilication treatments.

One-half of each type of plate was reexposed to the mercury light source for 30 seconds and redeveloped. The plates were dry inked. The plates which had only been anodized became slightly toned where subjected to single exposure, but the area subjected to double exposure readily scummed. The plates which had been anodized and electrosilicated remained clean in the background areas of the double exposed portion as well as on the single exposed portion.

Electrosilication of aluminum and aluminum alloy plates following anodization may be effected by batches, under the condition of operation disclosed in the aforesaid U.S. Patent and according to any one of the arrangements of FIGS. 1-4, substituting for the acid electrolyte 12 a sodium silicate alkaline electrolyte, connecting the plate 10 as an anode to the positive terminal of a DC power supply 18, using a stainless steel or other conductive cathode 16 connected to the negative terminal of the power supply (FIG. 1). If both faces of plate 10 have been anodized previously, both faces may be electrosilicated by using a pair of cathode electrodes 16 and 16', connected as shown at FIG. 2. Using an AC power supply 18, the arrangement of FIG. 3 or FIG. 4 may be used.

Referring now to FIG. 5, there is schematically illustrated a continuous process for making photolithographic plates according to the present invention. A web 20 of aluminum or aluminum alloy foil is unwound from a coil 22 mounted on an appropriate support 24. The web 20 is continuously fed in the direction of the arrows, appropriate feed means, such as shown at 26, being disposed at appropriate locations along the manufacturing line. By means of appropriate rollers, the continuously traveling web 20 is deflected into successive tanks in which appropriate steps of the process are

accomplished. The web 20 is first cleaned in the cleaning tank 28, containing an appropriate cleaning or degreasing fluid such as trichloroethylene, perchlorethylene, or the like, and from the cleaning tank the web is passed into a graining tank 30 in which a surface of the web 20 is grained under the action of a sand slurry 32 contained in the tank and frictionally applied to a surface of the web by means of a rotating brush 34. The web 20 is then rinsed, as shown at 36, and after rinsing the web is caused to pass through an anodizing tank 38 wherein it is linearly displaced in proximity to an electrode 16, the grained surface of the web being directed toward the electrode 16. In the process of FIG. 5, the electrode 16 is connected to the negative terminal of a DC power supply 18, while the positive terminal of the power supply 18 is connected to the web 20 by way of appropriate electrical contact making rollers 40. The anodizing tank contains an electrolyte 12 made of an aqueous solution of an appropriate acid such as sulfuric acid or the like, at the concentrations disclosed at Examples 1-4 hereinbefore, and the other parameters of operation, such as voltage of the power supply 18 and temperature of the electrolyte, may be one of the parameters hereinbefore disclosed. For example, and preferably, the power supply 18 has a voltage of 36 volts, the electrolyte 12 consists of a 5% aqueous solution of sulfuric acid and is maintained, by 36 of appropriate cooling means, not shown, at a temperature of 25°C. The grained surface of the web 20 is translated at a distance of 3 inches (75 mm.) from the electrode 16, and the relative length of the electrode 16 and the speed of translation of the web 20 are chosen to provide anodization of the grained surface of the web for about 15 seconds. At the selected continuous speed of translation of the web 20 of 12 feet per minute (3.65 meters/min.), which is a convenient speed of translation of the web, the electrode 16 has a length of 36 inches (91.5 cm.). The web 20 is conveniently obtained in 29½ inches (75 cm.), and the width of the electrode 16 is at least the width of the web 20. Preferably, the electrode 16 is a stainless steel plate or grid.

The web 20, having been now provided with a grained and an anodized surface, is subsequently passed through a rinsing tank 42 for removing traces of the acid electrolyte and is subsequently passed through an electrosilication tank 44. In the electrosilication tank 44, the web 20 is translated with its grained and anodized face disposed, for example, 3 inches (75 mm.) away from an electrode 46, made of stainless steel, for example, connected to the negative terminal of the power supply 18. As previously mentioned, the web is maintained connected to the positive terminal of the power supply by means of electrical contact establishing rollers 40. The electrolyte 48 in the electrosilication tank 44 consists of an appropriate aqueous solution of sodium silicate, as disclosed in the hereinbefore referred to U.S. Patent, for example an aqueous solution of 17% by weight of sodium silicate, such as the Star Brand sodium silicate marketed by Philadelphia Quartz Company, and the temperature of the electrolyte 48 is maintained at, for example, 70°C by means of appropriate thermostatically controlled heating coils, not shown. The grained and anodized surface of the web 20 is subjected to electrosilication for about 15 seconds, although other durations may be used, which necessitates providing the electrode 46 with a length of 36 inches (91.5 cm.).

After emerging from the electrosilication tank 44, the continuous web 20 is passed through a rinsing tank 50, and then dried by being passed through a tunnel oven 52 or the like. The grained, anodized and electrosilicated surface of the web 20, after drying of the web, is coated with an appropriate photosensitive material such as a conventional aqueous solution of diazonium resin. The coating operation is effected by any conventional means such as roller coating 54 or spraying followed by calendering. After coating of its grained, anodized and electrosilicated surface, the web is passed through a drying oven 56 for drying the coating of photosensitive material, and the coated web is fed to a cutting station 58 where it is cut to appropriate lengths, thus providing presensitized photolithographic plates 60 which, after further cutting to appropriate sizes if so required, are appropriately packaged and shipped to the user. The coating and subsequent steps are effected under yellow light which is nonactinic to diazo type photosensitive materials.

Although the continuous line process of manufacturing photolithographic plates schematically illustrated in FIG. 5 has been described as including a DC power supply 18 for the anodization and electrosilication steps, it will be appreciated that an AC power supply may be substituted for the DC power supply 18, or a pulse DC power supply may be used, for effecting both the anodizing step and the electrosilication step, or for effecting any one of these steps.

As previously explained herein, an AC power supply may be used for accomplishing the anodizing step and, as disclosed in the aforementioned patent, alternating current may be used for electrosilication of aluminum and aluminum alloys. When an AC power supply is used, it has been found advantageous to use higher voltages than normally used in direct current anodization and electrosilication process. It is convenient to utilize alternating current at 115 volts (RMS) as supplied directly from the mains.

When utilizing an AC power supply, it is further advantageous to utilize the arrangement schematically illustrated at FIG. 6, comprising two continuous lines of aluminum or aluminum alloy webs as shown at 20 and 20', respectively, adapted to be translated parallel to each other, in the same direction as shown, or in opposite directions to each other. As shown at FIG. 6, the first web 20 is obtained from a coil 22, and the second web 20' is obtained from a second coil 22'. Each web, while being translated, is successively passed through a cleaning tank 28, 28', a graining station 30, 30' to provide a surface of each web with a grained surface, and subsequently to graining each web is passed through a rinsing station as shown at 36 and 36', respectively. It is to be noted that the surface of the web 20 which is grained and the surface of the web 20' which is grained are caused to pass through the anodizing bath in the anodizing tank 38 facing one another. The two webs 20 and 20' are displaced through the anodizing tank 38, parallel to each other, in close relative proximity, 3 inches for example, through an appropriate electrolyte 12, made for example of an aqueous solution of sulfuric acid, having the concentration hereinbefore indicated, preferably maintained at a temperature of 25°C by means of appropriate cooling coils, not shown. One of the webs is connected to a terminal of an AC power supply 18', and the other web is connected to the other

terminal of the power supply by means of appropriate contact making rollers 40 and 40', respectively.

After anodization in the anodizing tank 38, the webs 20 and 20' are rinsed by being passed through a rinsing tank 42, and are passed through an electrosilication tank 48, being maintained parallel to each other with the grained and anodized faces opposite to each other and separated by a distance of, for example, 3 inches. After electrosilication in the electrosilication tank 44 for a period of time substantially equal to the period of time during which they are subjected to anodization, for example, 15 seconds, the two webs 20 and 20' are passed through a rinsing tank, as shown at 50, and they are dried in an oven, as shown at 52. Each of the webs are then caused to pass separately through a coating station, as shown respectively at 54 and 54', where the grained, anodized and silicated surface of each web is coated with a coating of photosensitive material, such as a diazo resin, as previously explained. The coating of photosensitive material is subsequently dried in the drying oven, as shown at 56 and 56', respectively. The coated webs are then cut at a cutting station, 58 and 58', respectively, to appropriate lengths for providing presensitized photolithographic plates 60 and 60'.

FIG. 7 schematically illustrates, in a grossly exaggerated manner, a section through an aluminum or aluminum alloy plate 10 provided with an anodized oxide film 62 on a surface thereof. The anodized film 62 is, as previously mentioned, hard and corrosion resistant, although not endowed with highly hydrophilic qualities. In addition, the anodized layer 62 is substantially porous and, if its surface was provided with a coating of, for example, photosensitive material such as a diazo resin, the oxide layer 62 would be easily penetrated in view of its porosity by the coating material, which may result in a spontaneous reaction occurring between the metal of the support base 10 and the material of the coating. This presents many disadvantages if a simply anodized aluminum plate is utilized as a support member for photosensitive coatings such as diazo resins for the purpose of providing a presensitized lithographic plate. Such a lithographic plate has a very short shelf life, as the reaction between the diazo resin having transpired through the oxide film 62 to the subjacent aluminum of the support base 10 tends to spontaneously react and spontaneously form black spots, that is spots resulting from areas of the diazo resin having spontaneously chemically reacted with the subjacent aluminum, the resultant material being highly oleophilic and incapable of being dissolved in the course of developing the lithographic plate following exposure.

However, when the anodized face of the aluminum or aluminum alloy plate 10 is subjected to electrosilication, according to the present invention, the electrosilication step actually seals the pores of the oxide layer 62, in addition to electrolytically transforming the surface 64 of the oxide layer 62 from a mildly hydrophilic to a highly hydrophilic surface. The result achieved is that an effective chemical barrier is created between the subjacent metallic support base 10 and a coating, such as a coating of diazo resin 66 (FIG. 8) which is subsequently applied to the surface 64 of the oxide layer 62. The resulting presensitized lithographic plate has a long shelf life because, as a result of the electrosilication step, the oxide layer 62 provided by the anodization step has been effectively sealed, thus creating an effective barrier preventing spontaneous reac-

tion between the diazo resin and the metal of the subjacent support base 10. In addition, the resulting lithographic plate, after exposure and processing, is provided with hydrophilic non-image areas as the surface 64 of the oxide layer 62 has been, in the course of the electrosilication step, further modified from a slightly hydrophilic surface to a highly hydrophilic surface, without any loss in the quality of the oxide layer to provide a corrosion and abrasion resistant film. The advantage procured by electrosilication of an aluminum or aluminum alloy surface relating to providing a good anchoring surface for paint, lacquer, and photosensitive materials, such as diazo resins, remains entirely unaffected by the prior anodization step with the result that presensitized lithographic plates manufactured according to the method of the present invention have a shelf life several times that of conventional presensitized lithographic plates, without formation of any black spots or other deterioration of the plates during storage, or after the plates have been exposed and developed.

Having thus described the invention by way of examples of methods for practicing the invention, modification whereof will be apparent to those skilled in the art, what is sought to be protected by United States Letters Patent is as follows:

1. A method of manufacturing presensitized lithographic plates, said method comprising the steps of graining a surface of an aluminum or aluminum alloy plate, anodizing the grained surface electrolytically in an aqueous acidic solution, anodically treating the anodized surface in an alkaline aqueous solution of sodium silicate, and coating the treated surface with a photosensitive material.

2. The method of claim 1 wherein said photosensitive material is a diazo resin.

3. The method of claim 1 wherein each of the steps of anodizing and anodically treating said plate is effected by connecting said plate and an electrode across a source of electrical energy such that said plate is anodic at least part of the time.

4. The method of claim 1 wherein said aqueous acidic solution is a solution of sulfuric acid having a concentration in acid of 5% to 15%.

5. The method of claim 3 wherein said source of electrical energy is an AC source and said electrode is a second aluminum or aluminum alloy plate having a grained surface disposed proximate to the grained surface of the first plate.

6. The method of claim 4 wherein said aqueous acidic solution is maintained at a temperature of about 25°C.

7. A method of manufacturing presensitized lithographic plates from a continuous web of aluminum or aluminum alloy, said method comprising the successive steps of cleaning said web, anodizing the grained surface of said web electrolytically in an aqueous acid solution, anodically treating the anodized surface in an alkaline aqueous solution of sodium silicate, rinsing said web, drying said web, coating the treated surface of said web with a photosensitive material, drying said coating and cutting said web to appropriate size.

8. The method of claim 7 wherein said photosensitive material is a diazo resin.

9. The method of claim 7 wherein each of the steps of anodizing and anodically treating said web is effected by connecting said web and an electrode across

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a source of electrical energy such that said web is anodic at least part of the time.

10. The method of claim 7 wherein said aqueous acidic solution is a solution of sulfuric acid having a concentration in acid of 5% to 15%.

11. The method of claim 10 wherein said aqueous acidic solution is maintained at a temperature of about 25°C.

12. A method of manufacturing presensitized lithographic plates from a pair of continuous webs of aluminum or aluminum alloy, said method comprising the successive steps of cleaning of said webs, graining a surface of each of said webs, anodizing the grained surface of each of said webs electrolytically in an aqueous acidic solution, anodically treating the anodized surface in an alkaline aqueous solution of sodium silicate,

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rinsing each of said webs, drying each of said webs, coating the treated surface of each of said webs with a photosensitive material, drying the coating and cutting each of said webs to appropriate size, wherein said webs are disposed parallel to each other in the course of said anodizing, and said anodically the grained surface of said webs disposed toward each other, and said webs are electrically connected each to a terminal of an AC source of electrical energy.

13. The method of claim 12 wherein said aqueous acidic solution is a solution of sulfuric acid having a concentration in acid of 5% to 15%.

14. The method of claim 13 wherein said aqueous acidic solution is maintained at a temperature of about 25°C.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,902,976
DATED : September 2, 1975
INVENTOR(S) : John E. Walls

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 25, after "extent", "is" should be --in--.

Col. 11, line 31, "ageous" should be --aqueous--.

Col. 11, line 62, after "anodizing" delete "the" and insert -- and --.

Col. 13, line 27, following "by" delete "36" and insert --way--.

line 38, "conveninetly" should be --conveniently--.

Col. 15, line 25, "is" should be --in--.

Col. 18, line 6, following "anodically" insert --treating steps with--.

Signed and Sealed this

sixth Day of *January* 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

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Commissioner of Patents and Trademarks