

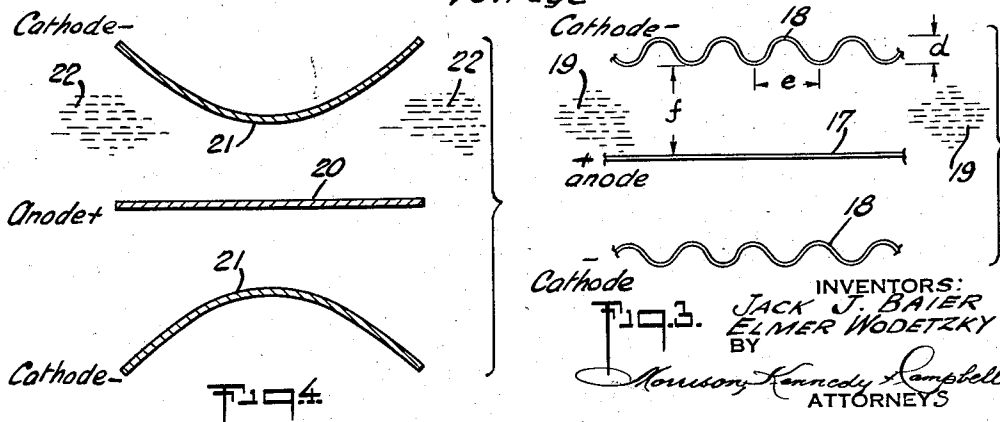
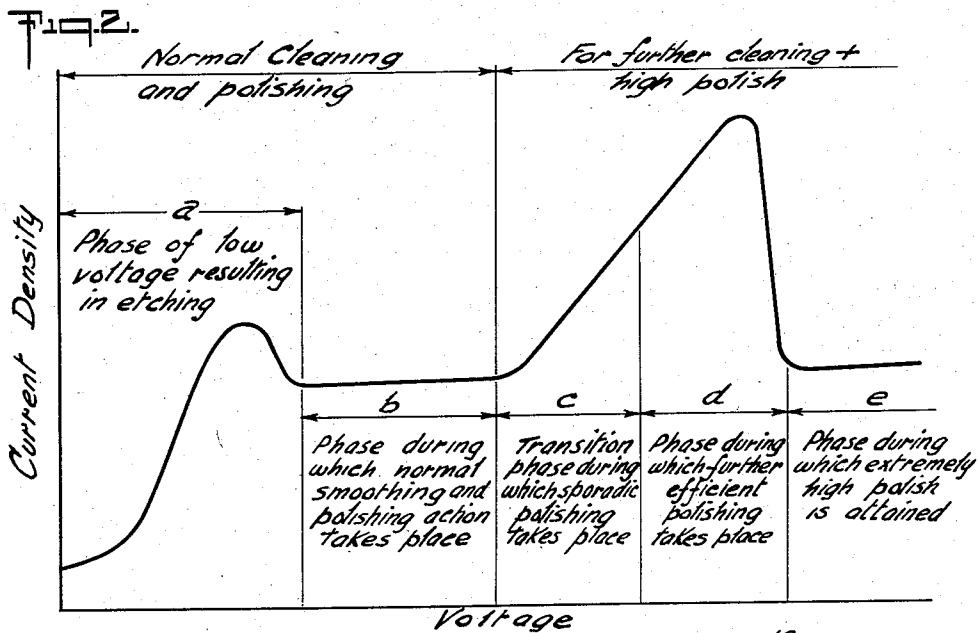
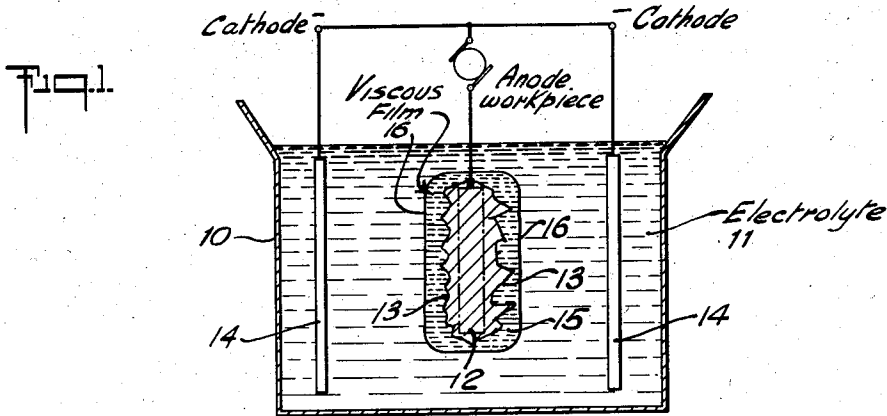
Jan. 13, 1959

J. J. BAIER ET AL
ART OF ELECTROLYTICALLY TREATING METAL TO
CLEAN, LEVEL, SMOOTH, POLISH AND/OR
PROTECT THE SURFACES THEREOF

2,868,705

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2 Sheets-Sheet 1



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2 Sheets-Sheet 2

Fig. 5.

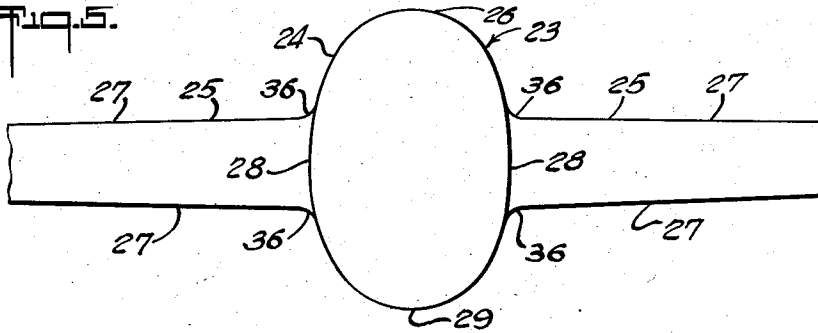


Fig. 6.

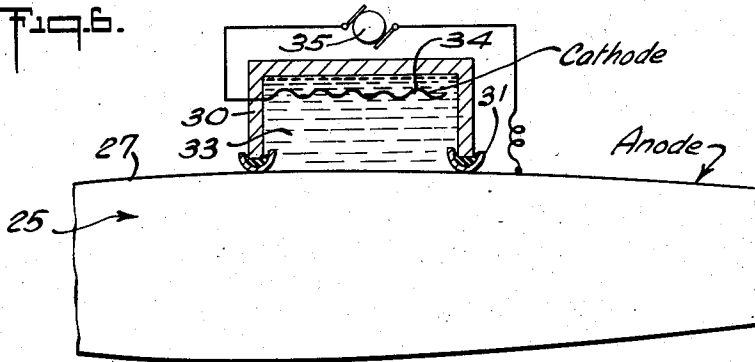


Fig. 7.

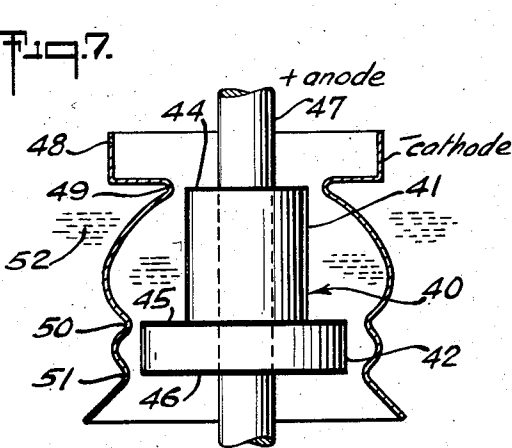


Fig. 8.

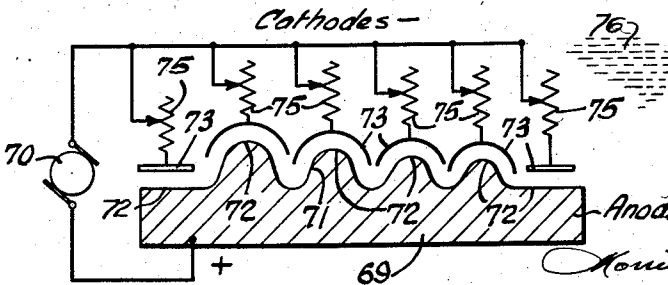
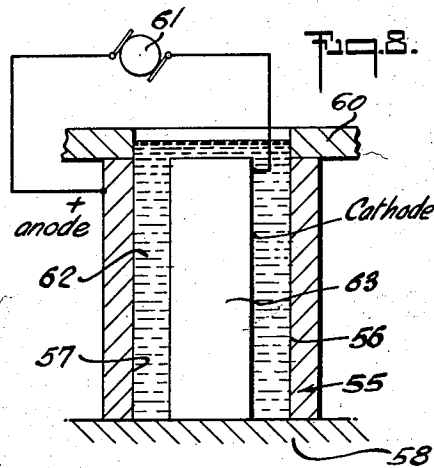


Fig. 9.

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2,868,705

ART OF ELECTROLYTICALLY TREATING METAL TO CLEAN, LEVEL, SMOOTH, POLISH AND/OR PROTECT THE SURFACES THEREOF

John J. Baier, Manhasset, and Elmer Wodetzky,
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Application January 19, 1955, Serial No. 482,832

4 Claims. (Cl. 204—140.5)

The present invention relates to the art of electrolytically treating metal to clean, level, smooth, polish and/or protect the surface thereof.

It is believed that in the anodic treatment of metals, a viscous layer or film of high electrical resistivity is formed on the surface of the anode being treated during the passage of current through the electrolyte. Since the electrolyte is of comparatively low electrical resistance, the formation of a layer of comparatively high resistance on the anode surface, causes the anodic potential in the different regions of the surface being treated to vary according to the extent to which these regions project into said layer. This causes the salient points on the surface to fuse at a rate according to their depth, thereby levelling off said points until an equipotential condition is attained over the surface. At this stage, the surface will be levelled and smoothed off.

One object of the present invention is to provide new and improved electrolyte for anodically treating a metal surface, which is fast acting and lends itself to continuous and mass production, which renders the surface even and extremely smooth, which imparts a permanent high lustre or polish having high reflectivity to the surface, which so acts on the surface as to impart thereto high resistance to oxidation and corrosion and high weldability, and which can be used for long periods under stable electrolytic conditions and without regeneration of the electrolyte.

Various other objects of the invention are apparent from the following description and from the accompanying drawings, in which

Fig. 1 is a diagrammatic view of an electrolytic tank, and associated parts for carrying out a process in its primitive form according to the present invention;

Fig. 2 is a graph showing the current density-voltage relationship of the different stages or phases of the process illustrated in Fig. 1;

Fig. 3 is a diagrammatic view of a cathode and anode assembly and design showing one way in which the electrolyte of the present invention can be used in cleaning and polishing flat continuously moving strip metal of substantial width;

Fig. 4 is a diagrammatic view of a cathode and anode assembly and design showing another way in which the electrolyte of the present invention can be used in cleaning and polishing flat metal plate of comparatively narrow width;

Fig. 5 shows diagrammatically the outlines of an airplane and especially the fuselage and part of the wing which may be cleaned and polished by the electrolyte of the present invention;

Fig. 6 is a side elevation of one of the airplane wings shown in Fig. 5 and shows diagrammatically the surface of said wing being cleaned and polished by an electrolytic box assembly containing the electrolyte of the present invention, said electrolytic box assembly being shown in section;

Fig. 7 is a section of a cathode and anode arrangement and design by which the burrs on a workpiece may be

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easily removed by the electrolyte of the present invention;

Fig. 8 is a section of a cathode and anode arrangement and design by which the internal surface of a tubular member, such as that of the cylinder or chamber of a combustion engine, steam engine or pump, may be cleaned and smoothed by the electrolyte of the present invention; and

Fig. 9 is a section of a cathode and anode arrangement and design by which a surface of intricate or complicated contour may be cleaned, smoothed and polished by a series of cathode elements shielding the different sections of the contour and supplying variable voltage according to the nature of the contour sections, using the electrolyte of the present invention.

In using the electrolyte of the present invention in the manner illustrated in Fig. 1, a tank 10 is provided containing an electrolyte 11, the special nature and composition of which will be described hereinafter. The metal piece 12 with its rough surface 13 to be treated, is suspended in the electrolyte as the anode. The irregularities on the surface 13 of this metal piece 12 are greater than would be encountered in practice, and are shown herein in exaggerated form only for the purpose of clarity in illustration.

The cathodes 14 which flank the metal piece 12 may be of any well known inert material, such as stainless steel. When direct current is applied between the cathodes 14 and the anode 12, the irregular surface 13 will be evened off and smoothed. The mechanism for this operation is believed as follows:

With the application of direct current, a viscous layer 15 of comparatively high electrical resistance is formed over the rough surface 13 of the metal plate 12, consisting of a mixture of ions from the electrolyte and ions from the dissolved anode. This layer 15 has its surface 16 opposite the rough surface 13 substantially flat, so that the thickness of this layer from the salient points on this surface to the layer surface 16 varies according to the depth of these salient points. Since the electrical resistance of the electrolyte is very low, the electrical resistance of the layer opposite these points varies according to the depth of these points. The salient points of greater depth on the surface 13 of the metal piece 12 therefore receive current of greater density than the points of lesser depth. The net result is that the high points on the rough surface 13 of the metal piece 12 are dissolved at a faster rate than the low points, thereby gradually levelling off this surface until a condition of potential equilibrium is attained. When this stage of equilibrium is reached, the surface will be flat and smooth, as shown in dot and dash lines in Fig. 1, and will have all the other desirable characteristics to be described.

An important feature of the present invention is the composition of the electrolyte 11 employed in the process described. The basic ingredients of the electrolyte are phosphoric acid and chromic acid. If the phosphoric acid is used alone without the chromic acid in the electrolyte, the layer 15 of high viscosity developed will contain numerous gas bubbles which cause spotty polishing. However, the viscous layer 15 produced by the phosphoric acid alone has some good characteristics which it is desirable to retain. For example, it has a low degree of adherence, and therefore is constantly renewed by successive new layer formations. If bubbling in this layer can be kept down, a smoother surface will be produced, but this requires a comparatively long time to attain.

If the chromic acid or its anhydride is used in the electrolyte without the phosphoric acid, the resulting layer 15 will be free of gas bubbles. However, if so exclusively used, the acid has a tendency to produce wavy surfaces which nevertheless have good reflectivity.

It has been found in accordance with the present invention, that by combining the phosphoric acid and the chromic acid in the electrolyte, the desirable characteristics of both are attained and the undesirable characteristics of each are substantially obviated or materially reduced. At the same time, it has been found that the action of effectively cleaning, polishing or otherwise treating the surface of the metal piece is faster with the combination of chromic acid and phosphoric acid, than it is with either one of these ingredients alone.

The proportions of chromic acid and phosphoric acid of the electrolyte depend on the type of metal to be treated and the finish that is desired. The phosphoric acid should preferably be at least 60% by weight (on a pure basis) of the electrolyte and the chromic acid should be at least 1.7% (on an anhydride basis). It has been found, that a good working range for these ingredients is 76.4 to 94.3 parts of phosphoric acid on the basis of an 84 to 85% syrup to 1.9-13.2 parts of chromic acid on the basis of the anhydride.

In addition to the specific ingredients described, it has been found in accordance with the present invention, that the addition of a small amount of sulfuric acid and a still smaller amount of hydrofluoric acid in the electrolyte, increases the current carrying capacity of the electrolyte, provides better current distribution, and prevents certain granulation on the surface of the anode. Also, with deterioration of the electrolyte due to age, the resistance or strength of the anode layer 15 is increased, and this has an adverse effect on the process. This sulfuric acid and hydrofluoric acid act as stabilizers to retard materially this deterioration. A good working range for the sulfuric acid is 0.7% to 2.7% of the final electrolyte and for the hydrofluoric acid is 0.004% to 1.014%.

As the electrolyte ages, the voltage necessary to attain the necessary polish increases, due to the increase in the resistance of the electrolyte. This is believed due to the deterioration of the chromic acid resulting from its reduction. It has been found in accordance with the present invention, that the addition of a small amount of sodium dichromate to the electrolyte, retards materially the reduction of the chromic acid and prolongs the useful life of the electrolyte to a substantial extent, so that satisfactory cleaning, smoothing and polishing is attained over the life of the electrolyte, without material increase in voltage. A good working range for the sodium dichromate is 0.6 to 2.6% of the electrolyte.

If under high current densities, excessive gassing results due to the resistance of the electrolyte being too low, an ounce or two of acetic acid may be added to the electrolyte as a stabilizer. This will tend to increase the resistance of the electrolyte and to decrease the current density, so that gassing will cease.

The electrolyte described should be maintained at a temperature of between 175° F. and 185° F. Below this temperature range, the process will be too slow and above this range, the electrolyte in the vicinity of the viscous layer 15 will bubble excessively. To maintain the electrolyte 11 at the required temperature, cooling of the electrolyte is resorted to, as for example, by cooling the tank 10 with cooling water.

It is also desirable that the electrolytic bath be kept under constant circulation while in use.

In order to assure an electrolyte mixture, which is chemically and physically stable, the different ingredients of the electrolyte must be put together in a definite manner. To that end, the bulk of the phosphoric acid and of the chromic acid preferably in anhydride form are mixed together to produce mixture No. 1. This mixture No. 1 is produced in a specific instance by mixing the phosphoric acid in the form of an extra pure syrup 84-85%, having a specific gravity of 1.70 equivalent to 59.5° Bé. with acid chromic anhydride. The proportions by weight of the ingredients in mixture No. 1 on

the basis of the final electrolyte are preferably as follows:

MIXTURE NO. 1

Posphoric acid (84-85%)—73.5% to 91.4% of the final electrolyte
Acid chromic anhydride—1.7% to 11.7% of the final electrolyte

A Mixture No. 2 is produced comprising phosphoric acid, acid chromic anhydride, sulfuric acid, hydrofluoric acid, dichromate of sodium, and water. In this Mixture No. 2, the proportions by weight of the ingredients are preferably as follows, on the basis of the final electrolyte:

MIXTURE NO 2

	Percent
Phosphoric acid -----	2.9-6.9
Acid chromic anhydride -----	0.2-1.5
Sulfuric acid -----	0.7-2.7
Hydrofluoric acid -----	0.004-0.014
Dichromate of sodium -----	0.6-2.6
Water (sufficient to make up 100% in the final electrolyte) -----	0.1-2.1

After Mixtures No. 1 and No. 2 have been separately formed as described, they are combined.

A specific example of an electrolyte formed in accordance with the present invention is as follows:

MIXTURE NO 1

1 gallon of phosphoric acid Extra Pure Syrup 84-85% (1.70 sp. gr.=59.5° Bé.) equivalent to 83.5% of the final electrolyte
500 grams of acid chromic anhydride equivalent to 6.7% of the final electrolyte

MIXTURE NO. 2

200 cubic centimeters of phosphoric acid Extra Pure Syrup 84-85% (1.70 sp. gr.=59.5° Bé.) equivalent to 4.9% of the final electrolyte
40 grams acid chromic anhydride equivalent to .5% of final electrolyte
70 cubic centimeters sulfuric acid equivalent to 1.7% of final electrolyte
1 cubic centimeter of hydrofluoric acid equivalent to 0.009% of final electrolyte
120 grams of dichromate of sodium equivalent to 1.6% of final electrolyte
80 cubic centimeters of water equivalent to 1.1% of the final electrolyte

In forming the final electrolyte, 100 cubic centimeters of Mixture No. 2 are combined with each gallon of Mixture No. 1.

In the operation of carrying out the surface treating process indicated above with the electrolyte described in the specific example, while the electrolyte is maintained at 180° F. and agitated, direct current is passed there-through between the anode and cathode immersed therein.

It has been found that with an electrolyte of the type indicated above, the average metal dissolution on normal metals, such as aluminum and steel, is in the neighborhood of 0.0003" per minute of current application with a current density of 0.2 to 0.5 ampere per square inch. It is seen that the entire process can be accomplished in a matter of seconds, in certain cases as little as 3 seconds, on work, where the roughness is very minute. Even in extreme cases of roughness, the entire process need not take over 30 seconds to accomplish a smooth highly polished surface. A surface appears polished to the eye, when the maximum depth of the pores or roughness is smaller than one-half of a light wave of visible light (one light wave is equivalent to 5000 Angstrom units).

In carrying out the electrolytic process of the present invention with the electrolyte of the present invention, the

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viscous layer 15 is brought up to its maximum temperature of 175° to 185° F. as quickly as possible, within practical limits of voltage and current density, by increasing the voltage at a rate, rapid enough to maintain the temperature of said layer a few degrees (5° to 7° F.) above that of the metal anode. By carrying out this initial phase of the cleaning and polishing cycle as described, a faster cleaning and polishing results, thereby cutting down the timing of a complete cleaning and polishing cycle to a matter of seconds.

In Fig. 2 is shown a current density-voltage curve which is characteristic of the process. During the entire cycle, since the temperature of the electrolyte as well as of the viscous layer 15 is increasing, the resistance of said viscous layer is also increasing. Therefore, the voltage to attain the necessary current density at the anode 12 must also be increased. During the initial phase indicated by the part *a* of the curve, the voltage is increased at a rapid rate to increase the temperature of the viscous layer 15 to the maximum level (175° F. to 185° F.) rapidly. Since, during this early phase, the temperature of the viscous layer 15 is still comparatively low, the resistance of the viscous layer is also low, so that the increase in voltage will increase the current density, until the current density reaches a maximum, after which it drops to a steady level and continues through the phase *b*. This initial phase *a* is the etching period, during which the rough spots are removed and etching results.

At the end of the etching phase *a*, as the voltage is increased to compensate for increase in resistance of the viscous layer 15, the current density at the anode 12 remains at a steady value for a period indicated by the interval *b* on the graph of Fig. 2. During this phase *b*, normal smoothing and polishing action takes place, until a point is reached at which the current density starts to increase, although the voltage rate increase might remain the same. The interval *c* of this part of the cycle is a transition period during which sporadic polishing takes place and continues into phase *d* during which the polishing becomes more efficient and more uniform. Phase *d* continues with progressive increase in voltage and progressive increase in current density until the current density reaches a peak and then drops suddenly to a level of current density substantially the same as that attained during phase *b*, to initiate phase *e*, even though the rate of voltage increase should remain the same. During phase *e* extremely high polish to a mirror finish is attained and this phase may be continued depending upon the degree of polishing required.

During the entire cycle, the rate of voltage increase may be maintained substantially constant, and due to the peculiar characteristics of the electrolyte, the process will undergo the different phases described, or the voltage rate of increase may be changed from phase to phase to attain the different phase described but with different periods. In any case, the temperature of the viscous layer 15 is desirably maintained at a temperature of between 175° and 185° F. Also, the voltage rate of change should be as rapid as possible to attain the quickest and most efficient cleaning and polishing with minimum of power consumption. If the voltage increase is at too rapid a rate, the power consumption might be comparatively high. In addition, undesirable bubbling of the electrolyte in the vicinity of the viscous layer 15 might result.

For normal smoothing and cleaning, the cycle need not be extended beyond phase *b*. However, for extreme cleaning and extremely high polishing, the cycle can be extended into phase *e*.

An example of a cycle which may be employed with the electrolyte described in the specific example above, and in connection with an aluminum workpiece to be cleaned and polished, is as follows:

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Phase *a*

The voltage is increased progressively from 0-18 volts during 3 seconds. The current density goes up to a maximum of 0.3 ampere per square inch and then drops to 0.21 ampere.

Phase *b*

The voltage is increased progressively from 18 to 28 volts during a period of 3-5 seconds. The current density during this phase remains constant at 0.21 ampere per square inch.

Phase *c*

The voltage is increased progressively from 38 to 40 volts during a period of 3-5 seconds. The current density increases progressively from 0.21 ampere per square inch to 0.45-0.50 ampere per square inch.

Phase *d*

The voltage is progressively increased from 40 to 45 volts during a period of 2-3 seconds. The current density increases progressively from 0.50 ampere to 0.75 ampere. At the end of the third second of this phase *d*, the current density will drop suddenly back to 0.21 ampere per square inch.

Phase *e*

The voltage rate of change is maintained the same as in the previous phase *d* for 2-3 seconds, to attain extremely high polish at a steady current density of 0.21 amperes per square inch.

It is seen therefore, that there must be proper control of the relationship between the voltage and current to carry the process through the different phases.

Losses of electrolyte under normal uses may be replaced by maintaining a supply reservoir to one side of the processing tank 10, and as the electrolyte is depleted by adherence of some electrolyte to the treated metal piece withdrawn from the tank, by running into the tank by gravity or pressure, sufficient electrolyte to make up the deficiency. If no electrolyte is removed from the treating tank, its strength may be kept up by the addition of chromic acid and sodium dichromate.

After one month of normal continuous use, it is advisable to replace the entire electrolyte. The condition of the electrolyte necessary to replace it can be ascertained by noting the color of the electrolyte, which changes from brown to green and which also manifests increased foaming, when it has deteriorated to the stage where replacement is required. The stale electrolyte can be used as a pre-cleaner for the metal workpiece to be cleaned before it is immersed in the fresh electrolyte, by heating the stale electrolyte to a temperature of between 200°-210° F., without using electric current.

The action of the improved electrolyte in the process described is fast acting and can be extended to produce a surface which is not only smooth but has a high lustre or polish. Tests have shown that the surface produced by the process of the present invention has characteristics not obtained by smoothing and polishing to a comparable degree by mechanical means. For example, a surface polished by the electrolyte of the present invention will retain its lustre and high reflectivity almost indefinitely, while a mechanically finished surface of equal initial smoothness and polish will lose its polish in a short time. Moreover, a surface treated by the electrolyte of the present invention will be highly resistant to atmospheric corrosion, and stainless steel surfaces so treated, manifest high resistance against corrosion and especially against the action of chlorides and organic acids indefinitely, while a mechanically finished surface of equal initial smoothness and polish will erode during the same period. This improved result is due to the fact that in conjunction with an extremely smooth and highly polished surface, there is produced by the electrolyte of the present invention, an extremely thin transparent pro-

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tective sealing coating on the smooth polished surface. This coating is believed to be an oxide, but unlike metals with the usual oxide coatings, the metals treated as described manifest improved weldability.

It has also been found that a plating applied in the usual manner to a metal surface cleaned and polished electrolytically in accordance with the present invention manifests better adherence to the base metal, greater durability and resistance to corrosion, and less porosity than in a case of a plating applied in the same manner to a surface, which has been mechanically cleaned and polished.

The electrolyte of the present invention can be used for cleaning, sealing and polishing all metals including alloys, except chromium and zinc. By cleaning and sealing is meant cleaning and smoothing to the extent of preventing further oxidation of the metal under normal conditions of usage. The process can be used, for example, to clean and polish aluminum, steel, brass and copper, and in addition it will seal the surface of the metal against deterioration in normal atmospheres.

In treating an anodically connected work sheet, it has been found that a flat cathode sheet on either or both sides of the work sheet does not produce as even a current distribution as might be desired. For example, it has been found that at the sides of the anodically connected sheet, the current density is greater than in the intermediate section of the sheet. It has been determined that a contoured cathode sheet adjacent to the flat anode sheet to be electrolytically treated, produces a more even current distribution. The cathode sheet or sheets may be contoured by corrugations in the sheets, especially in the case of a comparatively wide anode sheet, or by arching the cathode sheets, so that the sides of said sheets slant away from the sides of the anode sheet, especially in the case of a comparatively narrow anode sheet. Fig. 3 shows one of these arrangements in connection with a continuous anode sheet 17 flanked by two cathode sheets 18 of suitable inert material, such as stainless steel, these electrodes being immersed in an electrolyte 19 preferably of the improved character described. The anode sheet 17 is moved continuously through the electrolytic bath in the direction transverse to the plane of the drawing of Fig. 3 at a constant rate sufficient to attain the necessary surface treatment.

For the arrangement of Fig. 3, the cathode sheets 18 are corrugated in a direction transverse to the direction of motion of the anode sheet 17. The corrugations of the cathode sheets 18 are preferably of sinusoidal form, and in a specific example the depth d of each corrugation is between $\frac{3}{8}$ " and $\frac{1}{2}$ "; the length e from one point on a corrugation unit to the corresponding point on the next corrugation unit is between $\frac{7}{8}$ " and $1\frac{1}{4}$ " and the nearest distance f of the corrugated sheets 18 from the anode 17 is between 1 " and $2\frac{1}{2}$ ". In a specific installation, the distances d , e and f , may be $\frac{3}{8}$ ", $\frac{7}{8}$ " and $1\frac{1}{4}$ " respectively.

Where both faces of the anode sheets 17 are to be finished, two corrugated cathode sheets 18 are required on opposite sides of said anode sheet as shown.

Fig. 4 shows an arrangement in which the cathode sheets are contoured simply in connection with a comparatively narrow anode sheet up to a foot wide, to attain uniform current density across the anode. In this arrangement, there is provided a flat anode sheet 20 to be cleaned and polished on opposite faces. This sheet 20 may be stationary while being electrolytically treated or may be a continuous strip being advanced lengthwise while being treated. On opposite sides of this anode sheet 20 and equally spaced therefrom are two cathode sheets 21, arched and symmetrically arranged with their convex faces turned towards the anode sheet, so that the sides of said cathode sheets slant outwardly away from the sides of the anode sheet. This brings the middle section of the cathode sheets 21 closer

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to the anode sheet 20 than the side sections, the curvature of said cathode sheets being such as to attain uniform distribution of current density across the sheet. The cathode sheets 21 may, for instance, be circularly curved, and in a specific example, with an anode sheet 20, 6 inches wide, the intermediate sections of the cathode sheets 21 may be spaced 2 inches from the confronting faces of the anode sheet 20 and the sides of the cathode sheets at the regions directly opposite the side edges of the anode sheet may be spaced $3\frac{1}{2}$ inches from the confronting faces of the anode sheet.

The electrode arrangement of Fig. 4 when immersed in an electrolyte 22 preferably of the improved character described, and when the electrolytic circuit is closed, delivers to the anode sheet 20 current of uniform density across the width of said anode sheet.

The electrolyte of the present invention is useful, for example, in connection with the cleaning, polishing and sealing of the external surfaces of airplane bodies and wings made of aluminum, as shown in Figs. 5 and 6. For that purpose, there is shown an airplane 23 with a fuselage 24 and wings 35. The top section 26 of the fuselage 24 is usually painted to prevent absorption of heat, so that this section need not be cleaned or polished electrolytically or by any other process. The surfaces 27 of the wings 25, as well as the sides 28 and bottom 29 of the fuselage 24, require cleaning, polishing and sealing.

For cleaning the wing surfaces 27, there is provided a portable box 30, shown of rectangular form and inverted over the surface to be treated, this box having a gasket 31 of suitable resilient material, such as neoprene, around its bottom edge for hermetically sealing the box to the surface to be treated, while permitting said box to be pushed along said surface. This box 30 contains an electrolyte 33, which is preferably of the improved composition described above, and a corrugated sheet 34 of the type shown in Fig. 3 or of the arched type shown in Fig. 4, cathodically connected to a source 35 of direct current, while the wing surface 27 to be treated is anodically connected to said source.

For cleaning, polishing and sealing the surface 27, the box 30 is moved over this surface at a rate to effect the necessary treating operation. Because of the quick acting nature of the electrolyte 33, requiring only a matter of a few seconds to effectively treat any particular area, the cleaning, polishing and sealing operation of the entire surface can be accomplished in a comparatively short time.

The surfaces 27 of the airplane wings 25 are generally flat, so that a box 30 presenting a substantially flat open end or rim with the sealing band 31 around it will suffice to maintain the desired sealing contact with said surfaces, as the box is pushed along said surfaces. There are, however, certain parts of the external airplane surfaces that have curvatures which cannot sealably receive a box with a flat open end, as described, but which require a box having an open end of corresponding curvature to fit somewhat conformably and sealably over these curved surface parts. For example, the concave junctures 36 between the wings 25 and the sides of the fuselage 24 are of this curved nature. Also, certain parts of the fuselage 24 itself, as for example, the bottom part 29, may be curved enough to require an electrolytic box with a curved rim to conform sealably therewith. In any case, there are no more than two or three general types of contours requiring electrolytic boxes with rims of corresponding contours, so that the entire cleaning, polishing and sealing operation can be carried out with only two or three types of electrolytic boxes.

The electrolyte of the present invention lends itself to selective action on restricted sections of a surface of a metal piece, especially where such a piece has a shape more intricate than that of a plain sheet. For example,

after certain shearing or machining operations, a metal piece may have burrs along the sheared machine edges, which require to be removed. To remove such burrs, there is contemplated the use of a cathode, shaped to concentrate its action on these selected burred regions of the metal piece, so that other parts of this piece are not substantially affected by electrolytic action. Fig. 7 shows the use of the electrolyte for that purpose. In the arrangement of Fig. 7, the metal piece 40 is shown consisting of a sleeve or collar, having a cylindrical section 41 and a flange 42. This metal piece 40, after machining, will have peripheral burrs around the edges 44, 45 and 46. To electrolytically remove these burred edges 44, 45 and 46, there is provided an anode rod 47 on which the metal piece 40 is impaled, so that this metal piece is anodically connected in the electrolytic circuit. Around this metal piece 40 and concentric therewith, is an annular cathode 48 having peripheral annular sections 49, 50 and 51 projecting radially inwardly in position directly opposite the burred edges 44, 45 and 46 respectively, so that the electrode action of the cathode 48 is concentrated on these edges. The arrangement described is immersed in an electrolyte 52 preferably of the improved character described.

The general arrangement shown in Fig. 7 lends itself to deburring action on a mass production basis. For example, the cathode 48 may be stationary but the metal pieces 40 to be deburred may be slipped over the anode rod 47 in numbers and moved step by step thereon, to move said metal pieces successively in position inside the cathode 48, to be deburred thereby, and then successively out of said cathode when each deburring operation is completed.

The electrolyte of the present invention has great utility in connection with the cleaning and smoothing of the internal surfaces of tubular members, as for example, the inside bore surface of the cylinders of combustion engines or pumps. Fig. 8 shows such an arrangement, comprising an engine cylinder 55 shown somewhat diagrammatically, having a cylindrical bore 56 with a cylindrical internal surface 57. The bottom of this cylinder 55 is closed by a seal 58 and a head plate 60 is placed over the cylinder. This cylinder 55, which is anodically connected to a source 61 of direct current, is filled with electrolyte 62, preferably of the type described above, and immersed in the electrolyte in this cylinder is a cathode 63 of cylindrical form concentrically placed in relation to the internal surface 57. By subjecting the electrolyte to voltage in the manner described above, the internal surface 57 of the cylinder engine is cleaned and smoothed to a much greater degree than is possible by machining.

In cases where the contour of the anodically connected workpiece to be cleaned and polished is intricate, it is difficult to clean and polish electrolytically uniformly over the contour of said workpiece. Uniform cleaning and polishing for such a complicated contour may be accomplished by breaking up the cathode into a series of separate elements in conforming shielding relationship with respective sections of the workpiece to be cleaned and polished and by applying separate voltages to these

cathode elements, differing in values according to the configuration of the sections shielded. Fig. 9 shows an embodiment of this feature, comprising a workpiece 69 connected as an anode to a source 70 of direct current and having an intricate surface 71 consisting of a series of sections 72 of different contours, some of which may be in the form of rounded projections or beads and some of which are flat. Placed opposite each of these contour sections 72 and shaped therefrom in shielding relationship thereto, are a series of cathode elements 73 conforming in shape with the respective contour sections. These cathode elements 72 are separately connected to the source 70 of direct current through respective rheostats 75, by which the voltages on the individual cathode elements, and in turn the required current densities may be selected according to the shape of the cathode elements, to attain uniform cleaning and polishing over the entire contoured surface of the workpiece 69. The arrangement shown in Fig. 9 is operated in an electrolyte 76 preferably of the improved type described above.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and restricted solely by the scope of the appended claims.

What is claimed is:

1. An electrolyte for use in anodically treating metal surfaces, consisting essentially of phosphoric acid and chromic acid and containing 0.7 to 2.7% by weight of sulfuric acid and 0.004 to 0.014% of hydrofluoric acid.

2. An electrolyte for use in anodically treating metal surfaces, comprising at least 60% by weight of phosphoric acid on a pure basis, 2 to 12% of chromic acid on the basis of the anhydride, 0.7 to 2.7% of sulfuric acid and 0.004 to 0.014% of hydrofluoric acid.

3. An electrolyte for use in anodically treating metal surfaces comprising at least 60% by weight of phosphoric acid on the pure basis, 2 to 12% of chromic acid, 0.7 to 2.7% of sulfuric acid, 0.004 to 0.014% of hydrofluoric acid, 0.6 to 2.6% of sodium dichromate and 0.1 to 2.1% of water.

4. An electrolyte for use in anodically treating metal surfaces, consisting essentially of at least 60% by weight of phosphoric acid on the pure basis and 2 to 12% of chromic acid and containing 0.6 to 2.6% of sodium dichromate.

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