

July 14, 1953

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2,645,611

METHOD OF AND BATH FOR ELECTROLYTIC POLISHING

Filed Sept. 20, 1948

3 Sheets-Sheet 1

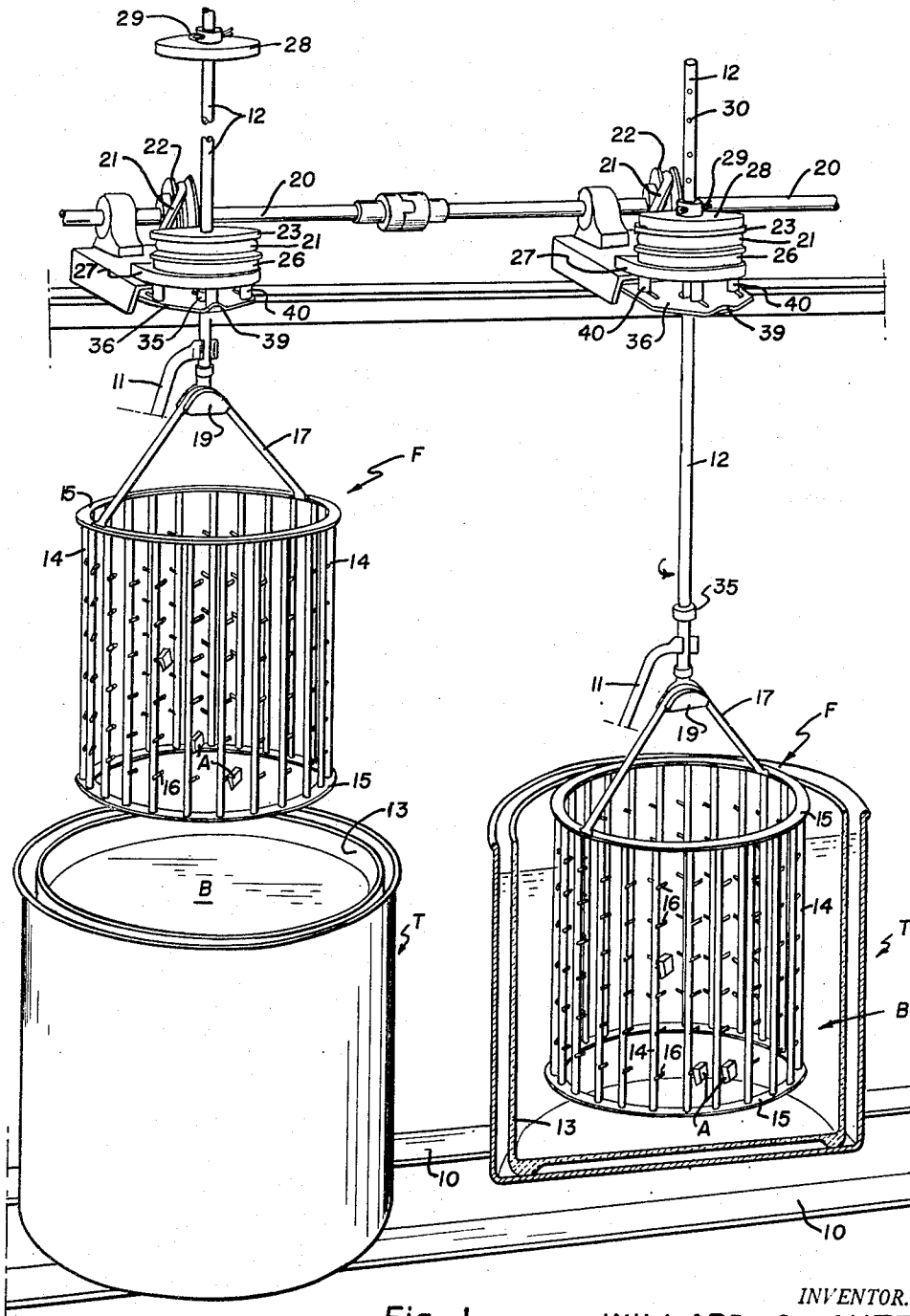


Fig. 1

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3 Sheets-Sheet 2

Fig. 4

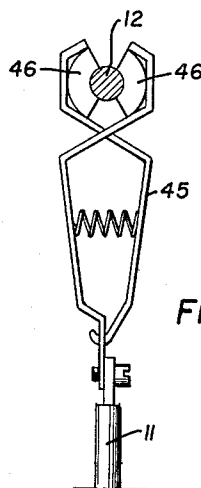
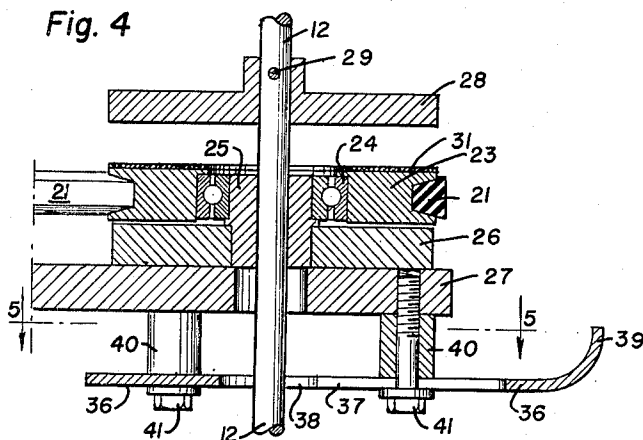


Fig. 6

Fig. 5

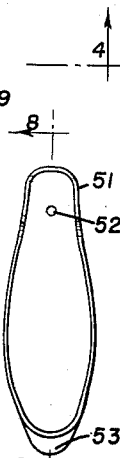
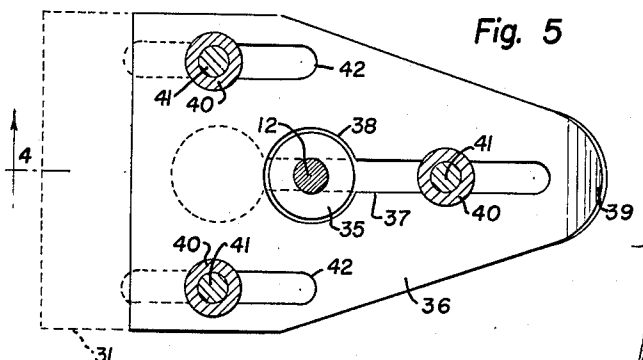


Fig. 7

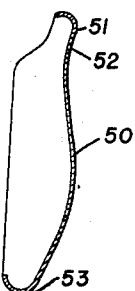


Fig. 8

Fig. 2

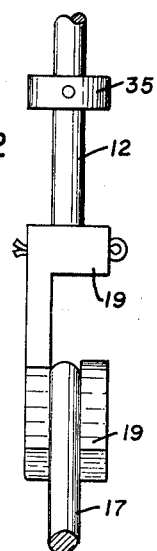
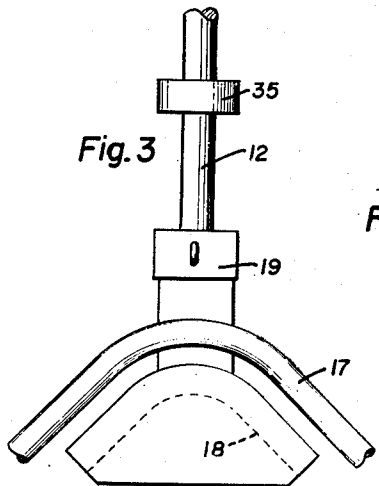


Fig. 3



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METHOD OF AND BATH FOR ELECTROLYTIC POLISHING

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3 Sheets-Sheet 3

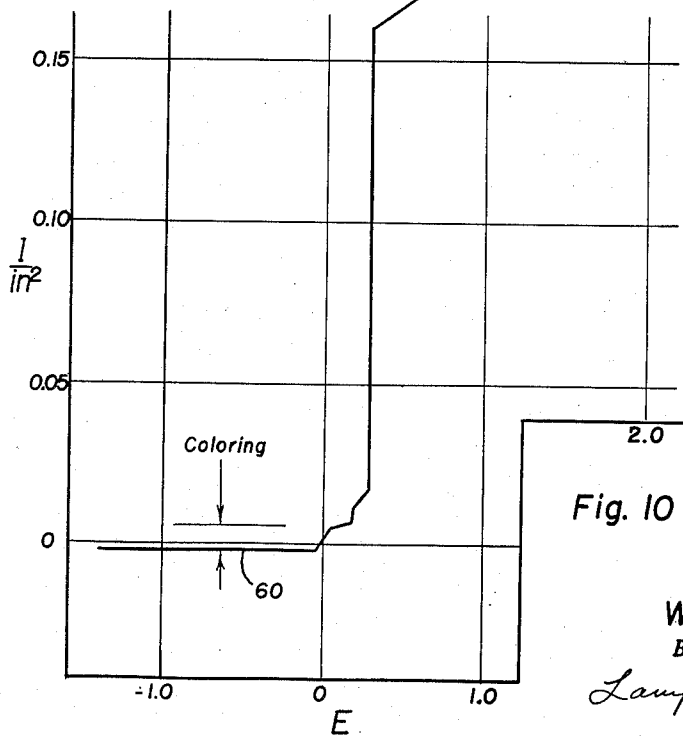
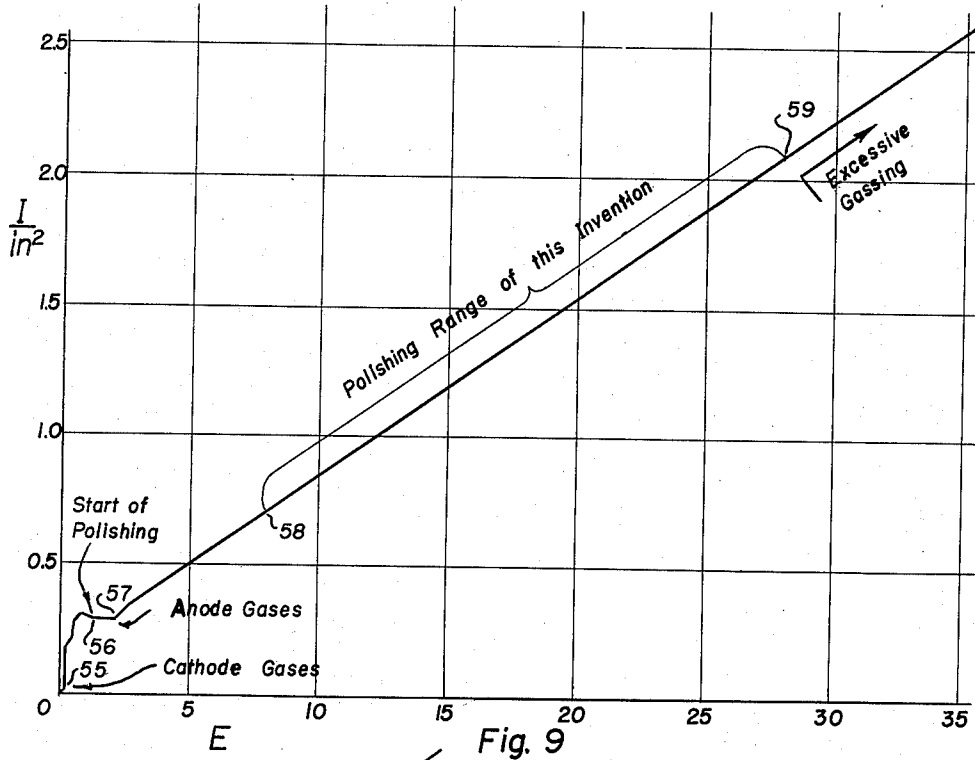


Fig. 10

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METHOD OF AND BATH FOR ELECTROLYTIC
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Application September 20, 1948, Serial No. 50,068

18 Claims. (Cl. 204—140.5)

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This invention relates to a method of and apparatus for, and also an electrolyte or bath used in, the electrolytic polishing of metals and alloys, including brass and also copper and other copper alloys, such as German silver, nickel silver and bronze, and certain other metals and alloys, such as stainless steel, nickel-copper alloys, such as Monel metal, cobalt-chromium-tungsten alloys, as of the "Stellite" type, nickel-molybdenum-iron alloys, as of the "Hastelloy A" and "Hastelloy B" types, nickel-molybdenum-chromium-iron alloys, as of the "Hastelloy C" or "Vitalium" types, and others.

Mechanical polishing of the surface of an article often requires difficult and costly grinding and buffing operations, particularly for articles having intricate or irregularly curved surface portions. Also, as a result of mechanical polishing, particles of abrasive may be embedded in the surface, and the heat developed during polishing sometimes adversely affects portions of the surface. However, with a proper electrolyte and suitably controlled conditions, the object to be polished being the anode, intricate or irregularly curved surfaces are readily polished electrolytically, in accordance with this invention.

The electrolytic polishing of metal, particularly stainless steel, has only recently received considerable attention from metallurgists and others interested in producing, by electrochemical reaction, a lustrous finish on various articles. A brightly polished but uniformly etched surface was stated to be produced on ferrous materials, in U. S. Patent No. 1,658,222, but the treatment was used in preparation for nickel plating, and the etched surface produced apparently did not have a sufficiently uniformly smooth surface to attract general interest in electrolytic polishing, per se. Thus, it was apparently not until after an article by Jacquet appeared in "Transactions of the Electrochemical Society," vol. 69, page 629 (1936), that wide general interest in the process was established. While this Jacquet article related to the electrolytic treatment of copper in aqueous solutions of phosphoric acid, in Jacquet French Patent No. 707,526, the electrolyte consisted of orthophosphoric acid and ether, for copper; and perchloric acid and glacial acetic acid, for nickel, aluminum, zinc, iron, lead and tin.

Because of the interest in the polishing of stainless steel, and the above disclosure of perchloric acid as a principal constituent of the electrolyte, a large amount of work and a considerable number of electrolytes involving perchloric acid were

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developed. However, perchloric acid is an extremely critical material to handle, and there have been several instances in which loss of life has been occasioned by explosions in plants using perchloric acid for electrolytic polishing purposes. An electrolyte consisting of phosphoric acid and ether is generally unsatisfactory for commercial purposes, due not only to the tendency for the ether to evaporate and reduce the useful life of the solution, but also to the hazard to workers due to the presence of ether vapors in the air.

While it is possible to electrolytically polish a flat surface of an article, in an aqueous solution of phosphoric acid, it is difficult and often impossible to secure satisfactory results, in the case of irregularly curved and shaped articles, or even on both sides of a flat article simultaneously. Also, the majority of previous electrolytes containing phosphoric acid also contained a stronger acid, such as sulfuric acid, but these were apparently developed for polishing stainless steel and experiments indicated that such electrolytes produced etching rather than polishing of brass and other copper alloys. Such experiments also indicated that none of the previous electrolytes are completely satisfactory for commercial operations, particularly in which relatively unskilled labor is used, rather than laboratory trained technicians or scientists, due to a short solution life or relatively narrow critical ranges of temperature or other operating conditions, in addition to those which are unsatisfactory due either to hazards involved in handling the electrolyte or its components, such as those containing perchloric acid, or the hazards involved in fumes due to the volatility of a component of the electrolyte, such as those including ether.

Among the objects of the present invention are to provide a novel electrolyte or bath and method of electrolytically polishing articles of brass and also certain other metals and alloys; to provide such a bath and method which can be used in polishing curved and irregular surfaces, as well as both sides of an article simultaneously; to provide such a method which can be carried out by non-technical workmen; to provide such an electrolyte which has a relatively long life; to provide such an electrolyte which does not produce noxious or dangerous fumes or vapors and which contains no components which are dangerous to handle or tend to produce explosions; to provide such a method and electrolyte which will operate successfully over a relatively wide range of temperature, and which does not require extremely

accurate control of voltage or current density; to provide a novel method of polishing and then producing a desired color of the polished surface of an article formed of brass, bronze or the like; and to provide such a method by which the polishing results can be duplicated with regularity and is therefore applicable to mass production.

Additional objects and the novel features of this invention will become apparent from the description which follows.

The novel electrolyte, or bath for electrolytic polishing, of this invention may consist, in one preferred form, of the following constituents, in the approximate proportions indicated, by volume:

Constituent	Proportion, percent
Orthophosphoric acid 85% ($H_3PO_4 \cdot H_2O$).....	41.5
Glycerin or glycerol (1,2,3-propanetriol).....	24.9
Ethylene glycol (1,2-ethanediol).....	16.6
Lactic (2-hydroxy propanoic) acid.....	8.3
Water.....	8.7
	100.0

The amount of water added is preferably that sufficient to adjust the specific gravity of the solution to approximately

$$\frac{20}{1.388}$$

although the specific gravity may be varied between 1.386 and 1.47. The water added to the solution is in addition to that contained in the phosphoric acid, so that if more concentrated acid, or pyrophosphoric acid ($H_4P_2O_7$), is utilized, then the water should be increased accordingly.

Another preferred form of the bath or electrolyte of this invention may consist of the following constituents, in the approximate proportions indicated, by volume:

Constituent	Proportion, percent
Orthophosphoric acid 85%.....	39.8
Glycerol.....	23.9
Ethylene glycol.....	15.9
Lactic acid.....	8.0
Monosodium glutamate.....	4.0
Water.....	8.4
	100.0

As will be evident, the difference between the above preferred forms is the presence in the second of monosodium glutamate, which thus may be termed an addition agent. Of course, the proportions of the various constituents may be varied within the ranges indicated below, while various constituents may be substituted for the preferred constituents. For instance, glycerol may be substituted for ethylene glycol and vice versa. Also, other water soluble polyhydric alcohols, such as propylene glycol and hexanehexol, may be substituted for ethylene glycol and/or glycerol, but the presence of at least two polyhydric alcohols is much preferred.

The substitutes for lactic acid are preferably mono-hydroxy mono-carboxylic acids, such as glycolic (hydroxyethanoic) acid, hydroxybutyric acid, and the like. It is to be noted that tests made with certain other acids, substituted for lactic acid, indicated that many carboxylic acids which might be thought to be probably satisfactory substitutes for lactic acid, did not produce equivalent or reasonably satisfactory results. Thus, tests with oxalic acid, which, of course,

contains no hydroxy group, produced very poor results, as did also tests with tartaric acid, a di-hydroxy di-carboxylic acid, and citric acid, a mono-hydroxy tri-carboxylic acid. It is further to be noted that when lactic acid, or a satisfactory substitute therefor, was omitted from the solution, some polishing took place, although the surface was noticeably less clean and less bright, but that much more satisfactory results were secured when at least two polyhydric alcohols were present.

Other agents which may be added in minor proportions, to increase the brightness of the surface produced, as determined by image reflection tests, and in some cases also the throwing power or ability to polish around curved surface portions or on the rear surface of an article, include mannitol (hexanehexol), amino acids such as glycine and glutamic acid, and amines such as ethylene diamine and monoethanol and tri-ethanol amines. Glutamic acid and monosodium glutamate are perhaps preferred addition agents, in view of the increased brightness produced when a minor amount, such as up to about 4%, is added to the bath of the first preferred form. In the case of monosodium glutamate, tests indicated that addition of from 1% to 4% produced an increase in the brightness or reflecting power of the polished surface, but that over 4% caused a decrease in the brightness, with 10% addition causing a decrease in brightness compared to the bath without an addition agent and also causing considerable etching.

In general, the bath of this invention preferably includes the constituents indicated in the following ranges of proportions:

Constituent	Proportion, percent
Orthophosphoric acid 85%.....	35-70
Polyhydric alcohol.....	8-64
Lactic acid or substitute.....	1-12
Water (including water in acid).....	5-30
Addition agent.....	0-10

The bath of this invention thus may be an aqueous solution of phosphoric acid and at least two polyhydric alcohols; an aqueous solution of phosphoric acid, at least one polyhydric alcohol, and lactic acid or substitute; a bath having the general range of proportions above indicated; or a bath having the approximate proportions of the preferred forms, as well as including the various addition agents disclosed. Such baths also preferably have no significant amount of an acid stronger than phosphoric.

In electrolytic polishing with the bath of this invention, a relative movement of the articles immersed in the bath is preferably utilized, although small articles can often be polished in stationary position.

The electrolytic bath of this invention may be used in polishing metals and alloys other than brass, which, of course, is an alloy of copper and zinc. Thus, a copper article is readily polished, as are also articles of copper alloys, such as beryllium copper; nickel silver and German silver, alloys of copper, nickel and zinc; Monel metal, an alloy of nickel and copper; and bronze, an alloy of copper, tin and zinc. Strangely, articles of substantially pure zinc were attacked but not really polished, tending to be blackened or stained, as was also the case with articles of nickel and of silver. Articles of stainless steel were readily polished, while those of carbon steel and soft iron were cleaned, but were difficult to

polish, since the anodic film could not be removed quickly enough. Also, articles of 24SO aluminum, which contains a small percentage (about 4.4%) of copper, were polished readily, while an article of 2SO aluminum (substantially pure aluminum) was anodically attacked but not polished.

There are several alloys which are used for hardness or strength at high temperatures, but which are difficult to machine and have required costly grinding operations for polishing. Such alloys, each of which is polished by the method and bath of this invention, include the cobalt-chromium-tungsten alloy known as "Stellite," used for hard facing cutting tools, drill bits, and the like; the nickel-molybdenum-iron alloys of "Hastelloy A" and "Hastelloy B" types, used for hard facing and wear resistance; and the nickel-molybdenum-chromium-iron alloys of the "Hastelloy C" or "Vitalium" type, the former also including tungsten and the latter also including a relatively large percentage of cobalt, used for strength at high temperatures, as in gas turbine blades, and in dental and medical work, because of neutrality in the human body. The principles of this invention may be utilized not only in polishing articles made of such alloys, but also in reducing the cross-sectional area thereof, or removing specific portions by masking, as for balancing in the case of gas turbine blades. As far as is known, none of these alloys have been hitherto successfully polished or otherwise treated electrolytically.

The method of electrolytic polishing of this invention may be carried out in apparatus, such as illustrated in the accompanying drawings, in which:

Fig. 1 is a three-dimensional view of such apparatus, certain parts being shown in section for clarity of illustration;

Figs. 2 and 3 are an enlarged fragmentary side and front elevation, respectively, of a rotating framework connection of the apparatus of Fig. 1;

Fig. 4 is an enlarged cross section of a pulley and clutch arrangement of the apparatus of Fig. 1;

Fig. 5 is a horizontal section taken along line 5—5 of Fig. 4;

Fig. 6 is a top view of an electrical connection;

Figs. 7 and 8 are bottom plan and longitudinal sectional views, respectively, of a typical article adapted to be electrolytically polished in the apparatus and in accordance with the method of this invention;

Fig. 9 is a chart illustrating voltage and current values for electrolytic polishing by use of the bath or solution of this invention; and

Fig. 10 is a chart illustrating voltage and current values during coloring, in further accordance with this invention.

As illustrated in Fig. 1, an electrolytic solution or bath B, having the constituents described above, is placed in a tank T, which is set on electrically conductive strips 10, as of copper or the like, the tank T being the cathode. The articles A to be polished are mounted on a basket or framework F, adapted to be rotated within the bath B, each of the articles A preferably being disposed at the same radial distance from the center of rotation, so that the relative speed of movement of each article through the bath is substantially the same. The framework F is preferably rotated at a speed so that the rate of movement of the articles through the bath is between 20 and 60 feet per minute, the preferred

velocity being approximately 40 feet per minute. It is to be noted that when the speed was above 60 feet per minute, the articles tended to be etched, rather than polished. A relative movement of the articles being polished with respect to the bath may be obtained by movement of the bath, or by movement of the articles other than rotative, such as vibratory. Calculations based on vibration of the articles in the bath showed an average speed of movement of the articles approximately the same as for rotation, i. e. a permissible range of 20 to 60 feet per minute, with a preferred rate between 35 and 40 feet per minute.

The framework F and the articles A form the anode within the bath B, current being supplied to the framework through a conductor 11, the connection between the conductor 11 and a vertical shaft 12 for rotating the framework F, and also the connection between the shaft 12 and framework F, being described in detail later. As the framework F and the articles A revolve within the bath B, a voltage of preferably between 8 and 28 volts is applied through the bath, between the articles A and the tank T. The preferred current density is between 0.5 and 2.0 amperes per square inch, and the temperature of the bath B is preferably maintained between 70° F. and 150° F., excellent commercial production results having been obtained with the bath solution at a temperature of about 95° F. to 104° F. (35° C. to 40° C.). As will be evident, with a constant speed drive, the speed of movement of the articles through the bath may be maintained relatively constant at the desired speed; with suitable electrical controls, the voltage and current density may be maintained relatively constant; and while the temperature of the solution is preferably maintained between 95° F. and 104° F., the bath temperature may be considerably higher without materially affecting the quality of the work, excellent results having been obtained with a bath temperature of about 130° F., so that the temperature of the bath may vary relatively widely, and the operations are therefore capable of being carried out by non-technical personnel.

As the articles A move through the bath B, and a current of the desired voltage and intensity passes therethrough, a complex, viscous layer which is difficult to analyze, forms thereon. One theory of the action, during electrolytic polishing, is that this layer causes a selective dissipation of the metal of the articles through electrolytic action, the high spots being removed faster, due to the layer being thinner thereover. The accuracy of this theory has not been definitely proven, but the result is that the surfaces of the articles A, after removal from the apparatus and washing to remove the viscous layer, have a high polish and luster, rivaling and often exceeding that produced by mechanical polishing. This is particularly true of curved or irregular surfaces, which may be uniformly polished electrolytically, but are difficult to polish uniformly mechanically. That is, a flat surface polished electrolytically in accordance with this invention, normally has a polish and luster equal to or greater than that of a mechanically polished surface, while a curved or irregular surface, almost without exception, has as high a polish and luster as the flat surface, which may not be true when the irregular surface is polished mechanically.

The articles are preferably removed as quickly as possible from the bath, as soon as polishing

is complete, and then washed, as discussed later. The bath may not be used indefinitely, without regeneration, at least in polishing brass articles, test results indicating a useful life of about 300 ampere hours per liter, which apparently corresponds to a concentration of between 60 and 70 grams per liter of copper and between 25 and 30 grams per liter of zinc. When brass articles are being polished, both the copper and zinc from the brass pass into the solution. Tests have indicated that the concentration of the copper reaches a maximum, and the copper then begins to deposit out at the cathode, i. e. at the tank T. Apparently, the zinc remains in solution, and the life of the solution is apparently determined by the concentration of the zinc.

Additional advantages are obtained when a porous wall or the like, such as provided by a porous, unglazed ceramic cylinder 13, is interposed between the anode and the cathode, the anode in this case being the articles A and the cathode the tank T. If desired, cooling coils may be disposed between cylinder 13 and tank T. When the copper separates out at the cathode or tank T, it is apparently substantially metallic copper, and the porous cylinder 13 prevents this metallic copper from being stirred about and perhaps contacting or interfering with the polishing of the articles A. In this way, more uniform polishing results are obtained, as the possibility of unpolished or less polished spots on the articles, due to the articles picking up metallic copper as they move through the bath, is avoided. The porous cylinder 13 further adapts the apparatus of this invention to use by unskilled or non-technical workmen, since it is unnecessary for such workmen to attempt to ascertain when the amount of copper, for instance, being stirred about in the solution, is interfering with the polishing operation.

As indicated previously, the framework F is rotated by the shaft 12, the framework being disconnected from the shaft when articles A are to be removed from the bath and washed, and another framework carrying a series of articles to be polished may be substituted therefor, the apparatus thus being capable of substantially continuous operation. The framework F may comprise a series of vertical bars or rods 14, extending between end rings 15 and provided with pins or pegs 16, preferably extending slightly upwardly in the direction of rotation and on each of which an article A may be hung. The spacing of the bars 14 and pins 16 is preferably such that no article will tend to touch or contact an adjoining or adjacent article during polishing, as such contact would tend to produce a surface portion or spot of less polish or luster. All of the framework which is subjected to the electrolyte is preferably painted with an electrical insulating material, such as a synthetic rubber cement of the "Pliobond" type, except the pins 16 on which the articles are mounted. The upper ring 15 is provided with a V-shaped handle 17, which is conveniently placed in a groove or socket 18, as in Fig. 3, open at the top and formed in a block 19, which is attached to the lower end of shaft 12. The upper midsection of handle 17 is preferably curved or arcuate, and the socket 18, as in Figs. 2 and 3, is correspondingly formed so as to receive the handle 17, and anchor the handle against tipping or pivoting about the socket, particularly during rotation in the bath. Since the framework F is suspended from the block 19, there is no tendency for the handle 17 to slip out

of the groove 18 during polishing. However, when the shaft 12 is lifted to its upper position, in a manner explained later and as shown at the left in Fig. 1, the framework F may be readily removed, and another framework having a new series of articles to be polished substituted therefor. After the framework is removed, the articles are washed, as by dipping, and then replaced by a new series of articles to be polished. As will be evident, when the shaft 12 and framework F are lifted to the upper position, the circuit through that particular tank is broken, so that no current is flowing through the tank, and it is unnecessary to turn off the current in order to remove a framework having polished articles thereon, or in order to place a framework having articles to be polished on the block 19.

Shaft 12 is rotated by a clutch mechanism which is automatically disconnected when the framework is lifted out of the tank, and since the framework revolves at a relatively slow speed, such as less than 10 R. P. M. for a framework diameter of 18 inches, the framework is relatively easily lifted out of the tank, to the upper position shown at the left in Fig. 1, without the necessity of stopping the drive shaft 20, or interfering with the operation of other polishing tanks.

As in Fig. 1, each automatic clutch mechanism may be driven by a V-belt 21 or the like, which passes around a drive pulley 22 on shaft 20, and also around a pulley 23, mounted for rotation about a vertical axis, as by a bearing 24, shown in Fig. 4. Bearing 24 is mounted on a bushing 25, shaft 12 being rotatable and also slidable in bushing 25, which is mounted in a spacing block 26, in turn mounted on a supporting plate 27. A circular drive plate 28 is attached to each shaft 12 adjacent the upper end thereof, as by a pin or the like, such as cotter pin 29. The position of drive plate 28 may be adjusted on the shaft 12, by insertion of the pin 29 in one of a series of holes 30 in shaft 12. The top surface of pulley 23 is preferably provided with a layer of friction material 31, such as similar to brake lining and the like, so that when the frame work is dropped to its lower position, as shown at the right in Fig. 1, the pulley 23 will drive plate 28, thereby rotating shaft 12 and the framework F.

The shaft 12, as in Figs. 1 to 3, is also provided with a collar 35 adjacent to but spaced above the block 19, which is adapted to rest on a sliding plate 36, as shown at the left in Fig. 1, so as to hold the shaft 12 in its upper position, as when a framework F is being removed or placed thereon. As will be evident, as soon as the framework F is lifted, preferably by the operator grasping the underside of block 19, so as to lift the shaft 12 along with the framework F, the drive plate 28 will no longer be in engagement with pulley 23, so that the shaft 12 no longer rotates. The framework and shaft are then lifted to the upper position, and plate 36 slid inwardly to support the collar 35, and thereby hold the shaft 12 in its upper position.

As in Figs. 4 and 5, the sliding plate 36 is provided with a central, longitudinally extending slot 37 having at its rear end a circular enlargement 38, through which collar 35 on shaft 12 is adapted to pass. Normally, the sliding plate 36, which may have an upturned end 39 which serves as a handle, is left in the full position of Fig. 5. However, as soon as shaft 12 has been lifted to its upper position, the plate 36 is slid to

the dotted position of Fig. 5, in which position the circular enlargement 38 will pass beyond collar 35, the latter then being supported by the plate, on the edges of slot 37, with the shaft 12 extending through slot 37. The sliding plate 36 may be supported in any suitable manner, as by three, or any other desired number of pins or the like, such as provided by spacing blocks 40 through which cap screws 41 extend, the heads of the cap screws 41 supporting the sliding plate 36. One of the cap screws 41 may pass through the central slot 37, while a side slot 42 for each of the other cap screws may be provided in plate 36.

The conductor 11 may be connected to shaft 12 just above block 19 but below collar 35, a connection between the conductor and shaft preferably being made so that the shaft may rotate without undue pull on the conductor. While any suitable means for connecting the conductor 11 to the shaft 12 may be used, a satisfactory connection is shown in Fig. 6, wherein the conductor 11 is provided at its end with a double arm spring clamp 45, adapted to hold a pair of arcuate blocks 46 against the shaft 12. The blocks 46 are preferably made of copper, copper-bearing graphite, or other suitable electrically conductive material, and the clamp 45 maintains the blocks 46 in engagement with the shaft 12 during rotation of the latter. An electrical connection to shaft 12 may also be made, if desired, at supporting plate 27, as by a spring pressed brush of carbon, copper-bearing graphite, or other suitable material.

A typical type of article, formed of brass, which has been successfully polished commercially by the method of this invention, is illustrated in Figs. 7 and 8. Such an article is a drawbolt cap for luggage, which has an elongated, rounded back 50, a neck 51 at one end, provided with an attachment hole 52, and a partly closed opposite end 53. As will be evident, the shape of this article is quite irregular, which caused mechanical polishing operations to be relatively difficult and costly. Also, before mechanical polishing, it is necessary to degrease and clean thoroughly, since grease from stamping and machining operations tend to interfere with mechanical polishing. However, when such a drawbolt cap was polished electrolytically in accordance with this invention, no degreasing was necessary. As a matter of fact, during tests, several drawbolt caps which were covered with grease and had been damaged by accidental partial crushing, to the extent that they contained an indentation or depression sufficient to prevent a uniform polish being obtained mechanically, were removed from scrap and, without degreasing, polishing electrolytically in accordance with this invention, a uniformly lustrous finish being obtained, even in the indentation. When the drawbolt cap of Figs. 7 and 8 is polished, it is merely hung by hole 52 on a pin 16 of framework F. Such drawbolt caps are made of brass, and other articles, also made of brass, which have been successfully polished commercially in accordance with this invention are handle loops for trunks, ferrule tie-backs for traveling cases, hooks for traveling case compartments, and rod ends for swinging partitions in traveling cases.

The articles on the framework F are subjected to a suitable current for a suitable period of time, to effect the desired polish, such as from 15 seconds to 30 minutes, dependent upon the surface condition, i. e. the amount of metal necessary to

be removed until a satisfactory polish or luster is obtained. The framework F is then removed from the tank T, and the framework, with the articles hanging on it, dipped into wash water, at about room temperature, which removes most of the bath solution adhering to the framework and the articles. This wash water is preferably used as makeup water for replenishing the bath solution, since electrolysis of water in the solution tends to cause a loss thereof. The framework and the articles are then dipped into hot rinse water, preferably maintained at a temperature of 150° F. to 160° F. or higher, which washes off the viscous, tenacious layer adhering to the articles. After removal from the framework F and drying, the articles may be lacquered, bake enameled or otherwise treated in accordance with the procedure in the particular factory. The rinse water is preferably maintained at or above 150° F., since a much lower temperature may not be sufficient to lower the viscosity of the tenacious layer to permit its ready removal. Thus, water as low as 100° F. to 120° F. has been found, in tests, to be too low to remove the layer completely from all of the articles.

The articles are removed from the polishing bath as quickly as convenient after polishing has been completed, or if it is necessary to let them stand in the bath after polishing is completed, a slight current flow is preferably maintained, to prevent discoloration. Also, the articles are preferably washed as soon as possible after removal from the bath, again to prevent discoloration due to galvanic action. The tendency for this discoloration may be taken advantage of, if a slightly different color is desired on the polished article, as when the article is made of an alloy such as brass, containing materials of different electrical potential, as described later. While the voltage may be varied over a relatively wide range, for economy purposes the voltage is preferably maintained as low as will produce the desired results. In general, the more viscous the bath, the higher the voltage necessary to produce maximum polishing results.

The curve shown in Fig. 9, in which voltage is plotted as abscissae, and current density, or amperes per square inch, is plotted as ordinates, is a typical curve illustrative of variations in voltage and current density during electropolishing in the bath of this invention. When a brass article was placed in the bath, and the current first started flowing therethrough, at a relatively low voltage, the cathode started gassing at about point 55, while with an increase in voltage and current density, polishing began at about point 56, but the results were not sufficiently satisfactory for commercial operations. Between points 56 and 57, the current density did not increase, as the voltage increased, but at point 57 the anode began gassing, and the current density then increased proportionally to an increase in voltage. The best results were obtained between points 58 and 59, i. e. between 8 and 28 volts and a current density of between about 0.5 and slightly over 2 amperes per square inch. Above point 59, excessive gassing at the anode apparently prevented sufficiently satisfactory results from being obtained. In some instances, as in the case of single articles, not too large, polishing may be satisfactory at less than 8 volts, sometimes even as low as point 56, but when a plurality of articles were being polished, operation in the preferred range, 8 volts and above, was necessary.

After the article has been polished, it may be colored, if desired, by a very slight or reverse

voltage, and a very small current, the coloration depending upon the amount of time the coloring current is passed through the article. In the case of a brass article, when the voltage is reduced below the single electrode potential of copper, i. e. +0.7618 volts, but above the single electrode potential of zinc, i. e. -0.344 volts, a color range from the light gold of brass to the copper hue of copper can be produced. The reason for such coloring is not definitely known, one probable explanation being that the zinc is removed while the copper stays on the surface.

The curve in Fig. 10, in which voltage is plotted as abscissae and current density as ordinates, represents conditions when the current and voltage were varied, for low values thereof. Thus, when the voltage was reduced to almost zero, such as +.04 volts, the current was correspondingly low, while when the voltage was reversed to a low value, such as from -.01 to -.4 volts, the current remained substantially constant, at approximately -.0005 amperes per square inch, such as along the portion 60 of the curve. The brass articles being colored were first polished, then removed from the polishing solution, rinsed and wiped dry, and then returned to the polishing solution. A voltage of -.044 volts produced, with the corresponding current density of -.0005 amperes per square inch, certain colors, dependent upon the time that the article was so treated. Thus, with the amount of time indicated, the following coloring was produced:

Time	Color
2 Seconds.....	Light Gold.
3 Seconds.....	Gold.
5 Seconds.....	Coral Gold.
8 Seconds.....	Red Gold.
12 Seconds.....	Copper.

The temperature of the solution for coloring may be maintained between 70° F. and 150° F., preferably around 140° F. The solution is preferably one which has been used for a sufficient period of time that the concentration of copper therein has reached or exceeded about 5 milligrams per milliliter, representing a use of about 100 ampere hours per liter or more.

Articles formed of alloys other than brass may be polished and then colored, the preferred voltage and current ranges, and times for coloring, varying in accordance with the alloy being colored. As will be evident, the colors which can be obtained are limited to the production on the surface of the article of a greater proportion of a metal which has a higher single electrode potential. In the case of binary alloys, the metal having the higher single electrode potential, such as copper in the case of brass, is the "coloring agent," as it were. In the case of ternary or quaternary alloys, the metal having the highest single electrode potential may be the coloring agent, or the two or more metals having higher single electrode potentials may be the coloring agent. As will be evident, coloring subsequent to polishing will be desired only when a different color than that naturally possessed by the alloy is desired, and the metal or metals providing the "coloring agent" will also produce the desired color.

From the foregoing, it will be evident that the method and the electrolytic bath of this invention, fulfill to a marked degree the requirements and objects hereinbefore set forth. None of the preferred ingredients of the bath, namely, phos-

phoric acid, glycerol, ethylene glycol, lactic acid and water, have explosive potentialities, are difficult or dangerous to handle, are toxic, or produce dangerous or noxious fumes, either alone or in association with the other ingredients. A solution containing the above ingredients is acidic, but not harmful to the skin, so that there is no danger of acid or alkali burns to workmen. Furthermore, heating the bath to a temperature, such as 150° F., or even higher, does not cause noxious or toxic fumes or vapors to be driven off. The substitutes for glycerol and/or ethylene glycol, namely, polyhydric alcohols such as propylene glycol and hexanehexol, and the substitutes for lactic acid, namely, mono-hydroxy monocarboxylic acids such as glycolic, hydroxybutyric and vinylglycolic acids, are also neither dangerous nor toxic, nor do they produce noxious fumes. It is to be noted that the monohydric alcohols, such as ethanol, methanol and isobutyl alcohol, tend to boil off and to be lost from the solution, thus producing not only a loss of constituent which must be replaced, but also noxious fumes, whereas the polyhydric alcohols, in general, have higher boiling points and therefore are not lost as readily nor produce objectionable fumes. The preferred addition agents, namely, monosodium glutamate and glutamic acid, as well as hexanehexol and glycine and other amino acids, are further neither toxic nor dangerous nor productive of noxious fumes, while the amines useful as addition agents, such as ethylene diamine, are neither dangerous to handle nor productive of noxious fumes or vapors. As indicated previously, the temperature of the bath may be maintained within a relatively wide range, and excellent results secured. While the voltage and current density may also be varied over a relatively wide range, these may be controlled more readily, and therefore no difficulty is encountered in maintaining optimum conditions.

A relatively large number of metals and particularly alloys, though not all metals or alloys, can be polished successfully, in addition to brass. In addition, the proportions of the solution constituents may be those of commercial compounds, such as 85% orthophosphoric acid, which, of course, contains water.

The electrolytic polishing of the cobalt-chromium-tungsten, nickel-molybdenum-iron, and nickel-molybdenum-chromium-iron alloys, of the types described previously, is an achievement of no small importance. Both from the standpoint of imparting a smooth, lustrous finish to the surface of articles made of such alloys, particularly useful in the case of articles such as gas turbine blades and dental and medical specialties, and reducing the cross sectional area or removing selective surface areas of an article made of such an alloy by electrolytic action, a valuable contribution has been made.

The apparatus constructed in accordance with this invention has many advantageous features. The provision of a porous wall between the cathode and the anode or article being treated prevents a metal or compound, separating out at the cathode, from being carried around in the solution and interfering with the polishing operation. The provision of a rotating framework on which a plurality of articles may be mounted for polishing, such framework preferably being circular so that each article will move through the bath at the same rate of speed, coupled with a readily detachable connection between the framework and a drive shaft or the like there-

for, is quite advantageous, and particularly so when coupled with an automatic clutch mechanism which causes the drive to be disconnected when the framework is lifted for removal of the articles from the bath. It will be evident, of course, that various changes may be made in the apparatus. Neither the tank nor the porous wall between the cathode tank and the articles being treated need be circular, but may have any other desired shape. For instance, the tank may be made of glass, with a copper or other suitable metal plate disposed in the bottom as the cathode, while the porous wall may be a layer of fiber glass disposed above the cathode plate, a shielded conductor preferably being connected to the cathode. Also, only a portion of the tank may form the cathode, such as one wall of a square or rectangular tank, and in such case the porous wall may extend in parallel, spaced relation to the cathode wall. The framework on which the articles are mounted may have shapes other than circular, such as planar when a single wall of the tank is the cathode, and the articles then may be vibrated or reciprocated, to effect movement thereof relative to the bath, rather than being rotated. While it is desirable that each article be disposed as nearly as possible the same distance from the cathode as the remaining articles, this may not be necessary in many cases. Also, the articles may be polished by a continuous conveyor system, whereby they are passed through the electrolytic bath, lifted out, washed, lifted, and then rinsed. After rinsing, the articles may be automatically discharged, as by being hung on hooks which are shaped so as to discharge the articles when a predetermined angular position is reached. Such hooks may extend from a plate or chain at about 45° to the horizontal, and be provided with an end extending vertically when in a depending position, with a stop opposite the end and extending at 90° to the main portion of the hook. When such a hook is moving down, and becomes nearly level, the article will drop off. The bath may be circulated, as for cooling, and also may be filtered or treated for regeneration, to remove metal separated out at the cathode or in solution in the bath. In addition, various other types of clutch mechanism and detachable connections between the framework and the drive, as well as electrical connections thereto, may be utilized.

It will further be understood that various other changes may be made in the method and bath of this invention, and that materials other than those specifically described herein may be added to the solution, without departing from the spirit and scope of this invention.

What is claimed is:

1. An electrolytic polishing bath comprising by volume, from approximately 35% to approximately 70% of orthophosphoric acid; from approximately 8% to approximately 64% of at least one water soluble polyhydric alcohol; from approximately 1% to approximately 12% of a mono-hydroxy mono-carboxylic acid; from approximately 5% to approximately 30% of water; and from 0 to approximately 10% of an addition agent adapted to increase the brightness of an article polished in said bath, the total of said constituents being approximately 100%.

2. An electrolytic polishing bath as defined in claim 1, wherein each said polyhydric alcohol is selected from the group consisting of glycerol, ethylene glycol, propylene glycol and hexanexol.

3. An electrolytic polishing bath as defined in claim 1, wherein said mono-hydroxy mono-carboxylic acid is selected from the group consisting of lactic acid, glycolic acid and hydroxybutyric acid.

4. An electrolytic polishing bath as defined in claim 1, wherein said addition agent is selected from the group consisting of monosodium glutamate, an amino acid, and an amine.

5. An electrolytic polishing bath as defined in claim 1, wherein said addition agent is hexanexol.

6. An electrolytic polishing bath consisting by volume of about 41.5% of 85% orthophosphoric acid; about 24.9% of glycerol; about 16.6% of ethylene glycol; about 8.3% of lactic acid; and about 8.7% of water.

7. An electrolytic polishing bath comprising by volume, about 39.8% of 85% orthophosphoric acid; about 23.9% of glycerol; about 15.9% of ethylene glycol; about 8.0% of lactic acid; about 4.0% of monosodium glutamate; and about 8.4% of water.

8. A method of electrolytically polishing an article of brass, comprising placing said article in an electrolytic bath as defined in claim 1; and passing an electric current through said article as the anode in said bath.

9. A method of electrolytically polishing an article of brass, as defined in claim 8, which includes maintaining said bath at a temperature between 70° F. and 150° F.

10. A method of electrolytically polishing an article of brass, as defined in claim 8, which includes moving said article relative to said bath at a speed of between 20 and 60 feet per minute.

11. A method of electrolytically polishing an article of brass, as defined in claim 8, which includes passing an electric current through said article as the anode in said bath, at a voltage between 8 and 28 volts and a current density between 0.5 and 2.0 amperes per square inch.

12. A method of polishing and coloring an article of brass, which comprises placing said article in an electro-polishing bath as defined in claim 1; passing an electric current through said bath and article as the anode, to polish said article; removing said article from said bath and washing the same to remove any viscous layer therefrom; replacing said article in said bath; and passing a current through said article for a relatively short period of time at a voltage between +.04 and -0.4 volts, to color the same.

13. A method of polishing and coloring an article of brass, as defined in claim 12, wherein said coloring voltage is approximately -0.044 volts and the current density is approximately 0.0005 amperes per square inch.

14. A method of electrolytically polishing an article formed of an alloy whose principal components are cobalt, chromium and tungsten, which comprises placing said article in a bath as defined in claim 1; and passing an electric current through said article as the anode in said bath.

15. A method of electrolytically polishing an article formed of an alloy whose principal components are nickel, molybdenum and iron, which comprises placing said article in a bath as defined in claim 1; and passing an electric current through said article as the anode in said bath.

16. A method of electrolytically polishing an article formed of an alloy whose principal components are nickel, molybdenum, chromium, iron and tungsten, which comprises placing said ar-

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article in a bath as defined in claim 1; and passing an electric current through said article as the anode in said bath.

17. A method of electrolytically polishing an article formed of a material selected from the group consisting of brass, copper, a copper base alloy, an alloy whose principal components are cobalt, chromium and tungsten; an alloy whose and iron; an alloy whose principal components are nickel, molybdenum, chromium, iron and tungsten; and an alloy whose principal components are cobalt, chromium, nickel, molybdenum and iron, which comprises placing said article in an electrolytic bath as defined in claim 1; and passing an electric current through said article as the anode in said bath.

18. A method of electrolytically polishing an article formed of an alloy whose principal components are cobalt, chromium, molybdenum and iron, which comprises placing said article in a bath as defined in claim 1; and passing an electric current through said article as the anode in said bath.

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