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ELECTROLYTIC POLISHING OF METALS

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FIG. 1

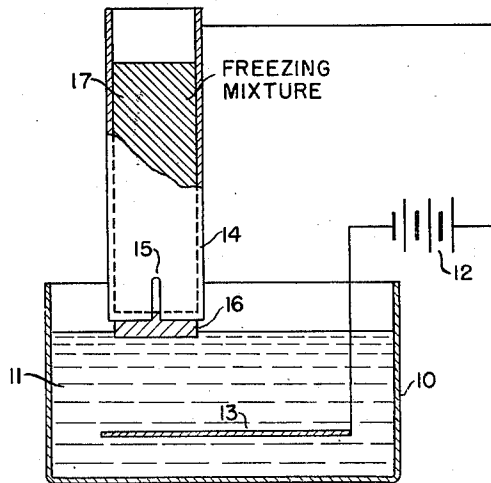
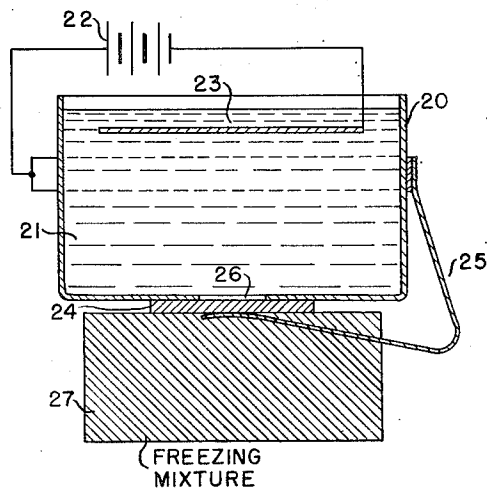


FIG. 2



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# UNITED STATES PATENT OFFICE

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## ELECTROLYTIC POLISHING OF METALS

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7 Claims. (Cl. 204—140.5)

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My invention relates to a method and an electrolytic bath for the anodic or electrolytic polishing of metals.

Electrolytic polishing methods used in the finishing of metal surfaces have remained highly empirical practices in which specific electrolytic solutions having polishing properties only for certain metals are effective. In general, the art shows that the solution used as the polishing electrolyte is strongly acidic and quite specific for the metal being polished in order to obtain the result usually described. Accordingly, it is an object of my invention to provide a composition for an electrolyte and a method of polishing which do not have such specificity and can be used to polish many metals with only minor adjustments in the composition of the electrolyte.

Polishing solutions frequently contain heavy concentrations of strong oxidizing agents, such as chlorates, and conditions in the electrolyte not infrequently develop which result in the occurrence of explosive reactions within the electrolyte. Hence, it is another object of my invention to provide an electrolytic polishing solution and method which can be carried out conveniently and in a manner such that the solution at all times will be free of high concentrations of oxidizing agents and, consequently, the danger of the occurrence of an explosion is eliminated.

It is another object of my invention to provide a method of electrolytic polishing whereby a solution of electrolyte prepared according to the principles of my invention can be caused to polish many metals.

It is a further object of my invention to provide an electrolyte and method of polishing and treating metals and alloys to produce finished surfaces of a degree of polish sufficient for reproduction for examination under the electron microscope.

It is another object of my invention to provide a method of polishing alloys having more than one phase present whereby one of the phases of the alloy can be selectively polished so that the surface of the alloy can be examined for the presence of that phase, the other phases remaining unpolished or etched.

Other objects and advantages of my invention will in part be obvious and in part appear hereinafter in the following detailed description of its principles and several of its embodiments.

My invention, accordingly, consists of electrolytic bath and the method of polishing metals including the relationship of one or more of the constituents of the bath to each of the others

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thereof and the relationship of one or more of the steps of the method to each of the others thereof as will be described herein, and my invention is not to be limited except as defined in the claims appended to this application.

In the drawings comprising Figures 1 and 2 I have illustrated two convenient apparatuses for practicing the method of polishing metals according to my invention.

In order to polish, an electrolytic bath should cause polarization of the anode and it should have the capacity for carrying a heavy current, for a necessary condition for the production of polarization within the cell is the employment of a high current density. The bath should also cause the anode metal, or the metal being polished, to go into solution and, at the same time, liberate oxygen at the anode. It should also produce concentration polarization within the cell.

I have discovered a composition for an electrolyte which permits the control of the above-named effects and includes simply a solution of a substantially neutral salt, such as an alkali metal salt of a mineral acid in water and an organic solvent such as alcohol. The concentration and pH of the solution are determined by the polishing problem on hand. The pH of the solution is adjusted until polishing takes place at the anode, which value of pH I call the "polishing pH" of the solution.

It is necessary that the salt used have a solubility high enough in the water-organic solvent mixture to carry a sufficiently heavy current to cause polarization of the anode. In general salts such as alkali metal salts of the mineral acids, i. e., sodium, potassium and lithium salts of nitric, hydrochloric, hydrobromic, hydroiodic, hydrofluoric, phosphoric, chromic and sulfuric acids, which are sufficiently soluble to give concentrated solutions can be used. In general, they are available as substantially neutral salts and will form aqueous solutions which, as electrolytes, are capable of carrying high currents, thus permitting the application of current densities to specimens sufficient to accomplish polishing. It is a matter of common knowledge that some salts of the mineral acids, particularly the phosphates are not neutral in solution.

However, in such cases, solutions of the salts can be made up with sufficient free acid to counteract the inherent buffer nature of the salt thus providing a substantially neutral salt solution as a starting point.

The organic solvent can be any completely water-miscible organic liquid or solvent such as ethyl alcohol, methyl alcohol, glycerine, ethylene

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glycol, acetone, isopropyl alcohol, Cellosolves, water-miscible esters and like organic compounds. Apparently the function of the organic material in the electrolyte is to reduce the ion velocity and thereby to aid in the establishment of concentration polarization at the cell anode.

The pH of the solution of the salt in the water-organic solvent mixture is adjusted by the addition of a small amount of a strong base or acid to adjust it to the "polishing pH." Sodium hydroxide can be used as the alkali and, for acidification of the solution, such acids as, acetic, nitric, oxalic, citric, sulfuric, or hydrochloric acids can be used. In general, it is preferable, although not essential, that the acid used to acidify the solution be one that will supply the same acid radical as that in the solution as part of the salt. This is particularly to be observed where there is possibility that ingredients of the electrolyte will react with each other.

When the electrolytic baths are freshly prepared, it is not immediately certain that they will polish the metal it is desired to polish. Simple experimental observation will tell the operator after a few seconds of electrolysis of his specimen whether or not the polishing is taking place for, if the polishing condition, that is, polishing pH, prevails in the solution, the outer corners and edges of the specimen will very quickly begin to appear bright. If inspection shows that the specimen is not being polished but is being etched, the solution is made slightly more alkaline by the addition of a few drops of strong alkali until observation shows that polishing is taking place. If inspection of the specimen after a few seconds of preliminary electrolysis shows it is being oxidized, the solution is made slightly more acidic until polishing takes place. It is a relatively simple matter to adjust the pH of the solution with a few drops of acid or alkali to the polishing value. Once this is attained, the polishing will proceed smoothly and a specimen, with little preliminary mechanical preparation or finishing, can usually be polished within a matter of 15 to 60 seconds at a current density of about 0.3 to 3.0 amperes per square-centimeter.

The polishing pH for the bath depends upon the temperature of the solution, the temperature of the anode and the current density as well as upon the anode material. I have found that best polishing conditions are attained by maintaining the anode as cold as possible without causing precipitation of electrolyte. For example, in carrying out the method, cooling of the anode by contacting it with a freezing mixture or solid carbon dioxide, either continuously or intermittently, will maintain the anode sufficiently cold to promote the polishing.

Referring to the drawing, Figure 1 illustrates a convenient polishing apparatus in which 10 represents a vessel for electrolyte 11. Battery 12 represents a source of current, 13 the cathode and 14 the anode which, for convenience in polishing small specimens, can be made from a piece of metal tubing one end of which has a slit 15 to provide a sort of spring grip for specimen 16. Since it is desired to chill the specimen to a temperature well below that of the solution, a freezing mixture 17, conveniently Dry Ice, is placed in the specimen holder.

As has been mentioned, adjustment of the solution to polishing pH is done empirically by observation of the specimen. Accordingly, Figure 2 illustrates a more convenient apparatus for so

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doing. In the drawing, 20 represents a vessel for holding electrolyte 21. Battery 22 supplies current to the cell by way of the cathode 23 and anode 24, the specimen to be polished. Electrical connection to the anode is made through spring 25 which is adapted to hold specimen 24 closely against the bottom of vessel 20. The electrolyte makes contact with the anode through the hole 26 in the bottom of the vessel. The anode can be cooled by placing it in contact with a freezing mixture 27 as shown. By using such an apparatus it is possible to adjust the solution to polishing pH readily for the anode is at all times visible. Also, no interruption in its cooling or electrolysis is necessary to determine its state. By making the hole in the bottom of the vessel a definite area, such as an integral number of square centimeters, control of the current density employed is facilitated.

The nature of the electrolytic bath and the method of polishing according to the principles of my invention will be more clearly understood by reference to the following specific examples which comprise brief descriptions of a few embodiments of my invention.

#### Example I

To 10 milliliters of a saturated aqueous sodium nitrate solution there was added 100 milliliters of ethyl alcohol. The solution containing the sodium nitrate and the alcohol was cooled to about 10° C. and was used to polish a specimen of relatively pure iron after adjustment to polishing pH of a value slightly more than 7 by the addition thereto of a few drops of 1.0 normal sodium hydroxide solution.

Cells like those shown in the drawings, consisting of the above electrolytic bath, a stainless steel cathode and the specimen as the anode were used. The anode was chilled to a temperature of about minus 30° C. by placing it in contact with a freezing mixture, which conveniently can be a cake of Dry Ice, and then dipped into the solution and subjected to electrolysis at a current density of 0.3 ampere per square centimeter.

#### Example II

A sample of pearlitic steel was polished according to the method described at a current density of 0.3 ampere per square centimeter in a bath consisting of 125 milliliters of ethyl alcohol and 10 milliliters of saturated aqueous sodium nitrate solution, which bath had been slightly alkalized with a few drops of 1.0 normal sodium hydroxide. Under such conditions twenty seconds were required to polish the specimen.

#### Example III

A sample of "Armco" iron, more than 99 per cent iron, was polished according to the method outlined at a current density of 0.3 ampere per square centimeter in a bath consisting of 100 milliliters of ethyl alcohol and 15 milliliters of saturated aqueous potassium nitrate solution, which bath has been alkalized with a few drops of 1.0 normal potassium hydroxide.

#### Example IV

A sample of austenitic steel was polished at a current density of 0.6 ampere per square centimeter in an electrolyte consisting of 10 milliliters of saturated aqueous sodium nitrate solution and 125 milliliters of methyl alcohol. The solution was alkalized with a few drops of 1.0 normal so-

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odium hydroxide and chilled to 0° C. The anode was chilled to about minus 30° C. by contacting it with solid carbon dioxide during the electrolysis. About forty seconds were required for complete polishing.

#### Example V

Samples of 0.45 carbon steel, air-cooled from 1550° F., were polished at 0.43 ampere per square centimeter in different baths consisting of 15 milliliters of saturated aqueous potassium nitrate solution and 125 milliliters of methyl alcohol, ethyl alcohol and acetone slightly alkalized with a few drops of 1.0 normal sodium hydroxide. The solutions were chilled to temperatures of about 0° to 10° C. and the specimens chilled with solid carbon dioxide during the electrolysis.

Similar samples of steel tempered at 1300° F. were polished in the same baths under like temperature conditions at current densities of 0.2 ampere per square centimeter.

#### Example VI

A sample of stainless steel of the 18-8 variety was polished in an electrolytic bath consisting of 15 milliliters of saturated aqueous sodium nitrate solution, 75 milliliters of methyl alcohol and 0.1 milliliter of 1.0 normal nitric acid. The polishing required 30 seconds in the aggregate and was accomplished by chilling the sample by contacting it with a freezing mixture giving a temperature of about minus 40° C., electrolyzing for about 10 seconds, cleaning the electrolyzed surface by gentle brushing and repeating the steps.

A similar sample of 18-8 stainless steel was polished in a solution consisting of 15 milliliters of saturated aqueous sodium nitrate solution, 75 milliliters of acetone and 0.2 milliliter of 1.0 normal sodium hydroxide.

A specimen of stainless steel was polished to a high luster using the technique described and a bath consisting of 10 milliliters of saturated aqueous sodium nitrate solution, 10 milliliters of water and 40 milliliters of glycerine alkalized with 0.2 milliliter of 1.0 normal sodium hydroxide solution.

#### Example VII

Nickel was polished using a bath consisting of 75 milliliters of methyl alcohol, 15 milliliters of saturated aqueous sodium nitrate solution and 0.1 milliliter of 1.0 normal nitric acid. The current density employed was 0.9 ampere per square centimeter and during the electrolysis the solution was maintained at room temperature while the anode was chilled with a freezing mixture giving the temperature of about minus 40° C.

#### Example VIII

A sample of brass composed of about 70 per cent copper and 30 per cent zinc was polished in a bath consisting of 5 milliliters of saturated aqueous sodium nitrate solution, 125 milliliters of ethyl alcohol and 0.1 milliliter of 1.0 normal nitric acid at a current density of 0.2 ampere per square centimeter in about 45 seconds. The anode was chilled with a freezing mixture during the polishing. The solution also polished without the addition of the nitric acid but it did not give a polish of as high luster nor did it polish as rapidly as the acidified solution.

The solution was also used in substantially the same manner to polish samples of phosphor bronze.

When polishing a binary or multi-component alloy such as brass or bearing metal, it is possi-

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ble by slow adjustment of the pH toward the ideal polishing value to find a point at which one phase is etched and the other polished. This was done with several brasses, bronzes and bearing metals.

#### Example IX

A sample of aluminum was polished in a solution consisting of 15 milliliters of saturated sodium nitrate, 75 milliliters of methyl alcohol and 0.1 milliliter of 1.0 normal nitric acid at a current density of 0.5 ampere per square centimeter.

It was found, also, that the following solution polished aluminum quite satisfactorily: 75 milliliters of ethyl Cellosolve, 15 milliliters of saturated aqueous potassium nitrate solution and 5 milliliters of water, which solution was made acid to indicator paper using nitric acid. The samples were polished at temperatures below that of the solution. It was found that 1.0 ampere per square centimeter as a current density was necessary to produce a satisfactory polish in a reasonably short time when the anode was not cooled to a temperature substantially lower than that of the bath.

The aluminum was also polished with the following solution: 75 milliliters of acetone, 15 milliliters of saturated aqueous sodium nitrate solution, 10 milliliters of water and a few drops of 1.0 normal nitric acid to acidify the solution.

The above examples have been given to illustrate the steps of the method and the general proportions of constituents used to make up the baths. In a similar manner, as mentioned above, and in like proportions, the alkalimetal salts of the mineral acids such as hydrochloric, hydrobromic, hydroiodic, hydrofluoric, phosphoric, chromic and sulphuric can be used as the electrolytes in baths for polishing purposes.

In general, in the polishing of any of the metals, the best conditions for obtaining the most lustrous polish seem to prevail when the solutions are adjusted to pH values such that uniform gelatinous layers of precipitate are observed on the surfaces being electrolyzed.

From these data and descriptions illustrating my invention, its features will be apparent. The method of polishing is generally applicable to all metals and consisting in employing a high enough current density to induce polishing, maintaining the sample being polished at a low temperature, preferably substantially below that of the polishing solution and adjusting the pH of the bath to a value which I have denominated the "polishing pH." This term is descriptive and defines the pH at which polishing occurs which, in general, is close to the neutral in the range of 6 to 8 and could also be described as that value of pH at which a gelatinous precipitate of metal oxide or hydroxide forms substantially uniformly over the surface being polished. The composition of the bath, as will be noted from the data given above, is not specific for the metal being polished as has been true of prior art electrolytic polishing baths. A general characteristic of electrolytic solutions of my invention is that they contain a relatively highly soluble salt, preferably a neutral salt, that is, a salt of a strong base and a strong acid, in order to provide for adjustment of the pH to the optimum polishing value on either the acid or the alkaline side. However, if the salt itself is inherently a buffer, either acid or alkaline, it can be used as the electrolyte in a polishing solution for a metal requiring a polishing pH of substantially the value to which such salt buffers itself. This class of materials is well exemplified by the

borates, some phosphates, acetates and citrates and other organic and inorganic salts as described in greater detail in my copending application Serial Number 600,631, filed of even date herewith, (now Patent Number 2,506,582). A second ingredient of the solutions is a completely water-miscible organic or non-ionizing liquid or solvent which apparently functions to reduce the ion velocity in the solution to aid in the establishment of concentration polarization at the anode. The final ingredient of the solutions is merely acid or base to adjust the pH to the polishing value.

The polished surfaces appear to develop a high degree of resistance to corrosion for I have found that polished spots on samples remain bright when left exposed to the atmosphere, whereas adjacent polished areas corrode rapidly.

All of the metals polished according to the examples given above were finished to a very high luster and the surfaces showed no signs of scratches or defects when reproduced and examined under the electron microscope at 50,000X.

Since certain changes in carrying out the electrolytic polishing method can be made in the individual steps thereof and wide modifications in the composition of the electrolytic baths which embody the invention can be made without departing from the scope of the invention, it is intended that all matter contained in the above discussion, description and examples shall be interpreted as illustrative and not in a limiting sense.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

Having described my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of electrolytically polishing metals of the group consisting of ferrous metals, nickel, brass and aluminum comprising making a specimen of the metal to be polished an anode in an electrolytic cell in which the electrolyte consists essentially of a mixture of a concentrated aqueous solution of an alkali metal salt of an acid selected from the group consisting of nitric, sulfuric, chromic, hydrochloric, hydrobromic, hydroiodic and hydrofluoric acids and a completely water miscible alcohol, adjusting the pH of the mixture to between about 6 and 8, chilling the anode to a temperature below that of the electrolyte, and passing an electric current through said cell.

2. The method of electrolytically polishing metals of the group consisting of ferrous metals, nickel, brass and aluminum comprising making a specimen of the metal to be polished an anode in an electrolytic cell in which the electrolyte consists essentially of a mixture of a concentrated aqueous solution of an alkali metal salt of an acid selected from the group consisting of nitric, sulfuric, chromic, hydrochloric, hydrobromic, hydroiodic and hydrofluoric acids and a completely water miscible liquid selected from the group consisting of methyl alcohol, ethyl alcohol, glycerine, ethylene glycol, acetone and isopropyl alcohol, adjusting the pH of the mixture to between about 6 and 8, chilling the anode to a temperature at least 10° C. below that of the electrolyte, and passing an electric current through said cell.

3. The method of electrolytically polishing stainless steel comprising, making a specimen of said metal the anode in an electrolytic cell in which the electrolyte consists essentially of a mixture of a concentrated aqueous solution of an alkali metal salt of nitric acid and ethyl alcohol, adjusting the pH of the mixture to between about 6 and 8, chilling the anode to a temperature at least 10° C. below that of the electrolyte, and passing an electric current through said cell.

4. The method of electrolytically polishing medium-carbon steel comprising making a specimen of said metal the anode in an electrolytic cell in which the electrolyte consists essentially of a mixture of a concentrated aqueous solution of an alkali metal salt of nitric acid and a mixture of methyl alcohol, ethyl alcohol and acetone, adjusting the pH of the mixture to between about 6 and 8, chilling the anode to a temperature at least 10° C. below that of the electrolyte, and passing an electric current through said cell.

5. The method of electrolytically polishing stainless steel comprising making a specimen of said metal the anode in an electrolytic cell in which the electrolyte consists essentially of a mixture of a concentrated aqueous solution of an alkali metal salt of nitric acid and glycerine, adjusting the pH of the mixture to between about 6 and 8, chilling the anode to a temperature at least 10° C. below that of the electrolyte, and passing an electric current through said cell.

6. The method of electrolytically polishing aluminum comprising making a specimen of said metal the anode in an electrolytic cell in which the electrolyte consists essentially of a mixture of a concentrated aqueous solution of an alkali metal salt of nitric acid and methyl alcohol, adjusting the pH of the mixture to between about 6 and 8, chilling the anode to a temperature at least 10° C. below that of the electrolyte, and passing an electric current through said cell.

7. The method of electrolytically polishing brass comprising making a specimen of said metal the anode in an electrolytic cell in which the electrolyte consists essentially of a mixture of a concentrated aqueous solution of an alkali metal salt of nitric acid and ethyl alcohol, adjusting the pH of the mixture to between about 6 and 8, chilling the anode to a temperature at least 10° C. below that of the electrolyte, and passing an electric current through said cell.

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