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METHOD OF REGENERATING ELECTROLYTIC POLISHING SOLUTIONS

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This invention relates to the regeneration of electrolytic polishing solutions, and more particularly to a method of regenerating an electrolytic polishing solution of the type disclosed in the application for U. S. patent of Willard G. Axtell, Serial No. 50,068, filed September 20, 1948, entitled "Method of and Apparatus and Bath for Electrolytic Polishing."

In the electrolytic polishing of metals, an article whose surface is to be polished is made the anode in an electrolytic cell, and metal is removed from the surface, rather than being deposited thereon, as in electroplating. In the application of Willard G. Axtell, Serial No. 50,068, supra, an electrolytic polishing solution is disclosed which is particularly adapted for use in polishing articles made of brass, an alloy of copper and zinc, but which is also adapted for use in polishing articles made of a number of other metals, such as other copper alloys, particularly beryllium copper, nickel silver and German silver (copper, nickel and zinc), Monel metal (nickel and copper), bronze (copper, tin and zinc), and 24 SO aluminum (about 4.4% copper), as well as stainless steel and certain alloys used for hardness or strength at high temperatures. The latter include cobalt-chromium tungsten alloys of the "Stellite" type, nickel-molybdenum-iron alloys of the "Hastelloy A" and "Hastelloy B" types, and the nickel-molybdenum-chromium-iron alloys of the "Hastelloy C" and "Vitallium" types, the former also including tungsten and the latter also including a relatively large percentage of cobalt.

Broadly, such polishing solution may comprise an aqueous solution of phosphoric acid containing at least two polyhydric alcohols, and preferably also an hydroxy monocarboxylic acid. The preferred polyhydric alcohols are ethylene glycol (1,2-ethanediol), and glycerol (1,2,3-propanetriol), although other polyhydric alcohols, such as propylene glycol or hexanehexol, may be used. Lactic acid (2-hydroxy propanoic acid) is the preferred hydroxy acid, although glycolic (hydroxyethanoic) or hydroxybutyric acid may be used. The proportions of phosphoric acid, which may be used in the form of 85% orthophosphoric acid, may vary between 35% and 70% on a dry basis, the proportions of the polyhydric alcohol or alcohols may vary between 8% and 64%, and the proportions of the lactic acid or substitute may vary between 1% and 12%. Water, including water in the phosphoric acid, may vary between 5% and 30%, while addition agents may vary between 0 and 10%. Certain addition

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agents, such as monosodium glutamate, mannitol, amino acids such as glycine and glutamic acid, and amines such as ethylene diamine and monoethanol and triethanol amines, may be added in the minor proportions indicated to increase the brightness of the surface produced, and/or increase the throwing power or ability to polish around curved surface portions or remote surfaces of the article.

Two preferred solutions or baths for the electrolytic polishing of brass, the difference between the two residing primarily in the addition agent, may have the following approximate proportions, by volume:

Constituent	Proportion, percent
Orthophosphoric acid 85%	41.5
Glycerol	24.9
Ethylene glycol	16.6
Lactic acid	8.3
Water	8.7
	100.0

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

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

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

although the specific gravity may be varied between 1.386 and 1.47.

As also disclosed in the above application of Willard G. Axtell, Serial No. 50,068, the cells which contain the solution or electrolytic bath are preferably so constructed that the articles being polished cannot accidentally come in contact with the cathode, and also so that small particles of metal deposited at the cathode cannot, by breaking away and adhering to the surfaces being polished, result in a stain or unpolished surface portion. For this purpose, a formaminous or ceramic jar may be placed within a metal tank, the latter being made the cathode, and the jar being preferably of such a size that

a small space, such as approximately one inch wide, is provided between the jar and the tank.

During electropolishing of brass articles in accordance with the above, it has been found that, as the copper and zinc of the brass are removed, the copper tends to be deposited at the cathode, but the zinc, and also the remaining copper, stay in the solution, either in ionized form, or as complex ions or compounds of copper and zinc with phosphoric acid, ethylene glycol and/or glycerol. The effective solution life, i. e. the time at which the solution is exhausted, as it were, and then must either be replaced or regenerated to produce satisfactory results for commercial purposes, is apparently limited by the concentration of copper and zinc ions in the solution. The effective solution life was found, in a number of operations, to be in the neighborhood of 300 ampere hours per liter. When the solution was utilized in an unseparated cell, i. e. in which the ceramic jar was not utilized and the copper was completely free to deposit out at the cathode, the exhausted solution was found to have a concentration of copper of approximately 0.5 gram per liter and of zinc of 33.5 grams per liter. However, when the ceramic jar was used, less copper appeared to precipitate at the cathode and the exhausted solution had a concentration of about 67.6 grams per liter of copper and 28.4 grams per liter of zinc. However, after the solution had previously been regenerated in accordance with the present invention, the concentration of the exhausted solution was about 55 grams per liter of copper and 74 grams per liter of zinc. The actual concentrations of copper and zinc may, of course, vary somewhat in accordance with the articles being polished, differences in operating conditions, and also differences in the constituents used or percentages thereof.

In general, by the method of regeneration of the present invention, the same solution can be used over and over again, with periodic regeneration, the only addition necessary being that to make up for loss of water by electrolysis, drag out loss by solution clinging to the articles being polished upon removal from the bath, or slight losses in removing the precipitate formed during regeneration, as hereinafter described. Regeneration of the solution need not wait until the actual end of the effective solution life, but may be done at predetermined intervals, so that little decrease in brightness is obtained during polishing.

In accordance with the present invention, an exhausted or partially exhausted electrolytic bath or solution of the above character is regenerated by adding thereto a reagent which is soluble therein and contains the following radical:

$$\begin{matrix} COO- \\ | \\ COO- \end{matrix}$$

The reagent caused copper and zinc in the solution to precipitate out as copper and zinc oxalates, and the preferred reagent is oxalic (ethanedioic) acid. The amount of oxalic acid added is preferably slightly less than the molar quantity required to precipitate all of the copper and zinc in solution, in order to minimize the possibility of any free oxalic acid being left in solution. The action of oxalic acid in this respect is quite surprising, since no other acid tested—and those tested included numerous dicarboxylic acids, such as malonic (propanedioic) acid, succinic (butanedioic) acid, fumaric (trans-butenedioic) acid, maleic (cis-butenedioic) acid, glutaric (pentanedioic) acid, tartronic (2-hydroxy propanedioic) acid and malic (2-hydroxy butanedioic) acid, as well as other acids, such as formic, acetic, citric and tartaric acids—was effective to precipitate either copper or zinc.

For regeneration, oxalic acid in a pure form may be used if desired, but is normally unnecessary since regeneration has been successfully accomplished on a commercial scale with commercial hydrated oxalic acid, preferably dissolved in hot water to form a concentrated aqueous solution. The oxalic acid solution may be poured into the solution to be regenerated, or the solution may be poured into the oxalic acid solution. In either case, the precipitation of the copper and zinc oxalates takes place relatively quickly. Thus, in most instances the precipitates will be in fairly finely divided form, so that it is desirable to permit the solution to stand for a period of time, such as from one to two or three days, so that the precipitate will settle to the bottom. The supernatant liquid may be poured off, and the residue separated from the precpitate by dilution and decantation, or, if desired, by centrifuging. However, the precipitate forms a relatively heavy, compact mass when finally settled, so that the loss of solution is relatively small if the supernatant liquid is poured off carefully. The zinc and copper oxalates so formed may, if desired, be discarded, or used for any other desired purpose.

Instead of oxalic acid itself, certain derivatives of oxalic acid may be used, such as calcium or barium oxalate. Also, glycol oxalate or glyceryl oxalate may be utilized, as well as methyl oxalate or ethyl oxalate. Butyl oxalate and oxamide were found to be too nearly insoluble in the solution and thus of much less practical value.

The zinc and copper oxalates, while formed rapidly when oxalic acid is mixed with an exhausted or partially exhausted solution, are usually relatively fine, as indicated previously. A slight increase in the size of the particles, and therefore a lesser tendency for the particles to stay in suspension, may be obtained by varying the manner of mixing, or by using a reagent which is less soluble in the solution, such as ethyl oxalate, and therefore dissolves more slowly therein, to retard the reaction rate. Thus, a heated saturated oxalic acid solution poured carefully on top of the exhausted solution, tended to diffuse slowly through the solution, instead of mixing with it immediately, and increased the amount of clear solution. When ethyl oxalate was used, it formed a layer above the solution which slowly disappeared. The ethyl oxalate was believed to hydrolyze slowly, with the slow liberation of oxalic acid, thereby providing a slower reaction rate and larger particles. In any event, a greater amount of supernatant liquid was produced. While ethyl oxalate, on hydrolysis, also formed ethyl alcohol, the same was not found to be harmful, and also tended to boil off on heating. Furthermore, it may be pointed out that the solubility of ethyl oxalate was found to be relatively low, compared with a concentrated oxalic acid solution, for instance. Thus, when the reagent is stated to be soluble in the solution to be regenerated, sufficient solubility for regeneration purposes is all that is required.

In further accordance with this invention, oxalic acid may be mixed with one or more of the non-aqueous constituents of the solution, for example, the resultant of mixing oxalic acid and

glycerol, or oxalic acid and ethylene glycol, or oxalic acid, glycerol, ethylene glycol and phosphoric acid, may be added to the solution to be regenerated. In this manner, at least a portion of the makeup of the solution constituents can be added, and at the same time a tendency to produce larger precipitating particles provided. In such mixtures, it appears that the oxalic acid combines with the other constituents to form larger molecules, which must decompose to produce free oxalic acid before a precipitate can be formed. This will retard the reaction rate, and thereby produce larger precipitating particles, which are a bit easier to separate from the remaining solution, and also usually require less time to settle out.

The regenerating reagents of this invention are, of course, those described above, e. g., a reagent having the radical

$$\begin{matrix} COO- \\ | \\ COO- \end{matrix}$$

and more specifically oxalic acid, or a derivative of oxalic acid, such as calcium oxalate, barium oxalate, methyl oxalate, ethyl oxalate, glycol oxalate or glyceryl oxalate, or the resultant of mixing oxalic acid with one or more of the non-aqueous constituents of the solution. In the latter instance, it will be understood that such a non-aqueous constituent is not a constituent already in the solution, but is an additional amount of such constituent or constituents.

The method of regeneration and the reagent of this invention appears to produce the best results with solutions which have been used in polishing certain metals, or alloys containing the same. As indicated previously, copper and zinc are readily precipitated, while tests indicated that cobalt and nickel are also. Ferrous iron, but not ferric iron, also readily formed a precipitate upon the addition of oxalic acid to the solution. Other ions tested, which did not produce as satisfactory precipitation results, included stanic, stannous, chromic, chromate (chromic acid), molybdate (molybdic acid), tungstate (sodium tungstate), aluminum, and beryllium. It will, of course, be recognized that if an exhausted solution contains a metal or ion which is readily precipitated and one which is not, the useful life of the solution can be extended by precipitating only the former. It is primarily a matter of cost, whether an exhausted solution should be replaced or regenerated, but in general, the amount of regenerating reagent is relatively small, compared with the amount of solution involved, so that regeneration is normally highly economical.

It is to be noted that a polishing solution of the preferred proportions has been used continuously for more than six months, in polishing several thousand brass articles a day, with periodic regeneration in accordance with this invention, yet there has been no indication of any end to the ultimate life of the solution, and the total loss of solution, from all factors, was less than 1% for each regeneration. In such commercial regeneration, a saturated oxalic acid solution, made by dissolving in hot water hydrated oxalic acid crystals, $C_2O_4H_2 \cdot 2H_2O$, was added to the exhausted or nearly exhausted solution until the latter became a pale blue-green in color. If the solution turned white, it was taken as an indication that complete precipitation had occurred, and that there was probably an excess of oxalic acid, which of course was undesirable. Therefore, additional spent solution was added to neutralize the excess oxalic acid, or until the pale blue-green color returned.

In further accordance with this invention, when copper or iron are present in the metal or alloy being polished, the solution may be regenerated, at least partially, by adding thereto metallic copper or iron, respectively, preferably in finely divided form. It is also possible to cause copper to precipitate by adding metallic iron, preferably in finely divided form, to the solution while excluding air, but this will in most instances be undesirable from an economic standpoint, since when the metal being polished includes copper, finely divided copper normally deposits out at the cathode, thus providing an excellent source of the same. When metallic copper or iron is added to the solution containing the same, the amount of precipitate obtained, in terms of metallic copper or iron, is in excess of the metallic copper or iron added. It is believed that, in the case of iron, the ferric ion or compound is reduced to ferrous, and the precipitate, when no oxalic acid or oxalate is added, is apparently primarily ferrous phosphate. Of course, oxalic acid or an oxalate may also be added to increase the amount of precipitate. In the case of copper, the finely divided metallic copper apparently reduces the cupric ion or compound to cuprous, and apparently causes the formation of a cuprous phosphate which tends to precipitate. When regenerating a solution used in polishing brass, since both copper and zinc are in solution, the addition of finely divided metallic copper to the solution tends to cause precipitation of a portion of the copper by reduction to cuprous copper, so that oxalic acid, for instance, which apparently is slightly preferential toward the precipitation of copper rather than zinc, will tend to precipitate additional zinc when added to the solution. In any event, the amount of oxalic acid or oxalate used may be reduced by using metallic copper or iron, as the case may be.

It will be evident, from the foregoing, that the method of regeneration and the regenerating agent of this invention are highly useful and involve totally unexpected results. It will also be evident that the invention is subject to numerous variations, without departing from the spirit and scope thereof.

What is claimed is:

1. A method of regenerating an electrolytic polishing solution containing initially approximately 41.5% of 85% orthophosphoric acid, 24.9% of glycerol, 16.6% of ethylene glycol, 8.3% of lactic acid, and 8.7% of water, each by volume, such solution having been utilized in the electrolytic polishing of brass, which method comprises adding oxalic acid to said solution in an amount sufficient to precipitate at least a portion of the dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

2. A method of regenerating an electrolytic polishing solution utilized in the polishing of brass and initially containing phosphoric acid, ethylene glycol, glycerol, lactic acid, and water, which comprises adding to said solution at least one of the group consisting of the resultant of mixing phosphoric acid and oxalic acid, the resultant of mixing ethylene glycol and oxalic acid, the resultant of mixing glycerol and oxalic acid, the resultant of mixing ethylene glycol, glycerol and oxalic acid, and the resultant of mixing ethylene glycol, glycerol, phosphoric acid and oxalic acid, the same being added in an amount

sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

3. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid, at least two polyhydric alcohols, lactic acid and water, which solution has been used in the electrolytic polishing of brass, which method comprises adding to said solution relatively finely divided copper metal, and also adding to said solution a reagent comprising a substantially saturated aqeuous solution of oxalic acid in an amount sufficient to precipitate at least a portion of the dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

4. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and initially containing water, phosphoric acid and at least two polyhydric alcohols, which comprises adding oxalic acid to said solution in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

5. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and initially containing water, phosphoric acid and at least two polyhydric alcohols, which comprises adding to said solution a reagent selected from the group which consists of oxalic acid, calcium oxalate, barium oxalate, methyl oxalate, ethyl oxalate, glycol oxalate and glyceryl oxalate in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

6. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and initially containing water, phosphoric acid, at least one water soluble polyhydric alcohol, and a hydroxycarboxylic acid, which comprises adding oxalic acid to said solution in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

7. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and initially containing phosphoric acid, water, at least one water soluble polyhydric alcohol, and a hydroxycarboxylic acid, which comprises adding to said solution a reagent which is the resultant of mixing oxalic acid with at least one of the said non-aqueous constituents of said solution in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

8. A method of regenerating an electrolytic polishing solution initially containing water, phosphoric acid, at least one polyhydric alcohol, and a hydroxycarboxylic acid, which solution has been used in electrolytic polishing and, as a result, has dissolved therein copper and iron, which comprises adding to said solution relatively finely divided iron and also oxalic acid in an amount sufficient to precipitate at least a portion of the dissolved copper and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

9. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and containing essentially phosphoric acid, water, at least one polyhydric alcohol and a hydroxycarboxylic acid, which comprises adding methyl oxalate to said solution in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

10. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and containing essentially phosphoric acid, water, at least one poylhydric alcohol and a hydroxycarboxylic acid, which comprises adding ethyl oxalate to said solution in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

11. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and containing essentially phosphoric acid, water, at least one polyhydric alcohol and a hydroxycarboxylic acid, which comprises adding glycol oxalate to said solution in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

12. A method of regenerating an electrolytic polishing solution utilized in polishing brass, and containing essentially phosphoric acid, water, at least one polyhydric alcohol and a hydroxycarboxylic acid, which comprises adding glyceryl oxalate to said solution in an amount sufficient to precipitate at least a portion of dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

13. A method of regenerating an electrolytic polishing solution which has been utilized in polishing brass, said solution initially comprising from 35% to 70% orthophosphoric acid, from 8% to 64% of at least one water-soluble polyhydric alcohol, from 1% to 12% of a mono-hydroxy mono-carboxylic acid, from 5% to 30% of water, and from 0 to 10% of an addition agent adapted to increase the brightness of an article polished in said solution, which comprises adding oxalic acid to said solution in an amount sufficient to precipitate at least a portion of the dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

14. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid, water, at least one polyhydric alcohol, and a hydroxycarboxylic acid, which has been utilized in electrolytic polishing and, as a result, has dissolved therein at least one metal of the group consisting of copper, zinc, nickel, and cobalt, which method comprises adding to said solution the resultant of mixing oxalic acid with at least one of the said non-aqueous constituents of said solution in an amount sufficient to precipitate at least a portion of the dissolved copper, zinc, nickel and cobalt and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

15. A method of regenerating an electrolytic polishing solution initially comprising from 35% to 70% of orthophosphoric acid, from 8% to 64% of at least one water-soluble polyhydric alcohol, from 1% to 12% of a mono-hydroxy mono-carboxylic acid, from 5% to 30% of water, and from 0 to 10% of an addition agent adapted to increase the brightness of an article polished in said solu-

tion, said solution having been utilized in electrolytic polishing, and, as a result, having dissolved therein at least one metal selected from the group consisting of copper, zinc, nickel, and cobalt, which method comprises adding to said solution a reagent selected from the group which consists of oxalic acid, calcium oxalate, barium oxalate, methyl oxalate, ethyl oxalate, glycol oxlate and glyceryl oxlate, said reagent being added in an amount sufficient to precipitate at least a portion of the dissolved copper, zinc, nickel and cobalt and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

16. A method of regenerating an electrolytic polishing solution containing phosphoric acid and water, which solution has been utilized in electrolytic polishing and, as a result, has dissolved therein at least one metal of the group consisting of copper, zinc, nickel and cobalt, such method comprising adding oxalic acid to said solution in an amount sufficient to precipitate at least a portion of the dissolved copper, zinc, nickel and cobalt and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

17. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid, ethylene glycol, glycerol, lactic acid, and water, which solution has been utilized in electrolytic polishing and, as a result, has dissolved therein at least one metal of the group consisting of copper, zinc, nickel and cobalt, which comprises adding to said solution the resultant of mixing oxalic acid with one of the said non-aqueous constituents of said solution in an amount sufficient to precipitate at least a portion of the dissolved copper, zinc, nickel and cobalt and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

18. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid and water, which solution has been utilized in electrolytic polishing and, as a result, has dissolved therein at least one metal of the group consisting of copper, zinc, nickel and cobalt, such method comprising adding to said solution a reagent selected from the group which consists of oxalic acid, calcium oxalate, barium oxalate, methyl oxalate, ethyl oxalate, glycol oxalate, and glyceryl oxalate, said reagent being added in an amount sufficient to precipitate at least a portion of the dissolved copper, zinc, nickel and cobalt, and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

19. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid, water, ethylene glycol, glycerol, and a hydroxy mono-carboxylic acid, said solution having been utilized in electrolytic polishing and, as a result, having dissolved therein at least one metal of the group consisting of copper, zinc, nickel and cobalt, such method comprising adding to said solution at least one of the group consisting of the resultant of mixing phosphoric acid and oxalic acid, the resultant of mixing ethylene glycol and oxalic acid, the resultant of mixing glycerol and oxalic acid, the resultant of mixing ethylene glycol and oxalic acid, and the resultant of mixing ethylene glycol, glycerol, phosphoric acid and oxalic acid, the same being added in an amount sufficient to precipitate at least a portion of the dissolved copper, zinc, nickel and cobalt and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

20. A method of regenerating an electrolytic polishing solution which initially includes approximately 41.5% of 85% orthophosphoric acid, 24.9% of glycerol, 16.6% of ethylene glycol, 8.3% of lactic acid, and 8.7% of water, each by volume, such solution having been utilized in electrolytic polishing and, as a result, has dissolved therein at least one metal of the group consisting of copper, zinc, nickel and cobalt, which comprises adding to said solution at least one reagent selected from the group consisting of the resultant of mixing phosphoric acid and oxalic acid, the resultant of mixing ethylene glycol and oxalic acid, the resultant of mixing glycerol and oxalic acid, the resultant of mixing ethylene glycol, glycerol and oxalic acid, and the resultant of mixing ethylene glycol, glycerol, phosphoric acid and oxalic acid, said reagent being added in an amount sufficient to precipitate at least a portion of the dissolved copper, zinc, nickel and cobalt and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

21. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid and water, which solution has been used in the electrolytic polishing of brass, which method comprises adding to said solution relatively finely divided copper metal, and also adding to said solution a reagent comprising a substantially saturated aqueous solution of oxalic acid in an amount sufficient to precipitate at least a portion of the dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

22. A method of regenerating an electrolyic polishing solution containing phosphoric acid and water, which solution has been utilized in electrolytically polishing brass, such method comprising adding oxalic acid to said solution in an amount sufficient to precipitate at least a portion of the dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

23. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid and water, which solution has been utilized in electrolytically polishing brass, such method comprising adding to said solution a reagent selected from the group which consists of oxalic acid, calcium oxalate, barium oxalate, methyl oxalate, ethyl oxalate, glycol oxalate, and glyceryl oxalate, said reagent being added in an amount sufficient to precipitate at least a portion of the dissolved copper and zinc and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

24. A method of regenerating an electrolytic polishing solution initially containing phosphoric acid, ethylene glycol, glycerol, lactic acid and water, which solution has been utilized in electrolytic polishing and, as a result, having dissolved therein at least one metal of the group consisting of copper, zinc, nickel and cobalt, which comprises adding to said solution a reagent selected from the group which consists of oxalic acid, calcium oxalate, barium oxalate, methyl oxalate, ethyl oxalate, glycol oxalate and glyceryl oxalate, said reagent being added in an amount sufficient to precipitate at least a portion

of the dissolved copper, zinc, nickel and cobalt and less than the amount which will result in free oxalic acid being present in the solution when utilized again.

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