

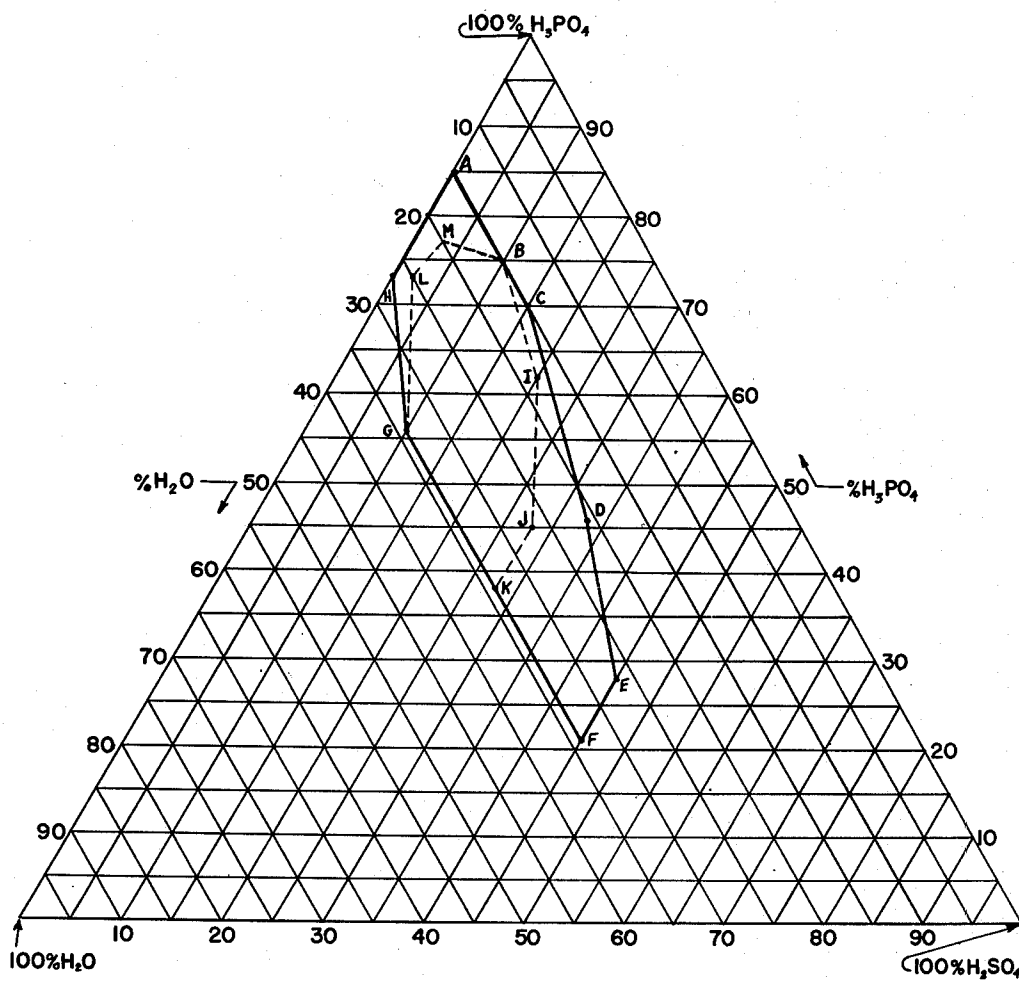
May 4, 1948.

C. L. FAUST ET AL  
CONTINUOUS METHOD FOR ELECTROPOLISHING  
NICKEL AND NICKEL-CONTAINING ALLOYS  
Filed July 23, 1943

2,440,715

4 Sheets-Sheet 1

Fig. 1.



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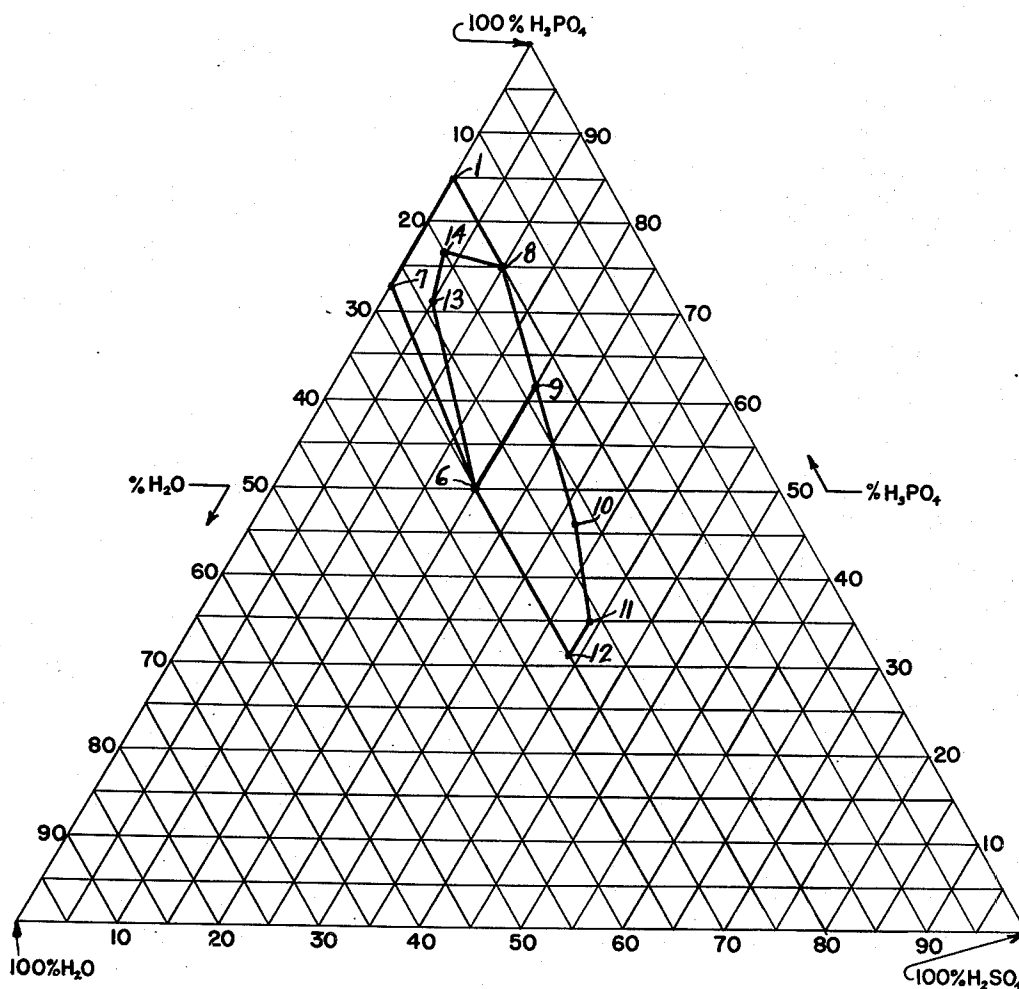
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4 Sheets-Sheet 2

Fig. 2.



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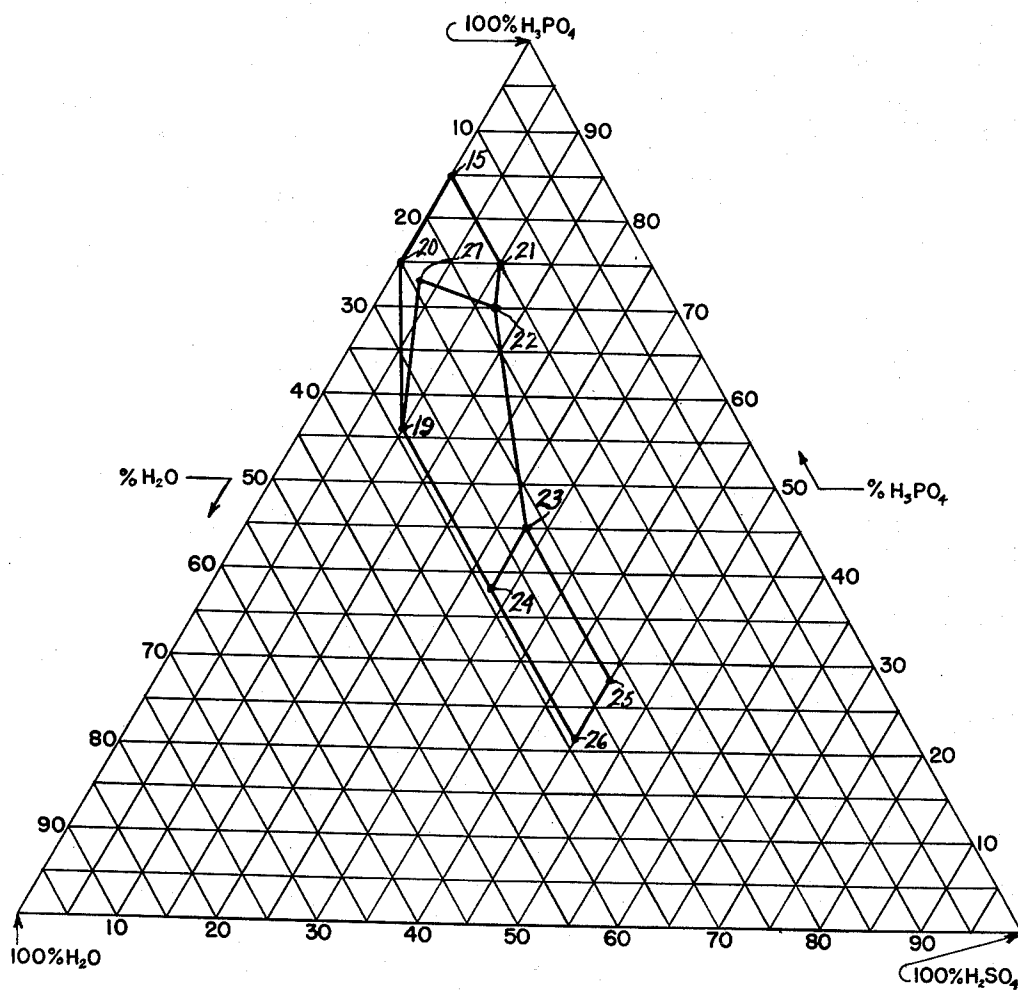
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4 Sheets-Sheet 3

Fig. 3.



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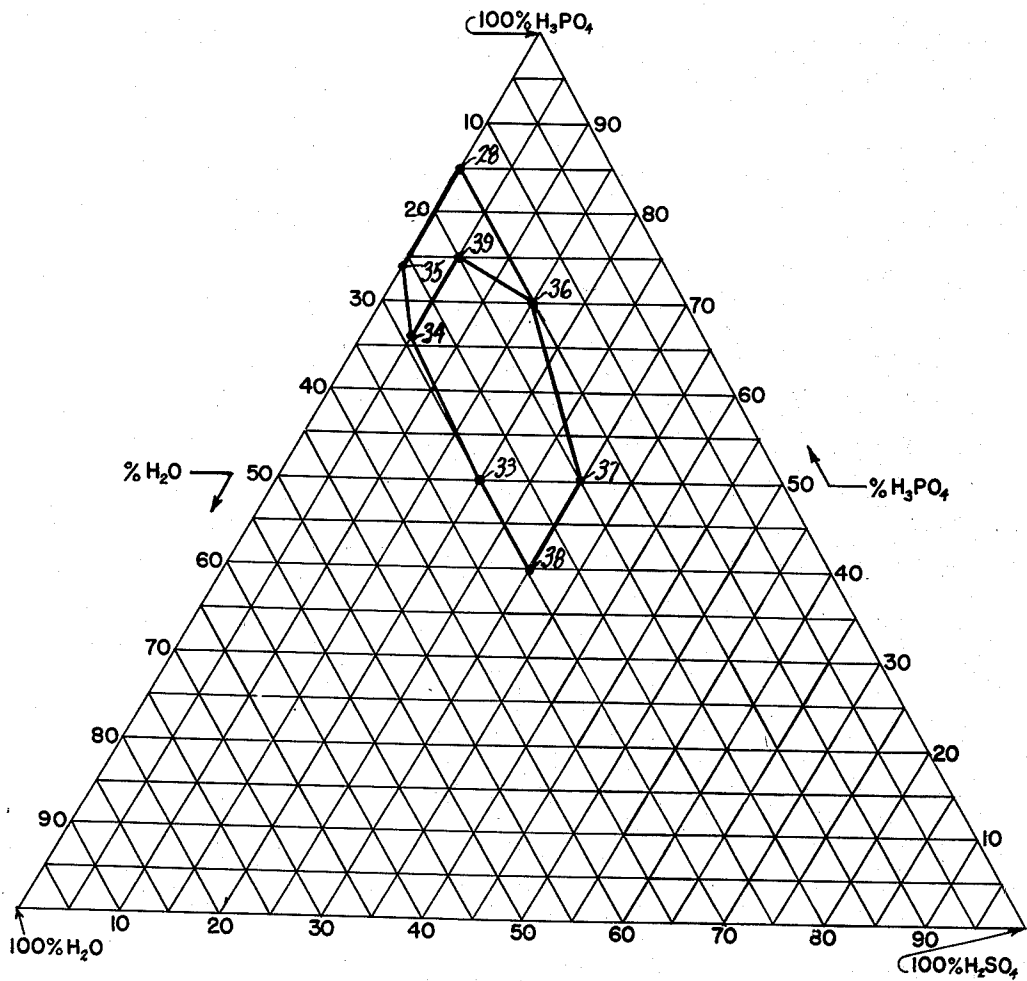
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2,440,715

4 Sheets-Sheet 4

Fig. 4.



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## UNITED STATES PATENT OFFICE

2,440,715

CONTINUOUS METHOD FOR ELECTRO-  
POLISHING NICKEL AND NICKEL-  
CONTAINING ALLOYS

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Application July 23, 1943, Serial No. 495,842

6 Claims. (Cl. 204-140)

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This invention relates to an improved electrolytic bath for anodically polishing nickel and nickel-containing alloys. More particularly, the invention pertains to a method of continuously electropolishing nickel by means of an electrolyte from which excess nickel dissolved during the electropolishing step is continuously plated out on the cathode as metallic nickel.

Nickel and its alloys that are rich in nickel may be anodically polished in an electrolyte containing, as an essential active ingredient, sulfuric acid or a mixture of sulfuric and phosphoric acids. The concentration of the sulfuric acid, when used alone, as well as the combined concentration of the mixed sulfuric and phosphoric acids should be at least 50% by weight of the solution and preferably not more than 95% by weight of the solution, the balance being largely water. For practical purposes, about 90% is the upper limit for the total acid concentration. While it is possible to produce good polishes with aqueous mixtures of sulfuric and phosphoric acids containing as much as 50% water, it has been found preferable to keep the water content of the bath relatively low, since, in general, baths containing lower proportions of water may be operated at lower current densities and, therefore, at a lower cost, to give satisfactory polishes. The relative proportions of the essential acids may vary between rather wide limits, as, for instance, from about 3 to about 76% of sulfuric acid and from 0 to about 78% of phosphoric acid, the total acid concentration being more than 50%.

Unless otherwise specified, all percentages referred to herein will be understood to represent percentages by weight rather than by volume. Also, references to acids should be understood to refer to the formula weights as  $H_2SO_4$  and  $H_3PO_4$ . Where phosphoric acid is referred to, orthophosphoric acid is meant, since that is the stable form under the temperature conditions obtaining in the operation. However, phosphoric acid may be added in some other form, such as pyro phosphoric acid or meta-phosphoric acid.

Thus, a mirror-like finish may be produced by

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anodically polishing nickel in aqueous solutions containing 15%  $H_2SO_4$  and 63%  $H_3PO_4$ , using a current density of 125 amperes per square foot and a bath temperature of 115 to 130° F. The time required to produce the polish is determined by the original physical character of the nickel being polished. However, during electropolishing under these conditions, a nickel compound is formed which breaks up at higher temperatures to form nickel sulfate. Consequently, a used bath precipitates nickel sulfate on the hot surfaces of the heating coils and the cathodes. As a result, the tank voltage increases because of the incrustation on the cathodes, and temperature control is impaired by the precipitation of the nickel salt on the coils during the warming up period. Therefore, in order to maintain continuous operation it is necessary to remove dissolved nickel from the bath.

The aforementioned difficulties can be temporarily overcome by reconditioning the bath. Reconditioning consists of heating at high temperature to precipitate nickel sulfate, filtering, adjusting the bath composition, and cleaning the cathodes. The bath can then be operated until reconditioning again becomes necessary. Since such reconditioning is not commercially feasible in the production tank, separate tanks and the attendant auxiliary equipment are needed. Thus, reconditioning adds to the operating cost.

Commercial operation can be greatly improved by having a bath which operates continuously without need for batch reconditioning, without impractical changes in composition, and without increase in operating voltage. In any case, continuous operation requires that nickel be removed from the bath.

If the aforementioned bath, containing 15%  $H_2SO_4$  and 63%  $H_3PO_4$ , is operated at a temperature high enough to precipitate nickel sulfate continuously, for instance, at 180° F., then a current density of more than 250 amperes per square foot must be employed, as otherwise the nickel surface, although given a brilliant finish, will be pitted.

Further developments have shown that additions of tri-valent chromium ions,  $\text{Cr}^{+3}$ , and tri-valent aluminum ions,  $\text{Al}^{+3}$ , to the 15%  $\text{H}_2\text{SO}_4$ -63%  $\text{H}_3\text{PO}_4$  bath, make it possible to electropolish nickel at temperatures sufficiently high to permit continuous precipitation of nickel sulfate. When the required amount of  $\text{Cr}^{+3}$  and  $\text{Al}^{+3}$ , or of  $\text{Al}^{+3}$  alone, is present, a brilliant, pit-free surface is produced if nickel is electropolished at a temperature of approximately 180° F. and at current densities of 125 to 250 amperes per square foot. This process has been described in a co-pending application of one of us, Charles L. Faust, S. N. 440,338, filed April 24, 1942, now Patent No. 2,429,676.

However, while the last mentioned bath is capable of fairly continuous operation, periodic filtration is necessary to remove the continuously precipitated nickel sulfate. Furthermore, the nickel is recoverable only in the form of a salt. The use of high temperatures is also objectionable because it increases the cost of operation.

It is therefore an important object of the present invention to provide an electrolyte and a method for electropolishing nickel and alloys rich in nickel that is capable of continuous operation at low current densities without need for bath reconditioning, without involving any objectionable amount of precipitation of nickel salts, and without impractical changes in composition.

Another object of this invention is to provide an electrolyte and a method for electropolishing nickel capable of being operated continuously without a progressive rise in operating voltages.

A further object of this invention is to provide an electrolyte and a method for electropolishing nickel capable of continuous operation at low temperatures.

Still a further object of this invention is to provide an electrolyte and a method for electropolishing nickel by the use of which excess nickel dissolved from the anode in the electropolishing step is continuously plated out as metallic nickel on the cathode of a degree of purity and in a physical state suitable for recovery and use as nickel.

Other and further objects and features of the present invention will become apparent from the following description and appended claims.

In the accompanying drawings, which show ternary systems of sulfuric acid ( $\text{H}_2\text{SO}_4$ ), orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and water ( $\text{H}_2\text{O}$ ) in percentages by weight:

Figure 1 illustrates areas representing bath compositions which, by the addition of between 0.04 and 2.5% of hydrochloric acid ( $\text{HCl}$ ), are operative at temperatures between 80° and 140° F. for effecting the electropolishing of nickel and nickel alloys with simultaneous plating out of excess dissolved nickel.

Figure 2 illustrates areas representing bath compositions which, by the addition of between 0.3 and 1.0% of hydrochloric acid ( $\text{HCl}$ ), are operative at a temperature of 115° F. for effecting the electropolishing of nickel and nickel alloys with simultaneous plating out of excess dissolved nickel.

Figure 3 is similar to Figure 2 except that it represents bath compositions operative at 90° F.

Figure 4 is similar to Figures 2 and 3, except it represents bath compositions operative at 135° F.

We have found that the addition of hydrochloric acid to straight phosphoric acid and to

mixed sulfuric acid-phosphoric acid baths within the general limits delineated in Figure 1 yields baths in which nickel or nickel-containing alloys can be polished to a bright, mirror-like, pit-free finish at temperatures in the general range of from 80° to 140° F. and at current densities from 50 to 300 amperes per square foot. We have further found that under these conditions the excess of nickel dissolved from the anode can be continuously electrodeposited as metallic nickel on the cathode. Thus, although hydrochloric acid is not essential for the production of a brilliant mirror-like electropolish in a bath containing sulfuric and phosphoric acids, the addition of minor percentages of hydrochloric acid does serve to make possible continuous operation without appreciable precipitation of nickel salts, change in viscosity, or increase in tank voltage.

Whereas the copending application, S. N. 440,338 of Charles L. Faust, relating to the electropolishing of nickel shows that electropolishing cannot be carried out so effectively in phosphoric acid baths containing no sulfuric acid, the present invention now makes this entirely practicable. Heretofore, the phosphoric acid baths, containing no sulfuric acid, electropolished nickel for a short period of time when they were fresh. However, the baths rapidly became very viscous, so that tank voltages and drag-out were high, polishing results were poor and the useful period was very short. The high viscosity apparently resulted from the fact that nickel is very soluble in straight phosphoric acid.

By virtue of the present invention, the phosphoric acid can be maintained in practically its original electropolishing condition because the nickel deposits out on the cathode during the operation of electropolishing. Thus, there is no build up in nickel concentration to render the bath viscous and of a short useful life. The straight phosphoric acid bath, however, does not have so good "throwing power" as the  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  combination. Therefore, the phosphoric acid bath is included only in the broad range of operable bath compositions.

In the case of baths containing more than about 45% of sulfuric acid, although hydrochloric acid additions according to the teaching of this invention tend to cause deposition of metallic nickel from solution, the solubility of nickel sulfate is so low that no significant, practical improvement results.

The effectiveness of the hydrochloric acid results from the chloride that it introduces into the bath. Consequently, any medium for introducing chloride additions can be used in place of the hydrochloric acid or in conjunction with it. We can, therefore, accomplish our improved results by introducing a soluble metal chloride such as the chloride of sodium, potassium, calcium, magnesium, nickel, aluminum, chromium, and the like.

The manner of introducing the chloride apparently is immaterial, but the simplest and most expedient method is to use hydrochloric acid. If a metal chloride were to be used, the quantity would be selected on the basis of equivalency to the chloride content of  $\text{HCl}$  specified in the operative ranges that are disclosed herein. Since the specified purpose of this invention is to remove metals from the electropolishing bath, it is preferred to use hydrochloric acid, for the metal chlorides introduce a metal into the bath. We have also found that the desired effect of chloride additions can be achieved by introducing small

concentrations of chlorinated organic acids, such as monochloroacetic acid.

The electropolishing bath as freshly made up with an addition of a chloroacetic acid gives no chemical test for a chloride. However, after a short period of use for electropolishing, the bath gives a positive test for chloride. It is, therefore, apparent that the chloroacetic acid effectively introduces chloride into the bath to accomplish the results of this invention.

The equilibrium condition of good operation is maintained simply by replacing water, HCl and drag-out losses. The cathode nickel, plated out during the electropolishing operation, consists of dense metal having a purity in excess of 98% and generally as high as 99.6%. Such a material is particularly well suited for use as anodes in nickel electroplating tanks.

Only minor percentages of chlorides are required to produce the desired effect. There is no practical way to add "chloride ions, per se" to the bath, or to determine what is the necessary chloride ion concentration. We have determined that an adequate chloride ion concentration results when a certain percentage of a chloride is present in the bath. For simplicity in maintenance and in expression of analysis, the chloride content is calculated as HCl. As shown by the data in Table I, satisfactory operation is obtained when the HCl concentration is but slightly in excess of 0.04%. These tests were made by adding HCl to a standard 15% H<sub>2</sub>SO<sub>4</sub>-63%

tained. In running these tests, the HCl was maintained at the proper value by periodic additions of concentrated hydrochloric acid. The amount to be added was determined by chemical analysis for chloride in the bath.

While HCl additions tend to facilitate the plating out of nickel in all H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub> baths, the efficiency of nickel deposition at the cathode and continued operation without precipitation problems depend upon the H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> ratio and the water content. In order for the deposition rate to equal the anodic dissolution rate, a certain minimum concentration of dissolved nickel apparently is required. The amount of nickel in solution depends upon the H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> ratio and the water content, which also determines the solubility limit. If the minimum concentration of nickel for a suitable deposition rate is greater than the solubility limit, precipitation will be unavoidable.

We have found that upon addition of HCl within the disclosed range, certain bath compositions are operable in continuous electropolishing without objectionable precipitation of nickel salts. These bath compositions are illustrated on the triaxial diagrams of the accompanying drawings. On the diagram of Figure 1 are represented two areas, a larger area delineated by the solid straight lines joining the points A, C, D, E, F, G, H and A, and a wholly enclosed smaller area delineated by the dotted straight lines joining the points B, I, J, K, G, L, M and B.

TABLE I

Per cent nickel plated at cathode for various HCl<sup>1</sup>  
Additions to the 15% H<sub>2</sub>SO<sub>4</sub>-63% H<sub>3</sub>PO<sub>4</sub>-22% H<sub>2</sub>O bath for electropolishing nickel

| Per cent Nickel Dissolved from Anode <sup>2</sup> | 0.000% HCl        | 0.001% HCl        | 0.01% HCl         | 0.04% HCl                     | 0.1% HCl | 0.3% HCl | 1.0% HCl | 2.5% HCl |
|---|-------------------|-------------------|-------------------|-------------------------------|----------|----------|----------|----------|
| 2.0   | 2.5               | 2.7               | -----             | 60                            | 92       | 56       | 75       | 66       |
| 3.0   | 7.0               | -----             | 42                | 84                            | 94       | -----    | 86       | -----    |
| 4.0   | ppt. <sup>3</sup> | -----             | 60                | -----                         | 95       | 90       | -----    | -----    |
| 4.5   | -----             | ppt. <sup>3</sup> | 42                | -----                         | 96       | -----    | -----    | 98       |
| 5.0   | -----             | -----             | -----             | 84                            | 97       | -----    | -----    | No ppt.  |
| 6.0   | -----             | -----             | 63                | -----                         | 98       | -----    | 101      | -----    |
| 7.0   | -----             | -----             | -----             | 90                            | -----    | -----    | -----    | -----    |
| 8.0   | -----             | -----             | 71                | -----                         | 100      | -----    | 108      | -----    |
| 9.0   | -----             | -----             | ppt. <sup>3</sup> | 102                           | -----    | -----    | 102      | -----    |
| 12.0  | -----             | -----             | -----             | Very slight ppt. <sup>3</sup> | 95       | -----    | No ppt.  | -----    |
| 34.0  | -----             | -----             | -----             | -----                         | 99       | -----    | -----    | -----    |
|   |                   |                   |                   |                               | No ppt.  |          |          |          |

<sup>1</sup> Values based on amount of nickel dissolved from the anode for the interval of electropolishing shown.

<sup>2</sup> Based on weight of the bath.

<sup>3</sup> Ppt. indicates formation of precipitate of nickel salt.

H<sub>3</sub>PO<sub>4</sub>-22% H<sub>2</sub>O electropolishing bath. Similar data for a 35% H<sub>2</sub>SO<sub>4</sub>-38% H<sub>3</sub>PO<sub>4</sub>-27% H<sub>2</sub>O bath are shown in Table II. The criterion for satisfactory bath operation is the efficient plating of nickel at the cathodes and the absence of an objectionable precipitate of nickel salts.

These data indicate that satisfactory results are obtained when HCl is present in amounts ranging from 0.04% to 2.5%. However, the lower range of from 0.04 to 0.4% is preferred because of the ease of maintenance and the absence of pitting tendencies on the work being electropolished.

Table I shows some fluctuation in per cent nickel plated out in baths containing 0.04% or more HCl. This small variation is considered to be caused by changes in water and HCl concentration. Periods of operation below 100% deposition are offset by periods of more than 100% so that no operational difficulties are encountered when water and HCl contents are suitably main-

TABLE II

Per cent nickel plated at the cathode<sup>1</sup>  
For various HCl additions to the 35% H<sub>2</sub>SO<sub>4</sub>-38% H<sub>3</sub>PO<sub>4</sub>-27% H<sub>2</sub>O bath for electropolishing nickel

| Per Cent Nickel Dissolved from the Anode <sup>2</sup> | 0.01% HCl               | 0.10% HCl | 0.3% HCl             | 0.65% HCl             |
|---|-------------------------|-----------|----------------------|-----------------------|
| 2.0   | 5.-----                 | 20.-----  | 56.-----             | 58.-----              |
| 6.0   | 24.-----                | 92.-----  | 80.-----             | -----                 |
| 9.0   | Heavy ppt. <sup>3</sup> | Some ppt. | 89.-----             | 91.-----              |
| 14.0  | do.-----                | do.-----  | 98.-----             | -----                 |
| 18.0  | do.-----                | do.-----  | 96.-----             | 100. very slight ppt. |
| 22.0  | do.-----                | do.-----  | 97. very slight ppt. | -----                 |

<sup>1</sup> Values based on amount of nickel dissolved from the anode for the interval of electropolishing shown.

<sup>2</sup> Based on weight of the bath.

<sup>3</sup> Ppt. indicates formation of a precipitate of nickel salt.

The larger area defined by the lines AC, CD, DE, EF, FG, GH and HA represents bath compositions as regards percentages of  $\text{H}_3\text{PO}_4$ , or of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ , which, when containing minor additions of HCl, are suitable for electropolishing nickel and nickel alloys at some or all temperatures within the broad temperature range of from 80° to 140° F. Within part or all of this temperature range, baths of a composition falling within the designated area and containing chloride additions within the limits above given, are operative to impart a bright polish to nickel and its alloys, while at the same time most of the dissolved nickel coming out of solution plates out at the cathode to permit continuous operation with only a slight precipitation of nickel salts, if any.

The values for percentages of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  at the points indicated on the boundary for this larger area are as follows:

|        | $\text{H}_3\text{PO}_4$ | $\text{H}_2\text{SO}_4$ | $\text{H}_2\text{O}$ |
|--------|-------------------------|-------------------------|----------------------|
| A..... | 85                      | 0                       | 15                   |
| C..... | 70                      | 15                      | 15                   |
| D..... | 46                      | 33                      | 21                   |
| E..... | 28                      | 45                      | 27                   |
| F..... | 21                      | 45                      | 34                   |
| G..... | 56                      | 10                      | 34                   |
| H..... | 73                      | 0                       | 27                   |

In general, therefore, the broad operative range lies between 21 and 85%  $\text{H}_3\text{PO}_4$ , 0 and 45%  $\text{H}_2\text{SO}_4$ , and 15 and 34%  $\text{H}_2\text{O}$ . The total acid concentration within this broad operative range has a minimum value of 66% and a maximum value of 85%.

It will be understood, of course, that the operative range of bath compositions for satisfactory electropolishing of nickel and its alloys is even broader than that represented by the larger area just defined, but upon continued operation of baths whose compositions lie outside of this larger area on the accompanying ternary diagram, there will be objectionable precipitation of nickel sulfate or else inefficient plating out of nickel, or both. Even within said larger area, some slight precipitation of nickel sulfate may occur for particular bath compositions at certain temperatures between 80° and 140° F., but such amount of precipitation will not, in general, be objectionable.

The wholly enclosed smaller area, lying within the straight dotted lines BI, IJ, JK, KG (full line), GL, LM and MB, represents the preferred ranges of bath compositions within which practically no precipitation of nickel sulfate occurs when the chloride content is within the limits given above and a proper temperature, within the range of from 90° to 125° F., is used for the composition selected. Under the conditions named, nickel and its alloys can be satisfactorily polished anodically, while, at the same time, dissolved nickel is plated out at the cathode at a rate sufficient to maintain the dissolved nickel content below its saturation point and thus prevent any substantial precipitation of nickel salts.

The values for the percentages of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  at the points indicating the boundaries of this smaller area are as follows:

| Point  | $\text{H}_3\text{PO}_4$ | $\text{H}_2\text{SO}_4$ | $\text{H}_2\text{O}$ |
|--------|-------------------------|-------------------------|----------------------|
| B..... | 75                      | 10                      | 15                   |
| I..... | 62                      | 20                      | 18                   |
| J..... | 45                      | 28                      | 27                   |
| K..... | 38                      | 28                      | 34                   |
| G..... | 56                      | 10                      | 34                   |
| L..... | 73                      | 2                       | 25                   |
| M..... | 77                      | 3                       | 20                   |

In this preferred operating area, therefore, the percentages of  $\text{H}_3\text{PO}_4$  lie between the limits of 38% and 77%, of  $\text{H}_2\text{SO}_4$  between the limits of 2% and 28, and of water between 15% and 34%. The combined  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  concentration within this same area lies between a minimum value of 66% and a maximum value of 85%, the same as in the larger composition area.

It will be understood that if plotted on the accompanying ternary diagram of Figure 1, the bath compositions giving little or no precipitation of nickel salts during continued electropolishing will all lie within the larger area ACDEFGHA if a proper temperature is selected between 80° and 140° F., and bath compositions within the smaller area BIJKGLMB will give substantially no precipitation of nickel salts if the proper temperature, within the range of from 90° to 125° F. is selected for the composition used.

The relationship between the compositions within the larger area in Figure 1 (defined by the lines AC, CD, DE, EF, FG, GH and HA) and the compositions within the smaller area in Figure 1 (defined by the straight dotted lines BI, IJ, JK, the full line KG and the straight dotted lines GL, LM and MB) is the following. The compositions within the smaller area are all operative within part or all of the temperature range of from 90° to 125° F. However, other compositions outside the smaller area but inside the larger area may also be operative at a temperature between 90° and 125° F. Note, for instance, that the area defined in Figure 2 by the lines drawn between points 1, 8, 9, 6, 7 and 1 in the order named includes only compositions operative at 115° F. This area in Figure 2 falls partly outside the smaller area in Figure 1. All compositions operative anywhere within the temperature range of from 80° to 140° are included within the large area of Figure 1, including those within the smaller area of Figure 1.

During the continued operation of a bath composition within the broader or preferred areas shown on the diagram of Fig. 1, the dissolved nickel remains at a concentration within the range of about 0.5 to 2.5%, calculated as Ni. Since the  $\text{H}_2\text{SO}_4$ : $\text{H}_3\text{PO}_4$ : $\text{H}_2\text{O}$  values shown in the diagram are based on 100% of the bath consisting only of the three mentioned components, the dissolved nickel and hydrochloric acid, or chloride content, alter all components to the same relative amount and to a degree that has no significant effect on the bath composition and control.

It can be seen that most efficient nickel electro-deposition, which means the absence of any objectionable amount of precipitate formation, can be obtained only in baths containing less than about 45%  $\text{H}_2\text{SO}_4$ . The diagram also shows that the water concentration in the bath must increase as the  $\text{H}_2\text{SO}_4$  content increases, if precipitation is to be avoided. In general,  $\text{H}_3\text{PO}_4$



concentrations between about 21 and 85% are practicable.

parent from the data in Tables V and VI. The uniformity of operating characteristics is evident.

TABLE III

*Operating characteristics of nickel electropolishing bath containing 15% H<sub>2</sub>SO<sub>4</sub>, 63% H<sub>3</sub>PO<sub>4</sub>, 22% H<sub>2</sub>O, 0.04% HCl*

[Bath temperature—115° F.]

| Per Cent Ni Removed from Anode <sup>1</sup> | Anode Current Density, Amps./sq. ft. | Anode Efficiency, Per Cent | Cathode Current Density, Amps./sq. ft. | Cathode Efficiency, Per Cent | Per Cent of Ni on Cathode <sup>1</sup> | Per Cent Ni in Solution | Cell Voltage | Per Cent HCl by Analysis | Per Cent of Ni Plated At Cathode <sup>2</sup> |
|---|--------------------------------------|----------------------------|--|------------------------------|--|-------------------------|--------------|--------------------------|---|
| 1.4   | 200                                  | 35                         | 40                                     | 17                           | 0.7                                    | 0.7                     | 4.5          | 0.040                    | 49  |
| 2.8   | 200                                  | 39                         | 40                                     | 32                           | 1.9                                    | 0.9                     | 4.0          | 0.048                    | 84  |
| 4.8   | 200                                  | 40                         | 40                                     | 31                           | 3.5                                    | 1.3                     | 4.0          | 0.048                    | 84  |
| 5.4   | 200                                  | 44                         | 40                                     | 35                           | 4.0                                    | 1.4                     | 4.0          | 0.048                    | 81  |
| 7.6   | 200                                  | 41                         | 40                                     | 38                           | 6.0                                    | 1.6                     | 4.0          | 0.048                    | 90  |
| 9.4   | 200                                  | 35                         | 40                                     | 37                           | 7.8                                    | 1.6                     | 3.0          | 0.048                    | 102   |
| 11.2  | 200                                  | 38                         | 40                                     | 42                           | 9.8                                    | 1.4                     | 4.0          | 0.048                    | 108   |
| 12.0  | 200                                  | 40                         | 40                                     | 39                           | 10.6                                   | 1.4                     | 4.0          | 0.037                    | 98  |

<sup>1</sup> Based on weight of the bath.

<sup>2</sup> Based on the amount of nickel dissolved at the anode for the interval.

TABLE IV

*Operating characteristics of electropolishing bath containing 35% H<sub>2</sub>SO<sub>4</sub>, 38% H<sub>3</sub>PO<sub>4</sub>, 27% H<sub>2</sub>O, 0.3% HCl*

[Bath temperature—115° F.]

| Per Cent Ni Removed from Anode <sup>1</sup> | Anode Current Density, Amps./sq. ft. | Anode Efficiency, Per Cent | Cathode Current Density, Amps./sq. ft. | Cathode Efficiency, Per Cent | Per Cent of Ni on Cathode <sup>1</sup> | Per Cent Ni Dissolved in Bath | Cell Voltage | Per Cent HCl by Analysis | Per Cent of Ni Plated At Cathode <sup>2</sup> |
|---|--------------------------------------|----------------------------|--|------------------------------|--|-------------------------------|--------------|--------------------------|---|
| 1.9   | 200                                  | 43                         | 50                                     | 24                           | 1.1                                    | 0.8                           | 3.5          | 1.0                      | 56  |
| 5.5   | 200                                  | 53                         | 50                                     | 43                           | 4.0                                    | 1.5                           | 3.5          | 0.11                     | 80  |
| 9.2   | 200                                  | 56                         | 50                                     | 49                           | 7.2                                    | 2.0                           | 3.5          | 0.30                     | 89  |
| 10.7  | 200                                  | 47                         | 50                                     | 51                           | 8.8                                    | 1.9                           | 3.5          | 0.30                     | 103   |
| 14.3  | 200                                  | 48                         | 50                                     | 44                           | 12.2                                   | 2.1                           | 3.7          | 0.31                     | 93  |
| 18.0  | 200                                  | 49                         | 50                                     | 45                           | 15.7                                   | 2.3                           | 4.0          | 0.31                     | 96  |
| 21.7  | 200                                  | 50                         | 50                                     | 48                           | 19.4                                   | 2.3                           | 4.0          | 0.31                     | 97  |

<sup>1</sup> Based on weight of bath.

<sup>2</sup> Based on the amount of nickel dissolved at anode for the interval.

The operating characteristics of electropolishing baths containing HCl additions are illustrated by the data in Tables III and IV. In general, the characteristics as regards current density and electropolishing results are similar to those of baths without HCl. It can be seen that there are several advantages to the 35% H<sub>2</sub>SO<sub>4</sub>-38% H<sub>3</sub>PO<sub>4</sub> bath shown in Table IV. It has a lower initial cost and it operates at higher anode and cathode efficiencies and a slightly lower cell voltage than does the 15% H<sub>2</sub>SO<sub>4</sub>-63% H<sub>3</sub>PO<sub>4</sub> bath shown in Table III. However, the 35% H<sub>2</sub>SO<sub>4</sub>-38% H<sub>3</sub>PO<sub>4</sub> bath has the disadvantage that it tends to form a slight precipitate on continued use. Therefore, some advantages result from using baths of intermediate composition between the 15% H<sub>2</sub>SO<sub>4</sub>-63% H<sub>3</sub>PO<sub>4</sub> and 35% H<sub>2</sub>SO<sub>4</sub>-38% H<sub>3</sub>PO<sub>4</sub> baths.

Further advantages of our invention are ap-

The HCl addition prevents rise in tank voltage during long use; whereas, without HCl, tank voltages are practically doubled after relatively short use of the bath. Nickel is suitably plated out to maintain low concentration in the bath. Consequently, no precipitation or voltage rise results. Likewise, the bath viscosity remains practically unchanged. This is important from the standpoint of losses by drag-out.

The cathode current density is not critical within satisfactorily wide limits of from 20 to 200 amp./ft.<sup>2</sup>. For reasons of simplicity in tank set-up, regarding electrode placement and areas, the preferred range is 50 to 120 amp./ft.<sup>2</sup>. In addition, the deposition rate is essentially the same as the rate of anodic dissolution during electropolishing so that the bath remains in proper balance.

TABLE V

*Operating characteristics of nickel electropolishing bath containing no HCl or chloride 15% H<sub>2</sub>SO<sub>4</sub>-63% H<sub>3</sub>PO<sub>4</sub>-22% H<sub>2</sub>O*

[Bath temperature—115° F.]

| Per cent Ni Dissolved from Anode <sup>1</sup> | Anode Current Density, Amp./ft. <sup>2</sup> | Anode Efficiency, Per cent | Cathode Current Density, Amp./ft. <sup>2</sup> | Cathode Efficiency, Per cent | Per cent Ni Remaining in solution | Cell Voltage Volts | Per cent of Ni Plated on Cathodes <sup>2</sup> | Per cent HCl in Solution by Analysis | Viscosity (poise) |
|---|--|----------------------------|--|------------------------------|-----------------------------------|--------------------|--|--------------------------------------|-------------------|
| 1   | 250  | 36                         | 20   | 1.7                          | 1.0                               | 3.6                | 0.2  | None.....                            | 22.7              |
| 2   | 200  | 36                         | 20   | 4.0                          | 1.8                               | 5.6                | 0.3  | do.....                              | -----             |
| 4   | 200  | 35                         | 20   | 4.8                          | 3.7                               | 6.2                | 0.5  | do.....                              | -----             |
| 5   | 200  | 35                         | 20   | 7.0                          | 4.5                               | 8.2                | 1.5  | do.....                              | 59.5              |

<sup>1</sup> Refers to total amount of nickel dissolved during electropolishing as weight per cent of the bath.

<sup>2</sup> Copious precipitation during the time interval between 2 and 4% nickel dissolved.

<sup>3</sup> Refers to total nickel plated out of bath as weight per cent of the bath.

<sup>4</sup> Heavy precipitate present.

TABLE VI

Operating characteristics of nickel electropolishing bath  
15%  $H_2SO_4$ -63%  $H_3PO_4$ -22%  $H_2O$ -(0.05-0.16)%  $HCl$

[Bath temperature—115° F.]

| Per cent Ni Dissolved from Anode <sup>1,2</sup> | Anode Current Density, Amp./ft. <sup>2</sup> | Anode Efficiency, Per cent | Cathode Current Density, Amp./ft. <sup>2</sup> | Cathode Efficiency, Per cent | Per cent Ni Remaining in solution | Cell Voltage Volts | Per cent of Ni Plated on Cathodes <sup>3</sup> | Per cent HCl in Solution by Analysis | Viscosity (poise) |
|---|--|----------------------------|--|------------------------------|-----------------------------------|--------------------|--|--------------------------------------|-------------------|
| 1.2   | 250  | 27                         | 20   | 24                           | 0.4                               | 4.6                | 0.8  | 0.08                                 | 22.7              |
| 2   | 200  | 33                         | 20   | 29                           | 0.5                               | 4.6                | 1.5  | 0.12                                 | 24.4              |
| 3   | 100  | 30                         | 20   | 28                           | 0.5                               | 3.5                | 2.5  | 0.05                                 | 23.6              |
| 4   | 100  | 34                         | 20   | 31                           | 0.6                               | 4.0                | 3.4  | 0.10                                 | 22.8              |
| 5   | 200  | 28                         | 40   | 26                           | 0.6                               | 5.5                | 4.4  | 0.16                                 | 22.8              |
| 10.3  | 200  | 28                         | 40   | 33                           | 0.6                               | 4.0                | 9.7  | 0.13                                 | 24.0              |
| 14.8  | 200  | 34                         | 40   | 32                           | 0.8                               | 4.3                | 14.0   | 0.16                                 | 23.2              |
| 22.0  | 200  | 35                         | 40   | 35                           | 0.7                               | 4.2                | 21.3   |                                      |                   |
| 28.5  | 200  | 34                         | 40   | 33                           | 0.9                               | 4.3                | 27.6   |                                      |                   |
| 34.0  | 200  | 36                         | 40   | 35                           | 1.0                               |                    | 33.0   |                                      |                   |

<sup>1</sup> Refers to total amount of nickel dissolved during electropolishing as weight per cent of the bath.

<sup>2</sup> No precipitation at any time.

<sup>3</sup> Refers to total nickel plated out of bath as weight per cent of the bath.

TABLE VII

Effect of  $HCl$  concentration on per cent nickel plated<sup>1</sup> at cathode in electropolishing bath containing 12.4%  $H_2SO_4$ , 56%  $H_3PO_4$ , 25.7%  $H_2O$ , 1.2%  $Cr$ , 2.3%  $Al$

| Per Cent Ni Dissolved <sup>2</sup> | $HCl$ 0.25% | $HCl$ 0.50% | $HCl$ 1.0% | $HCl$ 1.5% | $HCl$ 2.5% |
|------------------------------------|-------------|-------------|------------|------------|------------|
| 4.0                                | 120         | 105         | 110        | 100        |            |
| 4.5                                | 96          | 96          | 103        |            |            |
| 5.5                                | 101         | 105         | 97         |            |            |
| 6.5                                | 94          |             | 102        | 92         |            |
| 7.5                                | 100         |             |            | 103        |            |

<sup>1</sup> Values are for per cent nickel plated at cathode based on amount dissolved at anode for that interval.

<sup>2</sup> Based on weight of the bath.

Additions of chlorides may also be used effectively to cause dissolved nickel to be continuously deposited as metallic nickel at the cathode during electropolishing in the high temperature baths containing additions of trivalent aluminum, or of trivalent aluminum and trivalent chromium, as has been mentioned previously. Thus, if desired, the advantages of both high temperature operation, say, 180° F. to nearly boiling temperature, and continuous deposition of the dissolved nickel as metallic nickel on the cathode may be obtained. The effect of  $HCl$  concentration on these baths is illustrated by the data in Table VII.

The baths of the present invention are operative for the electropolishing of nickel and nickel alloys containing at least 90% nickel together with alloying ingredients in amounts (generally less than 10%) such as will not materially affect the behavior of the nickel for electrolytic treatment purposes. The principles of the invention include broadly electropolishing nickel in baths containing a minor chloride addition furnished by any compound selected from the group consisting of hydrochloric acid, metal (including ammonium) chlorides, and chlorinated organic acids.

Figures 2, 3 and 4, as previously noted, show the effect of operating at different bath temperatures.

When hydrochloric acid is added within the limits of 0.3 to 1.0% and the resulting baths are operated at 115° F., no precipitation of nickel salts occur if the  $H_3PO_4$ - $H_2SO_4$ - $H_2O$  values are kept within the area defined on Figure 2 by the straight lines joining the points 1, 8, 9, 6, 7 and 1 in the order named. In other words, this area represents baths in which simultaneous electro-

polishing and electrodeposition of nickel can be satisfactorily carried out. In the area delineated by the straight lines joining the points 9, 10, 11, 12, 6 and 8, in the order named, a slight amount of precipitation of nickel salts may occur, but such slight precipitation may not be objectionable.

In Figure 2, the preferred bath compositions, with respect to  $H_3PO_4$ - $H_2SO_4$ - $H_2O$  when containing from 0.3 to 1.0%  $HCl$  and operated at 115° F., lie within the area delineated by the straight lines joining the points 9, 9, 6, 13, 14 and 8, in the order named. Within this area, both electropolishing and nickel electrodeposition can be most satisfactorily performed. The broader bath composition limits for simultaneous polishing and plating are those lying within the area defined by the straight lines joining the points 1, 8, 9, 10, 11, 12, 6, 7 and 1 in the order named.

The following are the values for the various points indicated by reference numerals on Figure 2:

| Point | Per Cent $H_3PO_4$ | Per Cent $H_2SO_4$ | Per Cent $H_2O$ |
|-------|--------------------|--------------------|-----------------|
| 1     | 85                 | 0                  | 15              |
| 6     | 60                 | 20                 | 20              |
| 7     | 73                 | 0                  | 27              |
| 8     | 75                 | 10                 | 15              |
| 9     | 62                 | 20                 | 18              |
| 10    | 46                 | 32                 | 22              |
| 11    | 35                 | 39                 | 26              |
| 12    | 31                 | 39                 | 30              |
| 13    | 71                 | 5                  | 24              |
| 14    | 77                 | 3                  | 20              |

In general, for the operating conditions set forth in conjunction with Figure 2, the preferred bath compositions lie within the limits of from 50 to 77%  $H_3PO_4$ , 3 to 20%  $H_2SO_4$  and 15 to 30%  $H_2O$ , and within the area defined by the straight lines 8-9, 9-6, 6-13, 13-14 and 14-8. In the broader bath composition range, the limits are from 31 to 85%  $H_3PO_4$ , 0 to 39%  $H_2SO_4$ , and 15 to 30%  $H_2O$  and lie within the area defined by the straight lines 1-8, 8-9, 9-10, 10-11, 11-12, 12-6, 6-7, 7-1.

When hydrochloric acid is added within the limits of 0.3 to 1.0% and the resulting baths are operated at 90° F., no precipitation of nickel salts occurs if the  $H_3PO_4$ - $H_2SO_4$ - $H_2O$  values are kept within the area defined on Figure 3 by the straight lines joining the points 15, 21, 22, 23, 24, 19, 20 and 15 in the order named. In other words, this area represents baths in which simul-

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taneous electropolishing and electrodeposition of nickel can be satisfactorily carried out. In the area delineated by the straight lines joining the points 23, 25, 26, 24 and 23, in the order named, a slight amount of precipitation of nickel salts may occur but such slight precipitation may not be objectionable.

In Figure 3, the preferred bath compositions, with respect to  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$ , when containing from 0.3 to 1.0% HCl and operated at 90° F. lie within the area delineated by the straight lines joining the points 22, 23, 24, 19, 27 and 22, in the order named. Within this area, both electropolishing and nickel electrodeposition can be most satisfactorily performed. The broader bath composition limits for simultaneous polishing and plating are those lying within the area defined by the straight lines joining the points 15, 21, 22, 23, 25, 26, 19, 20 and 15.

The following are the values for the various points indicated by reference numerals on Figure 3:

| Point   | Per Cent $\text{H}_3\text{PO}_4$ | Per Cent $\text{H}_2\text{SO}_4$ | Per Cent $\text{H}_2\text{O}$ |
|---------|----------------------------------|----------------------------------|-------------------------------|
| 15..... | 85                               | 0                                | 15                            |
| 19..... | 56                               | 10                               | 34                            |
| 20..... | 75                               | 0                                | 25                            |
| 21..... | 75                               | 10                               | 15                            |
| 22..... | 70                               | 12                               | 18                            |
| 23..... | 45                               | 28                               | 27                            |
| 24..... | 38                               | 28                               | 34                            |
| 25..... | 28                               | 45                               | 27                            |
| 26..... | 21                               | 45                               | 34                            |
| 27..... | 73                               | 3                                | 24                            |

In general, for the operating conditions set forth in conjunction with Figure 3, the preferred bath compositions lie within the limits of from 38 to 73%  $\text{H}_3\text{PO}_4$ , 3 to 28%  $\text{H}_2\text{SO}_4$ , and 24 to 34%  $\text{H}_2\text{O}$ , and within the area defined by the straight lines 22-23, 23-24, 24-19, 19-27 and 27-22. In the broader bath composition range, the limits are 38 to 85%  $\text{H}_3\text{PO}_4$ , 0 to 28%  $\text{H}_2\text{SO}_4$  and 15 to 34%  $\text{H}_2\text{O}$  and lie within the area defined by the straight lines 15-21, 21-22, 22-23, 23-25, 25-26, 26-19, 19-20, and 20-15.

When hydrochloric acid is added within the limits of 0.3 and 1.0% and the resulting baths are operated at 135° F. no precipitation of nickel salts occurs if the  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  values are kept within the limits defined on Figure 4 by the straight lines joining the points 28 and 35. In other words, this line 28-35, representing from 74 to 85%  $\text{H}_3\text{PO}_4$ , 0%  $\text{H}_2\text{SO}_4$  and from 15 to 26%  $\text{H}_2\text{O}$ , represents baths in which simultaneous electropolishing and electrodeposition of nickel can be satisfactorily carried out. In the area delineated by the straight lines joining the points 28, 36, 37, 38, 33, 34, 35 and 28, in the order named, a slight amount of precipitation of nickel salts may occur but such slight precipitation may not be objectionable.

In Figure 4, the preferred bath compositions, with respect to  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$ , when containing from 0.3 to 1.0% HCl and operated at 135° F., lie within the area delineated by the straight lines joining the points 39, 36, 37, 38, 33, 34 and 39, in the order named. Within this area, both electropolishing and nickel electrodeposition can be most satisfactorily performed. The broader bath composition limits for simultaneous polishing and plating are those lying within the area defined by the straight lines joining the points 28, 36, 37, 38, 33, 34, 35 and 28.

The following are the values for the various

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points indicated by reference numerals on Figure 4:

| Point   | Per Cent $\text{H}_3\text{PO}_4$ | Per Cent $\text{H}_2\text{SO}_4$ | Per Cent $\text{H}_2\text{O}$ |
|---------|----------------------------------|----------------------------------|-------------------------------|
| 28..... | 85                               | 0                                | 15                            |
| 33..... | 50                               | 20                               | 30                            |
| 34..... | 66                               | 5                                | 29                            |
| 35..... | 74                               | 0                                | 26                            |
| 36..... | 70                               | 15                               | 15                            |
| 37..... | 50                               | 30                               | 20                            |
| 38..... | 40                               | 30                               | 30                            |
| 39..... | 75                               | 5                                | 20                            |

In general, for the operating conditions set forth in conjunction with Figure 4, the preferred bath compositions lie within the limits of from 40 to 75%  $\text{H}_3\text{PO}_4$ , from 5 to 30%  $\text{H}_2\text{SO}_4$  and from 15 to 30%  $\text{H}_2\text{O}$ , and within the area defined by the straight lines 39-36, 36-37, 37-38, 38-33, 33-34 and 34-39. In the broader bath composition range, the limits are 40 to 85%  $\text{H}_3\text{PO}_4$ , 0 to 30%  $\text{H}_2\text{SO}_4$  and 15 to 30%  $\text{H}_2\text{O}$  and lie within the area defined by the straight lines 28-36, 36-37, 37-38, 38-33, 33-34, 34-35 and 35-28.

Many details in composition and procedure may be varied within a wide range without departing from the principles of this invention, and it is therefore not our intention to limit the patent granted on this invention otherwise than necessitated by the scope of the appended claims.

What we claim is:

1. The method of electrolytically polishing metal selected from the group consisting of nickel and nickel alloys containing at least 90% nickel, which comprises making the metal the anode in an aqueous bath having a dissolved chloride ion content calculated as HCl of from 0.04 to 2.5% by weight of said bath, the remainder of said bath consisting essentially of a composition lying within the closed area defined on the accompanying diagram by the solid straight lines AC, CD, DE, EF, FG, GH and HA, passing through said solution while held within the temperature range of from 80° to 140° F. an electrical current of sufficient density and for a sufficient period of time to effect the polishing of said metal, and during said electropolishing maintaining said bath at that temperature within said range at which anodically dissolved nickel will be electrodeposited from said bath whereby the tendency of nickel salts to precipitate on continued operation of said bath is reduced.

2. The method of electrolytically polishing metal selected from the group consisting of nickel and nickel alloys containing at least 90% nickel, which comprises making the metal the anode in an aqueous bath having a dissolved chloride ion content calculated as HCl of from 0.04 to 2.5% by weight of said bath, the remainder of said bath consisting essentially of a composition lying within the closed area defined on the accompanying diagram by the dotted straight lines BI, IJ, and JK, the solid straight line KG and the dotted straight lines GL, LM and MB, passing through said solution while held within a temperature range of from 90° to 125° F. an electrical current of sufficient density and for a sufficient period of time to effect the polishing of said metal, and during said electropolishing maintaining said bath at that temperature within said range at which anodically dissolved nickel will be electrodeposited from said bath whereby the tendency of nickel salts to precipitate on continued operation of said bath is reduced.

3. For use as an aqueous electrolyte in the si-

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multaneous electropolishing of nickel and nickel alloys containing at least 90% nickel and the cathodic electrodeposition of nickel, an aqueous solution having a dissolved chloride ion content calculated as HCl of from about 0.04 to 2.5% by weight of said solution and containing dissolved nickel in an amount calculated as Ni of from 0.5 to 2.5% by weight of said solution, the remainder of said solution consisting essentially of a composition lying within the closed area on the accompanying diagram defined by the solid straight lines AC, CD, DE, EF, FG, GH and HA.

4. For use as an aqueous electrolyte in the simultaneous electropolishing of nickel and nickel alloys containing at least 90% nickel and the cathodic electrodeposition of nickel, an aqueous solution having a dissolved chloride ion content calculated as HCl of from about 0.04 to 2.5% by weight of said solution and containing dissolved nickel in an amount calculated as Ni of from 0.5 to 2.5% by weight of said solution, the remainder of said solution consisting essentially of a composition lying within the closed area on the accompanying diagram defined by the dotted straight lines BI, IJ and JK, the solid straight line KG, and the dotted straight lines GL, LM and MB.

5. For use as an aqueous electrolyte in the simultaneous electropolishing of nickel and nickel alloys containing at least 90% nickel and the cathodic electrodeposition of nickel, an aqueous solution having a dissolved chloride ion content calculated as HCl of from about 0.04 to 2.5% by weight of said solution and containing up to saturation of dissolved nickel, the dissolved nickel content calculated as Ni being at least equal to 0.5% by weight of said solution, the remainder of said solution consisting essentially of a composition lying within the closed area on the accompanying diagram defined by the solid straight lines AC, CD, DE, EF, FG, GH and HA.

6. For use as an aqueous electrolyte in the simultaneous electropolishing of nickel and nickel

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alloys containing at least 90% nickel and the cathodic electrodeposition of nickel, an aqueous solution having a dissolved chloride ion content calculated as HCl of from about 0.04 to 2.5% by weight of said solution and containing up to saturation of dissolved nickel, the dissolved nickel content calculated as Ni being at least equal to 0.5% by weight of said solution, the remainder of said solution consisting essentially of a composition lying within the closed area on the accompanying diagram defined by the dotted straight lines BI, IJ, and JK, the solid straight line KG and the dotted straight lines GL, LM and MB.

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