April 19, 1960 L. E. LANCY 2,933,438

ELECTRO PROCESSING AND APPARATUS THEREFOR

Filed Dec. 19, 1958

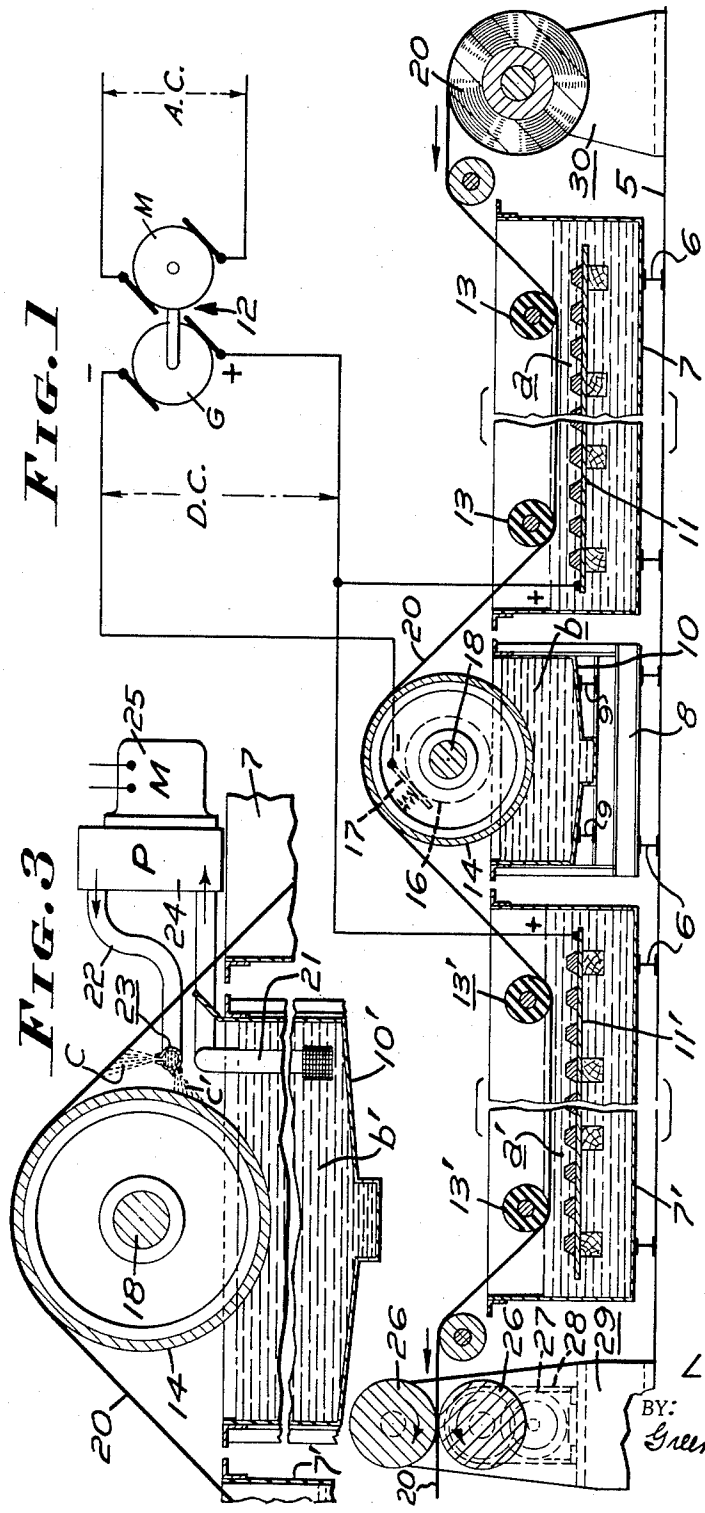

FIG. 1

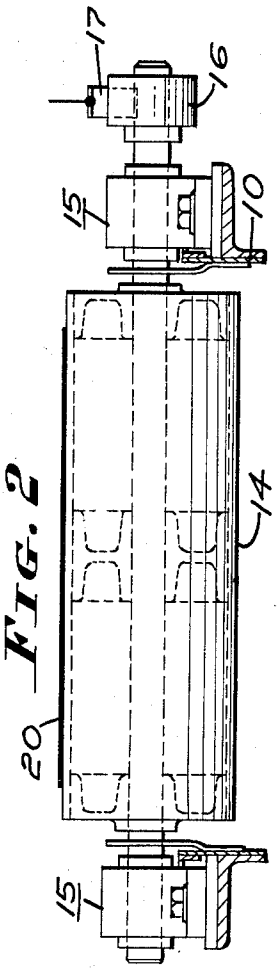

FIG. 2

FIG. 3

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United States Patent Office 2,933,438 Patented Apr. 19, 1960

2,933,438

ELECTRO PROCESSING AND APPARATUS THEREFOR

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Application December 19, 1958, Serial No. 781,805

18 Claims. (Cl. 204—28)

This invention pertains to the electroplating of continuous metal strip and particularly, to procedure and apparatus for improving the operation of contact rolls for the strip.

This is a continuation-in-part of my application Ser. No. 616,273 of October 16, 1956, now abandoned, of the same title.

Having been active in the field of electrotreating and plating of work articles, including strip metal, I found that there has been a limitation on the maximum speed at which the plating operation could be effected if good plating results were to be obtained. For example, about 800 feet per minute has been the maximum speed for a halogen tin plating line. In evaluating the problem, I found that the thickness, width, etc., of the strip did not appreciably enter into the factor of maximum speed, but that the tendency of carried-over plating solution to cause a plating of the contact roll was found to be a very important limiting factor.

In the continuous electroplating of the strip, it is usual to employ a plurality of electric contact rolls with contacting strips serving as conductors of the cathodic electric charge. The strip thus receives a metallic deposit in the plating solution due to this electric charge. It has been found advisable to position contact rolls in a non-immersed or above-positioning with respect to the plating solution and to employ them essentially as conductor and contacting members, although they do incidentally serve to guide the strip during its movement.

I have thus determined that if the speed of the plating operation or, in other words, the processing speed of the strip is to be increased to conform with higher mill speeds, that the problem centers around the tendency of drag-out or carry-over from the plating solution to deposit or plate a coating on the surface of the contact roll, itself. This is true, even if the contact roll is not immersed in the plating solution, since the moving strip carries sufficient quantities of the plating solution to keep the roll wet and covered with the same electrolyte contained in the plating tank or bath, itself.

Although great efforts have been made to make the electrical contact between the strip and the contact roll as good as possible, I have found that there is always electrical resistance between the two which results in a voltage drop across the two abutting surfaces, and that the potential is higher and more cathodic on the roll than on the strip. Thus, if the voltage drop due to this resistance is high enough to reach a decomposition potential of the plating solution, a metal deposit will develop on the contact roll with the strip acting as an anode.

It will be apparent that the greater the strip speed, the more solution that is carried on the strip, thus increasing the tendency to cause electrode deposition on the contact roll. A higher speed of strip plating also requires higher current densities that necessitate higher potentials. This causes the voltage drop between the contact roll and the strip to be greater along with a carry-over of more

solution from the electrolytic tanks or baths. This all leads to a faster plating build-up upon the contact roll.

Although those skilled in the art have recognized that contact roll plating is a limiting and disadvantageous factor, they have not realized that such plating will occur, even under the very best possible conditions. Thus, I have have found that the problem cannot be solved, as heretofore thought by those skilled in the art, by more tightly holding the strip on the contact roll, as by using a higher tension on the strip or more tightly pressing the strip against such roll by means of a separate rubber or plastic-coated pressure or back-up roll.

It has thus been an object of my invention to devise procedure and apparatus which will meet the problem or overcome an important limiting factor as to the maximum speed of operation of an electroplating line;

Another object has been to discover the features which enter into such factor and to at least control and limit it by a new approach to the problem;

A further object of my invention has been to devise new and improved procedure and to provide apparatus therefor which will substantially eliminate the heretofore somewhat inherent tendency to electroplate the contact rolls of an electroplating line;

A still further object of my invention has been to reduce or control roll plating caused by potential drop between the roll and the strip which is moving thereover and to do so without adversely affecting the over-all efficiency of the plating operation;

These and other objects of my invention will appear to those skilled in the art from the illustrated embodiments and the claims.

In the drawings,

Figure 1 is a side section in elevation through an electrolytic plating line constructed and employed in accordance with my invention. This view illustrates a so-called horizontal cell type of insatllation in which contact rolls are positioned between plating cells or baths during the continuous end progression of metal strip along the system. However, substantially the same principle is applied to a vertical pass type of installation, thus my invention as applied to the latter type of installation is also illustrated by this figure.

Figure 2 is a fragmental end view in elevation on the scale of and taken at right angles to Figure 1 and showing the construction and mounting of a contact roll of the plating line of the latter figure.

And Figure 3 is an enlarged fragmental side section in elevation of the plating line, showing the employment of spray means for the contact roll.

It is important to maintain a smooth contact roll surface since the strip is ordinarily of relatively thin gauge and is being moved under tension or pressure against the contact roll since any irregularity or roughness that appears on the contact roll will spoil the smooth surface of the strip. Scratches, pits, etc., are thus imprinted, embossed, or coined into the contacting surface of the strip. The unevenness also makes impossible a uniform and full electrical contact between all surface portions of the strip and corresponding portions of the contact roll. To provide a good plating operation on the strip, it is desirable to provide a full type of face-to-face abutment between the opposed faces of the contact roll and the strip during movement of the strip thereon or thereover.

As previously intimated, my study and evaluation in this connection indicates that the problem of contact roll plating is not primarily one of increasing the pressure or efficiency of contact between the roll and the strip. It may be noted that increasing the contact pressure increases the tendency to damage and break the strip.

My discovery is that a solution to the problem centers

on the factor of drag-out or carry-over of the plating solution and in controlling or conditioning the carry-over in such a manner as to eliminate its conduciveness to produce electroplating on the contact roll.

I have been able to non-adversely change the composition or nature of carried-over portions of the solution or, in other words, the nature of the drag-out at or before the time of its contact wtih the contact roll, so that it will no longer function as a plating solution. In this manner, I not only effectively eliminate roll plating, but also make possible lower pressures or tension on the strip, and thus the utilization of thinner gauge strip. A highly important factor that has heretofore minimized the maximum speed at which the strip could be moved through a plating line has been met.

Although I have discovered a number of ways of rendering the drag-out or plating solution ineffective, it should be appreciated that any method employed must essentially, if it is to be practical, not adversely affect the plating solution or plating operations in the plating baths or cells. For example, I could totally neutralize the drag-out portions of the solution at their point of contact with the contact roll, but neutralizing chemicals may block or at least in time render subsequent plating cells or baths inefficient or ineffective.

I have had to consider the make-up of the plating solutions to avoid harm being done by the drag-in of the contact roll solution or wash. I have determined that chemicals to be used for this purpose should be of such a nature that they are standard constituents of the plating solution involved, and that the out-of-balance condition of the wet film at the contact roll must not be of a type or be sufficient to ruin the efficiency of a subsequent strip plating step or of the solution employed. By employing standard contents or solution elements, I find that the quantity needed for rendering the solution ineffective as to the contact roll and for making it at least innocuous as to the plating bath, may be and is served by the addition of a beneficial chemical, such as one used in replenishing chemicals consumed in the plaitng process.

Strip plating solutions are usually formulated in such a manner that they are highly efficient, and this means that the maximum amount of electrical energy is converted into the deposition of metallic crystals. Cathodic efficiency is expressed by the relationship between the theoretical maximum amount of metal deposited for each coulomb of electrical unit and the actual efficiency of it. I have considered the use of a wash solution which would change the composition of the wet film on the strip by diluting the drag-out with water, adding chemicals, and removing the metallic ion content from the drag-out in an auxiliary system as (*a*) by electrolytic deposition, by (*b*) the use of an ion exchanger, by (*c*) the precipitation of metal ions, or by (*d*) removing them by physical means (such as by evaporation and crystallization, etc.). I have determined that a highly valuable approach involves the use of an anionic chemical addition to the drag-out, contact roll solution or wash water that is a standard or common constituent of the plating solution or bath and which is employed in a concentration sufficient to render the carried-over electrolyte inefficient or ineffective for plating the roll. The concentration is controlled in such a manner that solution or liquid drag-in of the strip from the contact roll station does not contain more than a normal maintenance chemical addition to the plating solution or bath for a subsequent plating operation.

In accordance with my invention, I alter the balance between the anions and cations by some suitable means, such as set forth in the previous paragraph, to provide cations in the conditioned carried-over or drag-out solution in an amount of not more than 50% of the cation concentration of the plating solution used in the preceding plating operation. I also provide by additions, a minimum anion content of the conditioned drag-out solution of at least 200%, or two times the content in the preceding plating solution. This provides the required minimum ratio of cations to anions in the drag-out solution, as conditioned for the contact roll, of 1 to 4 in favor of the anions. For example, if a plating solution has a normal amount of 1 ounce of free sodium or potassium cyanide in a zinc plating solution or of ½ an ounce in a copper plating solution, the minimum amount of the anion content of the sodium or potassium cyanide is two ounces per gallon of water for the conditioned drag out or contact roll solution for the line of the zinc plating bath and one ounce per gallon of water for the conditioned drag out solution for the line of the copper plating bath, or two times the normal content of the respective plating baths. The zinc concentration can be maintained at less than 50 percent of the concentration value found in the plating solution because the contact roll wash solution is made without the addition of any zinc (cation) and the zinc content of this solution is due only to the drag-in from the plating solution by the moving strip. The addition of a proper amount of fresh aqueous contact roll wash solution may thus be employed to provide the specified low cation concentration.

By way of example, in carrying out my invention, as applied to a zinc cyanide type of zinc plating solution, I have found that the addition of sodium cyanide to the contact roll wash water solution for conditioning the drag-out or carried-over solution may be employed to change the ratio in the latter between the zinc (cation) content of the film and the sodium cyanide (anion) content, and that this is a controlling factor as to plating efficiency. That is, the higher the sodium cyanide content and the lower the zinc content, the higher the numerical ratio between these two, the lower is the efficiency of the deposition. Thus, I provide a wash water or contact roll station solution containing more than about two ounces per gallon of sodium or potassium cyanide, but preferably at a concentration level of about 8 to 10 ounces per gallon. It will by its nature be low in zinc ion content and will act as a plating solution of extremely low efficiency. This gives an amount of about two times the free anion content of the plating solution (1 ounce normal) as a minimum and of about eight to ten times the free anion content for 8 to 10 ounces per gallon.

In another example as to an alkaline tin plating bath or solution, I provide a contact roll station solution that contains an alkali metal hydroxide in the nature of potassium or sodium hydroxide or both to greatly alter the balance between the tin salt and the caustic content of the plating solution and provide a contact roll solution film of very low plating efficiency. As an optimum, I will use more than about 2 ounces and may use up to about 6 to 8 ounces of the hydroxide per gallon of wash water. This gives an amount of about four times the free anion content of the plating solution (.5 ounce normal) as a minimum and of about twelve to sixteen times the free anion content for 6 to 8 ounces.

In plating solutions of an acid tin, zinc, copper or nickel type, I employ a relatively high concentration of the acid, so as to alter the pH provided for the contact roll solution. Thus, to provide the lowered pH desired, relatively high concentrations of the same acids used as in the plating bath are employed, either in the form of free acids or plating salts. As an example of a typical acid solution, a nickel solution will contain nickel sulphate, nickel chloride, boric acid and sulphuric acid. The wash solution is maintained at a low pH of, preferably less than one, by containing either free sulphuric or free hydrochloric acids or a mixture of them.

A fluoborate type of tin plating solution requires a wash solution containing free fluoboric acid or free fluoric acid. Thus, for a sulphate type of tin plating solution, I employ a wash solution containing free sulphuric acid. In this connection a .5 Normal acid (gram equivalent weight per liter) of the same type as the acid

constituent of the acid plating solution has been found to be an optimum in the conditioned contact roll solution. A common acid plating solution contains about .002 to .01 Normal free acid. I thus provide by my conditioning wash water solution a contact roll station solution of a minimum of about .05 Normal and a maximum of about 2 Normal. This gives a minimum of about twenty-five times the free anion content of the plating solution as based on .002 Normal and of five times as based on .01 Normal. It gives a maximum of about 1,000 times as based on .002 Normal and of about 200 times as based on .01 Normal.

For a cyanide type of copper plating solution, I provide the conditioned aqueous contact roll solution with more than about 1 ounce per gallon, and as an optimum, more than about 6 ounces per gallon of potassium cyanide (or of sodium cyanide if the general bath make-up in the plating solution uses this compound). Since the normal plating solution has about .5 ounce per gallon, I provide a minimum contact roll solution content of about two times the free anion content of the plating solution and of about twelve times for the free anion content of 6 ounces. The resultant conditioned solution film thus provided between the strip and the contact roll is relatively low in copper and high in free cyanide and thus, has a low cathode efficiency (non-plating effect).

From a broader aspect, my invention deals with at least limiting or effectively eliminating electroplating action between work strip and contact rolls therefor by controlling the content or nature of the drag-out of wash solution or film which is provided or is present at or between the opposed surfaces. This is done in such a manner as to supplement and not disadvantageously affect the efficiency or content of the plating cells or baths. The wash or aqueous conditioning solution may be applied in any suitable manner to the contact roll or underside of the strip, such as by dipping in an independent bath, as shown in Figure 1 of the drawings, by spraying the surface of the contact roll or by spraying the undersurface of the strip as it advances onto the contact roll.

My procedure is employed beneficially in replenishing the chemicals or the content of the plating baths, but in such a manner as to eliminate plating on the contact rolls as a factor in limiting increased strip speeds in a plating line. A surprising feature of the invention is that it has been found possible and practical to utilize an anionic chemical that is important in the plating solutions used and in such a manner or in such quantity that it hinders plating action as to the contact roll, but promotes plating action as to the strip and in the treating (plating) bath or solution. In accordance with my invention, the employment of an aqueous conditioning solution reduces the cation content of the conditioned resultant drag-out solution that is carried by the strip from a preceding plating solution treatment station, and the addition of an anion chemical to the conditioning solution that is a constituent of the plating solution increases the ratio of anion to cation content of the conditioned solution by at least 4 to 1 which is required to inhibit plating action as to the contact roll.

In Figure 1, I have illustrated an electroplating apparatus of a horizontal in-line or so-called horizontal cell type that is supported on a floor level **5** by a series of longitudinally spaced-apart transversely-extending cross I-beam supports **6**. The I-beams **6** not only support containers, tanks or electrolytic baths **7** and **7'**, but through extension structure **8** and supplemental cross I-beams or members **9**, also support a tank or container **10** for a contact roll treating or washing bath or zone. The tanks **7** and **7'** are shown as identical and illustrate the inbetween or intermediate station relationship of a contact roll **14** and its bath or treatment zone **10**.

The zones represented by the tanks **7** and **7'** carry an electrode table or assembly **11** or **11'**, therewithin and beneath the level of electrolyte, indicated as *a* or *a'*. The

electrode assemblies **11** and **11'** are energized by positive connections to a direct current source or a converter, such as a motor generator set or unit **12**. As shown, the unit **12** converts alternating to direct current for the system of Figure 1. The negative side of the direct current source from the unit **12** is connected to a contact roll or contactor **14** which may be of conventional construction.

Spring-pressed brushes **17** operate in a conventional manner on an electrical contact wheel portion or commutator **16** to energize the roll surface thereof which may be of a good conductor such as copper or steel. The contact roll **14** is carried on a shaft **18** which is journaled in suitable stands **15** (see Figure 2). Strip **20** to be electrolytically plated is shown as moving from right to left in Figure 1, substantially in a horizontal plane beneath the level of electrolyte in tank **7** (or **7'**), and above the electrode assembly **11** (or **11'**), as guided by at least a pair of hard rubber or plastic (dielectric) guide or tension rolls **13** (or **13'**). Although the roll **14** is of a positive or electric motor-driven type, as an alternate, the strip **20** may be pulled (under tension), as by a forward roll pass (see pinch rolls **26**), through the apparatus as a substantially continuous length to progressively subject it to electrolytic treatment in one or more electroplating baths or tanks **7**, **7'**, etc.

As shown in Figure 1, the strip **20** is fed from a coil mount **30**, under guide rolls **13**, over contact roll **14**, under guide rolls **13'**, and through a draw or tension pass provided by pinch rolls **26**. An electric motor **27** is shown positioned on roll stand **29** to positively drive the rolls **26** by means of a gear box **28**. Although not shown, the contact roll **14** may be directly driven, if desired.

The strip **20** is supplied with negative current, so that it may be properly plated, by the contact roll **14** of enlarged diameter. The contact roll **14** is operatively positioned above and outside of the tanks **7** and **7'** and its wash solution *b* is independent of the solutions *a* and *a'* of the tanks **7** and **7'**. If a spray treatment is to be applied (see Figure 3), it may be accomplished in the entry area to the right of the contact roll **14** that lies in the spacing between the under-face of the strip **20** and the outer or roll face of the contact roll **14**. Such a spray method may be exclusive of or may be combined with a bath treatment, such as illustrated.

In Figure 3, I have shown a pressure spray pump **24** that is supplied with solution by suction line **21**. The pump **24** is shown driven by an electric motor **25** to move the solution through discharge line **22**, through header **23**, and out through spray nozzles in the header, as sprays *c* and *c'*. It will be noted that one spray *c* is directed upon the underside of the strip **20** and that the other spray *c'* is directed upon the surface of the contact roll **14**, ahead of its area of contact with the strip **20**, during the counter clockwise movement of the contact roll.

Regardless of which way the washing or contact roll treating solution is applied, the principle is the same which involves progressively advancing the strip **20** out of one plating bath solution (such as **7**) upon the contact roll (such as **14**), and then back into a second plating bath (such as **7'**), while controlling the content, the nature or condition of the carry-over of plating solution by the strip from the bath **7** and of the drag-in from the contact roll **14** back to the bath **7'**. This is done in such a manner as to inhibit electroplating action on the surface of the contact roll without adversely affecting the electroplating action upon the strip.

What I claim is:

1. In a method of electroplating metal strip which is being progressively advanced out of a plating solution, upon a contact roll, and then into a plating solution; the steps of conditioning the content of the solution carried-over on the strip when the strip is advanced from the

plating solution to the contact roll by changing the ratio of cations to anions in the carried-over solution to at least 1 to 4 in favor of the anions to substantially inhibit electroplating action of the carried-over solution on the contact roll and renew the content of the plating solution when the strip is then advanced into it and without adversely affecting the electroplating action of the plating solution on the strip.

2. An electroplating method as defined in claim 1 wherein, the conditioning of the carried-over solution is effected by the application of an aqueous conditioning solution containing an anionic chemical constituent of the plating solution.

3. A method as defined in claim 2 wherein, the plating solution is of a zinc cyanide type, and the conditioning solution contains a cyanide of the class consisting of sodium and potassium cyanides.

4. A method as defined in claim 2 wherein the plating solution is of an alkaline tin plating type, and the conditioning solution contains a hydroxide of the class consisting of sodium and potassium hydroxides and in a sufficient concentration both to substantially alter a balance between the tin salt and the caustic content of the carried-over bath solution.

5. A method as defined in claim 2 wherein, the plating solution is of an acid metal plating type, and the conditioning solution contains a higher concentration of the same acid as used in the plating solution.

6. A method as defined in claim 2 wherein, the plating solution contains nickel sulfate, nickel chloride, boric acid, and sulfuric acid; and the conditioned carried-over solution is maintained at at least five times the free acid concentration of the plating solution with a pH of less than one, as effected by adding an acid of the class consisting of free sulphuric and hydrochloric acids.

7. A method as defined in claim 2 wherein, the plating solution is an alkaline tin plating type, and the conditioned carried-over solution contains a hydroxide of the class consisting of sodium and potassium hydroxides of more than about two ounces and up to about eight ounces per gallon of water in the solution.

8. A method as defined in claim 2 wherein, the plating solution is of an acid type, and the conditioned carried-over solution contains water and at least two times the amount of the acid in the plating solution.

9. A method as defined in claim 2 wherein, the plating solution is a tin fluoborate acid plating type, and the conditioning solution contains acid of the class consisting of free fluoboric and hydro fluoric acids.

10. A method as defined in claim 2 wherein, the plating solution is of a tin sulphate plating type; and the conditioning solution contains free sulphuric acid.

11. In a method of electroplating metal strip which is being progressively advanced from a plating solution, upon a contact roll, and then into a second plating solution of the same general type as the first solution; the steps of applying an aqueous conditioning solution containing a common anionic chemical constituent of the plating solutions to the solution carried-over on the strip when it is advanced from the first plating solution to the contact roll to inhibit electroplating action of the carried-over solution on the contact roll and renew the content of the common anionic chemical constituent of the second plating solution without adversely affecting the electroplating action of the second plating solution when the strip is advanced from the contact roll thereinto, and the conditioned carried-over solution for the contact roll having a maximum cation content of 50% of its content in the first plating solution and a minimum anion content of at least 200% of its content in the first plating solution.

12. A method as defined in claim 11 wherein the conditioning solution is sprayed between the contact roll and the metal strip in its movement from the first plating solution to the contact roll.

13. A method as defined in claim 11 wherein the conditioning solution is employed as a bath through which the contact roll rotates to pick up the solution on its surface and combine it with the solution carried-over by the strip from the first plating solution.

14. A method as defined in claim 11 wherein the ratio of cation to anion content of the conditioned carried-over solution is a minimum of 1 to 4.

15. A method as defined in claim 11 wherein, the plating solutions are of a copper cyanide plating type, and a cyanide of the class consisting of sodium and potassium cyanides is employed as a common chemical constituent of the conditioning solution to provide more than one ounce and up to about six ounces per gallon of water in the conditioned carried-over solution.

16. A method as defined in claim 11 wherein, the plating solutions are of a zinc cyanide type, a cyanide of the class consisting of sodium and potassium cyanides is employed as the common chemical constituent of the plating and conditioning solutions and is employed in an amount in the conditioning solution to provide more than two ounces of the cyanide per gallon of water in the conditioned carried-over solution.

17. A method as defined in claim 16 wherein the cyanide has a concentration level of about eight to ten ounces per gallon of water in the conditioned carried-over solution.

18. An integrated end-line electrolytic processing of metal strip which comprises, maintaining an electrolytically-active plating solution for first and second plating stations, providing a contact roll at an intermediate current-supply station for the strip, passing successive portions of the metal strip through the solution of the first station and electrolytically plating them thereat, passing successive portions of the metal strip from the first station over the contact roll of the intermediate station to electrically energize the strip, inhibiting electroplating action on the surface of the contact roll at the intermediate station due to electrical resistance between such surface and the contacting surface of the strip by changing the ratio of the cation to anion content of the solution drag-out from the first station to the intermediate station to at least 1 to 4 by the application of an aqueous wash solution containing an excess of an anionic chemical constituent of the first plating solution, and conditioning the drag-out solution to provide it with a minimum of about two times the free anion content of and to a maximum of not more than one-half the cation content of the first plating solution to thereby make the drag-out solution electrolytically inactive to the contact roll, and passing successive portions of the strip from the intermediate station into the plating solution of the second plating station and plating them thereat and renewing the solution of the second station by the conditioned drag-in solution carried by the successive portions of the strip from the intermediate station.

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