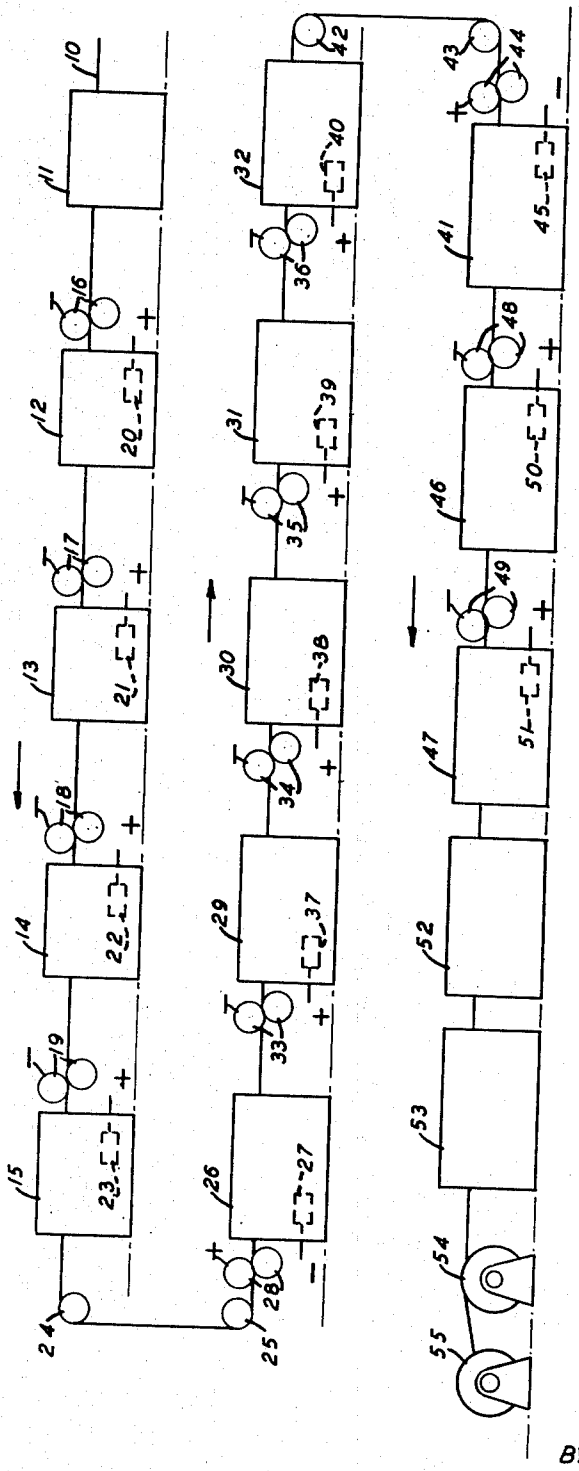
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ELECTROPLATING

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## ELECTROPLATING

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This invention relates to electroplating, and more particularly to methods of continuously electrodepositing smooth-surfaced, dense coatings of copper on moving steel wires.

In the manufacture of composite electrical conductors composed of copper covered steel cores, the known methods of continuously electroforming such conductors tend to produce products generally characterized by a nodular or rough surface. The problem of eliminating surface irregularities, while rapidly producing a dense deposit of copper on moving steel cores, has presented considerable difficulty. While a mechanical buffing operation may serve to improve the quality of a surface, such an expedient is obviously inadequate to improve the density and homogeneity of an electrodeposited coating.

An object of this invention is to provide new and improved methods of electroplating metallic articles.

Another object of the invention is to provide new and improved methods of electroplating copper on steel wires.

A further object of the invention is to provide new and improved methods of continuously electrodepositing smooth-surfaced, dense, homogeneous, thick copper coverings on steel wires at high rates of speed.

A method illustrating certain features of the invention may include the steps of immersing an electroconductive article as a cathode in an electrolytic bath to plate a layer of metal thereon, then immersing the article as an anode in another electrolytic bath to remove a portion of the electroplated layer and then immersing the article as a cathode in another electrolytic bath to plate more metal on the article.

A complete understanding of the invention may be obtained from the following detailed description, when read in conjunction with the appended drawing, in which the single figure is a schematic side elevational view of an apparatus for performing a method embodying the invention.

A steel wire 10 may be advanced through a series of cleaning baths (not shown) to prepare the wire for the electroplating process. The cleaning equipment customarily includes a carbon tetrachloride degreasing bath, an aqueous alkaline bath, a water rinsing bath to remove alkali from the surface of the wire, and a dilute sulfuric acid bath. An electrical potential may be impressed upon the wire in the alkaline and in the acid baths to aid the cleansing process. After being advanced through the sequence of

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cleaning baths, the wire 10 is passed through a water rinsing bath 11 to remove residual acid.

The wire 10, having been cleaned and rinsed, is then advanced through a series of copper plating baths 12, 13, 14 and 15. The wire 10 is engaged by a series of contact rollers 16—16, 17—17, 18—18 and 19—19, which are connected to a rectifier (not shown) from which current is drawn to make the wire 10 a cathode in each of the plating baths. The plating circuit is completed in the respective baths by anodes 20, 21, 22 and 23. Successive increments of copper are electrodeposited on the wire 10 during the initial plating operation performed in the tanks 12, 13, 14 and 15.

The plated wire 10 is then led around direction changing sheaves 24 and 25 into a deplating tank 26, in which the wire is made anodic. From another rectifier (not shown) a deplating circuit is completed through a cathode 27 in the deplating tank 26 and anodic contact rollers 28—28 which engage the wire 10. Since the wire 10 is anodic in the deplating tank 26, the copper plate applied in the plating tanks 12, 13, 14 and 15 tends to dissolve anodically. The conditions in the deplating tank 26 are so controlled that from about 5% to about 10%, of the initially deposited coating is removed during this operation.

A second plating operation is then performed in a sequence of tanks 29, 30, 31 and 32 wherein further increments of copper are deposited on the wire 10. Another rectifier (not shown) furnishes current through a series of cathodic contact rollers 33—33, 34—34, 35—35 and 36—36 and a series of anodes 37, 38, 39 and 40 which are located in the respective baths.

Deplating is then effected in a bath 41 through which the wire is advanced as an anode after passing around sheaves 42 and 43. Anodic contact rollers 44—44 and a cathode 45 are employed to make the wire 10 anodic in the bath 41. The function of the second deplating bath 41 is to remove approximately 5% to 10%, or more, of the coating which was deposited in the second series of plating baths 29, 30, 31 and 32.

The wire is then advanced through a bath 46 and a bath 47, in which additional increments of copper coating are caused to be deposited by cathodic contact rollers 48—48, and 49—49 in conjunction with anodes 50 and 51 and another rectifier (not shown). The total thickness of copper electrodeposited on the wire 10 by the time the wire reaches the baths 46 and 47, is sufficiently great to permit a higher amperage to be used with the same current density at

this stage of the process. Hence, only two plating baths may be required for depositing the final coating, whereas in the prior coating steps smaller increments were deposited using smaller amperages.

A number of factors, such as the diameter of the steel core, the lengths of the tanks, the speed at which the core is advanced through the baths, the concentrations of the plating solutions, the temperature of the baths and the current densities used, may make it desirable to have additional plating baths at any one stage of the process or to have added phases of plating and deplating. Although only a single tank has been used to illustrate the apparatus employed for each deplating phase, in practice it may be found to be desirable to employ two tanks for each deplating step with a correspondingly decreased rate of deplating in each of the two tanks. In such case, each of the two tanks should be provided with an internal cathode, but a single anodic contact roller may be located between the two tanks to serve both of them.

Upon completion of the last plating step, the covered wire is advanced from the tank **47** to a water filled dragout recovery tank **52**, and then through a water rinsing bath **53** to a capstan **54** and a take-up reel **55**. In the dragout recovery tank **52**, residual acidic plating solution is removed from the plated wire **10**, forming a dilute solution which may be used to replenish the several plating tanks to compensate for losses due to evaporation and other causes.

The electrolyte used in the plating tanks and in the deplating tanks is preferably of an acid type adapted for use with high current densities. For example, the electrolyte may be a copper fluoborate electrolyte containing equivalent copper from 7.2 to 18.6 ounces per gallon and hydrofluoboric acid from 2.5 to 8.6 ounces per gallon. Such an electrolyte might have a pH of from 1.0 to nearly zero, and preferably is maintained at a temperature of from 115° F. to 136° F. As another example, satisfactory results may be obtained by using a sulfuric acid electrolyte which may contain equivalent copper from 7.0 to 11.0 ounces per gallon and sulfuric acid from 3.0 to 6.0 ounces per gallon. Such an electrolyte preferably would have a pH of from 1.0 to 0.4, and would be kept at a temperature of from 60° F. to 85° F.

The current densities employed during the deplating steps of the process are preferably smaller than the current densities used during the plating steps. In practice, however, sometimes it may be found desirable to use higher current densities during the deplating steps. A rapid deplating action being more effective when excessively rough plated surfaces are encountered. Approximately 1800 amperes per square foot has been found to be an optimum current density for plating with the specified copper fluoborate or sulfuric acid electrolytes. The deplating current density may be varied from 500 to 3000 amperes per square foot.

An alkaline cyanide type electrolyte may alternatively be used in the several baths. In such case, the current density may be from 200–300 amperes per square foot and as many as twenty tanks may be used for the initial plating step, instead of four tanks as is illustrated for an acid type electrolyte. Furthermore, it may be considered desirable to use such alkaline type electrolytes for some stages of the process and acid type electrolytes for other stages of the process, with interposed washing tanks or neutralizing tanks.



Using the specified electrolytes and optimum current densities in the series of baths having alternate opposite potentials as has been described, the total thickness of the copper coating deposited is ordinarily from .003 to .004 inch. When three plating stages are used with two alternate intermediate deplating stages, a plurality of increments totaling over .001 inch may be deposited on the wire in each of the plating stages. Greater amounts may be deposited when correspondingly larger amounts are deplated.

The immersion length is a factor which affects the permissible rate of movement of the wire. Using an overall plating immersion length of about 160 feet, satisfactory results have been obtained by subjecting the wire to treatment while advancing it through the apparatus at speeds up to 100 feet per minute, although 84 feet per minute appears to be best related to other optimum conditions.

Manifold advantages are obtained from the above-described methods of alternately reversing the polarity of electrolytic baths through which a continuous wire is advanced. The wire receives an electrodeposited metallic coating having superior qualities of homogeneity, density and smoothness of its surface.

The deleterious effects resulting from the well known phenomenon of polarization are almost entirely eliminated by the alternate reversal of the potential and by the use of a plurality of tanks in each plating stage of the process. Polarization is related to the concentration of metallic ions in the electrolyte adjacent to the cathodic article, and the phenomenon becomes progressively pronounced as the concentration of the metallic ions is caused to become diminished by plating out. Since the effects of the phenomenon ordinarily are not significant until after a substantial amount of metal has been deposited, the successive deposition of small increments of metal in a plurality of tanks in conjunction with a moving cathodic article and a forced circulation of the electrolyte are effective to eliminate substantially all polarization.

In the present invention, the deplating action accomplishes considerably more than merely contributing to the reduction of polarization effects. Even when provisions have been made to control polarization, initially deposited metal usually exhibits superior density and uniformity. In a continuous plating operation, the metal deposited during the later stages of the process generally tends to be porous, coarse, nodular and otherwise heterogeneous. In the methods embodying the invention, from 5% to 10%, or more, of the thickness of a previously applied coating is removed by each deplating operation. By removing only subsequently applied portions of the coating and retaining only a series of increments of initially deposited metal, the resulting final product is a thick coating which is endowed with only the desirable qualities of initially deposited thin coatings.

The enumerated advantages accruing from the above-described aspects of methods embodying the invention are best realized by utilizing the apparatus illustrated. Furthermore, the apparatus described herein is manifestly more commercially feasible than any other conventional arrangement, and the coated wire may be manufactured at a high rate of speed. Installation and maintenance are simplified by having a plu-

rality of individual tanks, each of which performs a single operation and has a minimum of fittings. The series of tanks in tandem makes it possible to treat a multiplicity of wires running side by side through the apparatus, and individual wires can be introduced into and removed from the series of tanks with ease.

What is claimed is:

1. The method of making an electrical conductor having a steel core covered with a highly conductive layer of copper, which comprises impressing a cathodic charge upon a moving steel wire, continuously advancing the cathodically charged wire longitudinally through a series of electrolytic cells containing a copper-plating electrolyte to successively plate a plurality of thin layers of copper thereon, then impressing an anodic charge upon the plated wire, continuously advancing the anodically charged wire through an electrolytic cell containing a copper electrolyte, maintaining in said cell an anode current density sufficient to deplate from the wire during its passage through said cell from about 5% to about 10% of the previously electrodeposited layers of copper, then impressing a cathodic charge upon the partially deplated wire, continuously advancing the wire through another series of cells containing a copper-plating electrolyte to deposit another plurality of layers of copper thereon, and continuing to subject the advancing wire alternately to such a partial deplating step followed by such a depositing step until the resultant copper layer possesses a thickness sufficient to provide a highly conductive composite wire.

2. The method of making an electrical conductor having a steel core covered with a highly conductive layer of copper, which comprises impressing a cathodic charge upon a moving steel wire, continuously advancing the cathodically charged wire longitudinally through a series of electrolytic cells containing an acidic copper-plating electrolyte maintaining the cathode current density at about 1800 amperes per square foot in the series of plating cells to plate successively a plurality of thin layers of copper on the wire during its passage through these cells, then impressing an anodic charge upon the plated wire, continuously advancing the anodically charged wire through at least one electrolytic cell containing an acid copper electrolyte maintaining on the wire an anode current density of from about 500 to about 3000 amperes per square foot to deplate from about 5% to about 10% of the previously electrodeposited layers of copper from



the wire during its passage therethrough, then impressing a cathodic charge upon the partially deplated wire, continuously advancing the wire through another series of cells containing an acidic copper-plating electrolyte to deposit another plurality of layers of copper thereon, and continuing to subject the advancing wire alternately to such a partial deplating step followed by such a depositing step until the resultant copper layer is at least about .003 inch thick.

3. The method of making an electrical conductor having a steel core covered with a highly conductive layer of copper, which comprises impressing a cathodic charge upon a moving steel wire, continuously advancing the cathodically charged wire longitudinally through a series of electrolytic cells containing an alkaline cyanide copper-plating electrolyte maintaining the cathode current density at about 200 to about 300 amperes per square foot in the series of plating cells to plate successively a plurality of thin layers of copper on the wire during its passage through these cells, then impressing an anodic charge upon the plated wire, continuously advancing the anodically charged wire through at least one electrolytic cell containing an alkaline cyanide copper electrolyte, maintaining on the wire during its passage therethrough a current density sufficient to deplate from about 5% to about 10% of the previously electrodeposited layers of copper, then impressing a cathodic charge upon the partially deplated wire, continuously advancing the wire through another series of cells containing an alkaline cyanide copper-plating electrolyte to deposit another plurality of layers of copper thereon, and repeatedly subjecting the advancing wire to such a partial deplating step followed by such a depositing step until the resultant copper layer possesses a thickness sufficient to provide a highly conductive composite wire.


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