Jan. 26, 1954 G. E. MURRAY 2,667,453

METHODS OF ELECTROPLATING COPPER ON METAL ARTICLES

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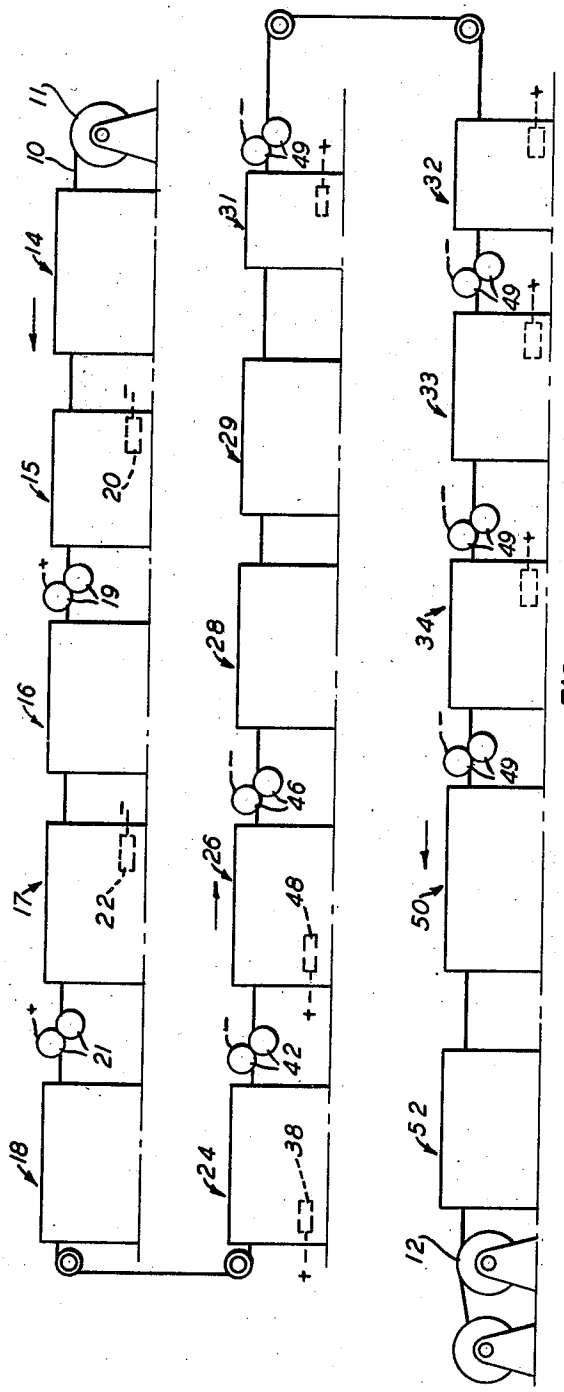


FIG. 1

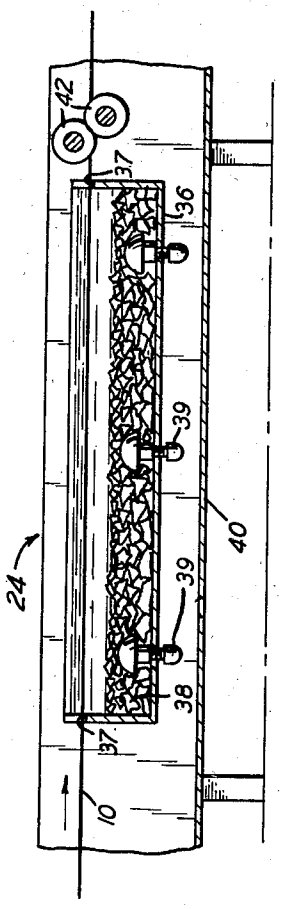


FIG. 2

INVENTOR
G. E. MURRAY
BY
ATTORNEY

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METHOD OF ELECTROPLATING COPPER ON METAL ARTICLES

Guy E. Murray, Towson, Md., assignor to Western Electric Company, Incorporated, New York, N. Y., a corporation of New York

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11 Claims. (Cl. 204—28)

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This invention relates to methods of electroplating copper on metal articles, and more particularly to methods of electroplating conductive layers of copper on steel wires.

In the manufacture of composite conductors including a steel core and a conductive copper covering enclosing the steel core, it has been proposed in the past to form the copper covering by electrodeposition upon the steel core. However, in the prior art methods it has been impossible to produce economically a composite conductor including steel wire having a thick, fine-grained, nonporous, copper covering, because whenever the current densities used on the core were sufficiently high to make the electroplating process economically feasible, the resulting coverings were coarse-grained and generally unsatisfactory.

An object of the invention is to provide new and improved methods of electroplating copper on metal articles.

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

Another object of the invention is to provide new and improved methods of electroplating tenaciously adherent, fine-grained, nonporous, thick copper coverings on steel cores at high rates of speed.

An additional object of the invention is to provide new and improved methods of electroplating heavy, electroconductive layers of copper on high strength steel wires to produce composite conductors suitable for use in communication systems, and the like.

A method illustrating certain features of the invention may include electroplating a very thin, fine-grained, copper flash deposit on a metal article in an alkaline bath having a predetermined low copper concentration therein, electroplating a heavier, protective deposit of copper on the fine-grained deposit in a second alkaline bath having a concentration of copper therein substantially greater than that in the first-mentioned bath, and then electroplating a heavy deposit of copper on the article in an acid copper plating bath.

A complete understanding of the invention may be obtained from the following detailed description of a method forming a specific embodiment thereof, when read in conjunction with the appended drawing, in which:

Fig. 1 is a schematic view of an apparatus for practicing a method forming one embodiment of the invention, and

Fig. 2 is a longitudinal, vertical section of a copper plating cell forming a portion of the apparatus shown in Fig. 1.

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A wire 10 composed of high tensile strength, high carbon steel is withdrawn from a supply 11 thereof by a capstan 12. In order to prepare the wire for electroplating copper thereon, it is advanced continuously by the capstan 12 through a degreaser 14, which applies trichloroethylene or other suitable degreasing solvent, to the wire to remove grease therefrom. The wire then passes successively through an alkaline electrolytic cleaning cell 15, which cleans the surface of the wire, a water rinsing bath 16, which washes the alklaine material from the surface of the wire, an acid electrolytic cell 17, which preferably contains sulphuric acid and further cleans the surface of the wire 10, and a water rinsing bath 18, which rinses the acid from the wire.

The cell 15 preferably contains an electrolyte consisting of a water solution of sodium orthosilicate having a concentration of from about 3.0 to about 7.0 ounces per gallon of water. The electrolyte in the cell 15 is kept at a temperature within the range of from about 140° F. to about 200° F. Positive contact sheaves 19—19 which engage the wire 10 and a suitable cathode 20 cause an electric current to flow through the wire and the electrolyte in the cell 15. The current density on the wire in the cell 15 is maintained at a value within the range of from about 50 to about 200 amperes per square foot.

The cell 17 preferably contains an electrolyte composed of a sulphuric acid solution having a concentration of from about 5% to about 25%, and the electrolyte is maintained at a temperature below 110° F. Positive contact sheaves 21—21 in engagement with the wire 10 and a cathode 22 cause an electric current to flow through the wire and the electrolyte at a current density on the wire from about 400 to about 1000 amperes per square foot.

The degreaser 14, the cells 15 and 17 and the baths 16 and 18 clean the surface of the wire 10 thoroughly so that the wire is very smooth and clean. The wire then is advanced as a cathode through a flash plating cell 24 having a low copper concentration, alkaline cyanide electrolyte to apply a very fine-grained, thin flash deposit on the wire. This thin copper deposit is applied at a cathode current density which, generally speaking, is low but which is a high current density for the copper concentration of the electrolyte. The grain structure of the flash deposit thus applied sets the pattern for subsequent deposits of copper substantially independently of copper concentration of the baths and current densities employed in applying those deposits. This flash deposit of copper adheres tenaciously to the wire.

The wire then is advanced as a cathode through

a plating cell 26 having a high copper concentration, alkaline cyanide plating bath to apply a further deposition of fine-grained copper on the flash deposit. A high cathode current density is maintained in the cell 26 to produce a high rate of copper deposition to build up the copper deposit rapidly to a thickness sufficient for plating thereon in subsequent acid plating baths without galvanic deposition of copper thereon. The wire is advanced continuously from the cell 26 through a water rinsing bath 28, and an acid bath 29 to wash off and neutralize any alkali on the wire. The wire then is advanced continuously as a cathode through acid plating cells 31, 32, 33 and 34, which plate copper on the previous deposit with very high current densities on the wire and very high rates of deposition.

The plating cell 24 may be constructed somewhat like that shown in Fig. 2, and consists of a conductive anode compartment 36 having slots 37—37 in the end walls thereof through which the wire 10 passes. A layer 38 of finely divided copper, such as scrap copper or small copper balls, rests on the bottom of the anode compartment 36, and the electrolyte employed is fed into the bottom of the compartment by means of inlet pipes 39—39. The electrolyte flows from the inlet pipes 39—39 through the layer 38 of finely divided copper, and out of the compartment 36 through the slots 37—37. The overflow falls into an outer compartment 40 from which it flows into a suitable tank (not shown), which serves as a reservoir from which the electrolyte is pumped through the inlet pipes 39—39.

The anode compartment 36 is connected to the positive side of a source of D. C. potential, thereby making the layer 38 of finely divided copper the anode in the cell 24, and the anode compartment is insulated from the outer compartment 40. The finely divided copper dissolves anodically to replenish the electrolyte with copper ions as copper is plated on the wire 10. Finely divided copper is added to the layer 38 from time to time to maintain an adequate supply of anode material. Contact sheaves 42—42, which are connected to the negative side of the D. C. source, are engaged by the wire 10, whereby the wire is made the cathode in the plating cell 24.

The copper concentration of the electrolyte in the cell 24 is low so that a very thin, fine-grained, flash deposit of copper is applied to the wire 10. This flash deposit is pure and very fine-grained in structure due to the diluteness of copper in the electrolyte in this cell, and it is tenaciously adherent to the wire because of the purity, denseness and fine-grained structure of the deposit. The cathode current density, which is kept sufficiently low for the low concentration of copper in the cell 24, should not be greater than about 75 amperes per square foot, and preferably should be between about 20 and about 50 amperes per square foot. The temperature of the bath is maintained at from about 140° F. to about 180° F.

A highly satisfactory electrolyte for use in the cell 24 is a mixed copper-potassium cyanide electrolyte having a composition within approximately the following limits:

	Oz. per gal.
Copper (as cyanide)	1.5 to 3.0
Potassium cyanide (free)	0.1 to 1.0
Potassium hydroxide (free)	3.0 to 6.0
Potassium carbonate	6.0 to 7.5

The most important elements of this type of electrolyte are the copper content and the free potassium cyanide content thereof. The preferred limits for the copper content are from 1.75 to 2.5 ounces per gallon, while the preferred limits for the free potassium cyanide content are from 0.3 to 0.7 ounce per gallon.

Negative contact sheaves 46—46 are provided adjacent to the cell 26 which is similar to the cell 24 and includes an anode 48 composed of divided metallic copper. A heavy deposit of copper is applied to the wire 10 in the cell 26 to protect the wire against galvanic cell copper deposition thereon in the acid plating cells 31, 32, 33 and 34. A deposit of from about 0.0001 inch to about 0.0002 inch is applied in the cell 26 under a substantially higher current density than was used in the cell 24. The deposit applied to the wire in the cell 26 is very fine-grained and dense inasmuch as the flash deposited on the wire in the cell 24 had already set the crystalline pattern of further deposits of copper.

A very satisfactory electrolyte for use in the cell 26 is a mixed copper-potassium cyanide bath having a composition within about the following limits:

	Oz. per gal.
Copper (as cyanide)	4.5 to 7.0
Potassium cyanide (free)	0.0 to 1.0
Potassium hydroxide (free)	3.0 to 6.0
Potassium carbonate	6.0 to 7.5

Here again, the concentrations of the copper and of the free cyanide are the most important elements of the electrolyte. The copper concentration preferably is within the range of from 4.5 to 6.5 ounces per gallon, and the free cyanide content preferably should be from 0.3 to 0.7 ounce per gallon.

The difference of potential between the contact sheaves 46—46 and the anode 48, the spacing of the anode from the path of the wire and the electrical resistance of the electrolyte are such that a cathode current density of from about 50 to about 200 amperes per square foot is maintained in the cell 26, the current density being kept substantially higher than that in the cell 24. The cell 26 is kept at a temperature of from about 140° to about 180° F.

The wire 10 emerges from the cell 26 having a plated copper covering thereon which is sufficiently thick to protect it against galvanic deposition of copper thereon. The water rinsing bath 28 and the acid bath 29 wash off or neutralize any alkali carried by the wire from the cells 24 and 26. The acid bath 29 may be a hydrofluoboric acid solution at a concentration of from about 1.0 to about 10.0 ounces per gallon, or a sulphuric acid solution at a concentration of from about 1.0 to about 10.0 ounces per gallon, depending on the type of electrolyte employed in the cells 31, 32, 33 and 34. The bath 29 is held at a temperature between about 60° F. and about 100° F. Since electrolyte used in the acid plating cells 31, 32, 33 and 34 may be a copper fluoborate or a copper sulphate solution, if copper fluoborate is used as the electrolyte in these cells, the hydrofluoboric acid solution is used in the neutralizing bath 29, while if copper sulphate is used in these cells, the sulphuric acid solution is used in the bath 29.

The wire 10 is advanced continuously through the cells 31, 32, 33 and 34 at a rate of speed between about 20 feet per minute and about 100 feet per minute, and the electrolytes in the cells are recirculated with a high degree of turbulence. Hence, high current densities may be employed

successfully in plating copper on the conductor without the deleterious action of hydrogen plating. The plating cells 31, 32, 33 and 34 are substantially like the cell 24 in construction, and have finely divided metallic copper anodes. The copper anodes dissolve electrolytically as the plating progresses to maintain the desired copper concentration therein. The wire in passing through the acid plating cells engages contactor sheaves 49—49.

A suitable copper fluoborate electrolyte for the acid plating cells will have a composition within substantially the following limits:

	Oz. per gal.
Copper (as fluoborate)	7.2 to 20.0
Hydrofluoboric acid (free)	2.5 to 3.6

The electrolyte preferably is operated at a temperature of from about 115° F. to about 136° F., and a cathode current density of from about 500 to about 3000 amperes per square foot is preferred. A good concentration range for these constituents is from about 15 to about 20 ounces per gallon of copper as fluoborate, and from about 3.5 to about 6.5 ounces per gallon of free hydrofluoboric acid. Good results are obtained when a cathode current density of from about 1000 to about 2500 amperes per square foot is employed.

A satisfactory sulphuric acid electrolyte for the acid plating cells will have a composition substantially as follows:

	Oz. per gal.
Copper (as sulphate)	7.0 to 11.0
Sulphuric acid (free)	3.0 to 6.0

The electrolyte preferably is kept at a temperature of from about 60° F. to about 85° F., and the acid plating cells using this type of electrolyte preferably are operated at a cathode current density of from about 500 to about 1200 amperes per square foot. Excellent results are obtained when the copper concentration is from about 8 to about 10 ounces per gallon, the free sulphuric acid concentration is from about 4.5 to about 5.5 ounces per gallon, and the cathode current density is from about 750 to about 1000 amperes per square foot.

The thickness of copper deposited in the cells 31, 32, 33 and 34 in one particular example has been from about 0.003 inch to about 0.004 inch. The deposit on the wire from the acid plating cells was very fine-grained and dense, being governed by the initial pattern of the grain of the copper deposit in the cyanide cell 24, even though a cathode current density as high as about 3000 amperes per square foot was used.

The covered wire 10 is advanced from the cell 34 to a dragout recovery bath 50 having water therein, and then through a rinsing bath 52. The water in the bath 50 washes any acid on the wire from the cell 34, and forms a dilute acid solution. This dilute acid solution is used to replace the water that is lost from the acid cells 31, 32, 33 and 34 from evaporation and other causes, and water is supplied to replenish it, from the bath 52, if desired.

Example I

In electroplating a high carbon, high tensile strength, steel wire having a diameter of 0.032 inch in one successful utilization of the invention, the wire was advanced continuously through the baths and cells 14, 15, 16, 17, 18, 24, 26, 28, 29, 31, 32, 33, 34, 50 and 52 at a rate of speed of 80 feet per minute. Trichloroethylene was used in the degreaser 14, and removed substantially all fats and grease from the wire. Any remaining grease and any other contaminants on the surface of the wire were removed by a sodium orthosilicate solution at a concentration of about 5.0 ounces per gal. in the cell 15, in which the wire was immersed as an anode for 18 seconds at an anode current density of 125 amperes per square foot. The wire was immersed in the acid cleaning cell 17 for 13 seconds as an anode at a current density of 550 amperes per square foot. The electrolyte in the cell 17 was a 15% sulphuric acid solution and was maintained at a temperature of 80° F. The cell 17 cleaned oxides completely from the surface of the wire, so that it was in excellent condition for the electrodeposition of copper thereon.

Each portion of the wire was immersed in the flash plating cell 24 for a period of 10 seconds at a cathode current density of 50 amperes per square foot, the period of time being just sufficient to form a thin film or flash thereon. The electrolyte was maintained at a temperature of 150° F. An alkali cyanide electrolyte having the following composition was used as the electrolyte in the cell 24:

	Oz. per gal.
Copper (as cyanide)	2.1
Potassium cyanide (free)	0.5
Potassium hydroxide (free)	5.0
Potassium carbonate	6.0

The flash deposit of copper produced on the wire in the cell 24 covered the wire completely, and was a thin, strongly adherent, flash film, which was very fine-grained in texture. This film was too thin to measure accurately.

Each portion of the wire advanced through the cell 26 was immersed therein for a period of 40 seconds at a cathode current density of 100 amperes per square foot. The cell was kept at a temperature of 150° F. A smooth, dense, very fine-grained deposit 0.00015 inch in thickness was formed on the flash deposit. The electrolyte in the cell 26 had the following composition:

	Oz. per gal.
Copper (as cyanide)	5.5
Potassium cyanide (free)	0.6
Potassium hydroxide (free)	5.0
Potassium carbonate	6.0

The acid neutralizing bath 29 was a 4% hydrofluoboric acid solution, and was maintained at room temperature (about 70° F.).

Each portion of the wire advanced through the acid plating cells 31, 32, 33 and 34 was immersed therein for a total period of 115 seconds at a cathode current density of 1800 amperes per square foot. The electrolytes in these cells were held at a temperature of 128° F. A smooth, dense, fine-grained deposit 0.003 inch in thickness was formed on the wire. The electrolyte in the cells 31, 32, 33 and 34 had the following composition:

	Oz. per gal.
Copper (as fluoborate)	18
Hydrofluoboric acid (free)	5.3

The entire deposit of copper on the wire was uniform, nonporous, dense, tenaciously adherent and fine-grained. There was no "treeing," and the peripheriy of the deposit was smooth. The temper of the steel wire core was substantially unaffected by the electroplating operation.

Example II

A high carbon, high tensile strength, steel wire having a diameter of 0.032 inch was advanced continuously through the baths and cells 14, 15, 16, 17, 18, 24, 26, 28, 29, 31, 32, 33, 34, 50 and 52 at a rate of speed of 80 feet per minute. Trichloroethylene in the degreaser 14 removed substantially all fats and greases from the wire, and this cleaning was completed in the cell 15, having therein an aqueous solution of sodium orthosilicate at a concentration of about 5.0 ounces per gallon in which the wire was immersed for 18 seconds as an anode at a current density of 125 amperes per square foot. The wire was immersed in the cell 17 for 13 seconds as an anode at a current density of 550 amperes per square foot. The electrolyte in the cell 17 was a 15% solution of sulphuric acid, and was kept at a temperature of 180° F. The cell 17 cleaned oxides from the surface of the wire and polished the surface of the wire to a matte condition.

Immersion time of the wire as a cathode in the flash plating cell 24 was 10 seconds, and a cathode current density of 50 amperes per square foot was employed. This immersion time was just sufficient to form a flash film at the current density employed. The temperature of the electrolyte was 150° F. An alkali cyanide electrolyte having the following composition was used in the cell 24:

	Oz. per gal.
Copper (as cyanide)	2.1
Potassium cyanide (free)	0.5
Potassium hydroxide (free)	5.0
Potassium carbonate	6.0

The flash deposit of copper applied to the wire in the cell 24 covered the periphery of the wire completely, and was a thin, strongly adherent, very fine-grained film.

Each portion of the wire advanced through the cell 26 was immersed therein as a cathode for a period of 40 seconds at a cathode current density of 100 amperes per square foot. The electrolyte was maintained at a temperature of 150° F. A smooth, dense, very fine-grained deposit 0.00015 inch in thickness was formed on the flash deposit. The electrolyte in the cell 26 had the following composition:

	Oz. per gal.
Copper (as cyanide)	5.5
Potassium hydroxide (free)	5.0
Potassium carbonate	6.0
Potassium cyanide	0.6

The acid neutralizing bath 29 consisted of a 10% sulphuric acid solution, and was maintained at a temperature of about 70° F.

Each portion of the wire advanced as a cathode through the acid plating cells 31, 32, 33 and 34 was immersed in these cells for a total period of 230 seconds at a cathode current density of 900 amperes per square foot and at a bath temperature of 70° F. A smooth uniform, dense, fine-grained deposit 0.003 inch in thickness was formed on the wire. The electrolyte in the cells 31, 32, 33 and 34 had the following composition:

	Oz. per gal.
Copper (as sulphate)	9.0
Sulphuric acid (free)	5.0

The entire deposit of copper on the wire was uniform, dense tenaciously adherent and fine-grained. The periphery of the deposit was smooth and free of nodes and other projections, the deposit was nonporous, and the initial condition of the steel wire core was practically unaffected by the electroplating operation.

The above-described methods are very rapid and economical. They provide a very fine-grained, dense, copper deposit on a steel article in a very short period of time, and the deposit of copper is uniform therearound. A very high tensile strength steel wire may be used as the steel core 10 without impairing the condition of anneal thereof by the above-described methods, inasmuch as the electroplating operations are conducted at relatively low temperatures. These results have been unobtainable by the use of processes heretofore known.

The resulting composite wire has a very high tensile strength, and also is electrically conductive, the conductivity of the wire produced in accordance with the above-outlined specific examples being about 30% of that of a pure copper wire of the same size. The composite wire may be used for communication purposes, and is excellent for the manufacture of drop wire, line wire, and other wires where a high tensile strength wire having good conductivity is required.

While it is possible to electroplate heavy coatings of copper upon cores solely by the use of cyanide baths, the copper deposits thus formed tend to be brittle, and composite conductors having a steel core provided with a heavy copper covering deposited from cyanide baths alone are unsatisfactory for communication purposes. When the grain pattern of the deposit is established in a low copper concentration cyanide bath in accordance with the methods described hereinabove, and the steel core is protected from reaction with an acid plating bath in the manner described hereinabove, a heavy deposit of copper may be formed upon a steel core quite rapidly by the use of an acid plating bath, and the deposite thus formed will not have the tendency to be brittle that is evident when a cyanide bath is employed to produce the copper plate.

Although in the specific embodiments outlined hereinabove, hydrofluoboric acid and sulphuric acid copper plating baths have been described, satisfactory results may be obtained when the plating performed in an acid bath is carried out in other baths that are acid in nature. For example, instead of hydrofluoboric acid or a sulphuric acid bath, an acid copper plating bath having as its principal constituent another suitable acid, such as sulfamic acid, fluosilicic acid, acetic acid or a sulphonic acid, for example, phenolsulphonic acid or benzene-di-sulphonic acid, may be used.

What is claimed is:

1. The method of electroplating copper on steel wires, which comprises continuously advancing a steel wire as a cathode seriatim through an alkaline cyanide flash coating bath containing copper dissolved therein at a concentration within the range of from about 1.5 to about 3.0 ounces per gallon, a second alkaline cyanide bath containing copper dissolved therein at a concentration within the range of from about 4.5 to about 7.0 ounces per gallon, and an acid plating bath containing a still higher concentration of copper dissolved therein, maintaining in the cyanide flash bath a cathode current density within the range of from about 20 to about 75 amperes per square foot for a period of time sufficient to deposit a very thin and very fine-grained flash coating of copper which sets a size pattern

that causes subsequent deposits on the wire to be similarly fine-grained, maintaining in the second cyanide bath a cathode current density substantially higher than the current density in the flash coating bath to deposit a fine-grained copper coating substantially thicker than the flash coating of copper, and maintaining in the acid plating bath a still higher cathode current density to form a thick copper deposit which increases materially the electrical conductivity of the resulting composite wire.

2. The method of electroplating copper on steel wires, which comprises continuously advancing a steel wire as a cathode seriatim through an alkaline cyanide flash coating bath containing copper dissolved therein at a concentration within the range of from about 1.5 to about 3.0 ounces per gallon, a second alkaline cyanide bath containing a higher concentration of copper dissolved therein, and an acid plating bath containing a still higher concentration of copper dissolved therein, maintaining in the cyanide flash bath a cathode current density within the range of from about 20 to about 75 amperes per square foot for a period of time sufficient to deposit a very thin and very fine-grained flash coating of copper which sets a size pattern that causes subsequent deposits on the wire to be similarly fine-grained, maintaining in the second cyanide bath a cathode current density within the range of from about 50 to about 200 amperes per square foot to deposit a fine-grained copper coating substantially thicker than the flash coating of copper, and maintaining in the acid plating bath a still higher cathode current density to form a thick copper deposit which increases materially the electrical conductivity of the resulting composite wire.

3. The method of electroplating copper on steel wires, which comprises continuously advancing a steel wire as a cathode seriatim through an alkaline cyanide flash coating bath containing copper dissolved therein at a concentration within the range of from about 1.5 to about 3.0 ounces per gallon, a second alkaline cyanide bath containing a higher concentration of copper dissolved therein, and a series of acid plating baths containing a higher concentration of dissolved copper than the concentration in the second alkaline cyanide bath, maintaining in the cyanide flash bath a cathode current density within the range of from about 20 to about 75 amperes per square foot for a period of time sufficient to deposit a very thin and very fine-grained flash coating of copper which sets a size pattern that causes subsequent deposits on the wire to be similarly fine-grained, maintaining in the second cyanide bath a cathode current density within the range of from about 50 to about 200 amperes per square foot to deposit a fine-grained copper coating substantially thicker than the flash coating of copper, and maintaining in the acid plating baths a cathode current density within the range of from about 500 to about 3000 amperes per square foot to form a series of increments of a thick copper deposit which increases materially the electrical conductivity of the resulting composite wire.

4. The method of electroplating copper on steel wires, which comprises advancing continuously a steel wire as a cathode seriatim through an alkaline cyanide, grain-pattern-setting bath having copper dissolved therein at a concentration within the range of from about 1.5 to about 3.0 ounces per gallon, an alkaline cyanide plating bath having copper dissolved therein at a concentration from about 4.5 to about 7.0 ounces per gallon and an acid plating bath having copper dissolved therein at a high concentration, maintaining a current density on the portion of the wire in the grain-pattern-setting bath within the range of from about 20 to about 75 amperes per square foot and for such a period of time as to just form a very thin, fine-grained, copper, flash deposit on the wire, maintaining a current density on the portion of the wire in the cyanide plating bath within the range of from about 50 to about 200 amperes per square foot to form a fine-grained copper deposit on the flash deposit to protect the wire against galvanic action in the acid plating bath, and electroplating a heavy deposit of copper on the second-mentioned deposit in the acid plating bath at a high cathode current density.

5. The method of electroplating copper on steel wires, which comprises advancing continuously a steel wire as a cathode seriatim through an alkaline cyanide, grain-pattern-setting bath having copper dissolved therein at a concentration of about 2.1 ounces per gallon, an alkaline cyanide plating bath having copper dissolved therein at a concentration of about 5.5 ounces per gallon and an acid plating having copper dissolved therein at a very high concentration, causing an electric current of such magnitude to flow through the grain-pattern-setting bath that the current density on the portion of the wire in that bath is from about 20 to about 75 amperes per square foot whereby a very thin, fine-grained, copper flash deposit is formed on the wire, causing an electric current of such magnitude to flow through the cyanide plating bath that the current density on the portion of the wire in that bath is from about 50 to about 200 amperes per square foot to form a fine-grained copper deposit on the flash deposit, and electroplating a heavy deposit of copper on the second-mentioned deposit in the acid plating bath at a very high cathode current density.

6. The method of electroplating copper on steel wires, which comprises advancing continuously a steel wire as a cathode seriatim through an alkali cyanide grain-pattern-setting bath having copper dissolved therein at a concentration from about 1.5 to about 3.0 ounces per gallon, through an alkali cyanide plating bath having copper dissolved therein at a concentration of from about 4.5 to about 7.0 ounces per gallon and through an acid plating bath having copper dissolved therein as copper fluoborate at a copper concentration of from about 7.2 to about 20.0 ounces per gallon, causing to flow through the grain-pattern-setting bath an electric current of such magnitude that the current density on the portion of the wire in that bath is from about 20 to about 75 amperes per square foot and for such a period as to form a very thin, fine-grained, copper, flash deposit on the wire, causing to flow through the cyanide plating bath an electric current of such magnitude that the current density on the portion of the wire in that bath is from about 50 to about 200 amperes per square foot to form a protective, fine-grained, copper deposit on the flash deposit, and electroplating a heavy deposit of copper on the second-mentioned deposit in the acid plating bath at a cathode current density of from about 500 to about 3000 amperes per square foot.

7. The method of forming an electroconductive layer of copper on steel wires, which com-

prises advancing a steel wire continuously as a cathode through a cyanide flash bath containing from about 1.75 to about 2.5 ounces per gallon of copper as cyanide and from about 0.3 to 0.7 ounce per gallon of free potassium cyanide, through a cyanide plating bath containing from about 4.5 to 6.5 ounces per gallon of copper as cyanide and from about 0.3 to 0.7 ounce per gallon of free potassium cyanide, and then through an acid plating bath containing from about 15 to 20 ounces per gallon of copper as fluoborate and from about 3.5 to about 6.5 ounces per gallon of free hydrofluoboric acid, electroplating each increment of the wire passing through the cyanide flash bath at a cathode current density of from about 20 to about 75 amperes per square foot for a period sufficient to form only a thin, fine-grained, flash deposit on the wire, electroplating each increment of the wire passing through the cyanide plating bath at a cathode current density of from about 50 to about 200 amperes per square foot for a period sufficient to form a fine-grained, protective deposit of copper on the flash deposit, and electroplating each increment of the wire passing through the acid plating bath at a cathode current density of at least 500 amperes per square foot for a period sufficient to form a deposit of copper on the protective deposit sufficiently thick to materially increase the electrical conductivity of the resulting composite wire.

8. The method of electroplating copper on steel wires, which comprises advancing continuously a steel wire as a cathode seriatim through a cyanide grain-pattern-setting bath having copper dissolved therein as cyanide at a concentration of 2.1 ounces of copper per gallon, free potassium cyanide at a concentration of 0.5 ounce per gallon, free potassium hydroxide at a concentration of 5.0 ounces per gallon and potassium carbonate at a concentration of 6.0 ounces per gallon, through a cyanide plating bath having copper dissolved therein as cyanide at a copper concentration of 5.5 ounces per gallon, free potassium cyanide at a concentration of 0.6 ounce per gallon, free potassium hydroxide at a concentration of 5.0 ounces per gallon and potassium carbonate at a concentration of 6.0 ounces per gallon, and through an acid plating bath having copper dissolved therein as copper fluoborate at a copper concentration of 18 ounces of copper per gallon, and free hydrofluoboric acid at a concentration of about 5.3 ounces per gallon, electroplating each portion of the wire in the grain-pattern-setting bath for about 10 seconds at a current density of about 50 amperes per square foot whereby a very thin, fine-grained, copper flash deposit is formed on the wire, electroplating each portion of the wire in the cyanide plating bath for about 40 seconds at a current density of about 100 amperes per square foot to form a fine-grained copper deposit on the flash deposit, and electroplating each portion of the wire in the acid plating bath for about 115 seconds at a current density of about 1800 amperes per square foot to form a heavy deposit of copper on the second-mentioned deposit.

9. The method of electroplating copper on steel wires, which comprises advancing continuously a steel wire as a cathode seriatim through an alkaline cyanide grain-pattern-setting bath having copper dissolved therein at a concentration of from about 1.5 to about 3.0 ounces per gallon, through an alkaline cyanide plating bath having copper dissolved therein at a concentration of from about 4.5 to about 7.0 ounces per gallon and through a sulphuric acid plating bath having copper dissolved therein at a concentration of from about 7.0 to about 11.0 ounces per gallon, maintaining a low current density on the portion of the wire in the grain-pattern-setting bath for such a period of time as to form on the wire a very thin, fine-grained, copper, flash deposit, maintaining a higher current density on the portion of the wire in the cyanide plating bath for such a period of time as to form on the wire a fine-grained copper deposit on the flash deposit to protect the wire against galvanic deposition in the acid plating bath, and electroplating a heavy deposit of copper on the second-mentioned deposit in the sulphuric acid plating bath at a cathode current density of from about 500 to about 1000 amperes per square foot.

10. The method of electroplating a conductive layer of copper on steel wires, which comprises advancing a steel wire continuously as a cathode through a cyanide flash bath containing from about 1.75 to about 2.5 ounces per gallon of copper as cyanide and from about 0.3 to 0.7 ounce per gallon of free potassium cyanide, through a cyanide plating bath containing from about 4.5 to 6.5 ounces per gallon of copper as cyanide and from about 0.3 to 0.7 ounce per gallon of free potassium cyanide, and then through an acid plating bath containing from about 8 to about 10 ounces per gallon of copper as sulphate and from about 4.5 to about 5.5 ounces per gallon of free sulphuric acid, electroplating each increment of the wire passing through the flash cyanide bath at a cathode current density of from about 20 to about 75 amperes per square foot for a period sufficient to form only a thin, fine-grained, flash deposit on the wire, electroplating each increment of the wire passing through the cyanide plating bath at a cathode current density of from about 50 to about 200 amperes per square foot for a period sufficient to form a fine-grained, protective deposit of copper on the flash deposit, and electroplating each increment of the wire passing through the acid plating bath at a cathode current density of at least 500 amperes per square foot for a period sufficient to form a deposit of copper on the protective deposit sufficiently thick to materially increase the electrical conductivity of the resulting composite wire.

11. The method of electroplating copper on steel wires, which comprises advancing continuously a steel wire as a cathode seriatim through a cyanide grain-pattern-setting bath having copper dissolved therein as cyanide at a copper concentration of 2.1 ounces per gallon, free potassium cyanide at a concentration of 0.5 ounce per gallon, free potassium hydroxide at a concentration of 5.0 ounces per gallon and potassium carbonate at a concentration of 6.0 ounces per gallon, through a cyanide plating bath having copper dissolved therein as cyanide at a copper concentration of about 5.5 ounces per gallon, free potassium cyanide at a concentration of 0.6 ounce per gallon, free potassium hydroxide at a concentration of 5.0 ounces per gallon and potassium carbonate at a concentration of 6.0 ounces per gallon, and through a sulphuric acid plating bath having copper dissolved therein as copper sulphate at a copper concentration of 9.0 ounces per gallon and free sulphuric acid at a concentration of 5.0 ounces per gallon, maintaining in the grain-pattern-setting bath a cathode current density of 50 amperes per square foot for a

period of 10 seconds to form on the wire a very thin, fine-grained, copper, flash deposit, maintaining in the cyanide plating bath a cathode current density of 100 amperes per square foot for a period of 40 seconds to form on the wire a fine-grained copper deposit on the flash deposit to protect the wire against galvanic deposition in the acid plating bath, and maintaining in the acid plating bath a cathode current density of 900 amperes per square foot for a period of 230 seconds to form a heavy deposit of copper on the second-mentioned deposit.

GUY E. MURRAY.

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