

June 4, 1957

W. D. BUCKINGHAM

2,794,775

ELECTROPLATING WITH TUNGSTEN

Filed May 21, 1954

2 Sheets-Sheet 1

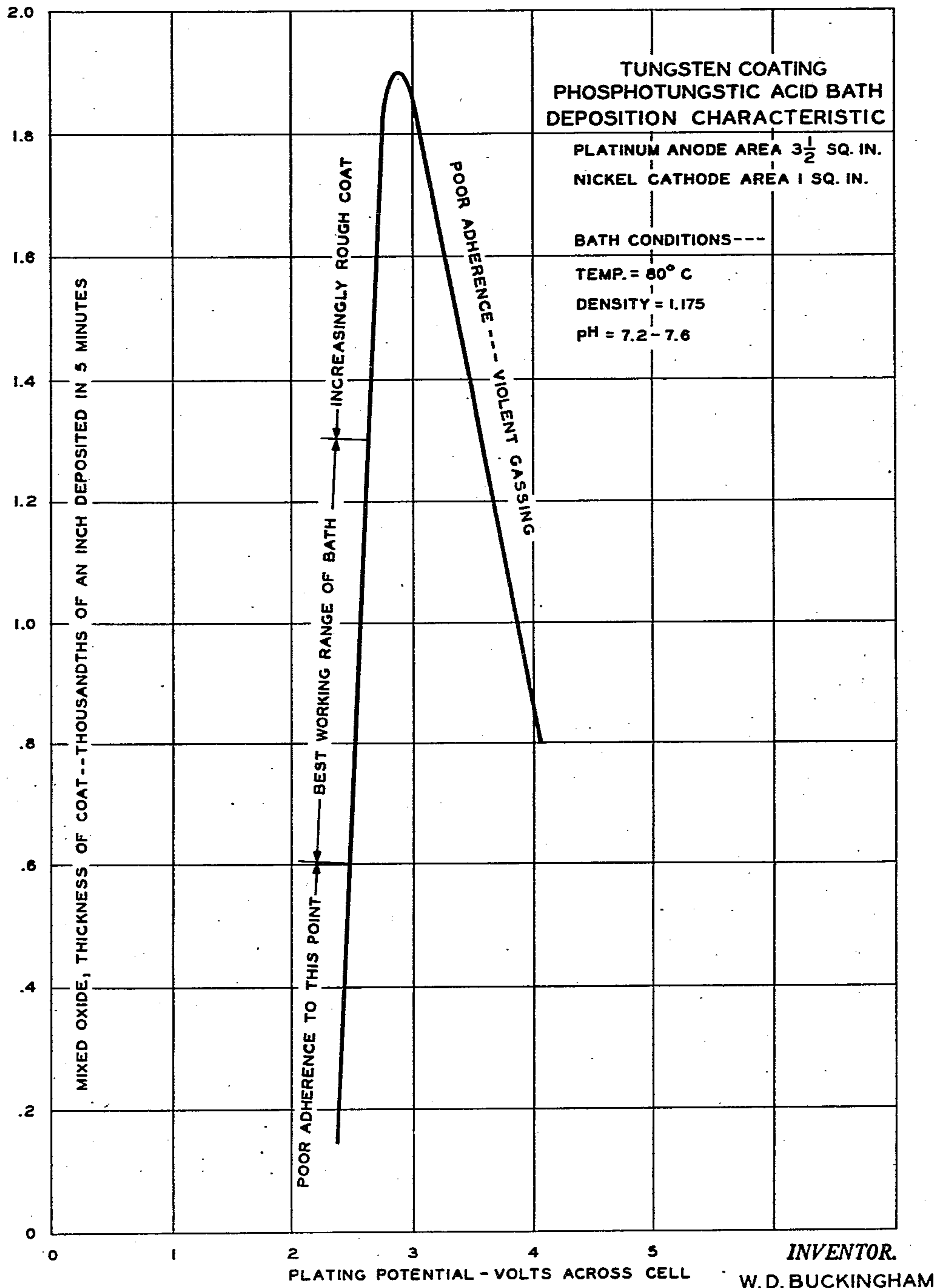


FIG. I

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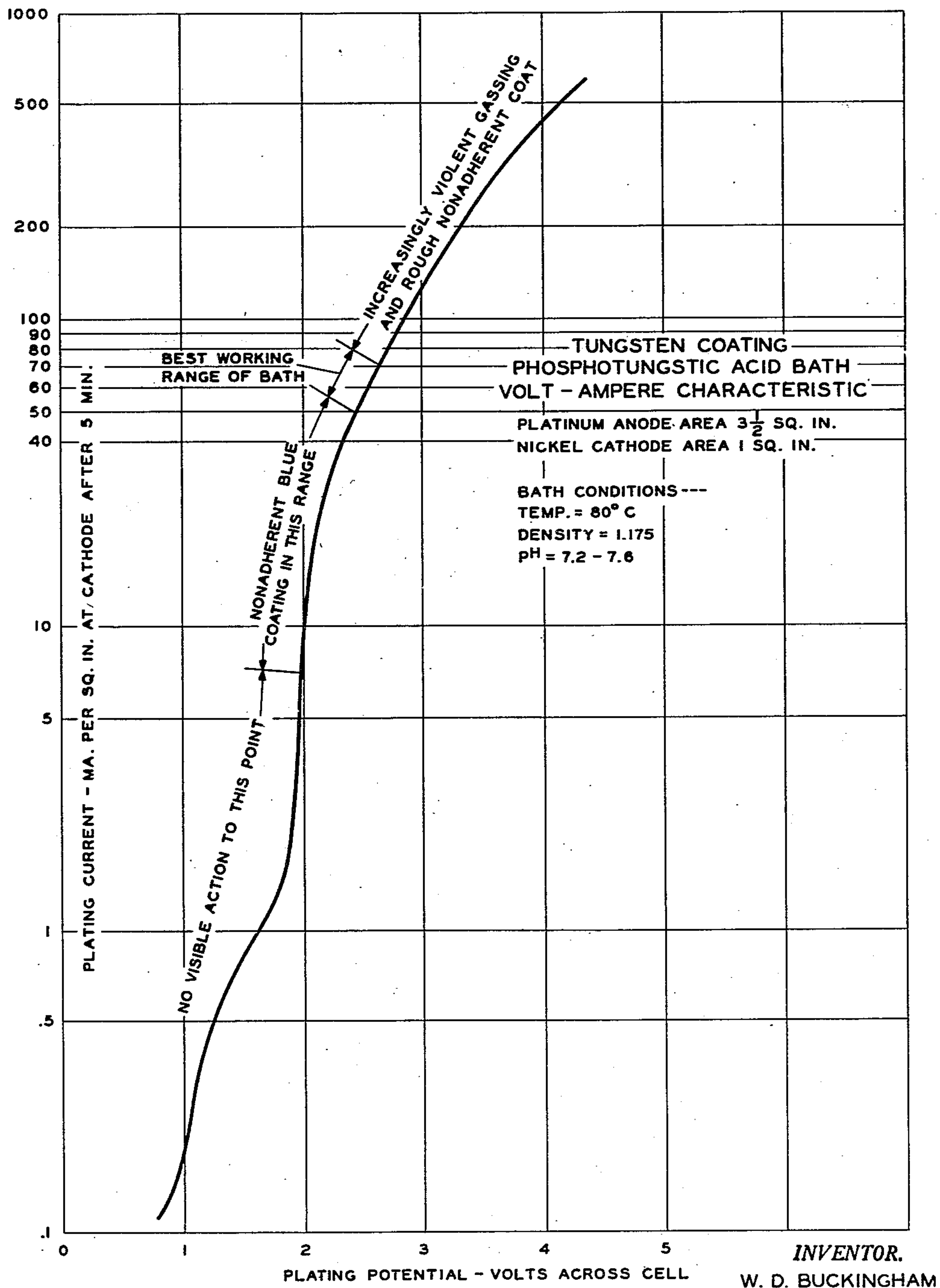


FIG. 2

INVENTOR.

W. D. BUCKINGHAM

BY

W. A. Presson

ATTORNEY

2,794,775

ELECTROPLATING WITH TUNGSTEN

William D. Buckingham, Southampton, N. Y., assignor
to The Western Union Telegraph Company, New York,
N. Y., a corporation of New York

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7 Claims. (Cl. 204—37)

This invention relates to a method of plating coatings of pure, or substantially pure, tungsten, and to an article having a plating of electrodeposited substantially pure tungsten.

Heretofore it has been possible to electrodeposit coatings of tungsten alloys or metals coplated with tungsten, for example, tungsten alloyed with nickel, iron, tantalum, cobalt and manganese, but so far as I am aware it has not been possible to produce a plating of pure, or substantially pure, tungsten by other than vapor deposition methods. Plating effected by vapor deposition has not proved entirely satisfactory; such a plating is not as dense or as adherent or as smooth as desired, and the thermal decomposition method is cumbersome and is wasteful of the plating material.

Various kinds and shapes of articles readily may be plated with the method of the instant invention, so long as they may be made the cathode in a plating bath. For example, in one type of an electromagnetic high speed relay a small round ball of iron or other magnetic material within an evacuated tube is employed as an armature which rolls back and forth alternately to engage two fixed contacts within the tube under the influence of the changing magnetic field of the relay in response to received telegraph signals. Such a delay is disclosed in my copending application Serial No. 352,355, filed May 1, 1953, and now Patent No. 2,732,454. The ball armature should revolve during operation of the relay and should have a surface of a material suitable for electrical contact purposes. An important characteristic of such a material is that it will not weld easily to the material of the fixed contacts. Tungsten satisfies this requirement to the highest degree.

To prevent the ball from sticking due to excessive residual magnetism it may be annealed to a degree such that it retains sufficient magnetism to cause rotation but not enough to cause sticking. The step of annealing, however, reduces the hardness of the ball so that after a period of use the ball generally will show a slight pattern on its surface produced by innumerable very small flat areas. To avoid this effect the ball may be plated with a hard coating, and a coating of tungsten offers an excellent solution, but heretofore no satisfactory method of plating a tungsten coating on such ball was available.

The objects of the instant invention are to provide a suitable method of plating tungsten by electrodeposition and to produce an article having a dense, smooth adherent plating of pure, or substantially pure, electrodeposited tungsten.

In the accompanying drawings:

Fig. 1 is a graph depicting the deposition characteristic of a phosphotungstic acid plating bath employed in the method of the invention; and

Fig. 2 is a graph, drawn on a logarithmic scale, depicting the volt-ampere characteristic of the plating bath.

The plating bath preferably is prepared as follows: A quantity of phosphotungstic acid is dissolved in water, the relative quantities being in the ratio of approximately 80

grams of the acid to 300 milliliters of water. This ratio may be varied within reasonable limits, for example, a solution of 20 grams of the acid and 100 ml. of water has also been employed, that is, the ratio of acid to water may vary from approximately 1:4 to approximately 1:5. The acid solution is then substantially neutralized by the addition of an aqueous solution of potassium hydroxide, the relative quantities being in the ratio of approximately 20 grams of the hydroxide to 50 milliliters of water. Sodium hydroxide or ammonium hydroxide in molecular equivalents may be used instead of the potassium hydroxide if desired.

The hydroxide solution is added, with stirring or other agitation, to the phosphotungstic acid solution until the pH of the latter solution equals approximately 7.2 to 7.6. As the hydroxide solution is added, a heavy white precipitate is formed which disappears when the neutral point is reached.

The article to be plated is then immersed in the bath and operates as the cathode in the forming circuit; a platinum electrode preferably is employed as the anode. Small articles, such as the ball armature above mentioned, may conveniently be suspended in the bath by means of a nickel-plated Alnico magnet. The bath is operated at a temperature of from 60° C. to 80° C. with the specific gravity or density in the range of 1.175 to 1.250.

The voltage across the electrodes of the plating both must be maintained within close limits. For example, with a nickel cathode area of 1 sq. in., a platinum anode area of 3½ sq. in., and a bath temperature of 80° C. with a density of approximately 1.175 and a pH value of 7.2–7.6, the following conditions have been found to prevail:

Volts	Current Through Bath in m. a.						Thickness of coat in 5 min., inches	See note—
	0 Min.	1 Min.	2 Min.	3 Min.	4 Min.	5 Min.		
1.5-----	5	1.1	.88	.84	.80	.80	0	#1
1.73-----	9	1.54	1.24	1.14	1.14	1.14	0	#1
1.9-----	12	3.2	2.9	2.6	2.4	2.2	0	#1
2.0-----	19	8.9	8.1	7.8	7.3	7.0	0	#2
2.1-----	32	26	23	21.5	19.5	19	0	#3
2.25-----	85	43	38	35	32	30	0	#3
2.35-----	115	53	44	34	30	29	.00015	#4
2.45-----	130	59	56	55.5	54	54	.0006	#5
2.65-----	200	85	73	70	68.5	65.5	.0013	#6
2.75-----	210	98	83.5	80	77	73.5	.0018	#7
2.87-----	250	114	102	97	92.5	90	.0019	#7
3.0-----	325	145	134	129	123.5	120	.0017	#7

Note #1: No visible action occurs at this point.
Note #2: A blue color becomes slightly visible about the cathode.
Note #3: A definite black coating forms on the cathode but comes off in solution.
Note #4: A black coat forms on the cathode with no visible bubbling.
Note #5: A very adherent coat forms.
Note #6: This coat slightly less adherent, than at 2.45 volts.
Note #7: Gassing at cathode knocks off flakes of coating resulting in very rough coat. Gassing becomes increasingly violent as voltage increases from this point. The coat is also increasingly more rough and less adherent.

From the foregoing table and the observed results it is shown that the permissible range of the plating voltage is critical, i. e., approximately 2.35–2.65 volts; the optimum value lies within the range of 2.4–2.6 volts, and preferably is 2.45 volts. Fig. 1 of the drawings graphically depicts the best working range of the bath; the ordinates show the thickness of the black or bluish-black coating of a complex intermediate oxide or hydrated oxide of tungsten that forms on the object, and the abscissas show the values of the plating potential for the best working range. Fig. 2 shows on a logarithmic scale the volt-ampere characteristic of the bath. It will be understood that the density of the current through the plating bath is that which obtains when the cathode has an area of 1sq. in. exposed to the bath. With a cathode having a smaller area, for example, a relay ball arma-

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ture of the character hereinbefore stated, the cathode area will be less than 1 sq. in. and the values of current density in milliamperes will be correspondingly smaller than those set forth in the table and depicted in the graphs for the same rate of deposit of the coating, since current density involves the concept of area as well as current. The plating voltage, however, is held within the limits above given by any suitable means, for example, a potentiometer or voltage divider across the output of a 6-volt storage battery and a galvanometer relay for controlling a charging circuit for the battery.

After the black or bluish-black oxide coating has formed on the object to a thickness of the order of a thousandth of an inch, the object is removed from the plating bath, and is then heated in a furnace in a reducing atmosphere, such as hydrogen, endogas, carbon monoxide or the like, at or above an incandescent temperature, and preferably about 1000° C., for approximately one-half hour. There then remains a very thin adherent coating of pure, or substantially pure, tungsten; if the thickness of the oxide coating was approximately 0.001 inch, in the reducing furnace the tungsten coating drops to about 0.0001 or 0.0002 inch which is approximately $\frac{1}{10}$ to $\frac{1}{5}$ that of the oxide coating. The object is again placed in the plating bath and a second coating plated thereon under the conditions above set forth, which second coating is also heated in a reducing atmosphere in the manner stated above. Successive thin coatings thus applied result in a dense and compact finished coating of desired thickness. The oxide coating which forms on the nickel plated magnet that holds the ball or other object in the bath is washed off after each plating operation. Between successive coating and heating cycles the ball preferably is worked in a raceway under pressure to increase the density, ductility and toughness of the tungsten layer; other objects of different configuration also may be worked by rolling under pressure or in any suitable manner for the same purpose.

The composition of the complex oxide coating which is formed on the object is not determinable by ordinary analytical methods including spectographic, and it is not known whether it is a single compound or a mixture. It has been determined, however, that in the reducing furnace the coating is reduced to pure, or substantially pure, tungsten. For brevity in the claims the expression "an oxide of tungsten" is employed to define this complex compound.

What is claimed is:

1. The method of forming a coating of tungsten on an object which comprises making said object the cathode in a plating bath of an aqueous solution of phosphotungstic acid to which has been added an aqueous solution of an alkali hydroxide in an amount to cause the pH of the bath to have a value of approximately 7.2 to 7.6 with a specific gravity in the range 1.175 to 1.250, passing a plating current through said bath, maintaining the temperature of said bath at approximately 60° C. to 80° C., controlling the plating voltage to a value of approximately 2.35 to 2.65 volts to cause to be deposited on the object

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a thin adherent coating of an oxide of tungsten, removing the object from the plating bath and heating the same in a reducing atmosphere at an elevated temperature until said coating is reduced to a thin adherent layer of substantially pure tungsten, and repeating the foregoing plating and reducing cycle until a layer of tungsten of desired thickness is deposited on said object.

2. The method according to claim 1, in which the object is kept in the bath during each plating operation until a coating of said oxide of tungsten of approximately .0006 to .001 of an inch has been deposited on the object, and in which said coating is heated in the reducing atmosphere until a layer of approximately $\frac{1}{10}$ to $\frac{1}{5}$ of that of the oxide-coating remains during each plating and reducing cycle.

3. The method according to claim 1, in which the tungsten layer is worked under pressure between successive plating and reducing cycles to increase the density and toughness of the coating.

4. The method of forming a coating of tungsten on an object which comprises making said object the cathode in a plating bath of an aqueous solution of phosphotungstic acid in which the ratio of acid to water is approximately 1:4 to 1:5 and to which has been added a sufficient amount of an aqueous solution of an alkali hydroxide of approximately 40% concentration by weight to cause the pH of the bath to have a value of approximately 7.2 to 7.6 with a specific gravity in the range 1.175 to 1.250, passing a plating current through said bath, maintaining the temperature of said bath at approximately 60° C. to 80° C., controlling the plating voltage to a value of approximately 2.35 to 2.65 volts to cause to be deposited on the object a thin adherent coating of an oxide of tungsten, removing the object from the plating bath and heating the same in a reducing atmosphere at an elevated temperature until said coating is reduced to a thin adherent layer of substantially pure tungsten, and repeating the foregoing plating and reducing cycle until a layer of tungsten of desired thickness is deposited on said object.

5. The method according to claim 4, in which said alkali hydroxide consists essentially of a compound of the class consisting of potassium hydroxide, sodium hydroxide and ammonium hydroxide.

6. The method according to claim 4, in which said basic compound is potassium hydroxide.

7. The method according to claim 4, in which said plating voltage is controlled to a value of substantially 2.45 volts.

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