March 20, 1951 J. M. BOOE **2,545,566**

ELECTRODEPOSITION OF METALS AND ALLOYS

Filed March 11, 1943 2 Sheets-Sheet 1

Fig. 1

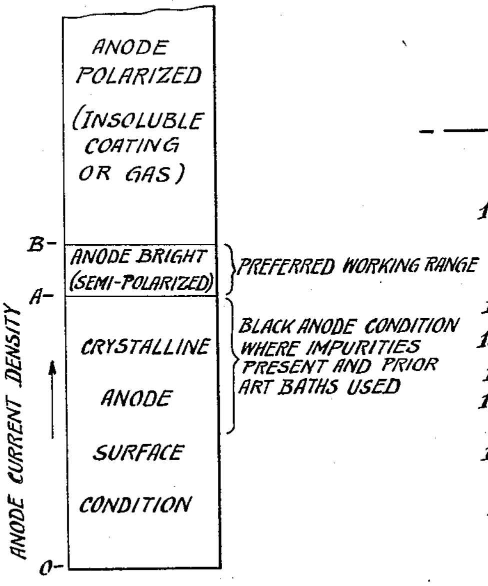


Fig. 2

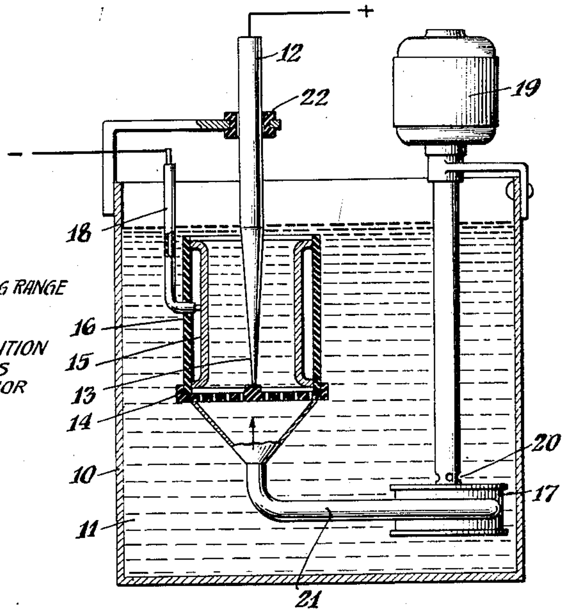


Fig. 3

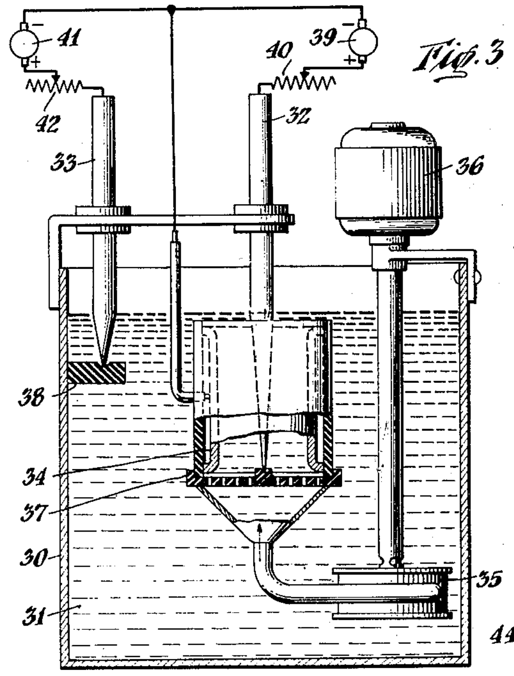
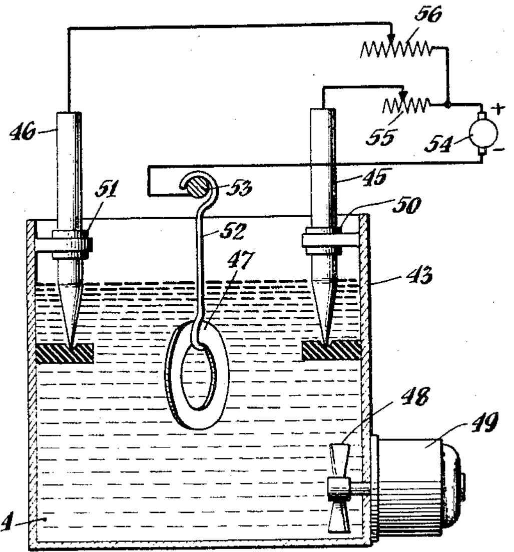


Fig. 4



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ELECTRODEPOSITION OF METALS AND ALLOYS

Filed March 11, 1943 2 Sheets-Sheet 2

Fig. 5

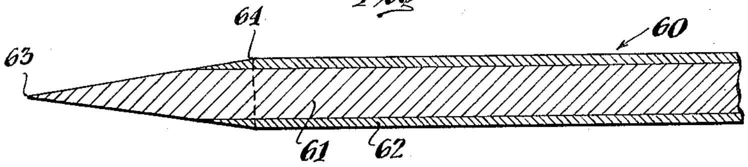


Fig. 6

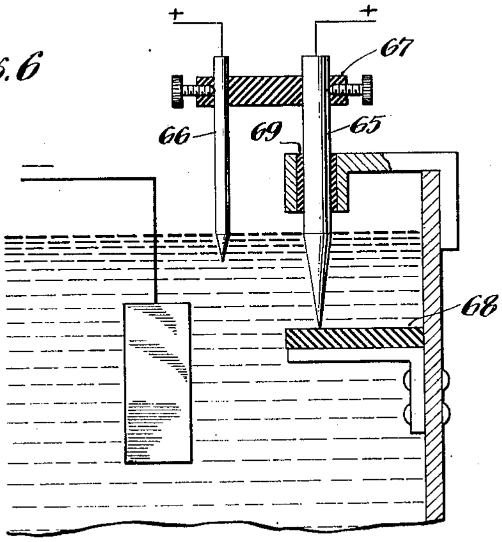
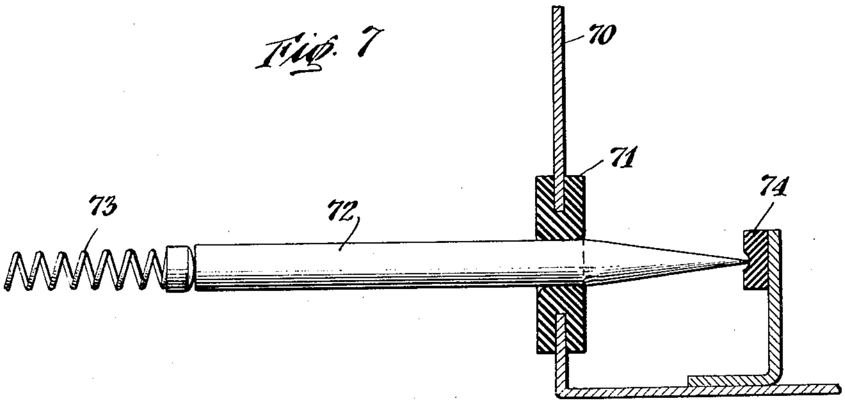


Fig. 7



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Patented Mar. 20, 1951 **2,545,566**

UNITED STATES PATENT OFFICE

2,545,566

ELECTRODEPOSITION OF METALS AND ALLOYS

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Application March 11, 1943, Serial No. 478,750

2 Claims. (Cl. 204—53)

This invention relates to the electric deposition of metals and alloys.

An object of the invention is to improve the methods, bath compositions and apparatus for the electrodeposition of metals and alloys.

Other objects of the invention will be apparent from the description and claims.

In the drawings:

Figure 1 is a diagram illustrating the preferred working range of anode current density for electrodeposition according to the present invention;

Figure 2 shows a plating tank and apparatus for plating the inside of a cylinder;

Figure 3 shows apparatus using two anodes and two power sources for alloy plating;

Figure 4 shows a tank plating apparatus using a single power source;

Figure 5 is a longitudinal section of an anode for alloy plating;

Figure 6 shows a modified anode feeding arrangement for alloy plating; and

Figure 7 shows another anode feeding arrangement.

In many plating operations of the prior art a great deal of trouble has been experienced in obtaining smooth uniform deposits over extended periods of time. While the plating bath may operate satisfactorily for the first few hours, the deposits produced by the bath may eventually become rough and useless necessitating renewal or replacement of the plating bath. While there may be several contributing factors, it is believed that the principal cause of the roughness is precipitation of fine particles from the solution. Most of these are probably fine metallic particles given off by the anode as it dissolves and metallic impurities from the anode which are not dissolved with the anode metal although some of them may also be due to metal compounds formed by reaction with one of the constituents of the plating bath such as the brightener.

The troubles are particularly marked in alloy plating such as in the deposition of silver-lead alloys. For example, a new solution for silver-lead plating will satisfactorily deposit silver-lead for the first several hours. However, with continued operation the deposit becomes increasingly rough and after ten to fifteen hours operation it is so rough as to be useless. Continuous or periodic filtering will not adequately keep the bath free of these fine particles originating at the anode or prevent them from reaching the cathode. On this silver plating the difficulties are not so marked but where heavier deposits are to be built up, such as those of several thousandths of an inch in thickness, these particles produce excessive roughness of the deposit.

The introduction of metal particles from the anode into the plating bath appears to result from a selective dissolution of the anode metal so that small particles or crystals of the anode metal become loosened and drop off the anode. This is borne out by the observable crystalline surface appearance of an anode while being used in the conventional electroplating processes.

Closely associated with this crystalline condition is the tendency in some plating processes to the formation of so-called "black anodes." This is perhaps the most important anode problem in large scale silver plating operations, for example. In usual prior art dissolution of silver anodes, the anode surface appears crystalline, matte or dull, and of a very light gray color. Under some conditions, however, the anode surface becomes much darker, or even black, and a fairly tenacious or adherent scum appears. Particles of this scum become loosened from the anodes and become suspended in the bath. The cause of these "black anodes" has been attributed to small amounts of impurities in the anode which are not readily soluble in the plating solution. These may amount to less than 0.05% of the anode weight and still produce this black condition.

I have found that the anode surface condition can be changed by increasing the anode current density. Various anode surface conditions are indicated in the diagram of Figure 1. With low anode current densities the anode takes on a crystalline, matte, or dull, appearance. Plating processes of the prior art operated the anodes in this range. This has resulted in metal particles falling into the solution. In this range, the current is roughly proportional to the applied voltage. The "black anode" condition, if present, occurs in this range.

As the voltage is increased, a point A is reached where the anode rather suddenly becomes smooth and bright and is no longer crystalline in appearance. This may be accompanied by fluctuating shadows playing over the anode surface. It is also accompanied by a sudden rise in voltage at the anode without a proportional rise in current. Further increase in voltage will not proportionally increase the current density. The anode may be said to be in a "semi-polarized" condition. Dissolution appears to take place uniformly over the anode surface.

The semi-polarized range has as its upper limit B the current density at which the anode becomes completely polarized as evidenced by formation of an insoluble dull coating on the anode surface or generation of gas.

The type of behavior described above applies to the platable metals generally, that is, to zinc and the metals below it in the electro-chemical series, such as cadmium, iron, the tin group, lead, copper, silver, gold, the platinum group and others, as well as to alloy anodes. The current densities A and B, marking the limits of the semi-polarized range, depend upon the anode metal as well as upon the composition of the plating bath, the temperature and the rate of circulation or agitation of the bath.

I have found that by operating the anode in the semi-polarized range the plating difficulties associated with fine metal particles in the bath can be eliminated and other advantages attained as well. Not only are no particles of the anode metal released into the bath, but the impurities associated with "black anodes" do not form particles in the solution. In the bright range apparently the oxidizing potential is sufficient to dissolve the impurities along with the silver so that no precipitate forms at the anode.

With ordinary alkaline plating baths, the bright range A—B is narrow and occurs at a fairly low current density. The current density for the bright range can be increased and the bright range broadened by the addition of corrosive ions to the plating bath. These are ions which form highly soluble compounds with the anode metal and hence promote dissolution of the anode. For example, in the case of a lead anode tartrate and citrate ions produce this result and hence the addition of one of their compounds, such as potassium tartrate, is desirable. With silver anodes cyanide is a corrosive ion.

When operated in the bright range with corrosive ions present the anode operates at 100% current efficiency.

Increase in temperature of the plating bath and increased circulation or agitation also raise and broaden the bright range and so are also desirable for better regulations, higher plating speeds and greater efficiency.

In raising the anode current density the anode size is reduced for a given cathode area. It has been conventional in electroplating practice to provide an anode area at least equal to the cathode area and usually greater than the cathode area. This was done because with smaller anode areas, under usual plating conditions, gassing takes place at the anode, causing a depletion of metal in the bath, and in the case of cyanide baths, acceleration of the formation of carbonates. In the present invention the anode area is greatly reduced. In the case of lead anodes, for example, the anode area may be only $^1/_{30}$ to $\frac{1}{10}$ that of the cathode and the anode current density may be 30 to 50 amperes per square foot. The small anode area also introduces mechanical advantages in plating certain shapes.

In summary, the following factors are combined to provide an electrodeposition process which prevents the introduction of metal particles into the solution, operates at greater plating speed and has 100% anode current efficiency;

1. Operation of anode in semi-polarized or bright range.
2. Use of corrosive ions in the plating bath. This is particularly applicable to alkaline baths.
3. Operation at high anode current density.
4. Anode area much smaller than cathode area.

It is preferable to combine with the above other factors which permit a fuller realization of the advantages of the process. One of these is the use of a brightener which does not form insoluble precipitates with the anode metal or plating bath. I have found the hydroxy-benzenes, such as pyrogallol, to be useful in alkaline plating baths generally. In an alkaline bath pyrogallol appears to take up oxygen and form a dark colored colloid which acts as the brightener. This brightener action takes place only in highly alkaline baths, namely those with a pH of 13 or above.

Another improvement resides in the means used for introducing the anode into the plating bath. The anode area in contact with the solution is small, and it must be kept within certain fairly close limits in order to preserve the semi-polarized condition and to regulate the cathode current density. I have devised a pointed anode rod which is allowed to rest on a support in the plating bath. If the semi-polarized condition is maintained along with fairly uniform agitation of the bath, the anode will dissolve uniformly and a sharply pointed condition is preserved and the anode settles so as to keep the same area always in the solution. This will be clearer from the more detailed description and the illustrations of the drawings.

The present invention has application to the plating of metals and alloys generally, but particularly to electrodeposition from alkaline baths. Following are examples of the invention as applied to lead plating, lead-silver alloy plating, silver plating and copper plating.

STRAIGHT LEAD PLATING

The following procedure is suitable for the plating of straight lead on a base such as steel, silver, copper and other metals.

The article to be plated is first degreased and then electrolytically cleaned in an alkaline cleaning solution. After removal it is desirable to thoroughly rinse the article in water. In case undercoating metals are applied to the base before lead plating, a brief rinse of the plated article in water is sufficient.

The article is then immediately transferred to the lead plating bath of the following composition, for example:

(*a*) *Alkaline lead bath*

	Grams per liter
Potassium tartrate	100
Potassium hydroxide	40
Basic lead acetate	42.5
(Equivalent lead content)	30
Pyrogallol	1

pH=13.5–14, temperature 50° C.

Plating is effected at 50° C. with a current density of 25 amperes per square foot of anode surface with agitation of 30 feet per minute past the electrodes. The cathode area being greater than the anode area, the cathode current density will be less than 25 amperes per square foot.

The plating apparatus is illustrated in Figure 2 of the drawing and comprises a tank **10** containing the plating bath **11**, the anode **12** which is tapered to a point **13** which rests on a perforated insulating plate **14**, the cathode **15** comprising a bearing sleeve resting on plate **14**, an insulating tubular mask **16** surrounding the exterior of the cathode, and a circulating pump **17**. A covered conductor **18** passes through mask **16** and connects the cathode to the negative terminal of a D. C. power source. The pump **17** is driven by electric motor **19** and draws in plating solution at **20** and forces it via pipe **21** through the holes in plate 14 and up through the center of the cathode bearing shell 15.

The anode 12 comprises a rod of lead (preferably round) which is tapered to a point 13 at its lower end. The taper is of such length as to provide the desired anode area in the tapered section. The support for the point 13 and the solution level are adjusted to bring the surface of the solution even with the upper end of the taper. The anode rod is supported loosely by an insulating sleeve 22 above the solution so that it may settle into the solution as the tapered portion is dissolved.

I have found that under these conditions, when the anode is operated in the bright or semi-polarized condition, and the circulation or agitation of the solution around the anode is fairly uniform, the current is uniformly distributed over the entire tapered area so that the tapered surface dissolves uniformly from the beginning of the taper to the tip, thus the same taper is always preserved as the anode rod settles into the solution and no particles or sections can become eaten away from the anode and drop off into the solution.

Another lead bath which is somewhat better than the above is as follows:

(b) *Alkaline cyanide lead bath*

	Grams per liter
Potassium tartrate	100
Potassium cyanide (total)	145
Lead acetate	52.5
Pyrogallol	1

pH=13.5–14, temperature 50° C.

With agitation of 30 feet per minute, an anode current density of 50 amperes per square foot is used with a cathode density of 5 to 25 amperes per square foot depending on its size.

While the above are the preferred conditions, given by way of example, it is contemplated that some deviation from these conditions can be made in some instances.

Other anodic dissolution producing ions may be substituted for the tartrates such as acetates, citrates, formates, malates, i. e., one which will dissolve lead to form a soluble compound.

SILVER-LEAD PLATING

For plating any base metal, such as a steel bearing shell with a silver-lead alloy, the steel blank is processed in the same manner as for lead plating. A copper strike followed by a silver strike may then be applied. However, I have found that a silver strike alone may be used. In this case the cleaned steel shell is soaked in the silver strike solution for one minute and then a strike current of 300 amperes per square foot of cathode surface is applied for one minute. A suitable silver strike solution may consist of:

Potassium cyanide, preferably at least 100 grams per liter

Silver cyanide, 0.5 to 1 gram per liter and preferably not over 1 gram per liter

The silver cyanide concentration is kept low and the potassium cyanide is kept high so as to maintain the silver ion concentration below that at which galvanic deposition of silver onto the steel will take place before current is applied. This insures that substantially all the silver which is deposited from the strike bath will be electrolytically deposited. After the silver strike, the

shell is transferred immediately to the silver-lead plating bath. This bath may consist of:

(c) *Silver-lead bath*

	Grams per liter
Silver-cyanide	120
Potassium cyanide (total)	205
(Free potassium cyanide	145)
Potassium tartrate	100
Lead tartrate	6
Potassium hydroxide	10
Pyrogallol	0.5

Before use the plating bath is clarified with 5 to 10 grams per liter of activated charcoal and filtered.

The high tartrate content affords the desired concentration of lead anode dissolution promoting ions. Tartrate alone gives a rather crystalline or spongy appearance to the lead anode which the presence of cyanide and/or hydroxide appears to overcome resulting in a very bright and smooth anode surface during plating. No finely divided lead particles are imparted to the solution during plating. The lead dissolves in the plumbous or bivalent condition.

Figure 3 shows a suitable apparatus for silver-lead plating. It comprises plating tank 30 containing silver-lead bath 31, silver anode 32, lead anode 33, cathode 34 and circulating pump 35 driven by motor 36. Both the lead anode 33 and the silver anode 32 are tapered, the tapered surfaces being proportioned to the relative areas required. Silver anode 32 rests on perforated plate 37 so that its tapered portion is located along the axis of the cathode cylinder. The lead anode 33 rests on an insulating table 38 outside the cathode. The silver anode is connected to D. C. source 39 through current regulating resistance 40 and the lead anode is connected to D. C. source 41 through regulating resistance 42. It is thus possible to adjust both anode currents independently.

This arrangement is suitable for depositing a high silver-low lead alloy on the cathode. While the lead anode is not symmetrically located with respect to all parts of the cathode surface, the circulation insures a uniform distribution of lead ions to all parts of the plating bath. The excess of current on the parts of the cathode nearest the lead anode is small in proportion to the total current so that the silver-lead alloy is deposited uniformly as to composition, and nearly uniform as to thickness over the entire cathode area.

The plating circuit and the amount of solution agitation, together with the relative size of the anodes and cathodes are arranged so as to provide a current density at the lead anode of 30 to 50 amperes per square foot, preferably 40 amperes, with a current density at the silver anode of 200 to 600 amperes per square foot, preferably 300 amperes, and a current density at the cathode of 45 to 90 amperes per square foot of cathode area. The lead anode has an area of about 1/10 to 1/30 of that of the cathode while the silver anode has an area of about 1/5 of that of the cathode.

The preferred operating temperature is 35 to 50° C. with moderate agitation, for example 45° C.

The percentage of lead and silver in the electrodeposited silver-lead alloy can be varied by adjusting the areas of the anodes under solution and the cathode current density is also controlled by adjusting the areas of the anodes under solution and the solution agitation. The proportion of lead deposited will be higher with the lower cathode current densities.

The process finds its most important use in producing silver-lead deposits containing up to 7 or 8% lead but is also applicable to the production of higher lead alloys. Heavy deposits can readily be produced by this process such as those used for silver-lead lined bearings. For example, it is possible to plate an alloy containing 3 to 4% lead and of ⅛″ in thickness.

While a suitable silver-lead plating bath is given in the above example, it is, of course, possible to vary the composition and proportions of the ingredients in the plating bath considerably and still obtain the desirable results of the present invention. For instance, the amount of silver cyanide may be varied over a considerable range as may that of the potassium cyanide. It is important, however, to have a high concentration of corrosive ion, such as tartrate, present. In the case of tartrate, it is also important to have considerable cyanide and/or hydroxide ion present as tartrate alone gives a rather crystalline or spongy appearance to the lead anode.

It will be noted that the above solution contains no carbonates. The literature on silver plating almost invariably recommends the addition of carbonates. I have found, however, that in a silver plating solution having a high concentration of silver and free potassium cyanide, the addition of carbonates, such as potassium or sodium carbonate, will not appreciably increase the conductivity of the solution. There is, however, a detrimental effect on the bright working lead anode in a silver-lead plating bath and the carbonates greatly limit the maximum anode current density obtainable. While the advantages of the present invention may be achieved to some extent in plating baths in which carbonates are present, I prefer to avoid their use.

STRAIGHT SILVER PLATING

An apparatus similar to that shown in Figure 2 may be used with a silver plating bath and silver anode. One suitable plating bath may consist of:

(*d*) *Silver bath*

	Grams per liter
Silver cyanide	120
Potassium cyanide (total)	205
(Free potassium cyanide	145)
Potassium tartrate	100
Potassium hydroxide	10
Pyrogallol	0.5

The conditions are about the same as for silver-lead plating.

STRAIGHT COPPER PLATING

Using the apparatus of Figure 2, copper may be deposited using a:

(*e*) *Copper bath*

	Grams per liter
Copper cyanide	165
Potassium cyanide (total)	247
(Free potassium cyanide	15)
Potassium hydroxide	15
Potassium tartrate	50
Pyrogallol	0.5
Sorbitol	60

The pH is adjusted to 13.5 by varying the KOH present. Temperature 70% C. Plating may be effected at a cathode current density of 45 amperes per square foot, an anode density of 180 amperes per square foot and an agitation of approximately 20 feet per minute.

Sorbitol is a hexahydroxy alcohol and is one of a class of organic compounds that will combine with metallic compounds in an alkaline solution. It has a beneficial effect on the operation of a bright-working copper anode and consequently produces a smoother deposit at the cathode. It may also have a direct effect on the cathode deposits.

COPPER-LEAD PLATING

For copper-lead plating using the apparatus of Figure 3, the following bath may be used:

(*f*) *Copper-lead bath*

	Grams per liter
Copper cyanide	165
Potassium cyanide (total)	247
(Free potassium cyanide	15)
Potassium hydroxide	15
Potassium tartrate	50
Lead acetate	10
Pyrogallol	0.5
Sorbitol	60

The pH is adjusted to 13.5 and the temperature to 70° C. The preferred cathode current density is 45 amperes per square foot, copper anode current density 180 amperes per square foot, lead anode current density 65 amperes per square foot and agitation approximately 20 feet per minute past the cathode surface. With 38% of the current from the lead anode and 62% through the copper anode, the lead anode voltage may be 0.75 to 1 volt and the copper anode voltage 1.0 to 1.4 volts.

Chlorides are also corrosive ions for copper plating.

TANK PLATING

Figure 4 shows a plating apparatus suitable for tank plating of miscellaneous parts. It comprises a tank 43 containing plating bath 44, tapered anodes 45 and 46 and cathode 47. The bath is agitated by a stirrer 48 driven by motor 49.

The anodes rest their pointed tips on insulating supports below the solution level and slide into the solution through guiding sleeves 50 and 51 of insulating material. The cathode parts are suspended by hooks 52 from bus bar 53 connected to the negative terminal of a D. C. source 54. The anodes 45 and 46 are connected to the positive terminal of the source through current regulating adjustable resistors 55 and 56 respectively. The current can thus be readily proportioned between the anodes.

The anodes may be of the same or different composition depending upon whether pure metal or an alloy is to be deposited, the plating bath being of suitable composition.

It is also contemplated that in the arrangements of Figures 2 and 4 the anodes can be formed of an alloy of the composition to be deposited. The oxidizing potential, when the anodes are operated in the bright range, is sufficient to dissolve both metals simultaneously.

Figure 5 shows in section a tapered anode for alloy plating comprising a core 61 of a first metal and a coating 62 of the second metal to be deposited. For example, the core may be of silver and the coating of lead. The anode is supported from the silver tip 63 in the plating bath with the level of the bath at the upper end of the taper **64**. With corrosive ions for both metals in the solution, it is possible to operate the anode with both metals working in the bright range so that uniform dissolution takes place and the same taper is preserved as the anode settles into the bath. With a silver-lead anode there is some tendency of the lead to polarize due to the high current density but this can be overcome by using sufficiently high pH solutions. The thickness of the metal coating **62** is selected to give a relative cross-section of the two metals in the proportions desired in the electrodeposited alloy.

Figure 6 shows a modification in which the two anodes **65** and **66** are clamped in an insulating yoke **67** at their upper ends and the point of anode **65** rests on table **68** under the solution and is guided by loose sleeve guide **69**. It will be apparent that dissolution of both anodes will take place at the same linear rate and hence the amount of the metals dissolved will be in proportion to their areas.

Figure 7 shows a method of introducing an anode below the surface of the plating bath. The plating tank **70** is provided with a circular aperture which is lined with a soft rubber or neoprene ring **71** through which anode **72** is fed by a spring **73** or feeding means. A stop **74** in the bath maintains the same tapered length in solution as the anode dissolves.

BRIGHTENERS

Pyrogallol, a trihydroxy benzene having the formula $C_6H_3(OH)_3$, is an exceptionally good brightener for metal plating. The amount required does not appear to be critical and I have successfully used it from a trace up to 5 grams per liter and found the bath capable of producing very bright metal and alloy deposits in this range. For the best functioning of this brightener to avoid roughness or nodules, the bath should contain a free hydroxide content to give a pH of 13 or above. The preferred ratio of pyrogallol to KOH is 1:100 on a weight basis but may be varied over a considerable range. Pyrogallol belongs to a group of organic compounds (hydroxy benzenes) having very strong reducing properties. Other compounds of this class which are also suitable as brighteners are:

Phloroglucinol (1,3,5 trihydroxy benzene)
Hydroxyquinol (1,2,4 hydroxy benzene)
Catechol (ortho dihydroxy benzene)
Resorcinol (meta dihydroxy benzene)
Hydroquinone (para dihydroxy benzene)
Phenol (mono hydroxy benzene)

The present invention makes possible not only improved electrodeposits of metals and alloys, but also introduces economies in the plating operation. Since the baths will operate satisfactorily for long periods of time without cleaning or filtering, a great deal of labor is saved which would otherwise be required in cleaning the solutions. Moreover, due to the use of higher current densities plating is effected at a greater rate and hence the number of plated pieces produced by a given plating bath in a predetermined length of time is increased. Moreover, since the metal dissolves at practically 100% efficiency, a saving in electric current is effected.

The invention also introduces advantages in the electroplating of certain shapes such as the inside of hollow members, such as bearing shells, gun barrels and the like. Heretofore, it has been difficult to obtain sufficient anode surface area inside the hollow article for plating under conventional conditions. By the present invention where the anode area is greatly reduced, the space problem is simplified since it is readily possible to insert an anode of much smaller surface area than the inside surface of the cathode to be plated and still maintain sufficient cathode current density.

While specific embodiments of the invention have been described, it is intended to cover the invention broadly within the spirit and scope of the appended claims.

What is claimed is:

1. The method of electrodepositing lead from an aqueous alkaline bath containing soluble lead salts which comprises employing a lead anode having an effective surface area less than 0.5 the surface area of the cathode to be plated and passing an electric current therethrough at an anode current density of about 30 to about 50 amperes per square foot of effective anode surface area, said current density being less than that required to polarize said anode and greater than that at which anode current density increases substantially proportional to the increase in impressed voltage.

2. The method of electrodepositing lead which comprises passing an electric current through an aqueous plating bath containing lead ions, tartrate ions and cyanide ions from a lead anode to a cathode to be plated at an anode current density of about 30 to about 50 amperes per square foot of effective anodic surface, said anode current density being less than that required to polarize said anode and greater than that at which anode current density increases substantially proportional to the increase in impressed voltage, said lead anode having an effective surface area about $\frac{1}{10}$ to about $\frac{1}{30}$ of that of said cathode.

JAMES MARVIN BOOE.

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