

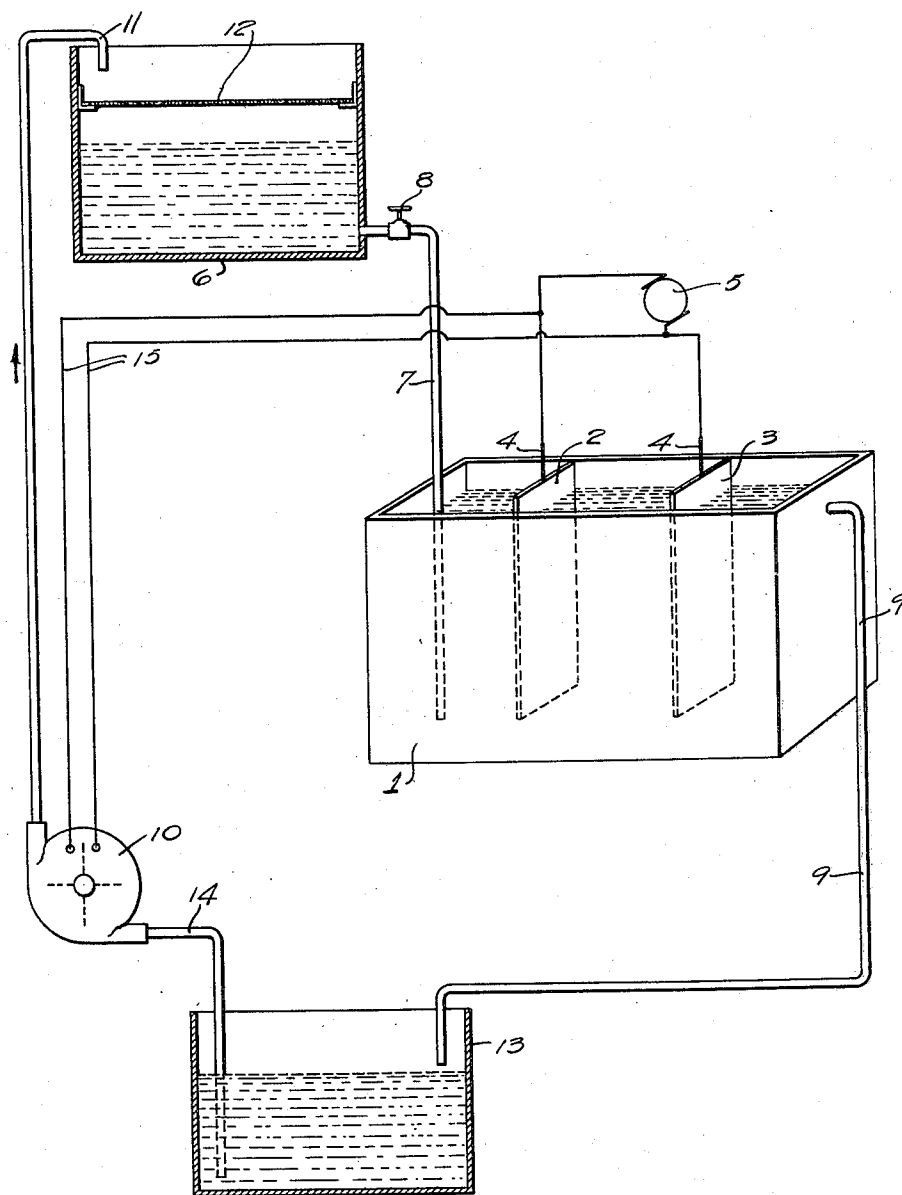
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SUBSTANTIALLY PURE TUNGSTEN PLATING AND PROCESS FOR PRODUCING SAME

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SUBSTANTIALLY PURE TUNGSTEN PLATING AND PROCESS FOR PRODUCING SAME

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This invention embodies a modification of the process disclosed in my pending application Ser. No. 183,235 filed April 12, 1927, and also a modification of the special carbonate bath process claimed in the application of Mr. Frank L. Jones and myself, Serial No. 362,854, filed May 13, 1929.

In both said previously described processes it has so far been found that when tungsten is the only plating metal present in the bath with the alkali metal salt, in any of the therein proposed manners, the tungsten plating proceeds up to a certain degree of thickness and then almost stops. If the plated cathode is then removed and a new one is substituted, normal plating speed is again resumed, but when the previously attained thickness of deposit has again been reached, further deposition apparently then almost ceases as before. Thus if operating under commercial conditions many successive articles of brass or other suitable material can be successively plated with pure tungsten from the same bath, but only to a substantially uniform limit of thickness of deposited layer.

As pointed out in my application Ser. No. 183,237 I had then found that the use of a supplemental anode of lead, or other cathode-depolarizing metal, would overcome this ultimate virtual cessation of plating action. Even a small quantity of such supplemental plating metal thus going into solution in the bath from any source seems to have a beneficial effect in similarly cleansing the surface of the tungsten film first deposited on the cathode, or otherwise depolarizing it, and thus permitting a continuous plating action so as to build up a thicker coating of substantially pure tungsten with which, however, a trace of the cathode depolarizing metal is alloyed. Subsequent more extensive study and experimentation have developed the fact that while the addition of any one of a number of metals other than lead, such as iron,

copper, cobalt or nickel, will serve to produce the apparent cathode depolarizing action resulting in the thicker substantially pure tungsten plating desired, nickel is the most satisfactory and efficient for this purpose.

As compared with the other depolarizing metals mentioned in the foregoing list, nickel has certain advantages as follows: It is cheap and can be obtained commercially in substantially pure condition. It alloys readily with tungsten and the alloys so formed are highly resistant to corrosion and have relatively high melting points. Most important of all, however, is the fact that nickel is only very slightly soluble in alkaline tungsten plating baths such as those described in the above recited prior applications. This low solubility of the nickel in the plating bath renders control of the concentration of the nickel in the bath comparatively easy from a commercial plating point of view.

This slight solubility of nickel above referred to is in accord with the statements of the recognized authorities on the subject.

Thus Comey-Hahn, pages 538 and 539 (McMillan 1921) states that the hydroxides of nickel, including $\text{Ni}(\text{OH})_2$, are insoluble in fixed alkali solutions, and are only slightly soluble in ammonium-hydroxide solutions, while Seidel, page 451 (Van Nostrand 1919) and the Hodgman-Lange Handbook of Chemistry & Physics (Chemical Rubber Company, Cleveland, 1928) on page 511, both state that nickel carbonate, (NiCO_3) is soluble in water at 25 degrees centigrade to the extent of only 0.0925 grams per litre of water. This would be about 0.3 of 1% of the WO_3 content of the tungsten plating baths, preferably used in accordance with the teachings of the above mentioned Fink & Jones application. As to what extent the solubility of nickel is affected by the presence of the tungsten salts is not definitely known.

Furthermore, since it is well recognized that nickel salts are readily precipitated

from aqueous solutions in the presence of alkali, it is probable that the net solubility of nickel carbonate in a sodium carbonate or a sodium hydroxide plating bath, such as described in said prior applications, will very likely not exceed one-tenth of that above given in pure water, or about 0.01 grams per litre, or less.

Obviously in order to produce a substantially pure tungsten plating with the least possible alloy of a metal introduced solely for cathode depolarizing purposes, it is desirable to reduce the amount of such supplemental metal in the plating bath to the lowest possible limit, and from the above considerations it appears that nickel automatically compels this desired condition when used in the tungsten plating process of the said prior applications, unless, of course, an excess of nickel, or of one of its salts, is added to the bath and maintained in suspension by mechanical means. There is another reason, however, for restricting the nickel content of the bath to a very low proportion such as above indicated (i. e. from one tenth of one per cent to one per cent of the WO_3 content of the plating bath, by weight) and that is that I have found that higher proportions of nickel, such as could be obtained by adding finely powdered metallic nickel to the bath or by using a nickel anode therein, produce a plating which, while of any desired thickness, peels or strips from the supporting base, doubtless as the result of the occurrence of large volumes of hydrogen liberated in my plating process at the cathode, this stripping phenomenon being also familiar in nickel plating where any considerable quantity of hydrogen is liberated at the cathode.

Controlling the amount of nickel solution in the plating bath within the narrow limits above outlined can best be done by slowly adding a predetermined amount of a standardized nickel solution to the plating bath at one point therein, as the operation proceeds, and removing a like amount of the resultant, partially spent, bath solution from a remote point in the plating cell, such nickel bearing tungsten plating solution being passed through the bath at a rate which permits about one-third of its nickel content to go into the plated deposit. The percentage of nickel in the plated layer is then extremely minute, amounting to little more than one thousandth of one per cent (0.001%) by weight and often less than this. A convenient apparatus for carrying out this process is illustrated in the accompanying sheet of drawing which shows a diagram of the apparatus in a vertical section taken through certain portions the plating cell and the circulating system for the nickel bearing solution being shown in side elevation.

Referring to the drawing, 1 represents the plating cell, 2 the anode and 3 the cathode

therein, and 4, 4, the terminals of the current supply circuit fed from generating source 5.

A tank is shown at 6 for holding the nickel bearing solution, such as an aqueous solution of sodium carbonate (Na_2CO_3) or hydroxide ($NaOH$) or sodium tungstate, of the same strength as that in use in cell 1, but also containing the small percentage of nickel above specified. 7 is a pipe leading from the bottom of said tank to the lower part of the cell 1 and controlled by valve 8. Preferably this pipe 7 discharges into the bath near the anode, as shown. The surplus, partially-spent, bath solution overflows from the other end of cell 1 through pipe 9 to the sump 13. Preferably this overflow pipe 9 leads from the upper portion of cell 1 at a point near the cathode. The overflow of partially spent bath solution collecting in sump 13 is intermittently pumped up through suction pipe 14 of pump 10 and delivered back to tank 6 through spout 11. Pump 10 may be electrically driven by current from source 5, blowing through shunt circuit 15 and any convenient form of float operated circuit breaker may control circuit 15, so that pump 10 will begin to operate only when the liquid level in sump 13 or tank 6 rises or falls to a predetermined point, and then is cut out when the liquid level reaches another point.

Tank 6 may have a filter bed 12 containing nickel carbonate ($NiCO_3$) for regenerating the partially spent bath solution so far as its nickel content is concerned, and also serving to free it from any suspended solid impurities. This regenerating action may, however, be produced in other ways, as by adding nickel in other forms, to the contents of tank 6. If nickel carbonate ($NiCO_3$) is used at any point of the process, care should be taken to make sure that it does not contain nickel chloride ($NiCl_2$) as an impurity, as commercial nickel carbonate is apt to do. The presence of such nickel chloride will increase the nickel content of any solution made from this material beyond the calculated limit.

One method of operating the herein described process, with the apparatus here illustrated, is as follows: The bath in cell 1 may be prepared by introducing fine nickel powder, such as is used as a catalyst for the hydrogenation of oils, into the predominantly alkaline sodium carbonate-tungstic oxide bath of the Fink & Jones application No. 362,854 and boiling the mixture with constant stirring; Or the nickel may be introduced by adding an excess of green nickel carbonate ($NiCO_3$) to such sodium carbonate-tungstic oxide bath, and then boiling and stirring as before. The solution produced will become saturated as to the nickel content at the low percentages given above and any excess, or remainder, of the nickel 130

carbonate will collect at the bottom of the container.

Tank 6 is filled with a nickel hydrate saturated sodium tungstate solution and this may be maintained at saturation as to nickel content by introducing fresh nickel hydrate ($\text{Ni}(\text{OH})_2$) from time to time as the plating process proceeds, or by the gradual solution in situ of the nickel carbonate (NiCO_3) filter bed 12.

Valve 8 is so adjusted that the flow of solution from tank 6 to the bottom of cell 1, for the purpose of maintaining the desired amount of nickel in the plating bath, will cause the surplus bath solution to overflow through outlet 9 at a rate which will result in the nickel bearing solution passing through the bath at a speed such that about one third or less of its nickel content will be consumed in the portion of the plating operation occurring during its passage through the cell. The bath solution with a reduced nickel content thus collecting beyond the cathode 3 at the upper portion of the cell and overflowing through pipe 9 to sump 13 is then returned to tank 6 for regeneration as before described.

The anode 2 may be composed exclusively of platinum, or it may be three-fourths platinum and one-fourth tungsten, or of any other usable composition except nickel,—if the low per cent nickel plating is desired. If a nickel anode is used a large quantity of that metal will be liberated and hydrated salts thereof maintained in suspension in the plating bath in cell 1 and no other nickel adding accessory will then be needed, but the quantity of nickel co-deposited with the tungsten may then become excessive, resulting in poor plating, as mentioned above. The cathode 3 may be made of any proper material which is electrically conductive which it is desired to plate, such as steel, brass, nickel, silver, etc.

By the above described process a substantially pure, closely adherent, tungsten plating can be produced of sufficient thickness for all ordinary commercial uses and free from pin holes, having practically the same resistance to the action of acids, alkalis, oxidizing agents and heat, as has an absolutely pure tungsten plating; the proportion of nickel present in it being so small that it cannot be accurately determined by ordinary methods of quantitative analysis, such for example as the dimethyl glyoxime method.

Any other cathode depolarizing metal, such as those hereinbefore suggested, may be substituted for nickel in this process, the proper compounds thereof being used as raw material and the proper reagents being employed to control the content thereof resulting in the electroplating bath within the minute limits desirable, and without destroy-

ing the predominant alkalinity of the bath, all as will be understood by those skilled in electro-chemistry, but on the basis of my investigations to date I believe the best results and most practical and economical operation can be secured with the use of nickel, in substantially the manner described.

So far as I am aware the use of a second metal for facilitating the electro deposition of the metal mainly relied upon for producing the desired plating layer, has not heretofore been suggested. Various non-metallic depolarizers have been used in the electroplating art, such as hydrochloric acid (HCl), or other non-metallic chlorides, for anodic depolarizers, and hydrogen peroxide (H_2O_2), or other oxygen compounds, for cathodic depolarizers. The accepted theory of such depolarizing action, however, has been that the gaseous element, chlorine in the one case and oxygen in the other, was the depolarizing agent, acting as such after liberation from the compound in which it was added to the bath, the other or base elements of such compound being neutral so far as any cathodic action was concerned.

Quite naturally metals were not heretofore used, or experimented with, as cathode depolarizers, because they would also be electro deposited on the cathode and adulterate the plating layer of the other metal used and intended to form a pure plating upon the cathode. Also the theory of depolarizing action heretofore has been that the depolarizer must be an element which would disintegrate or eat away the objectionable polarizing film on anode or cathode, and then evaporate, or go into solution in the bath with some of the original elements of such disintegrated polarizing film. Obviously no metal will operate in the way thus outlined, and for some or all of these reasons no metal or metallic compound has heretofore been proposed or used as a cathodic depolarizer.

So far as I know my recent investigations of the problem of electroplating with tungsten from an aqueous bath is the first instance in which has developed the phenomenon of a serious slowing down to practical extinction of plating action by some unexplained self polarizing action of the plating metal itself, or of one of its compounds, when layers of a given thickness have been deposited. When this developed the necessity for finding a remedy became acute and the idea of trying the effect of a small quantity of another metal which, when added to the bath, would be free from cathodic self polarizing action occurred to me and was tried out.

The theoretical objection that the use of a metal depolarizing addition would adulterate the primary plating desired also disappeared when it developed that a very minute quantity of the second metal was effective for cathode depolarizing purposes, and that the

trace of such second metal then present in the plated layer did not materially alter the characteristics derived by it from the primary plating metal.

In following out this method of overcoming the self polarizing difficulty it, of course, became important to keep the proportion of the added metal down to the lowest possible limit, if a substantially pure plating of tungsten was to be produced, and the fact that nickel is so slightly soluble in aqueous solutions, and still less soluble in the alkaline tungstate bath solutions of my process, ultimately rendered nickel the preferred metal for use as a cathodic depolarizer therein. I have, however, so far successfully tested out the other metals mentioned above, i. e. lead, iron, cobalt and copper, and believe that all other metals which are free from cathodic self polarizing action when used as the sole plating element will serve as cathodic depolarizing additions to electro plating baths (whether aqueous, organic or fused) of tungsten or of any other cathodic-self-polarizing metal.

The herein described method of preventing cathode depolarization is also operative in the similar processes of plating with thorium, titanium, aluminum and zirconium described in the copending application of Fink & Jones, Serial No. 362,854, filed May 13, 1929, when a proper amount of a cathode depolarizing metal is added to the bath, the effectiveness of the depolarizing action varying somewhat with different metals and baths. Thus zinc gives most satisfactory results in the thorium bath, copper is the best cathode depolarizer for the titanium bath, while nickel and cobalt are the most easily controlled in the tungsten bath, as above explained. Iron is perhaps the most efficient cathode depolarizer for the tungsten bath but there is difficulty in controlling the amount going into solution.

In all applications of the described aqueous bath plating processes to the metals hereinabove mentioned, this novel phenomenon occurs, i. e. the development of a cathode polarization, after a certain period of electrolyzation has fully covered the cathode with a complete layer of the plating metal.

Having described my invention, I claim:

1. An electrolytic bath adapted for use in producing substantially pure tungsten plating of any desired thickness, which bath comprises an aqueous solution of a tungstate with a trace of nickel dissolved therein.

2. An electrolytic bath adapted for use in producing a substantially pure tungsten plating of substantial thickness, which bath comprises a tungstate resulting from the addition of tungstic oxide (WO_3) to a predominantly alkaline solution, together with an amount of nickel not greater than one per

cent by weight of the tungstic oxide content of the bath so used.

3. An electrolytic metal plating bath containing a salt of the metal which is to form the dominant constituent of the plating to be produced therefrom and which develops a cathode-polarizing effect after a short period of electrolyzation and a minor proportion of a salt of a second metal having a cathodic depolarizing action when present in said bath.

4. A bath for use in electroplating with a metal which develops a cathode polarizing effect after a short period of electrolyzation when used alone as a plating element, which bath contains, in addition to such primary plating constituent, a minor quantity of a second metal which is devoid of such cathode polarizing characteristic when used alone and counteracts that of the first metal when thus used in combination therewith.

5. The herein described process of producing substantially pure tungsten plating of any desired thickness from a bath containing a tungstate solution, which process comprises maintaining the deposit-holding capacity of the progressively plated cathode surface by supplying an approximately predetermined quantity of a cathode-depolarizing metal to the bath.

6. A process such as defined in claim 5 in which nickel is employed as such cathode depolarizer.

7. A process such as defined in claim 5 in which said tungstate occurs in the bath as a predominantly alkaline, aqueous solution.

8. The herein described process of producing substantially pure tungsten plating of substantial thickness from a bath containing a tungstate solution, which process comprises maintaining the deposit-holding capacity of the progressively plated cathode surface by continuously supplying a regulated quantity of a cathodic non-polarizing metal to the bath at one point therein and continuously removing an equivalent volume of the spent bath solution from a point remote from that at which the said solution is being added.

9. A process such as defined in claim 8 in which said added solution is thus passed through the bath at a rate such that about one third of its metal component is consumed in the contemporaneous plating operation.

10. The herein described process of producing substantially pure tungsten plating of substantial thickness from a bath containing a tungstate solution, which process comprises maintaining the deposit-holding capacity of the progressively plated cathode surface by continuously supplying a regulated quantity of a cathode depolarizing metal to the bath at one point therein and continuously removing an equivalent volume of the spent bath solution from a point remote from that at which the depolarizing solution is being added, regenerating said spent solution by the addi-

tion of more of the depolarizing agent and returning said regenerated solution to the bath at a point remote from that from which it was removed.

5 11. A process such as defined in claim 10 in which said regenerating action is effected by passing the spent solution through a mass of nickel carbonate.

10 12. The product of the herein described process, being a continuous plated layer of tungsten of substantial thickness electrically deposited and containing a trace of nickel, said plated layer closely adhering to a base of electrically conducting material.

15 13. A process for producing a substantially pure plating of a cathode self-polarizing metal of any desired thickness from an aqueous solution which comprises maintaining and renewing the deposit-holding capacity of a progressively plated cathode surface by
20 supplying a small quantity of a cathode-depolarizing metal to the plating bath.

25 Signed at New York city, in the county of New York and State of New York, this 25th day of September, A. D. 1929.

COLIN G. FINK.

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