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CONTROL OF CHROMIUM PLATING SOLUTIONS

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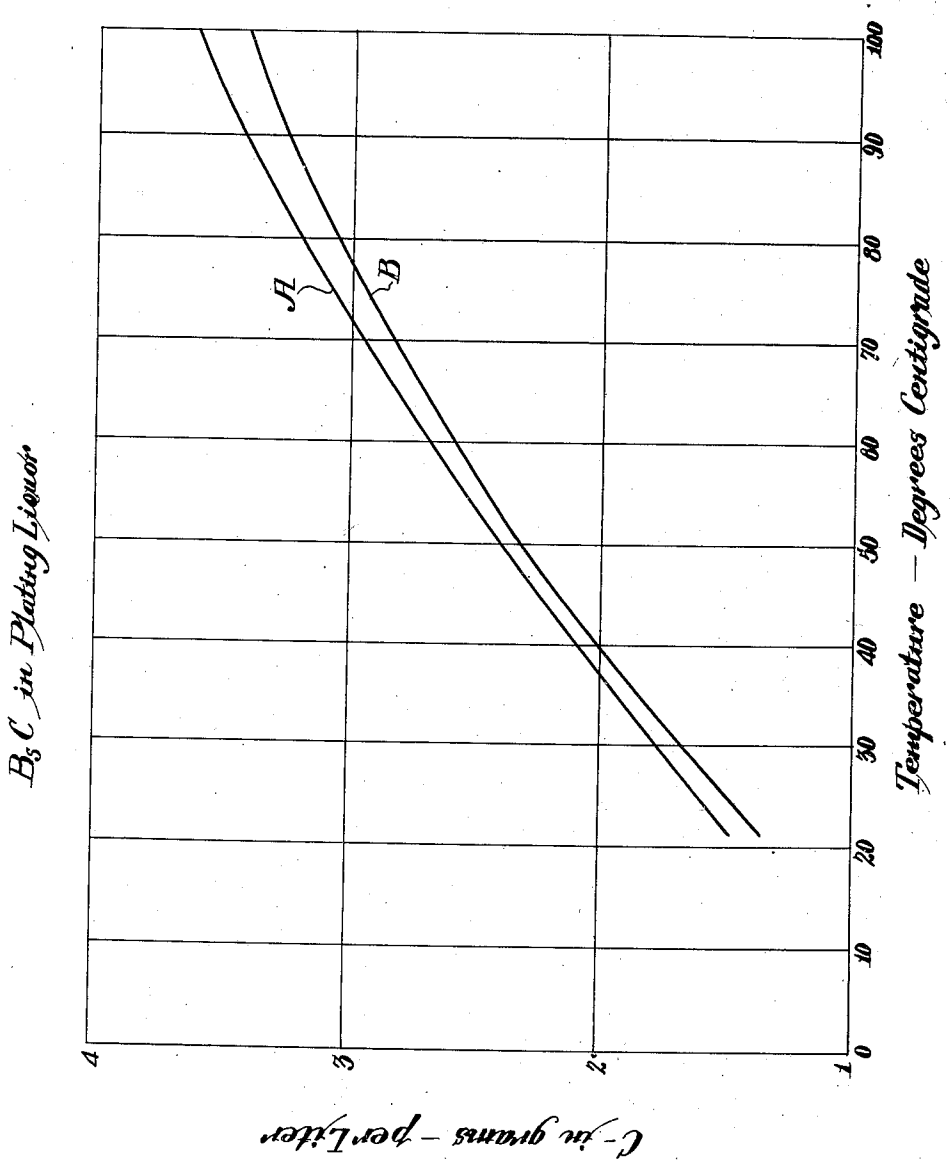

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CONTROL OF CHROMIUM PLATING SOLUTIONS

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27 Claims. (Cl. 204—1)

This invention relates to electrolytic solutions containing chromium and a catalyst and for use in electrolytic chromium plating, the invention being more particularly directed to the control of the concentration of the catalyst in the plating solution.

In present practice satisfactory electrolytic deposits of chromium are produced by passing a current from anode to cathode through an electrolytic solution containing chromium in the presence of a suitable catalyst, the object receiving the deposit of chromium being used as a cathode and the temperature of the solution, the anode current density, the cathode current density and the respective concentrations of the chromium and of the catalyst all needing to be kept within fairly well defined limits.

In continued use plating solutions have in the past tended to progressively change with respect to the concentration of the chromium and the concentration of the catalyst, tending to depart from, (fall below) the known limits essential for dependable satisfactory plating, and success in obtaining uniformly satisfactory chromium deposits has therefore depended not only upon careful control of temperatures and current densities but also upon careful periodically repeated adjustments in the concentrations of the plating solution with respect to chromium and with respect to the catalyst.

The control of the temperature of the solutions, the control of current densities and the control of chromium concentration can all be accomplished by relatively simple and well defined processes. The control of the catalyst concentration has hitherto however presented a more complex problem.

It has hitherto been necessary periodically to examine the plating solutions by more or less complex methods of analysis in order to determine periodically the concentration of the catalyst and thereby what additions of catalytic compound are necessary to keep the concentration of the catalyst within allowable limits known to be essential for the production of uniformly satisfactory deposits.

I distinguish between the catalyst, which in solution is an ion having catalytic properties, and the substance in which the catalyst is supplied to the solution, and which for convenience I refer to as the catalyst compound.

The different successfully used catalysts are acid radicals stable in the bath and stable under the actions which occur during plating when current is passing through the bath. Acid radicals conforming to these requirements and that are known to be suitable for catalysts are the sulphate, fluoride, phosphate and borate radicals. These may be used, by suitably introducing them in the form of one or more of the compounds of the catalyst with a metal or with a non-acid radical. I consider hydrogen as a non-acid radical.

A purpose of this invention is to provide a simple and effective means for keeping the concentration of the catalyst or catalysts in a plating solution of the character indicated constant and within the limits favoring the production of satisfactory commercial chromium deposits.

A further purpose is to limit the maximum solubility of the catalyst compound in a chromium plating solution, and thus to limit the maximum concentration of the catalyst (ion) in the solution to a value within the allowable range known to be essential for the production of uniformly satisfactory deposits of chromium, and simultaneously to prevent depletion of the catalyst.

A further purpose is to supply the catalyst or catalysts from a compound or compounds containing one or more other elements or positive radicals, said compound or compounds being distinguished by the fact that, if added in excess to electrolytic solutions containing chromium, enough and only enough of the catalyst or catalysts ionize to provide a total catalyst concentration favorable to the production of satisfactory electrolytic deposits of chromium.

A further purpose is to insure the continuous presence of an adequate concentration of the catalyst radical in a plating solution of the character indicated by maintaining the solution in continuous contact with an undissolved excess of a selected compound of the catalyst.

A further purpose is to maintain an electrolytic solution of the character indicated in a continuous saturation equilibrium with respect to a selected compound of the catalyst radical, using the solid compound, in continuous contact with the plating solution, as a source for an automatic supply of catalyst, and selecting a compound having the proper equilibrium solubility in the plating solution to give a catalyst cancentration within the limits of concentration required for the plating.

A further purpose is simultaneously and automatically to avoid, in a chromium solution, an excess of catalyst, received for example with make-up chromium compound or with make-up water, and automatically to insure an adequate

catalyst concentration, keeping up the concentration of the catalyst by maintaining the liquid in continuous contact with a solid compound comprising the catalyst acid radical and a selected positive radical or metal, and removing any excess catalyst by precipitation by means of a compound containing the said selected positive radical or metal.

A further purpose is to use the limited solubility of a suitable compound of a catalyst automatically to control the concentration of the catalyst within a chromium plating solution.

A further purpose is simultaneously to use temperature and the solubility characteristics of a compound of a catalyst in an electrolytic solution of a chromium compound to determine the content of the catalytic agent in the solution.

A further purpose is to maintain a plating solution containing a chromium compound and a sulphate radical in continuous contact with solid strontium sulphate.

A further purpose is to maintain a plating solution containing a chromium compound and a sulphate radical in continuous contact with solid strontium sulphate and upon the addition of make-up water or/and of make-up chromium compound to precipitate any excess sulphate radical, incident to any sulphate in the make-up water or/and in the make-up compound, by means of a strontium compound other than strontium sulphate, preferably strontium chromate.

Further purposes will appear in the specification and in the claims.

The figure comprises solubility-temperature curves of a catalyst compound in a solution of a chromium compound adapted to form a satisfactory plating liquor and to maintain in the liquor a concentration of the catalyst within the requisite limits. The ordinates are concentration in grams per liter and the abscissæ are degrees centigrade.

The curves are intended to show conventionally how to determine the suitability or unsuitability of any compound of a catalyst for use in automatic control of the catalyst concentration in a plating liquor, and the specific curves also give the results of an actual experimental investigation by the inventor to determine the adaptation of strontium sulphate as a medium for applying the invention to a sulphate catalyst. The curves show the solubilities of strontium sulphate in solutions of chromic acid of different concentrations, and indicate the suitability of strontium sulphate as a medium for controlling the concentration of the sulphate radical in chromium plating liquors represented by the range of chromic acid solutions indicated.

The catalyst in a chromium plating liquor has been found to comprise essentially an acid radical stable under conditions within the plating bath and in order to secure uniformly satisfactory deposits of chromium it has been found that the concentration of the catalyst in proportion to the concentration of chromic acid has to be maintained within fairly definite limits.

During the continued use of a plating liquor, the concentration of the catalyst as well as the concentration of the metal containing constituent in the liquor tend to change from different causes.

Causes of such changes are:

1. Loss of solution adhering to the objects plated on the removal of such objects from the plating bath and replacement of the lost solution by water, or by water and the compound containing the metal constituent which is to be plated or electrodeposited.

2. Consumption of the compound containing the metal constituent which is electrodeposited or plated on the article during the process.

3. Replenishment of the bath with the compound containing the metal constituent which is electrodeposited to replace the quantity consumed in electrodeposition.

4. Introduction of catalysts by compounds contained as impurities in the water and in the compounds containing the metal constituent which is to be electrodeposited, used for replenishment.

These changes are not only absolute as to the catalyst constituent, but relative as between the catalyst constituent and the compound containing the metal constituent which is to be electrodeposited.

In practice all of these factors are frequently material and variant and have hitherto frequently resulted in an impossibility to definitely predict the needed changes in the concentration of the catalyst except by troublesome and repeated analysis.

When the catalyst present as an impurity in the make-up materials has been unduly high, these materials have had to be purified from the catalyst or from a portion thereof preparatory to their introduction into the plating solution.

The object of the present invention is to correct automatically sometimes for an excess of catalyst, added for example with the make-up water or/and with the make-up chromium compound, and sometimes for a deficiency of catalyst from the repeated carrying away of small quantities of the catalyst in the plating liquor which adheres to objects removed from the bath.

Let L represent the plating liquor without the catalyst and having a chromium concentration within the requisite limits for satisfactory plating in the presence of the necessary concentration of catalyst.

Let C represent the catalyst, an acid radical. Let B represent any one of the metals or non-acid radicals, B_1, B_2, B_3 . . . B_s, each of which is adapted to combine with C to form a compound BC definitely soluble in L to a limited extent. If a solid compound BC be added in excess to the liquor L, the liquor dissolves BC to saturation and in saturation equilibrium contains a concentration of C determined by the maximum solubility of BC in L at the temperature of the liquor.

Among the non-acid radicals B_1, B_2, B_3 . . . B_s, let B_s represent a selected metal or non-acid radical B suited to the carrying out of the present invention with the liquor L.

In the past the liquor L has always been undersaturated with any compound BC added to provide a catalyst C.

One of the more important features of my invention comprises a selection and use from among the many available metals or non-acid radicals B of a radical B_s such that the concentration of the catalyst in the liquor L when determined by a complete saturation of the liquor with the compound B_sC will be within the known requisite limits of concentration for satisfactory plating.

In accord with this feature of the invention, I maintain the plating liquor L in continuous contact with undissolved B_sC and thereby in continuous saturation equilibrium with B_sC, the saturation concentration of B_sC in the liquor L providing a concentration of C in the liquor

within the said limits of concentration for satisfactory plating.

In practice the make-up materials may or may not be free from catalyst.

When the make-up materials are such as to be always substantially free from catalyst no catalyst being added from any other source except B_3C, and the equilibrium or saturation concentration of B_3C in L has been reached, the selected metal or non-acid radical B_3 being one to give a solubility or saturation concentration of C in the solution L within the requisite limits of catalyst concentration, the correction of any change in concentration, by reason for example of carrying away of the plating liquor on plated objects, is effected automatically by further solution from the excess solid B_3C.

In the event that the make-up materials are not free from catalyst, the catalyst may enter the solution L with the make-up chromium compound or/and with make-up water. It is also possible that catalyst may be added by mistake or in a misguided attempt to control the catalyst concentration by introducing the catalyst from a too-soluble compound.

The effect of such additional quantities of catalyst may obviously be to raise the quantity of catalyst beyond the requisite limits of concentration unless an additional means is provided for preventing such an increase in C.

I prevent any undue increase in C by precipitating any such excess out of the liquor in the form of B_3C, and obtain this solid precipitation by adding to the liquor a compound B_3R, which on solution yields the common ion B_3. R is optionally any one of a number of different acid radicals which will not be harmful in the liquor. The compound B_3R will react in a strong acid solution of chromic acid to produce a precipitation of B_3CrO_4—a compound that can be only sparingly soluble in the plating liquor.

The radical R will usually be preferably either the chromate radical CrO_4 or the carbonate radical CO_3. In most cases the radical R will be the chromate radical.

As an example of the reaction that takes place when an excess of C enters the liquor with the make-up material, assume this radical has been added in the form of a compound B'C.

The compound B'C will react with the B_3CrO_4 due to the added B_3R, for example in accord with the reaction:

$$B'C + B_3CrO_4 \rightleftarrows B_3C + B'CrO_4$$

The additional B_3C formed by this reaction causes a temporary supersaturation of the liquor with B_3C and the excess B_3C rapidly passes out of solution as solid B_3C, leaving that concentration of B_3C and therefore of C in the liquor which corresponds to a saturated solution of B_3C. Therefore the concentration of B_3C is unchanged except as the saturation concentration might be altered (somewhat reduced) by the presence of additional B_3 cations incident to any of the excess B_3CrO_4 having gone into solution.

If B_3 represents strontium, the B_3CrO_4 will be so nearly insoluble in the plating liquor as to have little effect on the saturation concentration of B_3C in the plating liquor, leaving the C within the requisite limits of concentration for satisfactory deposition of chromium, irrespective of whether or not the liquor is saturated with B_3CrO_4 as well as with B_3C. It is therefore important to use a metal or non-acid radical B_3 whose chromate is sparingly soluble.

This correction for the presence of catalyst in the make-up materials may be made with each addition of make-up materials, or more desirably, may be taken care of automatically by keeping the liquor in continuous direct contact with an excess of solid B_3R in addition to an excess of solid B_3C.

The presence of the solid B_3R will nearly always, to some extent, affect the saturation solubility of B_3C in the liquor L, normally tending to somewhat reduce this solubility. For this reason, when investigating the suitability of any metal or non-acid radical B_1 for limiting the minimum concentration of C in a range of plating liquors L, the different liquors L should preferably include not only those having the requisite range of chromium contents, but should also be preferably saturated with B_1CrO_4 before determining the saturation solubility therein of B_1C. This is true if the raw materials of the liquors in normal practice contain catalyst, or catalyst is dragged into the liquor as a result of the operation prior to plating, thereby making it desirable to keep the liquor in continuous contact with the solid phase of the chromate of the selected metal or non-acid radical B_3 and is also normally unnecessary if the solubility of B_3CrO_4 in L is known to be very small as compared to that of solid B_3C in L.

Any metal or non-acid radical B_1 may be used in carrying out my invention if its compound B_1C, when dissolved to saturation in the chromium liquor L, also saturated with the compound B_1CrO_4 gives a concentration of B_1C such as to make C within the requisite limits of concentration for satisfactory deposition of chromium.

Having considered the general principles, the application of my invention to a particular example will be discussed briefly before considering the actual operation of the invention. Let us assume that, in the liquor L containing a suitable compound of chromium, such as chromic acid, the catalyst C is the sulphate ion, whose concentration with respect to chromic acid must be maintained within specified upper and lower limits for satisfactory plating. The maintenance of these limits is the problem solved by the invention.

To reach and preserve the lower limit of sulphate ion concentration, I add to the liquor an excess of strontium sulphate (B_3 is strontium), which dissolves and ionizes to just the proper extent to give a sulphate ion (catalyst) concentration with respect to chromic acid within the required range. As liquor is withdrawn or evaporates, and water is added, more strontium sulphate dissolves, thereby building up the sulphate ion concentration automatically to the correct amount, as long as an excess of strontium sulphate remains in contact with the liquor.

If sulphate ions be brought into solution, as for example as an impurity in the make-up materials, some strontium sulphate will be driven out of solution by common ion effect, and the resulting total sulphate ion concentration will be less than the sum of the original sulphate ion concentration, plus the sulphate ion concentration due to the impurity.

There is the possibility, however, that the sulphate ion concentration will be increased beyond the proper upper limit of sulphate ion concentration. To prevent this, I add an excess of strontium chromate (B_3R is here strontium chromate) to the liquor. The strontium chromate is very sparingly soluble, and the chromate ion does

no harm in any case, as the liquor is intended for plating chromium.

The strontium ions due to the strontium chromate lower the solubility of strontium sulphate by common ion effect, since they increase the strontium ion concentration in the solubility product:

$$\frac{[Sr].[SO_4]}{SrSO_4}=K$$

In the same way, sulphate ions brought in as impurities will increase the sulphate ion concentration in the solubility product, decreasing the strontium ion concentration, and throwing down strontium sulphate from solution.

The figure illustrates curves of the solubility of a compound B_sC in different plating solutions that may or may not be also saturated with B_sCrO_4.

The curve A represents the solubility of B_sC in a plating solution so concentrated with chromium as to be near the upper limits of proper chromium concentration, and the curve B shows the solubiliy of B_sC in the solution after its chromium has been reduced by use to near its lower limit for uniformly satisfactory use.

The ordinates show the solubility, for example in grams of C per liter of the plating bath while the abscissae represent temperature.

Solubility is normally shown in grams per unit volume of the solution. It is probable however that in chromium plating solutions a more direct criterion of the concentration of the catalyst in the plating bath is represented by the ratio between the weights of the catalyst and CrO_3 per unit of solution volume.

Though an aqueous solution of chromic acid for L and the sulphate radical for the catalyst have been described, because the ingredients are commercially relatively cheap and free from impurities, a different liquor for L or/and a different stable acid radical for the catalyst may be used, in which even the metal or non-acid radical B_s found to fulfill the specified conditions might or might not be the same B_s (strontium) suitable when L comprises an aqueous solution of chromic acid and C comprises SO_4. Likewise B_sR, which is desirably strontium chromate when the liquor consists of chromic acid with a sulphate catalyst, may be some other substance when a different plating compound or/and different catalyst is used. And for the same plating compound and catalyst, any materials may be used for B_s and B_sR which meet the conditions.

Curve A specifically represents tests made by the inventor to determine the solubility of strontium sulphate in an aqueous solution of chromic acid having a concentration of 400 grams per liter of CrO_3.

Curve B represents the solubility of strontium sulphate in a chromic acid solution having a concentration of 200 grams per liter of CrO_3, the solubilities being shown in terms of grams of SO_4 (catalyst) per liter.

In using a sulphate catalyst in plating solutions containing 250 grams of CrO_3 per liter, or more, it has been found that uniformity satisfactory deposits of chromium are readily obtainable if the temperature of the plating liquor is maintained between 40° and 50° C., or even higher, and the ratio between the weights of SO_4 and CrO_3 in the plating solution is maintained between about .01 and .005. This weight ratio corresponds to a range of from 4 to 2 grams of SO_4 per liter for curve A, and 2 to 1 grams of SO_4 per liter for curve B.

In practice it is fairly easy to maintain the temperature of the plating bath between the prescribed limits, for example between 40° and 50° C., or above, whether the solution is concentrated with respect to chromic acid or relatively dilute.

Referring to the curves, it will be seen that if the temperature were maintained at 45° C., the ratio of SO_4 to CrO_3 in a solution saturated with strontium sulphate will be about .0056 for the conditions represented by curve A and about .0109 when the chromic acid content has reduced to the conditions of curve B. These figures are sufficiently close to the optimum ratio for satisfactory operation.

In practice any small lessening of the range of permissible variation in the concentration of the CrO_3 is of little importance as compared to the importance of being able to avoid the requirement for chemical tests, to determine the catalyst concentration incident to any such small lessening of the full permissible range of variation in the concentration of CrO_3 in the liquor.

In present practice it is possible to obtain commercial chromic acid substantially free from catalyst, and in view of this I may use the solutions represented by the curves without first saturating the liquor with strontium chromate or a similar compound. In fact, where pure make-up materials are available I will preferably employ only a compound containing the catalyst to control the catalyst concentration.

In many cases however it will be more desirable to use the somewhat cheaper raw materials that contain a somewhat indefinite amount of sulphate catalyst and, in this event, I prefer to keep the liquor continuously saturated with strontium chromate as well as saturated with strontium sulphate.

Any such sulphate radical in excess of that needed to maintain the liquor L saturated with strontium sulphate reacts with the strontium chromate and is precipitated as strontium sulphate, additional strontium chromate going into solution.

In making up a new plating solution, all that is necessary when the pure chromic acid is available is to dissolve chromic acid in water to a concentration of 250 grams per liter of CrO_3, and upward, add strontium sulphate until some of it remains parmanently undissolved, heat to 45° to 50° C. and start plating.

The concentration of the chromic acid solution may be determined with sufficient accuracy by an hydrometer reading. After the chromic acid liquor has been used sufficiently to reduce the concentration of the chromic acid it is replenished by adding fresh acid, water also being added as needed, usually from any ordinary tap supply, the strength of the liquor with respect to chromic acid being determined suitably by hydrometer reading as before.

The strength of the catalyst is taken care of automatically, the strontium sulphate dissolving until the new liquor is saturated with strontium sulphate.

When the make-up materials contain more than traces of sulphate, or when sulphate is introduced by mistake or in a soluble compound, I add to the solution some compound which will cause precipitation of strontium sulphate in the liquor. This addition may be an excess of strontium chromate or may conveniently be strontium carbonate.

It will, of course, be evident that the strontium sulphate need not be added as sulphate.

If the raw materials contain sulphate radical in excess of that needed for a production of a saturated solution of strontium sulphate in the liquor L, I may simply make up the chromic acid to the requisite strength, as for example 250 to 300 grams per liter of CrO_3, and add strontium carbonate to an amount in some excess of that required for the percipitation of the excess of sulphate radical, the result being a temporary evolution of carbon dioxide, precipitations of strontium sulphate and strontium chromate in the bath and saturated solutions in the bath of strontium sulphate and strontium chromate, the concentration of the strontium chromate however being very low as compared to that of the strontium sulphate.

It will be understood that the function of the solid strontium sulphate maintained in continuous contact with the liquor is to insure in the bath a concentration of sulphate as great as the minimum amount suitable for uniformly satisfactory plating, that is to keep the bath up to standard with respect to the sulphate radical, and that the function of the solid strontium chromate is to maintain the sulphate catalyst concentration below the upper range permissible for uniformly satisfactory plating with chromium, that is to keep the bath down to standard with respect to the sulphate radical.

While one only of the metals or non-acid radicals adapted to use in an automatic maintenance of the correct concentration of a catalyst has been discussed in full, the principles have been fully explained and can easily be applied to the selection of other suitable metals or non-acid radicals for use with chromic acid as a plating medium and with the sulphate ion as a catalyst and with other plating media or/and other catalysts—whatever the cost—; and the claims are intended to cover such other compound or compounds having the catalyst compound sparingly soluble in the plating bath.

I may use variation or regulation in temperature of the plating bath within the permissible limits of such variation to vary the weight ratio between the catalyst and CrO_3.

Thus if the plating liquor and catalyst are those adapted to be specifically represented by the curves of the figure, if the temperature for the conditions of curve A is maintained at 45° C. and continuously maintained at 45° C. until the conditions of curve B have been reached, the variation in the weight ratio of C/CrO_3 will, as already stated, be from about .0056 to .0109.

The .0056 ratio may readily be raised by increasing the temperature above 45° C. when the conditions are those represented by curve A and the ratio .0109 may readily be decreased by lowering the temperature as the chromic acid becomes gradually depleted. For example if the temperature were initially 50° C. under the conditions of curve A and 40° C. under the conditions of curve B, the weight ratios, as indicated by these curves, will be respectively .006 and .010.

It will be understood that such simultaneous variation of temperature and weight ratio may be made as the conditions of service require or render desirable.

It will be evident that, in the broad aspect of my invention, I control the catalyst content automatically. To do this, I maintain a plating solution, in which the liquid phase of the catalyst compound is present, continuously in contact with the solid phase of the catalyst compound.

It will be further evident that as a desirable, but not a necessary adjunct to my invention, I control the solubility of the catalyst compound by common ion effect. I preferably do this by maintaining the solid phase of a sparingly soluble compound containing the common ion in continual contact with the liquor.

While I have discussed rather fully the inhibiting of the catalyst solubility by common ion effect, it will be evident that my invention contemplates the use of any desired and suitable means for limiting the upper range of catalyst concentration, no matter what the inhibiting agent and without regard to the mechanism by which it acts upon the catalyst to limit the catalyst concentration.

The specific examples given have been largely limited to the employment of the sulphate ion as a catalyst, but, as pointed out, other ions such as the fluoride, borate and phosphate ions, are capable of use. It is also possible to employ several catalyst ions concurrently, and in this case if the upper range of catalyst concentrations is to be limited, I will either employ a single compound which restricts the concentrations of the various catalysts present or use separate compounds to inhibit the solubilities of the different catalysts.

In any case, the compound which inhibits the catalyst solubility must be specially selected with reference to the catalyst itself and to the chromium compound from which chromium is to be plated.

In view of my invention and disclosure variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying my specific disclosure, and I, therefore, claim all such in so far as they may fall within the reasonable spirit and scope of my invention.

Having thus described my invention what I claim as new and desire to secure by Letters Patent is:—

1. The method of maintaining the concentration of an acid radical catalyst in a chromium plating liquor containing chromic acid within a desired range of concentration, which consists in keeping the liquor in continuous contact with the solid phase of a selected compound of the catalyst acid radical and a metal or non-acid radical, the solubility of the compound in the plating liquor being such as to give the liquor, when saturated with the compound, a catalyst content within the desired range.

2. The method of maintaining the concentration of an acid radical catalyst in a chromium plating liquor containing chromic acid to a desired range of concentration, which consists in keeping the liquor at temperatures within a selected range thereof and in continuous contact with the solid phase of a selected compound of the catalyst acid radical and a metal or non-acid radical, the solubility of the compound in the plating liquor exclusive of the catalyst being such as to give the liquor, when at the said temperatures and saturated with the compound, a catalyst content within the desired range of concentration.

3. The method of maintaining the concentration of an acid radical catalyst in a chromium plating liquor containing chromic acid within a desired range of concentration, which consists in keeping the liquor at temperatures within a selected range thereof and in continuous contact with the solid phase of a selected compound of the catalyst, said compound comprising the cata-

lyst acid radical and a metal or non-acid radical, the solubility of the compound in the plating liquor being such as to give the liquor, when at the said temperatures and saturated with the compound, a catalyst content within the desired range of concentration and in adjusting the temperature to accommodate change of concentration of the liquor with respect to chromium.

4. The method of maintaining a permissible range of concentration of catalyst in a chromium plating liquor containing chromic acid, which consists in maintaining the liquor in contact with an excess of a compound which yields the catalyst upon dissolving and in limiting the solution of the catalyst by common ion effect.

5. The method of maintaining the concentration of an acid radical catalyst in a chromium plating liquor containing chromic acid within a desired range of concentration, which consists in keeping the liquor in continuous contact with the solid phase of a selected compound, the said compound comprising the chromate of a selected metal or non-acid radical, the said metal or non-acid radical being adapted to combine with the catalyst acid radical to form a second compound having a solubility in the plating liquor such that, when the liquor is saturated with the second compound, the catalyst portion thereof will have a concentration within the said range of catalyst concentration.

6. The method for maintaining the catalyst content of a chromium plating liquor containing chromic acid within a desired range of catalyst concentration, which consists in keeping the catalyst up to standard by maintaining the plating liquor in continuous contact with the solid phase of a compound of the catalyst, said compound comprising an acid radical and a selected metal or non-acid radical, maintaining the liquor saturated with the compound and thereby maintaining the concentration of catalyst up to the range of catalyst concentration for satisfactory plating and in keeping the solution down to a standard with respect to its catalyst content by maintaining the liquor in continuous contact with the solid phase of a chromate of the said metal or non-acid radical.

7. The method of maintaining the concentration of an acid radical catalyst in a chromium plating liquor containing chromic acid to a desired range of concentration, which consists in keeping the liquor at temperatures within a selected range thereof and in continuous contact with the solid phase of a selected compound, the said compound comprising the chromate of a selected non-acid radical, the said non-acid radical being adapted to combine with the catalyst acid radical to form a second compound having a solubility in the plating liquor such that, when the liquor is at the said temperature and saturated with the second compound, the catalyst portion thereof will have a concentration within the said range of catalyst concentration.

8. The method of maintaining the concentration of an acid radical catalyst in a chromium plating liquor containing chromic acid within a desired range of concentration, which consists in keeping the liquor at temperatures within a selected range thereof and in continuous contact with the solid phase of a selected compound, the said compound comprising the chromate of a selected non-acid radical, the said non-acid radical being adapted to combined with the catalyst acid radical to form a second compound having a solubility in the plating liquor such that, when the liquor is at the said temperatures and saturated with the second compound, the catalyst portion thereof will have a concentration within the said range of catalyst concentration, and in adjusting the temperature to accommodate change of concentration of the liquor with respect to chromium.

9. The method of controlling the concentration of sulphate ions in a chromic acid chromium plating liquor, which consists in dissolving strontium sulphate in the liquor and in further dissolving in the liquor a compound anf strontium free from sulphate.

10. The method of controlling the concentration of sulphate ions in a chromic acid chromium plating liquor, which consists in maintaining an excess of strontium sulphate in contact with the liquor and in further maintaining an excess of a strontium compound other than strontium sulphate in contact with the liquor.

11. The method of controlling the concentration of sulphate ions in a chromic acid chromium plating liquor, which consists in maintaining an excess of strontium sulphate and an excess of strontium chromate in the liquor.

12. The method of controlling the catalyst content of a chromium plating liquor containing chromic acid which consists in maintaining cations in controlled excess of the catalyst anions, selecting and maintaining in the bath a sparingly soluble substance containing a cation non-acid radical adapted to combine and precipitate any excess of the catalyst anions.

13. The method for keeping the catalyst content of a chromium plating liquor containing chromic acid to an amount within a standard range notwithstanding the addition of catalyst to an amount that would if uncorrected raise the catalyst concentration above the range, which consists in dissolving a catalyst compound in the liquor to substantial saturation, the said compound comprising the catalyst acid radical and a selected non-acid radical and in supplying the liquor with the non-acid radical as cations in controlled excess of the catalyst anions.

14. A chromium plating liquor comprising a solution of chromic acid, a sparingly soluble catalyst compound present in excess, yielding a catalyst ion within the desired range for plating and another ion, and a sparingly soluble compound present in excess yielding the other ion free from the catalyst ion.

15. A chromium plating liquor comprising a chromic acid solution, strontium sulphate present in excess and strontium chromate present in excess.

16. As a bath for electrolytic deposition of chromium, a solution of chromic acid with an addition agent adapted to promote the deposition of chromium, such addition agent being a compound which is soluble at plating temperatures in the chromic acid solution only to the extent which affords a working concentration of the addition agent in solution, there being in the bath an undissolved excess of such addition agent.

17. As a bath for electrolytic deposition of chromium, a solution of chromic acid with an addition agent adapted to promote the deposition of chromium, such addition agent being a compound which is soluble at plating temperatures in the chromic acid solution only to the extent which affords approximately the optimum concentration of the addition agent in solution, there

being in the bath an undissolved excess of such addition agent.

18. As a bath for electrolytic deposition of chromium, a solution of chromic acid with a strontium compound as an addition agent to promote the deposition of chromium, the strontium compound being soluble at plating temperatures in the chromic acid only to the extent which affords a working concentration of the strontium compound in solution, there being in the bath an undissolved excess of the strontium compound.

19. As a bath for electrolytic deposition of chromium, a solution containing approximately 250 to 300 grams per liter of chromic acid with a strontium compound as an addition agent to promote the deposition of chromium, the strontium compound being soluble at plating temperatures in the chromic acid only to the extent which affords a working concentration of the strontium salt in solution, there being in the bath an undissolved excess of the strontium compound.

20. As a bath for electrolytic deposition of chromium, a solution containing approximately 250 to 300 grams per liter of chromic acid and strontium sulphate in excess of the amount thereof soluble in the chromic acid.

21. As a bath for electrolytic deposition of chromium, a solution of chromic acid containing strontium sulphate in excess of the amount thereof soluble in chromic acid.

22. The method of depositing chromium electrolytically which comprises electrolyzing a bath containing chromic acid and an excess of an addition agent which promotes the deposition of chromium and which is soluble at plating temperatures to the extent only of providing in the chromic acid solution a working concentration of the addition agent in solution and permitting solution of the excess of the addition agent to maintain the working concentration.

23. The method of depositing chromium electrolytically which comprises electrolyzing a bath containing chromic acid and an excess of an addition agent which promotes the deposition of chromium and which is soluble at plating temperatures to the extent only of providing in the chromic acid solution approximately the optimum concentration of the addition agent in solution and permitting solution of the excess of the addition agent to maintain the optimum concentration.

24. The method of depositing chromium electrolytically which comprises electrolyzing a bath containing chromic acid and an excess of a strontium compound as an addition agent, which promotes the deposition of chromium and which is soluble at plating temperatures to the extent only of providing a working concentration of the addition agent in solution and permitting solution of the excess of the addition agent to maintain the working concentration.

25. The method of depositing chromium electrolytically which comprises electrolyzing a bath containing chromic acid and an excess of strontium sulphate as an addition agent and permitting solution of the excess of the addition agent to maintain the concentration of the addition agent.

26. The method of depositing chromium electrolytically which comprises electrolyzing a bath containing 250 to 300 grams per liter of chromic acid and an excess of strontium sulphate as an addition agent and permitting solution of the excess of the addition agent to maintain the concentration of the addition agent.

27. The method of depositing chromium electrolytically which comprises electrolyzing a bath containing chromic acid and an excess of a strontium compound as an addition agent, which promotes the deposition of chromium and which is soluble at plating temperatures to the extent only of providing approximately the optimum concentration of the addition agent in solution and permitting solution of the excess of the addition agent to maintain the optimum concentration.

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