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CHROMIUM PLATING BATH AND METHOD OF MAKING SAME

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7 Claims. (Cl. 204—1)

This invention relates to an improved chromium plating solution and to a process for its preparation.

The usual chromium plating solutions contain chromic acid and a relatively small amount of sulfuric acid or other source of sulfate radicle. We have now found that certain substances in combination, such as persulfates, perborates and peroxides, when added to such a chromium plating solution, will increase its throwing power, and make possible a rapid operation and the production of an improved deposit. Particularly, there is little or no oxide deposited even at high current density when a plating bath of our invention is used.

It is, then, an object of our invention to provide a chromium plating bath having superior throwing power and other characteristics.

Other and further objects of this invention will be evident from the following specification and the accompanying claims.

In general, our invention comprises an improved chromium plating solution to which has been added a small quantity of a persulfate and a perborate in addition to the usual chromic acid. In place of all or a part of the perborate content, a peroxide may be used, if desired.

It is not necessary when adding these substances to a chromium plating solution to add a sulfate also, since the decomposition of the persulfate when our process is followed will result in an increase in the amount of sulfate ion in the solution, and we find this to be sufficient in most instances without further additions of sulfate.

According to the literature, persulfates decompose to a considerable extent under the application of heat. We have not found, however that this decomposition is by any means complete even upon continued boiling. The addition thereto of a peroxide or a soluble perborate, such as sodium perborate, or of an insoluble perborate, such as zinc perborate, assures completion of the reaction. The products of the reaction appear to be sulfates, bichromates and borates, or their respective free acids.

We find that it makes little difference what positive radical, or metal is combined with the persulfate. However, we prefer to use ammonium, sodium or potassium persulfate. We have been able to find no substantial difference between the action of ammonium, sodium and potassium persulfate when used in our chromium plating solution. Other persulfates will also work.

As stated above, it is preferable that a perborate or peroxide be added to the solution. If perborates are to be used, any perborate may be employed, such as sodium or zinc perborate. If peroxides are employed, they may be substituted for part or all of the perborate. Many peroxides are suitable in our process, but we have found sodium, magnesium and zinc peroxides to be particularly satisfactory.

One of the advantages of our invention is that where persulfate is added to the plating bath, a wider latitude is possible in the ratio of chromic acid to sulfate than theretofore. For example, the chromic acid- sulfate ratio of our solution may be as high as 300 to 1 and still give a satisfactory deposit.

The following examples will serve to illustrate various modifications of our chromium plating solutions:

Example No. 1

Chromic acid	900 grams
Ammonium persulfate	2½ grams
Water	Sufficient to make one gallon of solution (3785 c. c.)

In preparing the above solution, the following procedure is to be preferred: Dissolve the chromic acid and the entire amount of ammonium persulfate in 1000 c. c. of water, which is then heated to 100° C. This hastens the decomposition of the ammonium persulfate. More water is then added until the volume of the solution reaches one gallon.

It will be noted that the above solution does not contain a perborate or peroxide. It has good throwing power, and the deposit is of good color. When tested for efficiency, a coating having an average thickness of .000054 inch is produced.

The test for efficiency is made by plating an area of 1/10th sq. ft. for a period of 20 minutes at a temperature of 105° F. using a current density of 100 amperes per sq. ft. The thickness of the coating produced in this manner is a measure of the efficiency.

Example No. 2

Chromic acid	900 grams
Ammonium persulfate	2½ grams
Sodium perborate	53 grams
Water	Sufficient to make one gallon of solution

In preparing this solution, the following procedure is to be preferred: Dissolve the chromic acid and the entire amount of ammonium persulfate in about 1500 c. c. of water and heat to 100° C. as in the preceding formula. The so-

dium perborate is separately dissolved in a small quantity of water and this solution is then added to the boiling solution of chromic acid and ammonium persulfate. When all of the ingredients are thoroughly dissolved, water is added in an amount sufficient to make one gallon (3785 c. c.).

This solution produces a deposit of very good color and with a throwing power superior to that exhibited by the solution of Example No. 1. The average thickness of the deposit secured in the above described efficiency test is .00007. Thus it will be seen that the addition of sodium perborate results in an increase in efficiency of about 23%.

Example No. 3

Chromic acid	900 grams
Sodium persulfate	2.6 grams
Water	Sufficient to make a total volume of one gallon

This formula may be mixed in the same manner as in Example No. 1. The resulting solution shows good throwing power and produces a coating having a good color. The thickness resulting from the efficiency test averages .00006 inch. It will be seen that these results are comparable with those obtained by the use of the solution of Example No. 1.

Example No. 4

Chromic acid	900 grams
Sodium persulfate	2.6 grams
Sodium perborate	53 grams
Water	Sufficient to make one gallon total volume

The mixing procedure given under Example No. 2 may be followed. It will be seen that this formula is like that of Example No. 3 except that a quantity of sodium perborate has been added. This increases the average thickness on the efficiency test to .000083 inch.

Example No. 5

Chromic acid	900 grams
Potassium persulfate	3.6 grams
Water	Sufficient to make a total volume of one gallon

The throwing power exhibited by this solution is good, but the color of the deposit is inferior to that produced using the formulas of Examples Nos. 1 to 4. Some oxide is produced on the deposit when the solution is held at 115° F. but none when the temperature is reduced to 105° F. The thickness of the coating produced by the efficiency test averages .000062.

Example No. 6

Chromic acid	900 grams
Potassium persulfate	3.6 grams
Sodium perborate	53 grams
Water	Sufficient to make a total volume of one gallon

This formula is identical with the formula of Example 5 above, except that a quantity of sodium perborate has been added. This produces a deposit having a good color and the solution shows a good throwing power. The thickness of the deposit produced on the efficiency test averages .000074. Thus it will be seen that the addition of sodium perborate is very effective in improving the properties of the solution when potassium persulfate is used.

The sulfate content of the chromic acid used in the above formulas is sufficient to add about 0.44 gram of sulfate, calculated as H_2SO_4, to each gallon of solution.

The addition, in the first instance, of boric acid or the borate ion is not equivalent to the addition of the perborate ion in the above formulas. The addition initially of an equivalent amount of a borate will not produce the same improvement in the characteristics of the solution notwithstanding the probable fact that the perborates used in our method ultimately are reduced to borates.

As stated above, various peroxides may be used to replace the perborate. When substituting peroxides for the perborate in the above formulas consideration must be given to the percentage of available oxygen contained in the various peroxides as compared with the available oxygen in the perborate. The following table gives several substances which may be used for this purpose, together with the percentage of available active oxygen and the number of grams of each substance which may be used in the above formulas:

	Percentage of available oxygen	Quantity to be used in above formulas
	Percent	*Grams*
Sodium perborate	9.5	53
Magnesium peroxide	4.3	117
Calcium peroxide	13.3	37
Zinc peroxide	7.4	69

When magnesium peroxide is substituted for the perborate in the formula of Example No. 6 above, the solution exhibits excellent throwing power and the deposit has an excellent color. The efficiency test described above has been found to give an average thickness of .000084 inch for this solution.

When calcium peroxide is used in a similar manner in the formula of Example No. 6 above, the solution shows good throwing power and the deposit has a good color, but in these two respects the results are slightly inferior to those produced by the magnesium peroxide described above. The efficiency test gives an average thickness of .000063 inch.

When zinc peroxide is used in the formula of Example No. 6, the color of the deposit is very fair, although not so good as with magnesium or calcium peroxide. The solution shows good throwing power at all current densities. The efficiency test shows an average thickness of .00008 inch.

In the above formulas, specific quantities for each ingredient are mentioned. In each case, these are the preferred quantities and the quantities mentioned will produce results superior to those produced by any wide variations therefrom. However, our invention is not limited to these precise proportions, since in each case the proportion of the ingredients may be varied through a wide range without departing from the principles of our invention. For example, when chromic acid, sodium perborate, and ammonium persulfate are used, the ranges through which they may be varied are as follows:

	Grams per gallon of solution
Chromic acid	450 to 1350
Ammonium persulfate	1 to 56
Sodium perborate	1 to 56
Chromium sulfate ($Cr_2(SO_4)_3 15H_2O$)	1 to 10

When making up other solutions from the ranges given above, it should be remembered that the ratio of chromic acid to sulfate radicle should not be greater than 300 to 1, and for best results should not be below 100 to 1.

The chromium sulfate in the above formula is an optional ingredient, and may be used when it is found undesirable to depend entirely upon the persulfate to supply the sulfate ion of the solution. It also serves to supply a quantity of trivalent chromium, which is considered desirable under some circumstances, although it will be understood that an addition of trivalent chromium in this manner is not essential to successful plating.

A preferred formula using chromium sulfate as an ingredient of the solution is as follows:

	Grams per gallon
Chromic acid	900
Chromium sulfate	2
Ammonium persulfate	1.5
Sodium perborate	28

When making up the above formula the method of dissolving the ammonium persulfate described above in connection with Examples Nos. 1 to 6 should preferably be observed.

It will be understood that when other persulfates or perborates are substituted for ammonium persulfate and sodium perborate in the permissible ranges of proportions given above, the ranges in each case will be approximately proportional to the quantity of persulfate and perborate ions available in the particular compound used. Also, when sodium perborate is replaced by some peroxide the ranges permissible will be proportional to the available active oxygen in the particular compound used. The available oxygen in several compounds, including sodium perborate, has been given above.

While the examples given above have been confined to soluble perborates, it will be understood that insoluble perborates may be used. In the case of zinc perborate, which is insoluble, it is desirable to modify the method of dissolving the ingredients of the solution. A preferable procedure when this particular compound is used is to dissolve the chromic acid and the potassium persulfate in a suitable quantity of water, 1500 cc. when the quantities specified in the above formulas are used, bring the solution to a boil and add zinc perborate to this same solution at the boiling temperature. The solution may then be diluted to 1 gallon.

When selecting the specific compounds to be used in the above formulas, it should be noted that while certain compounds may work slightly better than some others, the positive ions play no active part in the success of our plating solution. However, it is desirable to avoid the use of any substance, the positive ion of which will form an insoluble compound with any negative ion which is essential to the solution. For example, strontium peroxide is not to be preferred, since the strontium will react with the sulfate ion and produce a precipitate of insoluble strontium sulfate, thereby removing a portion of the desirable sulfate ions from the solution. To a lesser extent, calcium peroxide has the same objections, and this may explain, in part, the low efficiency observed above when the solution contains calcium peroxide. Of course, it will be understood that our invention is not rendered inoperative by the use of such substances, but merely that substances which do not form these precipitates are to be preferred.

While we do not commit ourselves to any particular theory as to the cooperation between various ingredients of our plating solution, it appears that there is a reduction reaction in the chromic acid bath between the peroxide or perborate used and the persulfate, since the peroxide or perborate adds considerably to the efficiency of the solution, but when the persulfate has not been added, the perborate or peroxide is incapable of showing the same improvements in the properties of the solution. The perborate or peroxide, whichever is present, serves to complete the reduction of the persulfate to sulfate and also to reduce a part of the six valent chromium to trivalent chromium. The presence of the trivalent chromium ions appears to result in a bath of better throwing power.

Thus it will be seen that we have provided a chromium plating bath of improved characteristics and a new and improved method of making such a bath.

We are aware that numerous details of the process may be varied through a wide range without departing from the principles of this invention, and we, therefore, do not purpose limiting the patent granted hereon otherwise than necessitated by the prior art.

We claim as our invention:

1. In the process of preparing a chromium plating bath containing chromic acid, the steps of adding a quantity of a persulfate thereto and reacting upon the persulfate at an elevated temperature with a substance selected from the group consisting of perborates and peroxides.

2. In the process of preparing a chromium plating solution, the step of adding a quantity of a persulfate thereto and reducing said persulfate into a sulfate by the action of heat and a member selected from the group consisting of perborates and peroxides.

3. A chromium plating solution containing the reaction products of chromic acid, a persulfate and a member selected from the group consisting of perborates and peroxides.

4. A chromium plating solution containing the stabilized products resulting from the subjection to heat of a solution of chromic acid, a substance selected from the group consisting of perborates and peroxides and a small quantity of a persulfate.

5. A chromium plating solution comprising an aqueous solution of chromic acid and the reduction products of chromic acid, a persulfate and a perborate.

6. A process for producing a chromium plating solution containing chromic acid, which comprises dissolving the chromic acid in water, heating the resulting solution to boiling and adding thereto a small quantity of a persulfate and adding a small quantity of a substance selected from a group consisting of perborates and peroxides thereto and diluting the solution to a predetermined volume.

7. A chromium plating bath having an initial composition of 450 to 1350 grams of chromic acid, 1 to 56 grams of a perborate and 1 to 10 grams of a persulfate per gallon of solution.

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CERTIFICATE OF CORRECTION.

Patent No. 1,967,789. July 24, 1934.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 67, for "theretofore" read heretofore; and page 2, line 148, for "56" read 10; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 11th day of September, A. D. 1934.

Leslie Frazer

(Seal) Acting Commissioner of Patents.