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CHROMIUM PLATING

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The invention relates to the electrodeposition of chromium and is more particularly concerned with a process employing a novel chromium plating solution and special preparation of the metal surfaces preliminary to the plating operation per se.

The object of the invention is to provide a process of chromium plating which is an improvement on present practices particularly in being less sensitive to variations in the factors involved in chromium plating and in the quality of the chromium plate produced.

A common practice in chromium plating is to use a plating bath composed essentially of a water solution of chromic acid (CrO_3) and a sulplate or sulphuric acid, the content of chromic acid varying, in general, from 150 to 450 grams per liter and the sulphate, estimated as SO_4, being preferably about 1% of the CrO_3 content. The extreme theoretical range for the ratio of SO_4 to CrO_3 is from 1 to 50 to 1 to 250, i. e. the SO_4 amounts to from 2% to 0.4% of the CrO_3 content. But in actual practice the ratio of SO_4 to CrO_3 is between 0.66% and 1.15%. Seemingly slight departures from the prescribed conditions of the SO_4 to CrO_3 ratio, the concentration of the CrO_3, and the temperature result in defective plating.

In contrast with the generally accepted practice, I have found that by the use of other metals than chromium and of their soluble salts of chromic acid, particularly bichromates, a chromium plating process is produced of lower sulphate content which has the desired advantages over known methods. In the following description I will refer specifically to salts of sodium, such salts being more readily available commercially, but it should be understood that it is not intended to confine the invention to the use of sodium salts, as soluble salts of potassium, ammonium, zinc, and other bases are suitable. The essential characteristic of the additional metal is that it forms with the chromic acid a soluble bichromate, the metal of which does not deposit or the salt precipitate or form a colloidal solution. Bichromates of limited solubility can be mixed with those of greater solubility.

There are several ways in which the plating bath can be made up. A preferred method, disclosed in my prior application, Ser. No. 686,069, filed August 21, 1933, of which the present application is in part a continuation, comprises mixing the following:

Chromic acid (CrO_3)	pounds	100
Sodium carbonate (Na_2CO_3)	do	36½
Alumina hydrate (commercial)	ounces	19
Water	pounds	8

The chromic acid and alumina hydrate are mixed first and then the sodium carbonate and water added in alternating increments, the final product being about 125 lbs. of a yellowish powder. (The final content of SO_4 in this mixture as shown by analyses is about .21–.22% of the powder or about .27% of the total CrO_3.) The plating bath is made up by dissolving the mixture in water, about three pounds to the gallon being preferred.

The composition may be obtained by direct admixture of CrO_3 and sodium bichromate or equivalent chromate, the choice of reagents to convert the CrO_3 into bichromates or to supply the chromate or bichromate being merely a question of relative cost of materials of the necessary purity.

The "alumina hydrate" employed is a commercial product containing a fairly definite proportion, about 12% of SO_3. The alumina hydrate, being a bulky material, facilitates uniform mixing. The commercial CrO_3 also contains sulphate as an impurity as may also the Na_2CO_3. But in the actual practice of my invention, the total sulphate is preferably around or below 0.1 oz. per gallon of bath as compared with three or four times as much in the conventional high acid bath. The above mixture will give about 0.1 oz. per gallon of plating solution containing 3 lbs. of the mixture. Of course, other sulphate carriers than the alumina hydrate can be used, such as sodium sulphate in proper proportions, the essential ingredients being free CrO_3, the salt of CrO_3 and the catalytic acid radical preferably SO_4.

The exact proportion of the hexavalent chromium present in the form of the salt (considering the salt to be bichromate) is not critical, 70% being generally sufficient. Solutions in which 80% is in the combined form have a slightly higher throwing power but lower conductivity. Much above 80% results in difficulties in obtaining a good plate. Operating conditions will therefore affect the ratio selected, for example, the relative desirability of lower resistance and of higher throwing power. In general, 70% is recommended and less than 60% is not preferred. The preferred method outlined above gives neutralization of chromic acid to bichromate of approximately 70%.

Variations in concentration of the bath content are also possible. These variations are limited on the upper side by solubility of the compound and on the lower side by a darkening or lack of uniformity of the deposit. I have, therefore, found it desirable to maintain the mixture at not less than 30 oz. per gallon. The concentration of free CrO_3, however, should be maintained at not less than 5 oz. per gallon even when lower concentrations of total chromium are used.

I have found that variations in the sulphate

concentration in this plating solution over a very wide range when operated as hereinafter described give results that produce a flat bright plate characteristic curve. This curve from a concentration of about .25 ounce of SO_4 per gallon on down to the lower limit practically possible by operating with commercial CrO_3 shows a substantially uniform bright plate range. The range, however, is somewhat wider at the lower SO_4 concentrations. It was for this reason and also for a minimum etching action of the solution that I prefer the .1 oz. SO_4 per gallon concentration, which concentration can be conveniently maintained with average commercial CrO_3 even when taking into account the consumption factor which tends to build up SO_4 from this impurity in the CrO_3 consumed. With much above the .25 oz. SO_4 per gallon, however, the bright plate range rapidly narrows, as reduced chromium oxides are formed at a faster rate than they are dissolved by the solution. This difficulty is of course greater at lower mixture concentrations, which is the reason for choosing the approximately 48 oz. per gallon solution concentration as the preferred one. While higher solution concentrations possess certain advantages, the drag out factor also increases, causing increased cost.

I have found that, by varying the proportions of chromic acid salts, the ratio of hexavalent chromium to SO_4 can be widely varied and plating solutions obtained which are very low in SO_4 content. For example, a solution of a high grade of chromic acid containing 0.085% SO_4, which without addition of more sulphate will give no indication of plating at normal current densities, can be made to plate upon neutralizing a substantial part of the chromic acid with sulphate-free NaOH. In such solution the ratio of hexavalent chromium to SO_4 is about 1180 to 1.

Good results with such solution have been obtained when the CrO_3 was neutralized to about 80% (estimating the neutralized CrO_3 to be in the form of sodium bichromate) leaving 20% of the CrO_3 as free acid, with the total original CrO_3 content about 40 oz. to the gallon. Consistent plating has been obtained with the neutralization from 75% to 85% but if as much as 90% of the CrO_3 is neutralized no plating at all is obtained. It will be noted that, with 75% neutralization, the SO_4 is 0.34% of the free or unneutralized CrO_3, and at 90% neutralization the SO_4 is 0.85% of the free CrO_3.

It is my belief that the salts thus introduced serve to dissolve or to maintain in solution the salts or oxides of reduced chromium which otherwise deposit along with metallic chromium and cause iridescence, splotches, or dark deposits. The bath differs, however, from all former chromium plating baths, of which I am aware, in the following particulars: first, the total sulphate radical relative to the total CrO_3 radical present is lower than is practicable in any known commercial bath. (This feature lowers the acidity and reduces the oxidizing and etching effect on the metal surfaces to be plated); second, the sulphate radical present has no definite relation either to the neutralized CrO_3 present or to the unneutralized radical present.

The maintenance of the solution is very simple. The proportions are much less critical than in the high acid baths in present use and commercial baths have been controlled over long periods by tests of the Baumé gravity only, by merely adding material of the original composition plus a percentage of CrO_3 to compensate for the consumption of the CrO_3. Frequent chemical analyses are unnecessary.

In plating with my low acid bath it has been found that the deposits are whiter, i. e., they are free from the bluish cast of conventional chromium plate. Also the deposit is less brittle and there is a practically complete absence of line cracks commonly experienced with higher acid ratios. This latter feature is highly advantageous in providing a protective coating for a metal like brass or in the heavy plating of objects which are to be ground to size.

The low acid content of my plating bath makes it possible to plate lustrous deposits of chromium directly upon metals which would be attacked by the conventional high acid bath, for example, zinc and zinc-base alloys. Solutions containing not more than about 0.1 oz. SO_4 per gallon will not etch zinc materially at room temperature. However, solutions containing more than 0.1 oz. SO_4 per gallon may be used without detrimentally etching the zinc at room temperatures with a reasonably short time of immersion. The etching action of these solutions, higher in SO_4 per gallon, is easily ascertained by flashing a coating of zinc upon a strip of brass and then dipping it in the solution. If the etching action is detrimental the brass color will rapidly reappear.

The following is given as a specific example of commercial practice in the plating of zinc-base die castings in my solution, or other metals which respond in the same way to the plating solution, such as lead, pewter and silver. The work is first cleaned in a solution of

NaOH	ounces per gallon	8
NaCN	do	⅓ to ½

The work is made a cathode and chromium tank voltage used. It is then rinsed well and put in the plating tank.

For metals of this type the solution temperature is preferably kept below 80° F. but no strict control of temperature is necessary, and the usual room temperature is satisfactory. Tanks without heating or cooling equipment have operated well as low as 55° F. in the winter and up to 85° in the summer. The current density should be about 100 amperes per square foot on metals of this type.

The work comes from the tank with a grey smut having a slight indigo blue cast. This smut colors off almost as readily as the smut on a good nickel plate. In practical operation the current is pushed up to the maximum limit at which the work, after a three minute plate, still shows the indigo blue cast. A further increase will result in a more greyish color, which is harder to "color" up. At the lower temperature the smut is often changed to a slight brownish color by the slower rate of dissolving of the Cr_2O_3 and other reduced compounds. This, however, has not proved to be detrimental either to the clearness of the plate or to the readiness with which it colors up. Allowing the piece to remain in the solution for a short time after disconnecting will dissolve these products to give the color control.

The characteristics of my bath not only enable it to plate chromium directly upon articles, such as zinc-base die castings, or articles of lead, pewter or silver, that cannot be satisfactorily plated in the usual bath, but also enables it to plate successfully on nickel, copper, brass, etc., after the work has been subjected to preliminary cleaning and etching operations which are adapted

to the particular metal surface to be plated.

The bright plate range is not controlled by the chemical composition of the solution and temperature alone, but is very largely dependent at the lower SO_4 concentrations on the preliminary treatment of the metal surface.

The invention accordingly contemplates the use of certain preliminary treatments adapted to and in combination with the subsequent plating in my low acid bath. By these treatments I apparently invisibly etch or roughen the metal surfaces so that the proper bond is produced in my plating solution to which the work is subsequently subjected.

In determining the ingredients of the etch solution, the products of their reaction should be soluble in the etch solution itself.

For nickel I use a mixture of an oxidizing reagent such as CrO_3 and an acid such as HCl. A properly etched surface, free from insoluble oxidation products, is obtained for the above preferred plating bath by the following solution:

CrO_3	ounces per gallon	2
NaCl	do	.04 to .06

The concentration of the chlorine radical is the determining factor; and the CrO_3 has to be made sufficiently concentrated to act as a dilute acid wash to neutralize any alkali which may carry over from the usual previous cleaning operation.

An etch solution involving an increased amount of acid radical and a bichromate, such as sodium or ammonium bichromate, results in a wider plating range for the truly bright plate. For example, such an etch solution may be as follows:

Sodium bichromate	ounces per gallon	20
CrO_3	do	2
NaCl	do	.04
H_2SO_4	do	.1

The .1 of an ounce of H_2SO_4 is substantially .5% of the 20 oz. of the sodium bichromate used. This is the normal sulphate impurity in commercial sodium bichromate.

Instead of adding sodium bichromate, equivalent amounts of soda ash and chromic acid may be added. As commercial soda ash contains sodium chloride as an impurity, the employment of this combination would operate to add additional sodium chloride.

The procedure for the plating of a nickel surface is:

(a) Clean work in cleaning solution and rinse with water.

(b) Etch for about ten seconds in nickel etch solution at room temperature. Time is not critical. Then rinse in water.

(c) Enter work in the chromium tank, making sure that it is well wet with the plating solution before making contact with the cathode bar.

For plating copper and brass, the proper etch can be obtained by using the correct proportions of cyanide in the cleaning solution.

An example of such an etch solution is as follows:

NaOH	ounces per gallon	8
NaCN	do	1½
Copper cyanide	do	½

This solution should be used at room temperature.

The procedure is:

(a) Clean electrically at cathode for 5 to 10 seconds in this solution using chromium tank voltage, and rinse in water.

(b) Rinse in a 1 to 2% HCl solution to remove alkali. Other acids, even as weak ones as acetic, can be used.

(c) Rinse well in water free from CrO_3 before entering chromium tank so that the presence of HCl in contact with the CrO_3 plating solution will not oxidize the copper or brass, which would make the work streaky or unplatable.

(d) Enter the work in chromium tank and plate.

The plating solution of my invention possesses a good bright plate range on copper, brass and nickel, even at temperatures of 110° F. but the best general range on these metals is 80–90° F.

While I have outlined different etching solutions for the different metals which I have found preferable for my preferred plating solution, I must make clear that these exact proportions for the etching solutions will not be the optimum for the entire range of variation in plating solutions having sulphate radical concentrations below approximately .65 percent, but would have to be varied according to the departures from the preferred plating solutions and directions given above. It should be understood that it is not intended to confine the invention to the use of the preferred nickel etching solution described above. Since I have found that the salts of both hydrochloric and sulphuric acid react as acids through ionization in the presence of weak acids, such as chromic acid, it is obvious that hydrochloric or sulphuric or other strong acids such as hydrofluoric acid can be used in combination with an oxidizing reagent, such as chromic acid to make suitable nickel etching solutions. In the substitution of other strong acids for hydrochloric acid, it should be observed that the most suitable proportions of acid will not depend upon the comparison with hydrochloric acid upon the basis of hydrogen ion concentration. Different acids have different etching characteristics in the presence of an oxidizing reagent, such as chromic acid. The proper proportions for other strong acids will easily be found. When the action of the etching bath is too strong, unplated areas form on the work in the plating operation; when too weak, the throwing power is poor and the resulting plate hazy.

It should also be understood that it is not intended to confine the invention to the use of the preferred copper and brass etching solution since the concentration of the cyanide (the etching medium) in the alkali cleaning solution and the concentration of the hydrochloric acid in the acid dipping bath are not critical. Too little cyanide, however, is detrimental to the throwing power and too much cyanide roughness the surface and gives a hazy plate.

Also it should be understood that it is not intended to confine the invention to the use of caustic soda, the preferred cleaning reagent for copper and brass, described above, since it is obvious that other known cleaning reagents can be used equally well.

I have found that it is possible to etch copper and brass in a properly proportioned oxidizing solution similar to, though considerably weaker than that used for etching nickel; but that the alkali cyanide solutions are preferable for these metals due to the uncertainty of the solubility of the oxides of copper in solutions of this type.

I have found also that even the above preferred plating solution when used for plating copper

and brass have some, though an insufficient etching action, on the surface to be plated. This mild etching action of the plating solution on the surface of the metal to be plated should be taken into account in determining the degree of etching action desired in the preliminary etching operation.

The etching action of the preferred plating solution on nickel is practically negligible; but if higher ratios of SO_4 to total CrO_3 are used, the etching action is not negligible and must be taken into account and allowed for in determining the degree of etching action desired in the preliminary etching operation.

While I have described the use of plating baths containing bichromate and low in SO_4 concentration with my etching baths, it should be understood that the invention is not to be confined to the use of my etching baths with such plating solutions, for my etching baths can be usefully employed with plating solutions containing little or no bichromate (representing neutralizations of CrO_3 from 60 per cent down to zero per cent) but containing SO_4 in lower concentrations than .65 per cent. Although such plating solutions have a greater etching action than similar baths containing substantial amounts of bichromate as described above, they are still useful for plating with my etching solutions. If the SO_4 concentration of such baths is reduced, the etching action is correspondingly reduced until it practically ceases at the lowest concentrations. Higher SO_4 concentrations though still below .65 per cent result in an etching action which must be taken into account and allowed for in determining the degree of etching action desired in the preliminary etching operation. This etching action of the higher SO_4 concentrations (though still below .65 per cent) is little affected by small amounts of bichromate. But if the proportion of bichromate is increased, the effect is to diminish the etching action until at the preferred percentages of neutralization, the etching action is reduced to minimum proportions.

The advantages of my process over the present high-acid method are as follows:

(1) Ability to plate metals of the type of zinc die castings direct with an adherent plate that will retain its luster for a long period.

(2) A much more adherent and lasting plate, free from line cracks, on brass and copper.

(3) On nickel the ease with which a true bright plate may be obtained even with irregular hand operation in the plating bath.

(4) No changes take place in the etching solution to upset the equilibrium so that control is greatly simplified.

(5) The plating solution is much less sensitive to the proportions of the chemical components present, e. g., Na, CrO_3, and SO_4, so that its maintenance is much less critical. There is no necessity to maintain a substantially constant ratio of SO_4 to either the total CrO_3 present or to the free CrO_3 present.

(6) The temperature may vary over a considerable range without affecting the results.

While I have referred above to the sulphate content, it should be understood that the invention is not limited to such acid radical additional agent or "catalyst." Other such addition agents known in the art, fluorides, fluosilicates, etc., may be employed in reduced amounts in accordance with the present invention. The impurity present in the CrO_3 and other materials, however, must be taken into account and corresponding reduction made in the additions of such catalysts. As sulphate is already present in the commercial raw material in amounts that roughly correspond with that used, the use of such equivalent known "catalysts" would largely depend on obtaining a raw material of greater purity than presently commercially available.

I claim:

1. A low-etching chromium plating bath for plating clear, adherent chromium comprising, a water solution of chromic acid in part free and in part combined as an alkali salt, the free acid constituting 20 to 40% of the total and not less than approximately 5 oz. per gallon, and sulphate to the amount of not over approximately .4% of the total chromic acid, the total chromic acid being 30 to 50 oz. per gallon.

2. A chromium plating bath for plating clear, adherent chromium comprising, a water solution of chromic acid in part free and in part combined as a metal salt of chromic acid, the metal of which does not deposit or the salt precipitate or form a colloidal solution, the total chromic acid being about at least 30 oz. per gallon and the free chromic acid constituting 20% to about 40% of the total, and a catalyst consisting of at least one of the acid radicals of the following class, sulphates, fluorides, and fluoscilicates, to the amount of not over approximately .4% of the total chromic acid.

3. A chromium plating bath for plating clear, adherent chromium comprising, an aqueous solution of chromic acid in part free and in part combined as an alkali salt of chromic acid, the free acid constituting approximately 30% of the total chromic acid, the total chromic acid being about 30 to 50 oz. per gallon, and sulphate to the amount of not over approximately .4% of the total chromic acid.

4. Process of producing a coating of clear, adherent chromium upon an article having a metallic surface composed preponderantly of a metal of the class consisting of copper, zinc, lead and silver, comprising immersing the article in an aqueous plating bath containing free chromic acid, a soluble bichromate and a sulphate catalyst promoting deposition of chromium, the total chromic acid being about 30 to 50 oz. per gallon and the free chromic acid constituting 20% to about 40% of the total, said sulphate catalyst being present to the amount of not over approximately .4% of the total chromic acid, and supplying plating current to said article.

5. A process of producing an adherent coating of clear, adherent chromium upon an article having a metallic surface composed preponderantly of a metal of the class consisting of copper, zinc, lead and silver, comprising immersing the article in a plating bath containing an aqueous solution of chromic acid in part free and in part combined as an alkali salt of chromic acid, the total chromic acid being about 30 to 50 oz. per gallon and the free acid constituting 20 to about 40% of the total and sulphate in amount of about .1 ounce per gallon, and supplying plating current to said article.

6. A process of plating clear, adherent chromium upon a metal surface composed preponderantly of copper comprising first treating the surface in a bath having an etching effect upon said metal the products of which are soluble in said bath, washing said surface, then immersing said article in a plating bath containing an aqueous solution of chromic acid in part free and in part combined as an alkali salt of chromic acid, the

total chromic acid being about 30 to 50 oz. per gallon and the free acid constituting 20 to about 40% of the total, and sulphate acid catalyst to the amount of not over approximately .4% of the total chromic acid, and supplying plating current to said article.

7. A process of plating clear, adherent chromium upon a brass or copper surface comprising first subjecting such surface to a cathodic treatment in an alkaline cyanide solution, washing with dilute acid to free from alkali, then plating directly thereon a coating of chromium in a plating bath comprising an aqueous solution of chromic acid in part free and in part combined as an alkali salt of chromic acid, the total chromic acid being about 30 to 50 oz. per gallon and the free acid constituting 20 to about 40% of the total, and sulphate acid catalyst to the amount of not over approximately .4% of the total chromic acid, and supplying plating current to said surface.

8. The process of making a chromium plating bath for plating clear, adherent chromium comprising mixing the following ingredients in substantially the proportions specified; chromic acid 100 pounds, sodium carbonate 36½ pounds, alumina hydrate (commercial) 19 oz., water 8 pounds, said constituents including sufficient sulphate to provide a sulphate content of approximately .2% of the dry composition resulting from mixing said ingredients in the proportions specified, and dissolving said mixture of ingredients in water in the ratio of about three pounds per gallon of water.

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