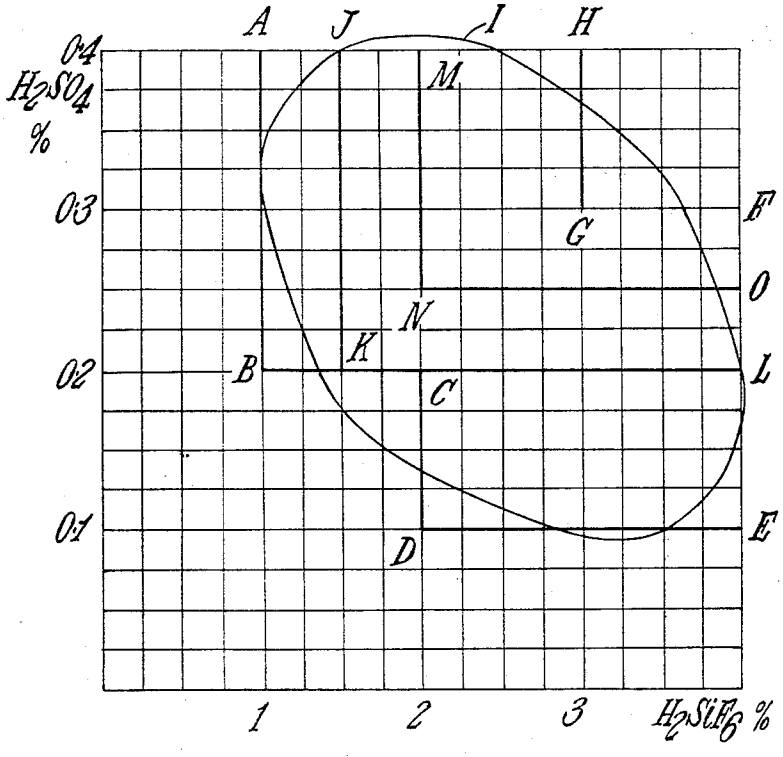
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ELECTRODEPOSITION OF CHROMIUM

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ELECTRODEPOSITION OF CHROMIUM

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ABSTRACT OF THE DISCLOSURE

A micro-cracked chromium coating having at least 600 micro-cracks per linear inch in any direction is obtained by a single-stage electrodeposition at less than 1920 amp-min. per sq. ft. from a solution consisting essentially of 100 to 225 g./l. of chromic acid, between 0.1 and 0.4% of sulphate ion, and between 1.5 and 4% of silicofluoride ion, with the percentages being based on the chromic acid content. If the sulphate ion content is less than 0.2%, the silicofluoride ion content is greater than 2% and if the sulphate ion content is greater than 0.3% the silicofluoride ion content is less than 3%.

This invention relates to the electrodeposition of chromium, and more particularly to the electrodeposition of chromium with a "micro-cracked" surface. A chromium coating is referred to as micro-cracked when it possesses a structure such that the surface is covered with a multitude of cracks in such quantity and in such a pattern that crossing any inch length of its surface in any direction are at least 600, and preferably 1,000 such cracks.

It is known that the use of so-called micro-cracked electrodepostied chromium coatings over an undercoat of nickel which has been electrodeposited on basis metals such as iron, copper, aluminum, zinc, or alloys of these metals confer excellent corrosion protection to these basis metals.

Commercial chromium-plating electrolytes consist of aqueous solutions of chromic anhydride (CrO_3), commonly termed chromic acid, which also contain small but vital quantities of so-called catalysts, without which no chromium could be electrodeposited. These catalysts are most frequently silicofluoride $(SiF_6)^{2-}$ and/or sulphate $(SO_4)^{2-}$ ions. It is essential in order to obtain the optimum conditions of chromium electrodeposition that these catalysts be present in certain specific ratios to the concentration of chromic acid present. For example, an electrolyte containing 1% of sulphate ions as compared with the chromic acid is frequently employed in commercial practice, as is one containing 0.5% of sulphate ions together with 1% of silicofluoride ions. While some tolerance can be allowed from the above ratios, it is essential for most effective electrodeposition that they are not departed from too far. For example, in the electrolyte containing sulphate ions only, the percentage is usually kept between 0.8% and 1.25%. Providing these ratios are compiled with, the concentration of chromic acid used is less critical and varies between 150 and 500 g./l. in commercial plating electrolytes. However, an electrodeposit with a micro-cracked structure is most readily obtained from a chromium plating electrolyte if the concentration of chromic acid is below 225 g./l. and contains both silicofluoride and sulphate ions. The total concentration of catalyst ions must also be raised above that normally considered appropriate for bright chromium electrodeposition. However, by doing so, the coverage of the electrodeposit is much reduced and no chromium is thereby deposited on the portions of the cathode where the current density falls below a certain limiting value, which

value is much greater than with conventional chromium-plating electrolytes. This means that any complex shaped article cannot be completely covered with chromium electrodeposited from such a solution. However, if the percentage of catalysts are lowered to give better coverage, the micro-cracked structure would be entirely absent, or else be confined to the edges of the plated article where the chromium thickness was greatest. (The development of a micro-cracked structure in any electrodeposit of chromium depends on a certain minimum thickness of chromium being electrodeposited and this thickness for commercial application must not be so great as to render it impracticable or uneconomical.)

Previously, therefore, electrodeposition of micro-cracked chromium coatings was done in two stages using two different chromium plating electrolytes, the first giving an electrodeposit having good coverage and the second producing the micro-cracked structure, which cracking extended through both layers of chromium to the underlying nickel. This is obviously not so convenient as electrodepositing micro-cracked chromium from one electrolyte only. It was formerly only possible to obtain micro-cracking in a single layer of electrodepostied chromium deposited by one electrolyte by adding an alkali metal selenate to the plating solution. This in turn creates difficulties as the concentration of selenate ions is very small and must be rigorously maintained within close limits, for if the content of selenate ions becomes too great, reduction occurs in the coverage given by the electrodeposit, or if it becomes too low the micro-cracked structure is no longer present in the electrodeposit. Also the selenate ions confer a much bluer color than usual to the chromium coating, which could be objectionable, particularly on components which are assembled on a structure adjacent to others plated with standard chromium deposits.

The use of this invention provides an electrodeposited chromium coating having a micro-cracked structure as defined above. It is readily carried out so as to use chromium plating operation only from a single chromium plating electrolyte containing only silicofluoride and sulphate ions as catalysts, the micro-cracked electrodeposit still having good coverage and attaining its micro-cracking structure at a reasonable thickness, i.e. in a fairly short plating time, considered to be 12 minutes on our particular standard specimens.

This is achieved by controlling three factors:

(1) Concentration of chromic acid.

(2) Percentage of catalysts.

(Not only must the total content of catalysts be raised but the proportion of silicofluoride to sulphate ions adjusted to a ratio not normally used for electrolytes employed for commercial electrodeposition.)

(3) Concentration of metallic impurities.

This invention consists in an electrodeposition solution containing between 100 and 225 g./l. of chromic acid, between 0.1 and 0.4% of sulphate ion and between 1 and 4% of silicofluoride ion, each reckoned on the basis of the chromic acid content, in which if the sulphate ion content is less than 0.2% the silicofluoride ion content is greater than 2% and if the sulphate ion content is greater than 0.3% the silicofluoride ion content is less than 3%.

Metallic impurities are often introduced into chromium plating electrolytes either by dissolution of the metals being plated such as iron, zinc or copper, or by reduction of hexavalent chromium at the cathode.

Preferably the solution should contain less than 8 g./l. of metallic impurities. If a higher concentration than this is present, more than 0.25% of sulphate ion and more than 2.0% of silicofluoride ion should also be present.

Preferred limits for chromic acid concentrations are 140–180 g./l. and for sulphate concentration 0.2% to 0.4% of this chromic acid concentration, and for silicofluoride 1.5% to 4% of this concentration.

The limits specified for sulphate, silicofluoride, metallic impurities and chromic acid are arrived at by consideration of the following factors:

(i) Below a certain concentration of total catalyst, micro-cracking will only occur at above 12 minutes plating time.

(ii) Above a certain concentration of total catalyst, chromium coverage will be too poor.

(iii) If one catalyst concentration is high, the other should be low, so the total does not exceed the level at which coverage will suffer. In the same way, the total catalyst content must not be too low or else micro-cracking will suffer.

(iv) Increase in chromic acid, at any given ratio of catalyst to chromic acid results in a lengthening of the time to give micro-cracking.

(v) Increase in metallic impurities necessitates a longer time for micro-cracking.

Since these limits are interdependent, an alternative expression of the invention can be given by drawing the graph of sulphate concentration against silicofluoride concentration and circumscribing the area of concentrations which would work by a closed loop.

The single figure of drawing shows such a graph, and the invention further consists in an electrodeposition solution containing between 100 and 225 g./l. of chromic acid and with a sulphate ion and silicofluoride ion content within the closed loop **1** on the figure of drawing provided.

It will be realized that the closed loop thus defined is not precisely the same as the figure with reentrant angles (see graph) earlier defined; however, it only differs by cutting of some of the angles which are in some respects not fully characteristic of the invention, and as a matter of substance the two definitions delimit the same invention.

For completeness of description the ranges and preferred ranges defined numerically above are also shown graphically. ABCDEFGH is the broadest such numerical statement, JKLFGH is the preferred range of concentrations, MNOFGH the preferred range of concentrations when more than 8 g./l. of metallic impurity is present.

To aid in maintaining the correct concentration of sulphate ions, the solution may contain dissolved strontium sulphate in the presence of solid strontium sulphate and also contain an innocuous strontium salt, e.g. the chromate to suppress the solubility of the strontium sulphate and maintain the sulphate ion concentration at a desired value.

In a further aspect, the invention consists in a method of electrodepositing a micro-cracked chromium coating in which an electrodeposition according to the invention and as described above is used as the electrolyte in a chromium plating bath. The micro-cracked chromium layer may be deposited in a single stage upon the basis metal, or be deposited, again if desired in a single stage, upon a previously formed nickel layer on the basis metal.

In a further aspect the invention consists in an article with a micro-cracked chromium coating produced by the method described in the preceding paragraph.

In a still further aspect, the invention consists in a liquid concentrate which when diluted with water gives an electrodeposition solution as described above. Such a concentrate may contain, e.g. up to 900 g./l. of chromic acid with sulphate and silicofluoride ions in proportion. Alternatively, in a further form the invention provides a solid mixture of chromic acid, a source of sulphate ion and a source of silicofluoride ion in such proportions that it can be dissolved in water to give an electrodeposition solution as described above. Such a solid mixture can also contain a source of strontium ion to give a solution as described three paragraphs above.

Another form such a solid mixture can take is a solid mixture of a source of strontium ion and of silicofluoride ion, e.g. of strontium chromate and sodium silicofluoride. This can be added to a conventional chromium plating solution (i.e. chromic acid and sulphate ion catalyst) to give a solution suitable to provide a micro-cracked coating according to the invention.

EXAMPLES

All these plating tests were performed on standard 2" x 2" steel panels, which had previously been coated with an electrodeposit of bright nickel. All tests were done under standard conditions (160 amps/ft.^{2} and 112° F.) and the solution composition varied to illustrate the effect of changes in its composition on the plating time and therefore thickness of chromium needed before micro-cracking occurred.

Example 1

This illustrates the effect of variation in chromic acid content.

Composition	Solution A	Solution B
Chromic acid, g./l.	150	200
Sulphuric acid, g./l.	0.55	0.55
Hydrofluosilicic acid, g./l.	3.0	3.0
Time for microcracking, min.	5	8

Example 2

This illustrates the effect of variation in sulphuric acid content.

Composition	Solution A	Solution B
Chromic acid, g./l.	150	150
Sulphuric acid, g./l.	0.25	0.55
Hydrofluosilicic acid, g./l.	3.0	3.0
Time for microcracking, min.	10	5

Example 3

This illustrates the effect of variation in hydrofluosilicic acid content.

Composition	Solution A	Solution B
Chromic acid, g./l.	150	150
Sulphuric acid, g./l.	0.35	0.35
Hydrofluosilicic acid, g./l.	3.4	1.8
Time for microcracking, min.	7	9

Example 4

This illustrates the effect of variation in metallic impurities.

Composition:	G./l.
Chromic acid	150
Sulphuric acid	0.45
Hydrofluosilicic acid	3.0

Time for micro-cracking with:

	Min.
(I) No metallic impurities present	6
(II) 3 g./l. trivalent chromium present	8
(III) 8 g./l. trivalent chromium present	9
(IV) 8 g./l. zinc present	9

Example 5

This gives examples of solution containing strontium compounds.

Composition:	G./l.
Chromic acid	150
Sodium silicofluoride	4
Strontium sulphate	2

Plus varying concentration of strontium chromate.

	Min.
(a) 8 g./l. gives micro-cracking in	5
(b) 17 g./l. gives micro-cracking in	8
(c) 24 g./l. gives micro-cracking in	10

Example 6

This is an example of a solid "conversion salt" mixture according to the invention. Such a salt can be added to the conventional (CrO_3/SO_4^{--}) chromium plating bath.

A solid mixture was made up of composition:

	Percent
Strontium chromate	62.5
Sodium silicofluoride	15.5
Chromic acid	22.0

The chromic acid was included for commercial reasons and was not an essential component of the mixture. 25 g./l. of this "conversion salt," added to a conventional chromium bath in the requisite range of CrO_3 and SO_4^{--} concentration gave a solution according to the invention.

Various modifications may be made within the scope of the invention as defined in the appended claims.

What we claim is:

1. A method of electrodepositing a microcracked chromium coating by a single-stage electrodeposition upon a nickel layer formed on basis metal which comprises passing current at less than 1920 amp-min. per sq. ft. from an anode to said nickel-coated metal as a cathode immersed in an aqueous chromium plating bath, said bath containing an electrodeposition solution which is an aqueous electrolyte consisting essentially of 100 to 225 g./l. of chromic acid, at least one soluble sulphate-containing compound which produces between 0.1 and 0.4% based on the chromic acid content of sulphate ion, and at least one soluble silicofluoride-containing compound which produces between 1.5 and 4% based on the chromic acid content of silicofluoride ion, the silicofluoride ion content being greater than 2% if the sulphate ion content is less than 0.2%, and the silicofluoride ion content being less than 3% if the sulphate ion content is greater than 0.3%, to produce a micro-cracked chromium coating having at least 600 micro-cracks per linear inch in any direction.

2. The method according to claim 1, wherein the electrodeposition solution contains from 140 to 180 g./l. of chromic acid and which has a sulphate ion content of from 0.2 to 0.4% and a silicofluoride ion content of from 1.5 to 4%.

References Cited

UNITED STATES PATENTS

2,640,022	5/1953	Stareck	204—51
2,787,589	4/1957	Stareck et al.	204—51
2,800,438	7/1957	Stareck et al.	204—51 X
3,157,585	11/1964	Durham	204—41

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