

1

3,457,147

CHROMIUM PLATING BATH AND PROCESS
Heinz Dettner, Berlin, Germany, assignor, by mesne assignments, to Dr. Heinz W. Dettner, Solingen, Germany
No Drawing. Filed Feb. 7, 1967, Ser. No. 614,424
Int. Cl. C23b 5/06

U.S. Cl. 204—51

5 Claims

ABSTRACT OF THE DISCLOSURE

Pyridine-, quinoline-, and isoquinolinesulfonic acids when present in otherwise conventional chromium plating solutions containing chromium trioxide and a plating catalyst, prevent the formation of chromium nodules during hard chromium plating without affecting the balance between the chromic acid and the catalyst.

Background of the invention

When heavy or so-called hard chromium deposits are formed on a cathode in the conventional chromium plating baths which are essentially aqueous solutions of chromic acid and of a relatively small amount of a catalyst, such as sulfuric acid, fluoride ion, or fluosilicate ions, nodules form on the chromium surface and mar its appearance. Nodule growth is particularly rapid in chromium plating solutions containing fluosilicate catalysts, and may interfere with proper use of the chromium plated object.

The tendency to nodule formation in fluosilicate-bearing plating solutions can be reduced by the addition of sulfates or of sulfuric acid, but such additions upset the balance between the chromium trioxide and the catalyst in the solution, the sulfate or the sulfuric acid respectively itself being a catalyst. A reduction in covering power results from the imbalance and may require use of auxiliary anodes.

It has been proposed heretofore to reduce nodule formation in chromium plating baths by the addition of alkyl-arylsulfonic acids (U.S. Patent No. 2,195,409), aromatic sulfonic acids (Dutch Patent No. 73,083), and m-benzenedisulfonic acid (German Patent No. 1,008,542); but it is a common feature of the known nodule-retarding addition agents that they are decomposed relatively rapidly after their addition to the electrolyte.

Summary of the invention

It has now been found that the pyridine-, quinoline-, and isoquinolinesulfonic acids and their soluble salts retard or prevent the formation of chromium nodules during hard chromium plating, that these sulfonic acids lack catalyst activity, thus do not upset the catalyst balance in the solution and that they resist decomposition by the electrolyte under plating conditions much longer than the aforementioned known sulfonic acids, 3-pyridinesulfonic acid being outstanding in this respect.

The addition agents of the invention are known, and may be prepared according to known methods. No benefits have been derived from the use of amounts greater than 75 grams per liter that could not be achieved with smaller concentrations of addition agent. Under most practical conditions, best results are achieved with amounts between 20 and 40 grams per liter. The addition agents of the invention may be added to otherwise conventional chromium plating solutions in the form of the free acids or of soluble salts of the acids with cations which do not interfere with chromium plating when present in the necessary amounts. The alkali metal salts, particularly the sodium and potassium salts, are most readily available, and therefore preferred. The nodule-retard-

2

ing or nodule-preventing activity of the addition agents is bound to the anion only, and the nature of the cation is immaterial.

If the catalyst in the chromium plating bath is fluoride or fluosilicate, the addition agents of the invention are most effective when used in conjunction with barium salts in amounts sufficient to precipitate any sulfate ion present. The addition agents of the invention are fully operative in chromium plating solutions containing sulfate ions as catalysts, and in self-regulating high-speed chromium plating solutions which rely on sparingly soluble sulfates for maintaining their electrolyte balance.

Description of preferred embodiments

The following examples further illustrate the invention, but it will be understood that the invention is not limited thereto.

Example 1

Steel plates were made the cathode in a conventional chromium plating solution which was an aqueous solution of 250 g. chromium trioxide and 15 grams potassium fluosilicate per liter, and had a temperature of about 53° C. The cathode current density was 50 amps. per sq. decimeter. After one hour, the chromium deposit showed uniformly distributed small nodules.

3-pyridinesulfonic acid was then added to the bath in an amount of 30 grams per liter, dummies were plated for a short period, and the afore-described plating procedure was repeated. The chromium deposits formed were entirely free from nodules.

Example 2

Freedom from nodules was also an outstanding feature of hard chromium deposits produced from the electrolytes and under the operating conditions listed in the following table.

TABLE

Chromic acid, grams per liter.....	400	300	350	300	250
Potassium fluosilicate, grams per liter.....	20			17	20
Calcium fluoride, grams per liter.....			18		
Sulfuric acid (d=1.84), grams per liter.....		3			
Barium carbonate, grams per liter.....	10				
Barium chromate, grams per liter.....				7	
3-pyridinesulfonic acid, grams per liter.....		10	25		
Sodium 3-pyridinesulfonate, grams per liter.....					
5-isoquinoline-sulfonic acid, grams per liter.....	50				
8-quinolinesulfonic acid, grams per liter.....				20	20
Cathode current density, amps./sq. dm.....	50	10	10	15	10
Temperature, ° C.....	42	40	45	40	40

8-isoquinolinesulfonic acid may be substituted for 5-isoquinolinesulfonic acid without significantly affecting the results. The pyridine-, quinoline-, and isoquinoline-monosulfonic acids not specifically referred to above have been found to have at least some nodule suppressing effect, but not to be as effective as the acids mentioned above and their salts with suitable cations.

The concentrations of the conventional electrolyte ingredients such as chromic acid and catalyst, the temperature and the current density may be varied within known limits and are not directly relevant to the suppression of nodule formation by the sulfonic acids and sulfonates of this invention. The beneficial effects increase, of course, with the thickness of the electrodeposited chromium, but some improvement can also be observed in decorative chromium coatings produced from electrolytes containing the sulfonic acids referred to above, or their soluble salts. The substrate on which the chromium is deposited has no influence on the nodule-preventing effect of this invention.

It should be understood, therefore, that the foregoing disclosure relates only to preferred embodiments of the invention, but that the invention is not limited to the ex-

3

amples chosen for the purpose of the disclosure but is defined solely by the scope and spirit of the appended claims.

What is claimed is:

1. In a chromium plating solution consisting essentially of an aqueous solution of chromium trioxide and a chromium plating catalyst the improvement which resides in the presence in said solution of an addition agent selected from the group consisting of pyridine-, quinoline-, and isoquinolinesulfonic acid, and soluble salts of said acids in an amount effective to reduce nodule formation on a chromium electro-deposit formed in said bath, but not substantially greater than 75 grams per liter.

2. In a solution as set forth in claim 1, said addition agent being 3-pyridinesulfonic acid or a soluble salt thereof.

3. In a solution as set forth in claim 1, said addition agent being 8-quinolinesulfonic acid or a soluble salt thereof.

4

4. In a solution as set forth in claim 1, said catalyst being a fluoride or fluosilicate, the solution further containing an amount of a barium salt sufficient to make sulfate ions substantially insoluble in said solution.

5. A method of electrodepositing chromium which comprises making a conductive substrate the cathode in the solution of claim 1.

References Cited

UNITED STATES PATENTS

2,195,409	4/1940	Flett	204—51 XR
2,750,337	6/1956	Brown et al.	204—51

FOREIGN PATENTS

274,913	1929	Great Britain.
---------	------	----------------

JOHN H. MACK, Primary Examiner

G. L. KAPLAN, Assistant Examiner