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CHROMIUM PLATING PROCESS

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The present invention is directed to the field of chromium electroplating, and more specifically directed to the preparation of nickel for subsequent chromium electrodeposits.

Certain nickel surfaces are relatively "inactive" as regards their receptivity to subsequent chromium electrodeposits. This relative inactivity may be caused by (a) the inherent nature of certain nickel electrodeposits, (b) inactivation due to film formation in air, and (c) buffing. Such inactive surfaces are poor surfaces for subsequent chromium electrodeposition, i.e., surface appearance is poor and it is also difficult to obtain good coverage with the chromium electrodeposited over the inactive nickel. To successfully electroplate chromium over inactive surfaces, it is necessary to use chromium baths containing large amounts of acid-catalysts which is often undesirable. To "activate" the nickel, it is usual to immerse it in mineral acid baths for surface activation prior to chromium electrodeposition. The most commonly used mineral acids, sulfuric acid and hydrochloric acid, are extremely undesirable contaminants in chromium plating baths. Drag-in of sulfate and chloride must be kept at a minimum. This necessitates the interposition of several water rinses between the mineral acid nickel activating bath and the chromium plating bath. There has long been a need for an activating bath which does not contribute any deleterious drag-in products to subsequent chromium electroplating baths.

It is an object of this invention to provide a process for activating nickel prior to chromium electroplating. It is also an object of this invention to provide a novel bath for the immersion activation of nickel. This invention also contemplates providing compositions of matter for making up and maintaining aqueous nickel activating baths. It is still another object of this invention to provide an improved chromium plating process utilizing a novel nickel activating processing step immediately prior to the chromium electrodeposition.

I discovered that nickel surfaces are activated for subsequent chromium electrodeposition by immersion in an aqueous bath containing between 1 g./l. (gram per liter) and 100 g./l. of at least one saturated dicarboxylic acid containing two to six carbon atoms in the chain. The solutions preferably contain between 5 g./l. and 50 g./l. of the dicarboxylic acid. Balancing technical and commercial considerations, baths containing about 25 g./l. are now considered optimum. The useful dicarboxylic acids include oxalic acid, malonic acid, tartronic acid, mesoxalic acid, succinic acid, malic acid, tartaric acid, glutaric acid, and adipic acid. Existing acid anhydrides of the useful acids are equivalents of the respective acid in the activation bath. The preferred acids are oxalic acid, succinic acid, and malic acid.

The minimum useful time of immersion in the activating bath is dependent on the particular dicarboxylic acid, its concentration, the temperature of the bath, and the degree of "inactivity" of the nickel. For commercial production, it is not contemplated that immersion of less than about 10 seconds will be used. It is preferred that the time of immersion be at least 60 seconds. Although longer immersion time may be used, the minimum time is usually used for large scale automatic production. The temperature of the immersion bath is not critical. It is advantageously at least 10° C. Using the dicarboxylic

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acid activating baths, it is unnecessary to rinse before inserting the nickel object into the chromium plating bath. The transfer time between the two baths should be kept to a minimum.

The nickel activating baths are made up by dissolving any one or a mixture of two or more dicarboxylic acids in water to the desired dilution. I find that solid mixtures of at least two acids containing between 50 parts (by weight) and 90 parts of oxalic acid, between 5 parts and 50 parts of malic acid, and between 5 parts and 50 parts of succinic acid are especially useful in making up and for maintaining the baths because of their availability, effectiveness as nickel activators, ease of handling, and harmless effect when dragged into the chromium plating bath. Examples of suitable solid mixtures containing the specified parts by weight of the various dicarboxylic acids are illustrated in the six examples in the following table:

Table I

	Parts by Weight					
	50	75	70	50	80	90
Oxalic acid.....	50	25	15	-----	-----	5
Malic acid.....	-----	-----	15	50	20	5
Succinic acid.....	-----	-----	15	-----	-----	5

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given.

Six samples of aqueous solution each containing a total of 20 g./l. of the specified acids (as shown in Table II) were prepared for testing as activating dips. Hull cell panels which had been nickel plated at least twenty-four hours earlier and were slightly inactive were immersed in the activating bath for one minute. The panels were transferred without rinsing, over a 15 second interval, to the chromium plating Hull cell and immersed directly. After a 15 second dwell time, current was applied and increased to ten amperes during a 10 second interval. Chromium was then electrodeposited for one minute at 49° C. These conditions are representative of production plating conditions. As controls, a water dip and a sulfuric acid activating dip were tested. Effectiveness of nickel activation was measured by the coverage and appearance of the subsequent chromium electrodeposit. Coverage of chromium was measured in millimeters along the panel. Chromium electrodeposited over poorly activated nickel has poorer visual appearance and poorer coverage over the low current density portion of the panel being plated.

Table II

Activating Dip	1	2	3	4	5	6	7	8
Oxalic acid g./l.....	20	-----	-----	10	13	-----	-----	-----
Malic acid g./l.....	-----	20	-----	10	-----	13	-----	-----
Succinic acid g./l.....	-----	-----	20	-----	7	7	-----	-----
Sulfuric acid g./l.....	-----	-----	-----	-----	-----	-----	50	-----
No activation.....	-----	-----	-----	-----	-----	-----	-----	-----
Coverage, mm.....	82	82	83	80	82	82	78	73

Although the illustrative baths utilize oxalic acid, malic acid, and/or succinic acid, useful baths are also obtained utilizing the equivalent dicarboxylic acids and their anhydrides.

The chromium plating baths were tested for their tolerance to the dicarboxylic acids by plating chromium from plating baths containing 1 g./l., 10 g./l. and 25 g./l. additions of the dicarboxylic acids. Short run tests at all three concentrations were satisfactory; as were longer tests at 1 g./l. and 10 g./l. (the 25 g./l. bath was not given a long run test).

By using the activating baths of the present invention, it is possible to (a) utilize "poorer" nickel plate (i.e., less active) and still obtain acceptable chromium coverage, (b) improve the chromium coverage over any given nickel, and (c) use chromium baths containing lower catalyst concentrations. This last advantage results in the possibility of obtaining increased thicknesses of bright crack-free chromium electrodeposits. These advantages are all achieved without the use of rinse tanks between the activating dip tank and the chromium plating tank, resulting in an important saving of space and money.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

I claim:

1. In a process for electroplating chromium over a nickel surface, the improvement comprising immersing a nickel surfaced article in an aqueous carboxylic acid bath consisting essentially of between 1 g./l. and 100 g./l. of at least one dicarboxylic acid selected from the class consisting of oxalic acid, malonic acid, tartronic acid, mesoxalic acid, succinic acid, malic acid, tartaric acid, glutaric acid and adipic acid; and removing said nickel surfaced article from said aqueous bath; and inserting said nickel surfaced article into a chromium plating bath and electrodepositing chromium on said article.

2. The process defined in claim 1 wherein the nickel surfaced material is immersed in a bath consisting essentially of between 5 g./l. and 50 g./l. of the acid.

3. The process of claim 2 wherein the acid is oxalic acid.

4. The process of claim 2 wherein the acid is succinic acid.

5. The process of claim 2 wherein the acid is malic acid.

6. The process of claim 2 wherein the nickel-surfaced material is immersed in the bath for at least sixty seconds.

7. In a process for electroplating chromium over a nickel surface, the improvement comprising immersing a nickel surfaced article in an aqueous carboxylic acid bath consisting essentially of between 1 g./l. and 100 g./l. of a saturated dicarboxylic acid containing from two to six carbon atoms in the chain for at least 60 seconds; and removing said nickel surfaced article from said aqueous bath; and inserting said nickel surfaced article into a chromium plating bath and electrodepositing chromium on said article.

8. The process defined in claim 7 wherein the bath contains about 25 g./l. of said saturated dicarboxylic acid.

9. A mixture of acids suitable for making up and for maintaining nickel activating baths consisting essentially of between 50 parts (by weight) and 90 parts of oxalic acid, between 5 parts and 50 parts of malic acid, and between 5 parts and 50 parts of succinic acid.

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