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[54] **ELECTROPLATING A DECORATIVE CHROMIUM-PLATING RESISTANT TO CORROSION**
5 Claims, No Drawings

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[56] **References Cited**

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ABSTRACT: A method for coating by electrolysis the surface of objects with a coating of chromium having a microfissured structure, in which the objects are subjected before chromium-plating to an electrolytic treatment for the purpose of depositing an intermediate layer of nickel effected in such manner that it becomes fissured and causes fissuration of the deposit of chromium during the chromium-plating operation, the crackle-finish nickel-plating being carried out by means of an electrolyte comprising a constituent selected from the group of strong acid nickel salts constituted by the chloride, sulfamate and fluoborate of nickel, characterized by the fact that the said electrolyte contains a second constituent formed by at least one alkaline salt of a strong acid.

ELECTROPLATING A DECORATIVE CHROMIUM-PLATING RESISTANT TO CORROSION

This invention relates to methods of covering the surfaces of objects by electrolysis with a coating of chromium having a microfissured structure.

Reference is made to my copending applications Ser. No. 440,019, filed Jan. 27, 1965, now Pat. 3,388,049 and Ser. No. 482,902 filed Aug. 26, 1965. Said applications disclose a method consisting in depositing prior to the chromium coating a thin nickel coating under conditions such as to cause the metal to be highly stressed and barely ductile. During the subsequent chroming operation, this last coating of metal and the coating of chromium undergo simultaneous microcracking, thereby imparting excellent resistance to corrosion to the object treated in this way.

The thinner the nickel coating deposited for subsequent cracking, the more advantageous it will be for it s electrochemical potential to lie between that of the subjacent metal and that of the terminal chromium plating (in the state of surface oxidation to which it is normally brought after a few hours or a few days have elapsed). By "thin coating" is to be understood a coating whose thickness is included between a fraction of a micron and approximately 3 or 4 microns.

The two examples given hereinafter of processes of obtaining a microcracked chromium layer according to said applications do not describe such preliminary operations involving degreasing and depositing metals such as copper, brass, zinc, levelling nickel, and so forth, as may be considered useful for reasons unconnected with the obtainment of the microcracking.

EXAMPLE 1

—Principal protective nickel plating, for example bright nickel plating.
—Rinsing operations
—Depositing of the cracking nickel under the following conditions:

		Optimum
· anhydrous nickel acetate	50 g./l. to saturation	100 g./l.
· hydrated nickel chloride	100 g./l. to saturation	375 g./l.
· pH	2 to 6	5 to 5.5
· current density	1 to 15 A./dm.²	10 A./dm.²
· duration	15 sec. to 2 min.	30 sec.
· temperature (below 35° C.)		20° to 25° C.

· agitation optional (with compressed air, say)

—Rinsings
—Chromium plating
—Rinsings
—Drying

EXAMPLE 2

—Principal protective nickel plating (bright nickel plating, for example)
—Rinsings
—Depositing of cracking nickel, in the following solution:

		Optimum
· hydrated nickel chloride	100 g./l. to saturation	400 g./l.
· anhydrous ammonium acetate	50 g./l. to saturation	100 g./l.
· pH	2 to 6	5 to 5.5
· current density	1 to 15 A./dm.²	10 A./dm.²
· duration	15 sec. to 2 min.	30 sec.
· temperature	below 35° C.	20° to 25° C.

· agitation optional (using compressed air, say)

—Rinsings
—Chromium plating
—Rinsings
—Drying.

It is to be noted that the nickel or ammonium acetate can be replaced by other compounds. Generally speaking, there can be employed as an additive to the nickel chloride a compound selected from the group of products constituted by nickel acetate, gluconic acid, nickel gluconate, tartaric acid, nickel tartrate, formic acid, nickel formate, malic acid, nickel malate, lactic acid, nickel lactate, citric acid, nickel citrate, succinic acid, nickel succinate, a mixture of at least two of the above compounds, and finally ammonium acetate.

The baths comprising acetic, gluconic, formic and succinic acids, associated with their nickel salts, in combination with nickel chloride, are those which lead to the production of deposits of microfissured chromium over the whole range of current densities at which the decorative chromium deposits are brilliant. They are therefore the most perfectly appropriate to the object of said applications.

However, the other acids or salts shown in the group listed above give very satisfactory results when the shape of the parts does not result in too great differences of current densities.

In this case, it is also possible to substitute nickel sulfamate or nickel fluoborate for the nickel chloride, this latter product remaining however preferable.

The cracking-nickel-plating baths used in the conditions specified in the two foregoing examples give, for plating times of less than 2 minutes, a coating of brightness such as to ensure the subsequent obtainment of very bright chromium plating.

In certain special cases, however, it may be necessary to extend the duration of the cracking-nickel-plating operation for a considerably greater time. This may be the case, for instance, when the parts to be protected have heavily recessed portions, since the thickness will increase less rapidly in such places than on the raised portions. It may also happen that certain installations, by their very design, will not permit of reducing the duration of the cracking-nickel-plating to 2 minutes or less.

It is then necessary to add to the bath one or more suitable brightening substances. Such brightening substances must not appreciably affect the potential of the cracking-nickel deposit, so that the electrochemical protective process may be maintained as described precedingly. Nor must they reduce the propensity for cracking of the ultimate coat of nickel which generates the microcracking in the subsequent chromium plating.

By way of brightening agents it is possible to utilize the sulfonates, the sulfonamides and the sulfonimides of aromatic compounds. More specifically, the sodium salt of sulfonimide ortho-benzoyl acid (saccharine) can be added in proportions ranging from 0.5 to 3 g./l., the optimum being around 1 g./l., though this is by no means critical.

If added to the cracking-nickel-plating baths, butyne 1-4 diol will enable very bright deposits of cracking nickel to be obtained, regardless of the thickness of the deposits. This compound is added to the bath in the proportion of 0.1 to 3 g./l.

Other brightening agents which will enable particularly bright cracking-nickel deposits to be obtained, regardless of their thickness, are the amino derivatives of heterocyclic compounds such as 2-amino-thiazole.

Lastly, when cobalt is added to the cracking nickel baths, it also enables the brightness of the deposit to be enhanced for concentration ranging from 1 to 30 g./l.

The following compositions and procedures were mentioned by way of complementary examples of the depositing of cracking nickel according to said applications:

EXAMPLE 3

Bath with addition of butyne 1-4 diol		Optimum
Anhydrous nickel acetate	50 g./l. to saturation	100 g./l.
Hydrated nickel chloride	100 g./l. to saturation	375 g./l.

Butyne 1-4 diol	0.1 g./l. to 3 g./l.	0.2 g./l.
pH	2 to 6	5 to 5.5
Current density	1 to 15 A./dm.²	10 A./dm.²
Duration	15 sec. to 5 min.	
Temperature	below 35° C.	20° to 25° C.

Optional agitation (with compressed air or by displacing the cathodes).

EXAMPLE 4

Bath with addition of 2-amino-thiazole		Optimum
Anhydrous nickel acetate	50 g./l. to saturation	100 g./l.
Hydrated nickel chloride	100 g./l. to saturation	375 g./l.
pH	2 to 6	4
2-amino-thiazole	5 mg./l. to 100 mg./l.	10 mg./l.
Current density	1 to 15 A./dm.²	10 A./dm.²
Temperature	below 35° C.	20° to 25° C.

Optional agitation (with compressed air or by displacing the cathodes).

EXAMPLE 5

Bath with addition of cobalt		Optimum
Anhydrous nickel acetate	50 g./l. to saturation	100 g./l.
Hydrated nickel chloride	100 g./l. to saturation	375 g./l.
Cobalt chloride	4 g./l. to 120 g./l.	40 g./l.
pH	2 to 6	5 to 5.5
Current density	1 to 15 A./dm.²	10 A./dm.²
Duration	15 sec. to 5 min.	
Temperature	below 35° C.	20° to 25° C.

Optional agitation (with compressed air or by displacing the cathodes).

The thickness of the cracking-nickel deposit can be considerably increased by the aid of the brightening agents utilized in accordance with said applications. This enables the method to be used in existing installations with minimum or no modification.

Indeed, this leads to the possibility of a simplified application: for when the electrolysis baths permit of obtaining bright and cracking deposits of a thickness appreciable greater than a few microns, for instance 10 to 20 microns, then in accordance with said applications these deposits can be substituted for the terminal protective nickel coating instead of being superimposed thereon.

The following was mentioned by way of nonlimitative examples:

a. The sequences customarily consisting of a superimposed copper (or brass) deposit and a conventional nickel deposit, in which the latter deposit is replaced by a thick bright deposit of cracking nickel or nickel alloy.

b. The sequences comprising a coating of dull or levelling nickel followed by a coating of bright nickel, this double nickel coating being obtained by the so-called "binickel" or "-duplex" method, in which the customary coating of bright nickel is replaced by a thick bright coating of cracking nickel.

It is to be noted that this operating sequence permits of combining the advantages offered by duplex nickel plating and microcrack chromium-plating; moreover, this sequence can be executed without the need to seek a more noble cracking of nickel than the subjacent coating of levelling nickel.

Lastly, in accordance with said applications, in the case of certain bright or semibright nickel-plating baths in which the additives may result in a degree of surface passiveness, perfect adhesion of the cracking-nickel deposit is ensured by initially depassivating the bright or semibright nickel deposit. This is achieved by means of the following operations:

—careful rinsing of the bright or semibright nickel deposit;

—treatment in an alkali cyanide-base depassivation bath, for which the following formulation represents a nonlimitative example:

Caustic soda	45 g./l.
Anhydrous sodium carbonate	45 g./l.
Sodium cyanide	20 g./l.
Temperature: ambient	
Current density	5 to 10 A./dm.²
Duration of cathode pass	20 to 30 sec.

—careful Careful rinsing before insertion into the bath, thereby ensuring a deposit of cracking nickel.

In cases where the initial nickel deposit is strongly passivated, provision may be made for an anode pass lasting approximately 5 seconds prior to the cathode pass.

While cracking-nickel-plating baths as a whole are not more sensitive to impurities than nickel-plating baths in general, recourse may be had, in order to maintain such baths in good condition, to intermittent or continuous filtering, or else to some method well know per se such as electrolysis on low-current-density cathodes for eliminating foreign metal, or neutralization and filtering on active charcoal in order to get rid of undesirable organic substances and the like.

It should be noted that the deposit of cracking nickel cracks slowly even in the absence of subsequent chromium plating. It is therefore necessary to avoid unduly long waits between the deposit of cracking nickel and the chromium plating, for otherwise the final chromium plating would mask the cracks already formed in the nickel, which would run counter to the aim sought.

This delay will vary with operating conditions and with the structure and stress specific to the subjacent nickel deposit. By way of indication, however, it may be stated that spontaneous cracking in the ultimate nickel deposit begins after approximately a quarter of an hour has elapsed.

By applying the method according to said applications, the microcracked structure can be developed over all the chromium-plated surfaces, using conventional chromium plating baths comprising, as catalysts, the sulfuric, hydrofluoric, fluosilicic, and like ions.

It must be added that the use of special chromium plating baths containing, say, selenium or additive particles insoluble in the intermediate-deposit solution, while not bringing marked benefits to the method, is not incompatible with the use of the cracking deposits specified hereinabove.

In order to reduce the production cost of the nickel baths according to said applications and to reduce the expense of losses by carrying away, efforts have been made to find a more economical composition of the baths.

According to the invention, good results have been obtained by replacing parts of the nickel ion by ammonium or alkaline ions. Thus, according to the principle of the present invention, it is possible to replace:

—a part of the strong acid salt of nickel by a strong-acid salt of sodium, potassium or ammonium;

all or part of the weak-acid salt of nickel by a weak-acid salt of sodium, potassium or ammonium.

The crackle-finish nickel-plated baths according to the invention will therefore be composed, in general:

—of a strong-acid salt of nickel such as the chloride, sulfate sulfamate, fluoborate;

—of a strong-acid alkaline salt, such as the chloride, sulfate fluoborate;

—of a salt of a weak acid selected from the group of weak acids cited above, it being understood that the above-mentioned weak acid may be added in the form of acid, or alkaline salt or of nickel salt.

It should be observed that by varying the concentration of the constituents of the bath, and in particular, the content and the nature of the weak acid, it is possible to obtain at will systems of fissures which are more or less close together. This density of fissuration may also be modified by varying the pH value of the bath and its temperature. Similarly, the variation of the content of dissolved nickel makes it possible to obtain variable margins of current density so as to determine, as a function of existing installations and of the shape of the parts to be treated, the most economical bath for the final produc-

tion of the deposits of chromium having a microfissured structure.

The following examples, according to the method of the present invention, are given by way of information and not in any limitative sense, the values indicating being considered as approximate.

EXAMPLE I

Nickel chloride	150 g./l.
Nickel acetate	50 g./l.
Ammonium chloride	120 g./l.
pH value	4
Current density	1 to 10 amp./sq.dm.
Temperature	25° C.
Duration	1 min.
Density of fissuration	Of the order of 300 fissures/cm.

EXAMPLE II

Nickel chloride	200 g./l.
Gluconic acid	100 g./l.
Ammonium chloride	150 g./l.
Ammonia	Q.S. for pH=3.5
Current density	1 to 15 amp./sq.dm.
Temperature	25° C.
Duration	1 min.
Fissuration density	Of the order of 500 fissures per cm.

EXAMPLE III

Nickel chloride	150 g./l.
Ammonium acetate	50 g./l.
Ammonium chloride	120 g./l.
pH value	3.5 to 4
Current density	1 to 10 amp./sq.dm.
Temperature	25° C.
Duration	1 min.
Fissuration density	Of the order of 700 fissures per cm.

EXAMPLE IV

Nickel chloride	150 g./l.
Ammonium acetate	50 g./l.
Ammonium chloride	120 g./l.
pH value	3.5 to 4
Current density	1 to 15 amp./sq.dm.
Temperature	35° C.
Fissuration density	Of the order of 500 fissures per cm.

EXAMPLE V

Nickel chloride	150 g./l.
Sodium acetate	50 g./l.
Sodium chloride	150 g./l.
pH value	4
Current density	1 to 10 amp./sq.dm.
Temperature	25° C.
Fissuration density	Of the order of 300 fissures per cm.

The above series of baths is compatible with the use of appropriate brightening agents such as those mentioned in said applications. In the same way, and as described in said applications, the bright or semibright nickel deposit may be depassivated if necessary.

I claim:

1. In a method of producing a corrosion-resistant microcracked coating of chromium on a substrate wherein nickel is electrodeposited on said substrate from an aqueous acidic solution containing a nickel salt of a strong acid and at least one compound selected from the group consisting of nickel salts of carboxylic acids and carboxylic acids, said nickel being deposited with a high-internal stress level, said stress level being sufficient to produce microcracks therein during the deposition thereon of the chromium layer which in turn produces a microcrack pattern in the chromium layer and thereafter electrodepositing chromium on said nickel, the improvement which comprises electrodepositing said nickel from an aqueous acidic solution consisting of about 200 g. and said nickel salt of a strong acid, about 150 g. of said alkaline salt of a strong acid, about 100 g. of said compound selected from the group consisting of nickel salts of carboxylic acids and carboxylic acids, and ammonia sufficient to produce pH of about 3.5.

2. A method of producing corrosion-resistant microcracked coating of chromium on a substrate which comprises electrodepositing nickel on said substrate from an aqueous acidic solution consisting of, per liter, about 150 g. of nickel chloride, about 50 g. of nickel acetate and about 120 g. of ammonium chloride, said nickel being deposited with a high-internal stress level, said stress level being sufficient to produce microcracks therein during the deposition of the chromium layer which in turn produces a microcrack pattern in the chromium layer, and thereafter electrodepositing chromium on said nickel.

3. A method of producing a corrosion-resistant microcracked coating of chromium on a substrate which comprises electrodepositing nickel on said substrate from an aqueous acidic solution consisting of, per liter, about 200 g. of nickel chloride, about 100 g. of gluconic acid, about 150 g. of ammonium chloride and ammonia sufficient to produce a pH of about 3.5 said nickel being deposited with a high-internal stress level, said stress level being sufficient to produce microcracks therein during deposition of the chromium layer which in turn produces a microcrack pattern in the chromium layer, and thereafter electrodepositing chromium on said nickel.

4. A method of producing a corrosion-resistant microcracked coating of chromium on a substrate which comprise electrodepositing nickel on said substrate from an aqueous acidic solution consisting of, per liter, about 150 g. of nickel chloride, about 50 g. of ammonium acetate and about 120 g. of ammonium chloride, said nickel being deposited with a high-internal stress level, said stress level being sufficient to produce microcracks therein during the deposition of the chromium layer which in turn produces a microcrack pattern in the chromium layer and thereafter chromium on said nickel.

5. A method of producing a corrosion-resistant microcracked coating of chromium on a substrate which comprises electrodepositing nickel on said substrate from an aqueous acidic solution consisting of, per liter, about 150 g. of nickel chloride, about 50 g. of sodium acetate and about 150 g. of sodium chloride, said nickel being deposited with a high-internal stress level, said stress level being sufficient to produce microcracks therein during the deposition of the chromium layer which in turn produces a microcrack pattern in the chromium layer, and thereafter electrodepositing chromium on said nickel.

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