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2,900,707

## METALLIC PROTECTIVE COATING

Henry Brown, Huntington Woods, Mich., assignor to The Udyllite Corporation, Detroit, Mich., a corporation of Michigan

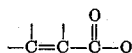
No Drawing. Application August 6, 1954  
Serial No. 448,365

4 Claims. (Cl. 29—183.5)

This invention relates to the electrodeposition of nickel from an acid bath.

The object of this invention is to produce a fine-grained lustrous ductile nickel deposit that is of high uniformity under conditions of steady electrolysis.

This object can be accomplished by the addition to the Watt's type of nickel bath of a small percentage of either chloral hydrate or bromal hydrate or mixtures of these two halogenated aldehydes, together with a compound carrying the



group selected from the compounds listed in Table II.

TABLE I

|                                                                             | Optimum conc.,<br>grams/liter |
|-----------------------------------------------------------------------------|-------------------------------|
| Chloral hydrate, $\text{CCl}_3\cdot\text{CHO}\cdot\text{H}_2\text{O}$ ----- | 0.1-6                         |
| Bromal hydrate, $\text{CBr}_3\cdot\text{CHO}\cdot\text{H}_2\text{O}$ -----  | 0.1-1.0                       |

TABLE II

|                                                                      | Optimum conc.,<br>grams/liter |
|----------------------------------------------------------------------|-------------------------------|
| Trimethyl aconitate -----                                            | 0.1-1.2                       |
| Dimethyl fumarate -----                                              | 0.1-1.6                       |
| Dimethyl itaconate -----                                             | 0.1-1.5                       |
| Methoxyethyl acrylate -----                                          | 0.1-1.0                       |
| Ethoxyethyl acrylate -----                                           | 0.1-1.0                       |
| Phenyl acrylate -----                                                | 0.1-6                         |
| Eethoxy propyl acrylate -----                                        | 0.1-1.0                       |
| Phenoxyethyl acrylate -----                                          | 0.1-0.6                       |
| Di-(methoxyethyl) maleate -----                                      | 0.1-2.0                       |
| Di-(methoxyethyl) itaconate -----                                    | 0.1-2.0                       |
| Di-(methoxyethyl) fumarate -----                                     | 0.1-2.0                       |
| Reaction product of coumarin and concentrated<br>sulfuric acid ----- | 0.2-1.2                       |
| Coumarin -----                                                       | 0.1-0.6                       |
| 3-chlorocoumarin -----                                               | 0.1-0.5                       |
| 6-, or 7- or 8-methoxy coumarin -----                                | 0.1-0.8                       |
| Methoxyethoxyethyl acrylate -----                                    | 0.1-1.5                       |
| Ethoxyethoxyethyl acrylate -----                                     | 0.1-2.0                       |

The reaction product of coumarin and sulfuric acid listed above in Table II refers to the product obtained by reacting coumarin with sufficient and preferably a minimum of concentrated sulfuric acid to completely solubilize the coumarin.

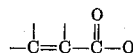
The chloral hydrate or bromal hydrate may be added to the bath, for example, as alcoholates or acetals, since the latter regenerate the aldehydes or the hydrates in the aqueous acidic nickel bath. The chloral or bromal compound can be added to the bath from water solutions or alcohol solutions or mixed water and alcohol solutions, and when dissolved in the bath are considered to be dissolved therein as the hydrates. Mixtures of the halogen atoms can be on the same molecule, for example  $\text{CCl}_2\text{Br}\cdot\text{CHO}$ ,  $\text{CBr}_2\text{Cl}\cdot\text{CHO}$ , and also mixtures of chloral hydrate and bromal hydrate may be used. The preferred

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concentration as hydrates usually is 0.2 to 0.4 gram/liter, though slightly higher or lower concentrations can be used, depending on the temperature of the bath, pH, and degree of agitation of the cathode or solution around the cathode. The higher the temperature, the higher the pH up to about 5.2, and the higher the agitation, the lower the concentration necessary for optimum results.

Chloral and bromal hydrate when present in the Watt's type bath or low chloride type bath make possible the deposition of fine-grained, lustrous ductile nickel deposits over a rather wide plating range, and with increasing plate thickness tend to smoothen out polishing lines and other surface imperfections in the underlying metal that is plated as is disclosed in United States Patent No. 2,321,182, issued June 8, 1943. Furthermore, these compounds of Table I do not seem to form any harmful breakdown or degradation products at either the cathode or anode during extended electrolysis, and this has been confirmed by the results of commercial baths which have been operated over long periods (3 to 6 months and longer) without the need of activated carbon treatments.

The



compounds of Table II, on the other hand, when used alone in the Watt's type or low chloride nickel baths while giving fine grained (but not as fine-grained deposits as the compounds of Table I), ductile deposits of very good leveling qualities (smoothening of polishing lines in the basis metal), have the shortcoming of forming harmful reduction or degradation products at the cathode during electrolysis. The baths using the compounds of Table II have to be purified after a given number of amperes-hours are passed through the plating solution, not because of any drag-in of impurities, but because of the formation of organic by-products from the compounds themselves by the process of electrodeposition or electrolysis. Thus, baths containing the addition agents of Table II have to be treated with activated carbon as often as every three to four weeks in commercial use. This treatment is expensive, and furthermore there is a variation of the quality of the plate, ductility, leveling properties, etc. as the baths deteriorate from the accumulation of the harmful by-products.

It has now been found that if the compounds of Table I are used in conjunction with the compounds of Table II, a remarkably improved result is obtained over either one alone in the Watt's type or low chloride type nickel baths. The fine-grained ductile plate obtained is much more lustrous than the plate obtained with the compounds of Table I or II used separately at their optimum concentration in the bath. Furthermore, the breakdown or degradation product or products formed during plating with the compounds of Table II are greatly reduced not only from the fact that smaller concentrations of the compounds of Table II can be used than when used alone, but also apparently from a co-action effect in the reduction processes occurring at the cathode when the compounds of Table I are also present in the bath. For example, if 8-methoxy coumarin, or coumarin, or di-(methoxy ethyl) maleate or trimethyl aconitate are added in concentration of 0.2 gram/liter for the first two materials, or of 0.8 to 1.5 grams/liter for the latter two materials, separately to Watt's baths of pH=4.2 temperature 130° F.-140° F., it is possible to obtain areas of plate in the intermediate current densities that are not as fine-grained as in other areas. These duller areas are immediately removed or prevented from forming by the addition of 0.2 gram/liter of, for example, chloral hydrate, to obtain a uniformly lustrous plate. This is not accomplished by other aldehydes such as

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acetaldehyde, formaldehyde, or propionaldehyde. It thus appears that chloral or bromal hydrate exert a definite carrier effect on the compounds of Table II. This carrier effect is not obtained, however, when the compound is a substituted coumarin such as hydroxy or carboxy substituted coumarin, or if a substituent such as hydroxy, alkoxy or alkyl group is in the 3- or 4-position on the coumarin ring.

As a result of this co-action in the reduction processes at the cathode, nickel deposits obtained with the conjoint use of the compounds of Table I with those of Table II are free from dull gray streaks, and are much more uniformly lustrous over a wider current density plating range and have a better rate of brightening (increase in luster) with increased plating thickness. Additionally there is greatly improved brightness in the low current density areas. This result is very important when buffing the deposit, since a fine-grained plate with a given leveling is easier to buff than a coarser grain plate with the same leveling properties. Also if instead of buffing, a bright plate is deposited thereon, a thinner bright plate can be used to obtain a finished bright plate without buffing than if the original plate was coarser-grained.

A preferred bright plate to be used over the deposits of this invention is a nickel-cobalt bright plate containing at least 10% cobalt in the plate deposited from a bath containing o-benzoyl sulfimide therein. This latter bath can be of the Watt's type, all chloride, or high chloride or fluoborate type or mixtures, and the deposits of nickel and cobalt obtained in the presence of o-benzoyl sulfimide can be chromium plated without appreciable hydrogen embrittlement, unlike the case when the cobalt is absent or present in amounts below about 10%.

The below examples set forth preferred bath formulations which are typical of the baths suitable for use in practicing this invention.

## Example 1

|                          |                      |
|--------------------------|----------------------|
| Nickel sulfate.....      | 150-300 grams/liter. |
| Nickel chloride.....     | 20-60 grams/liter.   |
| Boric acid.....          | 40-45 grams/liter.   |
| Trimethyl aconitate..... | 0.6-1.0 gram/liter.  |
| Chloral hydrate.....     | 0.2-0.4 grams/liter. |
| pH.....                  | 3.8-4.5.             |
| Temperature.....         | 50° C.-60° C.        |

## Example 2

|                               |                      |
|-------------------------------|----------------------|
| Nickel sulfate.....           | 150-300 grams/liter. |
| Nickel chloride.....          | 20-60 grams/liter.   |
| Boric acid.....               | 40-45 grams/liter.   |
| Di(methoxyethyl) maleate..... | 0.8-1.2 grams/liter. |
| Chloral hydrate.....          | 0.2-0.4 grams/liter. |
| pH.....                       | 3.8-4.5.             |
| Temperature.....              | 50° C.-60° C.        |

## Example 3

|                          |             |
|--------------------------|-------------|
|                          | Grams/liter |
| Nickel chloride.....     | 100         |
| Boric acid.....          | 50          |
| Trimethyl aconitate..... | 0.6-1.0     |
| Chloral hydrate.....     | 0.2-0.4     |

## Example 4

|                                                                  |         |
|------------------------------------------------------------------|---------|
| Nickel sulfate.....                                              | 150-300 |
| Nickel chloride.....                                             | 20-60   |
| Boric acid.....                                                  | 40-45   |
| Reaction product of coumarin and concentrated sulfuric acid..... | 0.3-0.5 |
| Bromal hydrate, chloral hydrate or mixtures.....                 | 0.2-0.4 |

## Example 5

|                         |         |
|-------------------------|---------|
| Nickel sulfate.....     | 150-300 |
| Nickel chloride.....    | 20-60   |
| Boric acid.....         | 40-45   |
| 8-methoxy coumarin..... | 0.2     |
| Chloral hydrate.....    | 0.2-0.4 |

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## Example 6

|                       |         |
|-----------------------|---------|
| Nickel sulfate.....   | 150-300 |
| Nickel chloride.....  | 20-60   |
| Boric acid.....       | 40-45   |
| 3-chlorocoumarin..... | 0.2     |
| Chloral hydrate.....  | 0.2-0.4 |

## Example 7

|                      |         |
|----------------------|---------|
| Nickel sulfate.....  | 150-300 |
| Nickel chloride..... | 20-60   |
| Boric acid.....      | 40-45   |
| Coumarin.....        | 0.2     |
| Chloral hydrate..... | 0.2-0.4 |

The preferred pH ranges are from 3.5 to 5.2 with a pH of about 4.2 optimum, though with higher bath temperatures the optimum pH shifts toward the lower values. The preferred or optimum bath temperatures are from 50° C.-60° C., though higher or lower temperatures can be used. The hotter baths require slightly smaller concentrations of the addition agents of Tables I and II. Also the more rapid the agitation of the cathode or the solution, the less the concentration of the addition agents needed.

Besides boric acid as buffer, other buffers such as formate, citrate or fluoborate may be used, but preferably in conjunction with boric acid. It is preferred to have none or minimal quantities of sodium or ammonium ions present.

A preferred bright plating bath for use in producing a bright deposit over the lustrous but cloudy nickel deposits obtained in Examples 1 to 7 inclusive is given in Examples 8 and 9 and is to be used prior to the deposition of the usual chromium plate.

## Example 8

|                                     |                      |
|-------------------------------------|----------------------|
| Nickel chloride.....                | 100-200 grams/liter. |
| Cobalt sulfate or chloride.....     | 30-50 grams/liter.   |
| Boric acid.....                     | 40-45 grams/liter.   |
| o-Benzoyl sulfimide.....            | 0.1-3 grams/liter.   |
| Benzene or toluene sulfonamide..... | 0.1-3 grams/liter.   |
| Temperature.....                    | 40° C.-70° C.        |
| pH.....                             | 2.5-4.8.             |

## Example 9

|                                 |                      |
|---------------------------------|----------------------|
| Nickel sulfate or chloride..... | 100-300 grams/liter. |
| Cobalt sulfate or chloride..... | 30-50 grams/liter.   |
| Boric acid.....                 | 40-45 grams/liter.   |
| o-Benzoyl sulfimide.....        | 0.1-3 grams/liter.   |
| Temperature.....                | 40° C.-70° C.        |
| pH.....                         | 2.5-4.8.             |

Baths given in Examples 8 and 9 may contain, in addition, small concentrations of a



compound as exemplified in U.S. Patents 2,648,628 and 2,647,866, as well as compounds from Tables I and II, and pH values as low as 1.5 may be used. Instead of cobalt sulfate or chloride or fluoborate, the corresponding ferrous salt (or even ferric salt) may be substituted in part or entirely for the cobalt salt concentration, and the bright nickel-cobalt, nickel-iron, or nickel-cobalt-iron alloy plates consequently obtained are also not appreciably hydrogen embrittled by the final chromium plate. When iron is present in the bath, it is preferred to have fluoborate ions also present in sufficient concentration to prevent or retard iron hydroxide precipitation in the bath. While from the economic standpoint it is highly desirable to use iron, nevertheless for highest atmospheric corrosion resistance it is preferred that less than about 10% of iron be present in the bright nickel alloy plates if the final thin chromium plate that is applied is porous as is the usual case. That is, the atmospheric corrosion resistance of the nickel-iron alloy plate when containing more than about 10% iron is decreased somewhat when

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covered with the usual final relatively thin chromium plate.

In Examples 1-7, nickel fluoborate may be present or be substituted in part or for the whole concentration of total nickel salts. However, the rate of brightening or leveling is not optimum with high fluoborate content or with high content of buffers other than boric acid, for example, formate. The nickel chloride content may be lower or higher than the values given in Examples 1-7, but the ductility of the plate and the luster is not optimum with high nickel chloride concentrations.

The above described bright nickel alloy plates which can be chromium plated without appreciable hydrogen embrittlement, and which have a high rate of brightening, can be used as thin bright plate over a relatively thick, cloudy, lustrous plate obtained from baths similar to examples 1-7, and obtain a final bright finish requiring no buffing before bright chromium plating. For example, 0.5 mil to 2 mils thicknesses of cloudy lustrous plate obtained from baths of Examples 1-7 can be made fully bright with as little as 10% of the thickness of the cloudy plate, with the bright nickel alloy plate. Furthermore, thicker bright nickel-alloy plate as already described can be applied up to 50% or more of the thickness of the softer cloudy plate, without appreciable hydrogen embrittlement after chromium plating. The chromium plate is usually applied directly over the final bright plate in thicknesses of about 0.01 mil to 0.1 mil.

The nickel alloy plate preferably contains a minimum of 50% nickel. Nickel-cobalt alloy plate may satisfactorily contain up to as much as 50% cobalt. Nickel-iron alloy plate may satisfactorily contain as much as 40% iron. When both iron and cobalt are present the sum of iron and cobalt may be as high as 50%.

By careful combination of the compounds of Table I and Table II under optimum conditions, it is possible to obtain a plate which is practically completely bright except for a faint bluish haze which is obscured upon chromium plating by the bluish bright chromium layer.

What is claimed is:

1. A metallic bright protective coating on a metallic base consisting of a firmly adherent layer of a substantially sulphur-free lustrous nickel deposit having a thickness from 0.5 mil to 2 mils, and an overlying layer which is firmly adherent to said nickel deposit consisting of a nickel-cobalt bright plate containing at least 50% nickel and about 10% to 50% cobalt in the plate and having a thickness from 0.05 mil to 1 mil.

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2. A metallic bright protective coating on a metallic base consisting of a firmly adherent layer of a substantially sulphur-free lustrous nickel deposit having a thickness from 0.5 mil to 2 mils, and an overlying layer which is firmly adherent to said nickel deposit consisting of a nickel-cobalt bright plate containing at least 50% nickel and about 10% to 50% cobalt in the plate and having a thickness from 0.05 mil to 1 mil, and a layer of chromium of a thickness of about from 0.01 mil to 0.1 mil firmly adherent to said nickel-cobalt plate.

3. A metallic bright protective coating on a metallic base consisting of a firmly adherent layer of a lustrous nickel deposit having a thickness in the range of about 0.5-2 mils, and a layer overlying said lustrous nickel deposit consisting of a nickel alloy and having a thickness of about 0.05-1 mil, said nickel alloy being an alloy of nickel with at least one metal selected from the group consisting of cobalt and iron and containing at least 50% nickel, the cobalt, when present, being present in an amount of about 10% to 50%, and the iron, when present, being present in an amount less than 40%.

4. A metallic bright protective coating on a metallic base consisting of a firmly adherent layer of a lustrous nickel deposit having a thickness in the range of about 0.5-2 mils, and a layer overlying said lustrous nickel deposit consisting of a nickel alloy and having a thickness of about 0.05-1 mil, said nickel alloy being an alloy of nickel with at least one metal selected from the group consisting of cobalt and iron and containing at least 50% nickel, the cobalt, when present, being present in an amount of about 10% to 50%, and the iron, when present, being present in an amount less than 10%.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 2,900,707

August 25, 1959

Henry Brown

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 2 and 12, name of assignee, for "The Udyllite Corporation" read --- The Udyllite Research Corporation ---; in the heading to the printed specification, lines 3 and 4, name of assignee, for "The Udyllite Corporation" read --- The Udyllite Research Corporation ---.

Signed and sealed this 12th day of April 1960.

(SEAL)

Attest:

KARL H. AXLINE  
Attesting Officer

ROBERT C. WATSON  
Commissioner of Patents