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ELECTRODEPOSITION OF NICKEL

Harry C. Mougey and Ralph J. Wirshing, Detroit, Mich., assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware

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The invention relates to the electrodeposition of nickel and is more particularly concerned with the production of lustrous or mirror-like deposits. That such deposits could be obtained under certain conditions and in the presence of certain addition agents has been known for years. The processes hitherto used, however, have been subject to objectionable features, especially with reference to the character of the deposit and the cost of materials. Coatings applied in accordance with prior processes generally have a tendency to brittleness particularly upon increase of thickness of the deposit. Furthermore, some at least of the addition agents used are expensive and, since they are destroyed or dissipated in the operation of the bath, render the maintenance of the bath costly.

We have found that improved operation can be obtained from the standpoint of first cost and maintenance as well as satisfactory character of deposit by the use of a novel addition agent containing selenium. It is necessary that the selenium be present in some form or compound from which it may be deposited along with the nickel, at least in very small amounts, and for this purpose it is, of course, essential that such compound be dispersed or dissolved in the electrolyte. It is also desirable to maintain the electrolyte free of non-essential foreign and possibly deleterious substances. Cost or commercial availability is also naturally an important factor.

As meeting most fully the above conditions we have preferred to employ the acids or acid anhydrides of selenium of which two are commercially available, namely, the selenic and selenious. Selenic acid is marked in the form of an aqueous solution of H_2SeO_4 while the selenious compound is obtainable as selenious acid or selenious oxide, SeO_2 , which is readily soluble in water to form H_2SeO_3 .

The selenium compound is effective to cause deposition of bright coatings in nickel electrolytes of the usual compositions some of which may be mentioned as examples. In the acetate bath the following solution has given satisfactory results:

Nickel acetate, $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$	grams.....	100
Nickel chloride, $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$	do.....	100
Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$	cc.....	35
Selenic acid (approximately 40% solution).....	cc.....	3
Water to make up 1 liter and sufficient HCl to adjust the pH to the desired acidity, for example, 3-3.5.		

Instead of selenic acid solution in the above bath we may use selenious oxide, the amount required being in the neighborhood of 0.1-0.3 gram per liter.

As an example of a nickel sulphate electrolyte the following may be given:

	Grams
Nickel sulphate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	240
Nickel chloride, $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$	30
Boric acid, H_3BO_3	30
Selenious oxide, SeO_2	0.2-0.3
Water to make up one liter, sulphuric acid being added in quantity sufficient to adjust the acidity as desired, for example to a pH of 1.5-5.5.	

Selenic acid may also replace the selenious oxide in this formula. As an example of a high sulphate bath, such as may be used for nickel plating zinc-base die castings, the following may be given:

	Ounces
Nickel sulphate.....	10-12
Sodium sulphate.....	9-11
Ammonium chloride.....	2
Boric acid.....	3
Selenious oxide.....	0.025-0.05
Water sufficient to make up one gallon, the pH being adjusted as desired, for example to approximately 5.8.	

It will be understood that the formulas given are merely illustrative and that variations thereof or different types of electrolytes are not excluded. In each example given, bright deposits are obtainable at current densities of 24-48 amperes per square foot and temperatures around 110° F.

The amount of the selenium compound may be varied over a rather wide range and increases with concentration of nickel salts, more of the addition agent being used in heavier solutions. Amounts up to 0.5 gram of SeO_2 per liter are satisfactory in an ordinary commercial bath, such as the examples above. In general, the amount required may be given as from 0.05 to 0.5 gram per liter of bath. The amount added should generally be restricted, however, to that necessary to produce the desired mirror-like deposit as excessive amounts tend to increase brittleness of the deposit. The selenious acid has been found more effective per unit of weight than the selenic. For this reason as well as the lower cost of the selenious acid, the latter is at present preferred. The production of a bright or mirror-like deposit is affected by a number of factors, particularly concentration of electrolyte, character and

amount of addition agent, temperature, current density and acidity at the cathode or pH. Obviously, there will be a range for each of these factors within which most desirable results are secured, which range is dependent also to some extent upon the quantum relations of the other factors, and suitable control of these factors is necessary. Therefore, while we have given specific examples by way of illustration, it will be understood that variation of the specific conditions within a range easily determinable by experiment is within the scope of our invention.

One difficulty met with in nickel deposition is the occurrence of small depressions or "pits." "Pitting," as this phenomenon is commonly termed, is generally remedied by the addition to the electrolyte of strong oxidizing agents such as hydrogen peroxide. Such additions may be used in our selenium compound baths but have in some cases the effect of destroying the effectiveness of the selenium addition agent, thus rendering it necessary to make new additions of the latter after treatment with H_2O_2 . We have found, however, that soaps of sulphated higher alcohols such as those sold under the trade name "Gardinol," are effective to reduce pitting in our bright nickel baths and appear to have no deleterious effect.

One of the commercial preparations of these alcohol soaps that is satisfactory for the purpose contains sodium alkyl sulphates which may have 10-14 carbon atoms, the principal constituent of which may be sodium lauryl sulphate,



The amount to be used depends upon the extent of the tendency to "pit." As little as 0.01 gram per liter has an appreciable effect and 0.1 gram is usually sufficient even for baths that tend to pit badly. Amounts larger than one gram have not been found necessary although the larger amounts have not been found detrimental.

In some cases, particularly with bright deposits produced with our process from the nickel sulphate bath, difficulty may be found in depositing bright chromium over the nickel. The chromium may tend to deposit only in spots or streaks or with a milky film. We are not at present able to give a definite explanation of this phenomenon but it seems to be due to passivity of the nickel-selenium surface induced by some peculiar condition or conditions in the bath or procedure, or to the effect of selenium in the plated surface. The difficulty is readily overcome by lightly buffing or scouring the plated surface before placing it in the chromium plating bath.

We have also found that treatment of the electrodeposited nickel in an electrolytic alkaline cleaner followed by treatment with hydrochloric acid eliminates any difficulty in regard to a subsequent coating of chromium. For this purpose the nickel plated article is placed in a bath comprising a solution of sodium carbonate, sodium hydroxide, or other alkali or alkaline mixture ordinarily employed for removing grease from metals, and connected as cathode in a suitable electric circuit. As a specific example, a cleaner compound may comprise 35% by weight of soda ash, 55% of trisodium phosphate and 10% sodium hydroxide. The bath may be made by dissolving 2-6 oz. of this compound per gallon of water. The bath should be heated and the article treated therein for a period of 1-3 minutes, the current being supplied at a voltage of 1-6 volts. The article should then be rinsed and dipped in a bath of dilute HCl and again rinsed before being

placed in the chromium plating bath. The latter may be of any usual type, for example, the chromic acid, chromium sulphate bath generally known as the "Sargent solution," the usual conditions for depositing bright chromium being maintained.

The selenium-containing addition agent is gradually depleted in use both by drag-out or like losses of solution and by actual combination with the cathodic deposit by electrodeposition or otherwise. Replenishment must be made, therefore, as required to maintain the initial proportions. The selenium deposited on the cathode apparently combines as metallic selenium with the nickel and we therefore regard the bright deposit as a compound or alloy of nickel and selenium, the latter, of course, being present in extremely small proportions.

We claim:

1. An electrodeposited combination of nickel and selenium the latter being present in relatively small proportion.

2. An electrolyte for electrodeposition of nickel containing an aqueous solution of nickel salts and an addition agent soluble in the electrolyte containing selenium in sufficient quantity to cause deposition of the nickel in brilliant form.

3. An electrolyte as in claim 2, the addition agent being a selenium acid.

4. An electrolyte for electrodeposition of nickel comprising a solution containing nickel sulphate, nickel chloride, and selenious acid, the selenious acid being present in amounts corresponding to about .05 to .5 gram of SeO_2 per liter of solution.

5. An electrolyte for electrodeposition of nickel containing an aqueous solution of nickel salts, a selenium compound soluble in the electrolyte and a sulphated higher alcohol having at least 10 carbon atoms in the molecule.

6. Process of electrodepositing nickel in bright form upon a base, comprising passing an electric current through a nickel electrolyte to said base as cathode, said electrolyte containing a solution of nickel salts and a compound of selenium soluble in the electrolyte.

7. Process as in claim 6, said compound being selenious acid.

8. Process of electrodeposition comprising passing an electric current through an electrolyte to a cathode to be coated, said electrolyte containing substances yielding simultaneously cathodic deposits both of nickel and selenium.

9. The process of electroplating a base comprising coating the base with a bright deposit containing nickel from a bath containing nickel sulphate, nickel chloride and a selenium compound soluble in the bath, subjecting the surface to a treatment to eliminate passivity and then plating chromium thereon.

10. Process as in claim 9, said treatment including rubbing the surface with abrasive.

11. Process as in claim 9, said treatment including subjecting the surface to the cathodic action of an alkaline electrolytic cleaner.

12. An electrolyte for deposition of nickel containing nickel acetate, nickel chloride, acetic acid and a compound containing selenium soluble in the electrolyte.

13. An article comprising a conducting base and an electrolytically deposited coating predominantly of nickel, said coating having a content of selenium to an amount sufficient to cause deposition of the nickel in brilliant form.

14. An article comprising a conducting base and a coating thereon consisting of an adherent

and brilliant-surface deposit predominantly of nickel but containing selenium to the amount obtained by electrodeposition of the nickel from a nickel plating bath containing the equivalent of approximately 0.05 to 0.5 gram per liter of SeO_2 .

15. The process of electrodeposition, which comprises electrodepositing nickel from an acid solution of nickel salts and an addition agent containing selenium in sufficient quantity to cause deposition of the nickel in brilliant form, the addition agent being a compound soluble in said solution containing an acid radical of a selenium acid.

16. An electrolyte for electrodeposition of nickel comprising an acid solution of nickel salts and an addition agent containing selenium in sufficient quantity to cause deposition of the nickel in brilliant form, the addition agent being a compound soluble in said solution containing an acid radical of a selenium acid.

17. An electrolyte for electrodeposition of nickel comprising an acid solution containing nickel sulphate, nickel chloride, and selenic acid in amount sufficient to cause deposition of the nickel in brilliant form.

18. The process of electrodeposition, which comprises electrodepositing nickel from an acid solution of nickel salts in the presence of an amount sufficient to insure a bright nickel deposit of a selenium compound, said compound being a compound soluble in said solution containing an acid radical of a selenium acid, and a minor amount of a sulphate of lauryl alcohol.

19. An electrolyte for electrodeposition of nickel, comprising an acid solution of nickel salts and containing an amount sufficient to insure a bright nickel deposit of a selenium compound, said compound being a compound soluble in said solution containing an acid radical of a selenium acid, and a minor amount of a sulphate of lauryl alcohol.

20. An electrolyte for electrodeposition of nickel comprising an aqueous acid solution containing nickel sulphate, nickel chloride, boric acid and to which has been added a minor quantity of a selenium acid soluble in the electrolyte sufficient to cause deposition of the nickel in brilliant form.

21. An electrolyte for the electrodeposition of nickel comprising an aqueous acid solution of a

compound of nickel and to which has been added a small amount of selenium di-oxide sufficient to cause deposition of the nickel in brilliant form.

22. An electrolyte for electrodeposition of nickel comprising an aqueous acid solution containing nickel sulphate, nickel chloride, boric acid and to which has been added a minor quantity of selenious acid sufficient to cause deposition of the nickel in brilliant form.

23. An electrolyte for electrodeposition of nickel containing an aqueous solution of nickel salts and an addition agent containing selenium in sufficient quantity to cause deposition of the nickel in brilliant form, the addition agent being selenious acid to the amount produced by the addition of approximately 0.05 to 0.5 gram SeO_2 per liter of solution.

24. An article comprising a metallic base and having a brilliant and adherent electrodeposited coating thereon composed predominately of nickel and containing a relatively minute amount of selenium.

25. An article comprising a conducting base, a brilliant electrodeposited coating thereon predominately of nickel and containing a small amount of selenium, and a brilliant electrodeposited coating of chromium upon said first mentioned coating.

26. An electrolyte for electrodeposition of nickel comprising an acid nickel electrolyte containing a small amount of a compound of selenium soluble in the electrolyte.

27. An electrolyte for electrodeposition of nickel comprising an aqueous acid nickel electrolyte containing selenic acid in amount sufficient to cause deposition of nickel in brilliant form.

28. An electrolyte for electrodeposition of nickel comprising an acid nickel electrolyte containing selenious acid in amount sufficient to cause deposition of nickel in brilliant form.

29. The process of electroplating a base which comprises coating the base with a bright deposit containing nickel from an acid nickel electrolyte containing a selenium compound soluble in the electrolyte, subjecting the deposit to a treatment to eliminate passivity and then plating chromium thereon.

HARRY C. MOUGEY.
RALPH J. WIRSHING.

CERTIFICATE OF CORRECTION.

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HARRY C. MOUGEY, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 37, for "marked" read --marketed--; line 39, after "acid" insert --anhydride--; and second column, line 9, for " $\text{NiCl} \cdot 7\text{H}_2\text{O}$ " read -- $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$ --; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of February, A. D. 1944.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.