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METHOD OF ELECTROPLATING NICKEL AND COBALT, BATHS AND AGENTS THEREFOR

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This invention is concerned with addition agents for use in the electrodeposition of nickel group metals, such as nickel and cobalt, with electroplating baths containing the addition agents and with the process of electrodeposition carried out in solutions containing the addition agents.

While the invention is generally applicable to the electrodeposition of nickel group metals, such as nickel and cobalt, its immediate important applicability is in the electrodeposition of nickel. Therefore, for convenience the invention may be illustrated by its use in nickel plating, although it is not to be restricted thereto.

The recent trend toward developments for the direct deposition of the so-called bright nickel has shown some progress in the desired direction. However, among the various agents tried in attempting to reach the end sought, each has exhibited some undesirable shortcoming to restrict its general application.

The weakness of some of the agents is the limited operating conditions under which they may be employed, requiring very close and expensive control and supervision. Others do not actually produce a satisfactorily finished bright surface, which may, for example, be subjected to a succeeding deposit of another metal without intermediate treatment to prepare the first deposited surface to take on the subsequently deposited plate. Still others are too fleeting in their activity in the plating bath and too hard to follow during the plating operation by practical analytical methods, thereby presenting difficulties in their use insurmountable to commercial application. Other examples require the use of still other agents simultaneously in the bath to prevent pitting. Many of them, in addition, require agitation to yield even their limitly available results.

The present invention provides for the preparation of a nickel plating bath free of the shortcomings characteristic of the earlier addition agents and permitting the operation of an easily controlled process of electrodeposition yielding a brilliant, ductile nickel deposit over a wide range of operating conditions even on the most intricate base surfaces.

Particularly useful as an addition agent according to the invention is ortho-sulfobenzaldehyde, the presence of which makes possible an electroplating bath exhibiting unusual throwing power of the character hereinafter demonstrated. With an electroplating bath comprising ortho-sulfobenzaldehyde, the plating operation can be

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carried out with minimum supervision and analytical control over an extensive period, within a broad range of hydrogen ion concentrations and under current densities suitable to a wide variety of shop needs to consistently yield an evenly ductile nickel deposit on even the most intricately formed surfaces, and possessing admirable adhesion even on steel.

Broadly described, ortho-sulfobenzaldehyde is a sulfonated aromatic aldehyde. Other addition agents capable of exhibiting the different properties in varying degrees are thus generically referred to as sulfonated aromatic aldehydes, which may be mono- or poly-sulfonated, such as the sulfonated aryl aldehydes, which may be polynuclear, as exemplified by the sulfonated naphthaldehydes or sulfonated anthraldehydes. Particularly desirable are the mononuclear aryl derivatives, illustrated by sulfonated cinnamaldehyde, exemplifying the unsaturated alkyl or vinyl derivatives, and sulfonated salicylaldehyde and other sulfonated benzaldehydes, including the saturated alkylated compounds, such as tolualdehyde, or especially the non-alkylated compounds as ortho-sulfobenzaldehyde, or the alkoxylated derivative as in sulfonated para-methoxy benzaldehyde (anisaldehyde). The nickel salt of 2.5 disulfobenzaldehyde illustrates the polysulfonated form.

The various types of the addition agent may be employed either as the free sulfonic acid derivative of the aldehyde or as a salt thereof. Therefore, the terms "sulfonic acid," "sulfonate," and "sulfo-" employed herein and in the appending claims are each used in the generic sense as if each is represented as the radical $-SO_3X$ in which X may be hydrogen or a salt forming cation such as a metal, for example, an alkali metal, as sodium or potassium, or an alkaline earth metal, as magnesium, or a nickel group metal, as nickel or cobalt, or other metal as cadmium, mercury, zinc and the like, or an amine type cation including ammonium and those derived from an amine or alkylamine as methylamine or ethylamine, or from an alkylolamine as mono-, di-, or triethanolamine, or other suitable salt forming base.

Distinctly effective as an addition agent is orthosulfobenzaldehyde, either in the form of the free sulfonic acid derivative or of any of the salts of any of the salt forming cations just above described.

The addition agents of this invention may be applied to any commonly employed nickel plating bath containing any of the usual nickel plating

salts and which may also include salts commonly employed for promoting anode corrosion and conductivity, such as the chlorides or sulfates, and ingredients effecting the hydrogen ion concentration of the bath, such as sulfuric, boric and citric acids.

Any convenient concentration of the brightening agent suitable to give the brilliance sought in the electrodeposit may be employed. A desirable effective range, for example, with orthosulfobenzaldehyde, is from about one-half (½) gram to twenty (20) grams per liter, although under some operating conditions less than one-half gram and in others more than twenty grams per liter can be used.

An attractive feature of the process of the invention is the wide range of hydrogen ion concentration over which it is operable. Particularly unique in this respect is ortho-sulfobenzaldehyde which is effective over a wide range from as little as around a pH of 1.5 to around 5.5, and admirably effective at any point in the range of pH from about 2.0 to about 5.0, measured electrometrically. In fact, it is possible to permit the hydrogen ion concentration of the plating bath to vary over the duration of the plating operation of the bath at any point within the indicated zone. It is thus found that little control of hydrogen ion concentration is necessary over a long period of operation thereby eliminating to a large degree the necessity for close supervision and analysis of the bath during long extended operation with regard to this particular operating condition.

At the same time, as found with ortho-sulfobenzaldehyde, the current density may be selected to suit a wide variety of shop needs for the electroplating bath may be operated at a current density of from about 5 or less to around 75 or more amperes per cathode square foot, and even up to about 100.

Along with the just described operating conditions possible by the process of electrodeposition with the electroplating baths of the invention, an unusual throwing power is observed. This characteristic makes agitation unnecessary in the operation of the plating bath, although agitation may be employed if desired. It has thus been possible by the process of the invention, without agitating the electroplating bath, to deposit nickel brilliantly and evenly over the entire surface of a bent cathode including the crevices and to produce an evenly brilliant nickel deposit over not only the outside, but also the inside of a cylinder without employing an inside anode, for example, when using ortho-sulfobenzaldehyde as an addition agent.

Electroplating baths according to the present invention, in which the above indicated results are obtained may be illustrated by, but not restricted to, the following:

Example 1

	Ounces for gallon
Nickel sulfate ($6H_2O$)	37
Nickel chloride ($6H_2O$)	8
Boric acid	5
Ortho-sulfobenzaldehyde	½

The electroplating bath can be operated at a temperature of from about 100° F. or less to about 140° F. or more, but a good operating range is between 110° and 120° F.

The concentration of the plating salts in the bath of the example may be varied to include the following ranges, although more or less of each of the primary constituents may be used, if desired:

	Ounces per gallon
Nickel sulfate ($6H_2O$)	28 to 50
Nickel chloride ($6H_2O$)	3 to 8
Boric acid	2 to 5

It has also been found that when an addition agent, such as ortho-sulfobenzaldehyde is present in the plating bath, it is not necessary to employ in the bath an anti-pitting agent, i. e. an agent that lowers the surface tension and avoids pitting.

Other organic addition agents are found to be applicable only within a limited range of hydrogen ion concentration and yield only a reasonably bright nickel deposit. It has been found that if part of the amount of such agent present is replaced by the addition agent of this invention exemplified by ortho-sulfobenzaldehyde, then the plating bath in which the combination of the two agents is present can be operated without the necessity of adjusting the hydrogen ion concentration during the extent of the operation while the pH varies between about 2.0 and about 5.5. Such plating bath will then also yield a brilliant nickel deposit.

Thus when ortho-sulfobenzaldehyde is added to a given bath ordinarily operated with a naphthalene sulfonate, e. g., a disulfonate, as a brightening agent, in a quantity to replace an equal quantity deducted from the customary charge of the naphthalene sulfonate, the bath may be operated over an extended period without the necessity of testing or adjusting the pH while this characteristic of the bath may change within the range from about 2.0 to about 5.5 and agitation, otherwise required, may be omitted.

Articles plated by the method of this invention do not require re-activation if the plating operation has been interrupted and is to be resumed or when the plated article is to be subjected to a subsequent deposit of another metal, or the nickel plated article can be subject to a chromium plating, after it has been exposed to the air, without the application of the customary so-called light wipe.

The present invention, particularly as exemplified by the use of ortho-sulfobenzaldehyde, includes among its advantages over the use of other addition agents, the fact that it is not critical in its operation and yields a brilliant deposit of the nickel group metal, e. g. nickel or cobalt, as compared with solely a reasonably bright deposit obtainable by the use of the others, and furthermore yields such brilliant deposit at decreased cost because of the reduction in supervision and analytical control and the elimination of agitation and the need of an anti-pitting agent.

While the invention has been illustrated by description of specific embodiments of it, it is understood that many modifications, alterations and equivalents may be employed within the scope of the invention as covered by the appending claims.

I claim:

1. An aqueous, acid electroplating bath which comprises in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of one of the metals selected from the group consisting of nickel and cobalt, together with an amount of a sulfonated aryl aldehyde sufficient to permit a brilliant cathodic deposit of the metal to be obtained upon the passage of an electric current

from an anode comprising said metal through the bath to a cathode, under the operating conditions.

2. An aqueous, acid electroplating bath which comprises in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of one of the metals selected from the group consisting of nickel and cobalt, together with an amount of a mononuclear aryl aldehyde having its benzene nucleus sulfonated sufficient to permit a brilliant cathodic deposit of the metal to be obtained upon the passage of an electric current from an anode comprising said metal through the bath to a cathode, under the operating conditions.

3. An aqueous, acid electroplating bath as in claim 2, in which the sulfonated aryl aldehyde is a sulfonated phenyl aldehyde.

4. An aqueous, acid electroplating bath which comprises in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of one of the metals selected from the group consisting of nickel and cobalt, together with an amount of ortho-sulfobenzaldehyde sufficient to permit a brilliant cathodic deposit of the metal to be obtained upon the passage of an electric current from an anode comprising said metal through the bath to a cathode, under the operating conditions.

5. An aqueous, acid electroplating bath as in claim 1, in which the sulfonated aryl aldehyde is selected from the class consisting of sulfonated phenyl, sulfonated naphthyl and sulfonated anthryl aldehydes.

6. An aqueous, acid electroplating bath as in claim 2, which in addition to the sulfonated aryl aldehyde contains a second aryl sulfonate brightening agent which is free from the aldehyde group, the two organic agents being present in a combined quantity sufficient to permit a brilliant deposit of the metal to be obtained.

7. An aqueous, acid electroplating bath as in claim 2, which in addition to the sulfonated aryl aldehyde contains as a second brightening agent a naphthalene sulfonate which is free of the aldehyde group, the two organic agents being present in a combined quantity sufficient to permit a brilliant deposit of the metal to be obtained.

8. An aqueous, acid electroplating bath as in claim 2, which in addition to the sulfonated aryl aldehyde contains as a second brightening agent a naphthalene polysulfonate which is free of the aldehyde group, the two organic agents being present in a combined quantity sufficient to permit a brilliant deposit of the metal to be obtained.

9. An aqueous, acid electroplating bath which comprises in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of one of the metals selected from the group consisting of nickel and cobalt, together with an amount of ortho-sulfobenzaldehyde and of a naphthalene disulfonate, the two organic agents being present in a combined quantity sufficient to permit a brilliant deposit of the metal to be obtained upon the passage of an electric current from an anode comprising said metal through the bath to a cathode, under the operating conditions.

10. The process of depositing a bright electrodeposit of a metal selected from the group consisting of nickel and cobalt, which process comprises passing an electric current from an anode comprising said metal to a cathode through an aqueous, acid electroplating bath comprising in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of said metal, in the presence of a mononuclear aryl aldehyde in an amount sufficient to permit a bright cathodic deposit of the metal to be obtained under the operating conditions having its benzene nucleus sulfonated.

11. The process as in claim 10, in which the sulfonated aryl aldehyde is a sulfonated phenyl aldehyde.

12. The process of depositing a bright electrodeposit of a metal selected from the group consisting of nickel and cobalt, which process comprises passing an electric current from an anode comprising said metal to a cathode through an aqueous, acid electroplating bath comprising in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of said metal, in the presence of orthosulfobenzaldehyde in an amount sufficient to permit a bright cathodic deposit of the metal to be obtained under the operating conditions as the brightening agent.

13. The process as in claim 10, in which the sulfonated aryl aldehyde is polysulfonated.

14. The process as in claim 10, which is carried out in the presence of both the sulfonated aryl aldehyde and a sulfonated aryl brightening agent which is free of the aldehyde group.

15. The process of depositing a bright electrodeposit of a metal selected from the group consisting of nickel and cobalt, which process comprises passing an electric current from an anode comprising said metal to a cathode through an aqueous, acid electroplating bath comprising in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of said metal, in the presence of both a mononuclear aryl aldehyde having its benzene nucleus sulfonated and a naphthalene sulfonate in a combined quantity sufficient to permit a bright deposit of the metal to be obtained under the operating conditions.

16. The process as in claim 15, in which the naphthalene sulfonate is a polysulfonate.

17. The process as in claim 15, in which the sulfonated aryl aldehyde is a sulfonated phenyl aldehyde and the naphthalene sulfonate is a polysulfonate.

18. The process as in claim 15, in which the sulfonated aryl aldehyde is a sulfonated benzaldehyde and the naphthalene sulfonate is a disulfonate.

19. The process as in claim 15, in which the sulfonated aryl aldehyde is ortho-sulfobenzaldehyde and the naphthalene sulfonate is a naphthalene disulfonate.

20. An aqueous, acid electroplating bath which comprises in the aqueous medium a nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with an amount of ortho-sulfobenzaldehyde sufficient to permit a brilliant cathodic deposit of the metal to be obtained upon the passage of an electric current through the bath, under the operating conditions.

21. An aqueous, acid electroplating bath which comprises in the aqueous medium nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with a sulfonated cinnamaldehyde as the sole addition agent capable of causing a brilliant cathodic deposit and in an amount sufficient to permit a brilliant cathodic deposit of the metal to be obtained upon the passage of an electric

current through the bath, under the operating conditions.

22. An aqueous, acid electroplating bath which comprises in the aqueous medium a nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with an amount of a sulfonated benzaldehyde sufficient to permit a brilliant cathodic deposit of nickel to be obtained upon the passage of an electric current from the anode through the bath to the cathode, under the operating conditions.

23. An aqueous, acid electroplating bath as claimed in claim 2, in which the benzene nucleus in the aromatic aldehyde is monosulfonated.

24. An aqueous, acid electroplating bath as claimed in claim 2, in which the sulfonated aryl aldehyde is a monosulfonated phenyl aldehyde.

25. An aqueous, acid electroplating bath which comprises in the aqueous medium a nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with ortho-sulfobenzaldehyde as the sole addition agent for causing a brilliant cathodic deposit of the metal to be obtained upon the passage of an electric current through the bath, under the operating conditions.

26. The process of depositing a bright electrodeposit of a metal selected from the group consisting of nickel and cobalt, which process comprises passing an electric current from an anode comprising said metal to a cathode through an aqueous, acid electroplating bath comprising in the aqueous medium a metal-ion yielding material consisting essentially of a mixture of the sulfate and of the chloride of said metal, in the presence of a sulfonated benzaldehyde.

27. A nickel electroplating bath addition agent composition comprising a brightening agent consisting essentially of a mononuclear aryl aldehyde having its benzene nucleus sulfonated and a naphthalene disulfonate, said addition agent composition being capable, upon addition to an aqueous, acid nickel plating bath containing nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, of causing a substantially uniform luster and brilliant cathodic deposit of nickel to be obtained upon the passing of an electric current from the anode through said bath to the cathode when the benzene-nucleus-sulfonated mononuclear aryl aldehyde and the naphthalene disulfonate are present in the bath respectively in combined quantities sufficient to permit a brilliant deposit of the nickel to be obtained under the operating conditions.

28. A nickel electroplating bath addition agent composition as claimed in claim 27, in which the benzene-nucleus-sulfonated, mononuclear aryl aldehyde is a sulfonated-phenyl aldehydic compound selected from the sulfobenzaldehydes and sulfocinnamaldehydes.

29. A nickel electroplating bath addition agent composition as claimed in claim 27, in which the benzene-nucleus-sulfonated, mononuclear aryl aldehyde is ortho-sulfobenzaldehyde.

30. A nickel electroplating bath addition agent composition as claimed in claim 27, in which the benzene-nucleus-sulfonated, mononuclear aryl aldehyde is sulfonated cinnamaldehyde.

31. An aqueous, acid electroplating bath which comprises in the aqueous medium a nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with an amount of a sulfonated-phenyl aldehydic compound selected from sulfobenzaldehydes and sulfonated cinnamaldehyde present in quantity sufficient to permit a brilliant cathodic deposit of nickel to be obtained upon passage of an electric current through the bath, under the operating conditions.

32. An aqueous, acid electroplating bath which comprises in the aqueous medium a nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with an amount of a sulfonated aryl aldehyde sufficient to permit a brilliant cathodic deposit of nickel to be obtained upon the passage of an electric current from the anode through the bath to the cathode, under the operating conditions.

33. An aqueous, acid electroplating bath which comprises in the aqueous medium a nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with an amount of a sulfonated mononuclear aryl aldehyde sufficient to permit a brilliant cathodic deposit of nickel to be obtained upon the passage of an electric current from the anode through the bath to the cathode, under the operating conditions.

34. An aqueous, acid electroplating bath which comprises in the aqueous medium a nickel ion yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, together with an amount of a sulfonated phenyl aldehyde sufficient to permit a brilliant cathodic deposit of nickel to be obtained upon the passage of an electric current from the anode through the bath to the cathode, under the operating conditions.

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