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ELECTRODEPOSITION OF METALS

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This invention relates to electrodeposition of metals; and it has to do more especially with electrodeposition of metals of the nickel group comprising nickel, cobalt and iron, employing plating baths or solutions containing an inorganic salt of the metal to be deposited, together with a relatively small quantity of an organic compound, particularly a sulfonic acid compound, as a catalyst, promoter, or assisting agent; the plating baths being operated relatively hot and at relatively low pH (hydrogen ion concentration); whereby electrodeposits of superior characteristics are produced. The invention comprises the novel process aforesaid, as well as the novel plating baths or solutions and the novel electrodeposits produced therefrom.

While the invention in its broader aspects is not restricted to electrodeposition of any particular metal or group of metals, but is applicable in a very wide field with varying degrees of utility, its greatest practical utility at the present time is in the electrodeposition of metals of the nickel group aforesaid, and preeminently of nickel itself. In explaining the underlying principles of the invention, therefore, reference will be made herein more particularly to nickel plating; but it will be understood that this is merely for purposes of illustration and that in its broader aspects the invention is of wider scope, as indicated.

A principal object of the invention is to produce electrodeposits of nickel or other metal which are bright and lustrous, i. e., image-reflecting or mirror-like. In the field of decorative plating, the final bright, glossy finish usually required and sought has ordinarily been obtained heretofore by buffing nickeled articles, which are then given a thin coating of chromium, for example. This sequence of operations necessitates a re-racking of the articles between the nickel and chromium plating tanks, and, what is more important, also results in a loss of nickel removed by the buffing or mechanical polishing operation, not to mention the expense of the labor involved. A method of plating whereby the nickeled articles come from the bath with a bright and lustrous finish, such as is afforded by the present invention, is therefore highly desirable.

Another object of the invention is to attain the foregoing desirable results while at the same time permitting rapid deposition of relatively thick or heavy metal coatings as required by modern plating practice, and to do this relatively simply and economically.

With the foregoing objects in view, as well as

others which will become apparent as the description proceeds, the invention consists in the novel plating processes and baths, as well as the resultant novel electrodeposits, which will be described in certain concrete illustrative examples hereinafter and will then be more particularly pointed out in the appended claims.

It has been proposed heretofore to produce bright or image-reflecting deposits of nickel directly in the plating bath, but all such prior proposals have involved serious disadvantages rendering them unsuitable for economically successful application in actual practice. What little is to be found in the literature on the subject of bright nickel plating has to do with cold nickel solutions or baths operated at ordinary room temperature and producing relatively thin deposits. Although the use of certain addition agents, chiefly colloidal, as brighteners in nickel plating baths has been suggested heretofore, they have not been widely used because of the difficulty in controlling their effect and because of the very narrow range of operating conditions within which satisfactory deposits could be obtained even experimentally. Nickel and other metal solutions are very susceptible to the action of colloids, and the amounts used, as well as other details of operation, must be carefully regulated to avoid production of cracked and curled deposits. Due either to their inherent character or to the particular manner in which it has been recommended to use them, the addition agents heretofore suggested for use were operative only for low current densities and thin deposits and are therefore not available for use in the more recent plating practice which calls for the rapid deposition of relatively heavy coatings. Addition agents thus suggested heretofore have included a wide variety of organic compounds, as well as certain metals such as zinc or cadmium. But it has not been possible heretofore, by the use of any of these addition agents, as proposed, to obtain satisfactory bright nickel deposits of appreciable thickness such, for example, as a thickness of more than 0.0002 inch; and even in the case of thinner deposits, an approach to satisfactory brightness or luster was obtainable only by using baths of relatively high pH value or by operating at low current densities impractical or very undesirable to use in modern plating practice, the resultant deposits, furthermore, being ordinarily brittle and poorly adherent.

According to the present invention, nickel plating baths, for example, are employed which in most respects may much resemble those now com-

monly used but which contain one or more addition agents serving to promote production of bright or mirror-like deposits, which novel baths are, furthermore, operated within a temperature range above ordinary room temperature and within a pH range that is relatively low (i. e., relatively strongly acid). The particular temperature and pH vary within the indicated ranges depending upon the particular addition agent or agents employed in any given plating bath, but may be adjusted and controlled in accordance with the present invention to give optimum results. In general the process of the invention involves operating at bath temperatures ranging from about 35° C. to about 60° C., a range of 40° to 50° C. being found especially desirable in the case of most of the addition agents most suitable for practicing the invention. The pH of the plating baths may range from 5.5 to 1.5, electrochemically determined, e. g. with the quinhydrone electrode; a pH of approximately 2.5 being found especially suitable in the majority of cases. Under these conditions of plating bath control or adjustment, and with the use of a proper addition agent or agents, employment of relatively high current densities in producing thoroughly satisfactory coatings becomes feasible and is also characteristic of the invention in its best embodiments. Current densities of from 30 to 50 amperes per square foot are especially suitable and are typical, although in many cases current densities as high as 60 to 100 amperes per square foot are practical and desirable. Lower current densities, e. g., on the order of 10 amperes per square foot, are also permissible; and it is to be understood that the use of such lower current densities is within the scope of the invention in its broader aspects, although higher current densities can advantageously be employed, as above pointed out, and are preferred in practice.

With respect to the addition agent or agents to be employed, a rather wide range of choice is afforded within the broadest scope of the invention, provided the conditions of bath control with respect especially to temperature and pH are observed as herein recommended. However, certain of these addition agents are of outstanding effectiveness and value for the purposes of the invention because of their especially marked influence in enhancing the desirable character of the electrodeposits within operating condition ranges sufficiently wide to render them practical and economical for use in commercial plating operations. These addition agents, therefore, are regarded as of peculiarly great importance for the purposes of the invention and their use is especially recommended and much to be preferred in practice. Other addition agents, although not excluded from the scope of the invention in its broadest aspect, are distinctly distinguishable from those just referred to in that they either exhibit much less specific potency for enhancing the desirable characteristics of the electrodeposits, or else are operative for this purpose within operating condition ranges which are so narrow, relatively, as to render their use more or less difficult or even impractical in commercial plating operations as now generally carried out. Accordingly, this latter group of addition agents is not to be regarded as the equivalent of the first mentioned group for the purposes of the invention in its more specific aspects, although not excluded from the invention in its broadest aspects, as already stated.

Generally speaking, addition agents suitable for use in the present invention are organic in character and, as a rule, are sulfonated compounds, that is, they comprise the sulfonic acid radical, being either sulfonic acids or suitable metal salts thereof. Sulfonated aryl compounds in particular are found suitable, whether containing the benzene nucleus or the naphthalene nucleus. Among the classes of compounds found practical to use as addition agents may be mentioned naphthalene sulfonic acids, naphthol sulfonic acids, naphthylamine sulfonic acids, toluidine sulfonic acids and tolidine sulfonic acids. It is also found that the desirable action of these agents is appreciably enhanced if they are mildly chlorinated, as, for example, by the use of a chlorine-in-water solution as the chlorinating agent. It is further found that in some cases especially good results are obtained when a small quantity of a metal promoter, zinc or cadmium, is associated in the bath with the addition agent. The organic addition agents may be used singly or in combinations of two or more within the scope of the invention; but from the standpoint of simplifying control of the composition of the plating solution, it is generally more desirable to employ only one. For the same reason, it is generally better to employ only one metal addition agent or promoter (in the form of a salt) in conjunction with one organic addition agent.

Another important feature of the invention in its best embodiments is the fact that the addition agent used is employed in only relatively very small quantity, so small indeed as not to combine with or bind chemically any substantial proportion of the amount of the plating metal present in the bath or solution to be deposited therefrom. In other words, in the practice of this invention, the metal to be deposited ordinarily exists in the bath wholly or almost wholly as a salt of an inorganic acid; but the term "inorganic acid" as here used is not intended to exclude the presence in the bath of variable proportions of acetate, formate, and/or oxalate, for example, of the plating metal, which salts may be employed as buffering agents. In other words, the organic addition agents as employed in the present invention seem to function very much in the role of catalysts in promoting the production of the superior electrodeposits obtainable in the practice of the invention, said addition agents being present in relatively small and generally only minute proportion, as compared with the amount of plating metal salt or salts in the bath and apparently undergoing very little depletion in operation except for the unavoidable drag-out. In referring to the action of these addition agents as catalytic, however, it is not intended thereby in any sense to rest the present invention upon a theoretical basis, but only to characterize conveniently and in a general way their promoting and assisting action, in contrast to the prior proposed use, in connection with tin, copper or lead plating, of certain sulfonic acid compounds in relatively large quantities for the purpose of binding chemically approximately half or more of the total plating metal present as a metal sulfonate. In contradistinction to methods heretofore proposed in applying the process of the invention to bright nickel plating, for example, the deposit may be made, and most desirably is made, at the relatively high temperatures and high current densities commonly employed commercially in 75

ordinary non-bright nickel plating practice; and the luster of the deposit becomes greater with increase of the thickness of the deposit. In fact, the present process enables plating upon a surface which is originally dull and, by continuing the deposition for a sufficient length of time and thus obtaining a relatively thick deposit, securing a deposit that is image-reflecting or mirror-like. This remarkable result can be accomplished, moreover, by using nickel plating baths which, except for the employment of an addition agent or "catalyst" as herein described, have compositions otherwise usual in present commercial practice. A typical plating bath of this character may contain, for example, 180 to 360 grams of hydrated nickel sulfate, 8 to 75 grams of nickel chloride and 8 to 45 grams of boric acid, per liter of solution.

Among the specific organic addition agents which have been found especially desirable to employ as assistants or catalysts in accordance with the invention may be mentioned the following: the alpha and beta naphthalene monosulfonic acids, the 1.5 and the 2.7 naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid; the toluidine sulfonic acids, 2 amino toluene 5 sulfonic acid, 2 amino toluene 4 sulfonic acid, 4 amino toluene 2 sulfonic acid; and o-tolidine disulfonic acid. The products resulting from mild chlorination of these compounds are also very effective. Of the compounds found to be specifically satisfactory for use as assistants or catalysts, those considered at present to be particularly desirable are the naphthalene disulfonic acids, particularly the alpha or 1.5 disulfonic acid, and beta naphthalene monosulfonic acid.

A bath containing any of the materials mentioned in the next preceding paragraph produces brighter deposits if the pH is decreased (acidity increased) down to a pH of 2.5 or even lower in some instances; while increase of temperature up to approximately 45° C., or in some cases higher, also causes an increase in the brightness of the deposit. Moreover, the deposits so obtained are characterized by good adherence and substantial freedom from cracking or curling, these eminently satisfactory results being obtainable over a relatively wide working range of temperature, pH value and current density, within the limits hereinabove indicated.

It is of course to be understood that, in general, salts (e. g., the sodium or other alkali metal salts, the calcium salts, etc.) of the sulfonic acids mentioned not detrimental to the plating bath may be used as addition agents or "catalysts" in place of the sulfonic acids themselves. Unless otherwise expressly indicated, therefore, the expression "sulfonic acid" is to be understood broadly to include both the free acids and salts thereof.

The amount of organic addition agent or catalyst which is desirably employed in practicing the invention may vary, in the case of the free sulfonic acids, for example, from 1 gram per liter up to saturation. Saturation in the case of the naphthalene 1.5 disulfonic acid is approximately 15 grams per liter, and in the case of beta naphthalene sulfonic acid is approximately 2 grams per liter at 40° C., in a bath containing 315 grams nickel sulfate, 15 grams nickel chloride and 30 grams boric acid in one liter of solution. Generally speaking, lowering the pH of the bath increases the solubility of the addition agents.

Deposits of even greater brightness are obtain-

able when the plating solution contains not only an organic addition agent but also a small quantity of either cadmium or zinc; and such conjoint use of such materials in plating solutions, particularly in nickel plating, is an important feature of the present invention. The addition to a dull nickel plating solution of a small amount of a soluble compound of an assistant or promoter metal, e. g., cadmium or zinc, for the purpose of getting some brightening effect, was long ago proposed but did not result in production of satisfactory plating deposits. As is well known, that use as heretofore proposed was too ineffective and too unsafe to be practical, especially under the operating conditions characterizing modern high-speed plating practice; and no way of overcoming the difficulties was known. But by employing a promoter metal in a nickel plating bath in conjunction with an organic brightening agent in accordance with the principles of the present invention, nickel plate of any desired thickness and of exceptional brightness may be easily produced, such deposits also being highly satisfactory in respect to their other required properties, including adequate ductility and good adherence. The promoter metal, which may be defined for the purposes of this invention as a metal having the effect, when used by itself in a bath from which a nickel group metal is electrodeposited, of enhancing the brightness of the plating metal deposit but tending to render it brittle and non-adherent, is usually added in the form of the sulfate although the specific method of adding it is in general immaterial. For example, the metal chloride may be employed, the oxide may be dissolved in the acid bath, or the metal to be introduced into the solution by dissolving it from an anode. It may also be used in the form of its compound with the sulfonic acid (e. g.) used as the principal addition agent or "catalyst". For example, excellent results are obtainable from a plating solution containing one of the organic addition agents or catalysts before mentioned together with from a trace up to about 1.6 grams of zinc per liter of solution, expressed as metal. Likewise, excellent results are obtained by the use of cadmium as the promoter in concentrations ranging from a trace upward to about 2.3 grams per liter, expressed as metal. Because these promoters have the property of reducing the ductility of the resultant electrodeposits as their concentration is increased, the concentration of either of them in a given solution should be adjusted in accordance with the degree of ductility required in the electrodeposited metal.

In order to further illustrate the principles of the invention, a few detailed examples illustrating typically good practice in employing the invention will now be given.

Example 1

With respect to concentration of plating metal to be deposited, nickel in this instance, the approximate composition of the solution or bath per liter may be 293 grams nickel sulfate, 12 grams nickel chloride and 25.5 grams nickel acetate, the last mentioned compound being relied upon for buffering effect; while the addition agent or catalyst used in such a bath may be either beta naphthalene sulfonic acid, alpha naphthalene sulfonic acid, or alpha naphthylamine 3.6.8 trisulfonic acid (amino H acid). A good working range for the bath temperature is 40° to 60° C., with the cathode current density ranging from 10 to 50

amperes per square foot. Under these operating conditions, the optimum concentration for both the alpha and beta naphthalene sulfonic acids is about 2 grams per liter (practical range about 0.5 to 4.0 grams per liter); while the optimum concentration for alpha naphthylamine 3.6.8 trisulfonic acid is about 40 grams per liter. Bright deposits of satisfactory character are obtained at all pH values within a working range of about 3.3 to 4.4, an average pH of 3.7 giving good results in all cases. The best results are obtained with beta naphthalene sulfonic acid, however.

Example 2

In this case the plating bath may contain about 320 grams nickel sulfate and 12 grams nickel chloride per liter, with boric acid present as a buffering agent in concentration equal to about 31 grams per liter. A bath of this general constitution is particularly desirable because it is a type of nickel plating solution in widespread use on account of its desirable characteristics when operated to produce relatively thick deposits rapidly. Using beta naphthalene sulfonic acid as the addition agent in this bath at a concentration of about 2 grams per liter, bright or mirror-like nickel deposits of excellent properties are obtainable when operating at cathode current densities of from 30 to 100 amperes per square foot, temperature of from 40° to 60° C., and pH of from 1.8 to 5.3.

Example 3

(a) Employing the same general type of plating solution as in Example 2, alpha naphthalene 1.5 disulfonic acid is employed as addition agent in concentration most desirably from about 4 to 10 grams per liter, in place of beta naphthalene sulfonic acid. The optimum operating conditions in this case are found to be approximately as follows: current density 25 to 60 amperes per square foot, temperature from 40° to 60° C., and pH range 1.8 to 5.3, a pH of 2.6 being a good working average.

(b) Naphthalene 2.7 disulfonic acid, employed at a concentration of about 2 grams per liter may be used in place of the 1.5 disulfonic acid with similar good results, although use of the 1.5 acid is considered on the whole to be more satisfactory and is therefore particularly recommended.

Example 4

In this case the type of plating solution and the conditions of operation are the same as in Example 2, except that the addition agent is mildly chlorinated. The nickel deposits obtained are of somewhat enhanced brightness and of otherwise equally satisfactory physical characteristics. Chlorination of the addition agents employed in Examples 1 and 3, as well as in the further examples to be given hereinafter, also gives excellent results.

Example 5

In this case one of the toluidine sulfonic acids is employed as addition agent or catalyst in a plating both otherwise similar in character to that used in Example 2. Bright deposits of excellent character are obtained, although over a somewhat narrower range of operating conditions than with some of the other addition agents recommended herein.

(a) When employing 2 amino toluene 5 sulfonic acid as the addition agent at a concentration of about 24 grams per liter of the plating solution (a range of about 9 to 24 grams per

liter is practical), the best pH range for bright deposits of satisfactory character is approximately from 2.2 to 4.25, operating at about 50 amperes per square foot cathode current density and a bath temperature of about 40° C. The practical desirable range of cathode current density for bright deposits at pH of 2.4 and bath temperature of 40° C. can be taken as approximately from 30 to 75 amperes per square foot.

(b) Using 2 amino toluene 4 sulfonic acid as the addition agent, in place of the 2-5 acid employed in (a), but with the plating solution otherwise similarly constituted, a range of from 10 to 20 grams of the addition agent per liter is practical, about 12 grams being optimum. At this optimum concentration, the best working conditions are (approximately): pH 2.0 to 5.0, cathode current density 20 to 50 amperes per square foot, and temperature 40° to 50° C.

(c) Again employing the general type of plating bath of Example 2, and using 4 amino toluene 2 sulfonic acid as the addition agent at an optimum concentration of 4 grams per liter (a range of about 4 to 12 grams per liter is practical), the best working pH range for bright deposits is approximately from 2.5 to 5.2, with a cathode current density of 50 amperes per square foot and bath temperature of 40° C. At a pH of 2.5 and bath temperature of 40° C., the practical desirable range of cathode current density for bright deposits may be taken as approximately from 30 to 75 amperes per square foot.

Example 6

A bath of the same general character as that described in Example 2 is used; but, in place of beta naphthalene sulfonic acid, ortho toluidine disulfonic acid is used as addition agent or catalyst at a concentration which most desirably lies between about 6 and 12 grams per liter. Within this concentration range, bright deposits of satisfactory character are obtained when operating at pH 2.0 to 3.0, cathode current density 40 to 60 amperes per square foot, and temperature 40° to 50° C.

Example 7

In this instance a small quantity of metal "promotor" is present in the solution, as well as an organic addition agent or catalyst.

(a) The plating bath may be like that employed in Example 3, with alpha naphthalene 1.5 disulfonic acid as the addition agent; but it also contains cadmium, added (e.g.) as the sulphate or chloride, at a concentration of about 0.2 gram per liter expressed in terms of the metal. From such a plating solution, deposits noticeably brighter than those produced without the cadmium addition are obtained when operating, for example, at a cathode current density of 50 amperes per square foot, bath temperature of 40° C., and a pH range of from 2.05 to 4.7. Maintaining the pH substantially constant at 2.05, the current density may range from approximately 10 to 100, or even 125, amperes per square foot, with production of satisfactory deposits.

(b) Although using cadmium as a promoter gives especially good results when alpha 1.5 disulfonic acid is employed as the addition agent or catalyst, the brightness of the deposits obtained with the monosulphonic acids or with any of the other addition agents mentioned herein is perceptibly enhanced by such use of cadmium.

(c) Similarly the brightness of deposits obtained from plating solutions containing any of 75

the organic addition agents herein disclosed is enhanced, without undesirably affecting the character of the deposits, when zinc is employed as the promoter in concentrations up to about 1 gram per liter, expressed as the metal. The zinc is conveniently added in the form of sulfate. Increase of the zinc concentration to as high as 3 grams per liter tends to cause brittleness in the deposit, and any addition as a promoter should therefore be desirably kept safely below this concentration for best results. This tendency to cause brittleness is less marked in the case of zinc, however, than in the case of cadmium.

In general, with lower concentrations of the plating metal in the bath, the concentration of the promoter metal (whether cadmium or zinc) should also be lower, although not necessarily proportionately lower. In general, the concentration of the promoter metal dissolved in the bath should not substantially exceed one-tenth normal

$$\left(\frac{N}{10}\right)$$

In the foregoing examples, the concentration of the plating metal in the bath is specified as approximately 2.5 N in each instance as illustrative of typical good practice, and the amounts of the various addition agents or "catalysts" specified are generally indicative of satisfactory concentrations thereof in such plating baths. It is to be understood, however, that considerable variation from these optimum concentrations and other operating conditions is permissible within the scope of the invention in its broader aspects.

It is found that during the plating operation the addition agents or "catalysts" and/or promoters may in some cases become concentrated at the surfaces of the cathodes or work being plated, this being especially characteristic of beta naphthalene sulfonic acid. When the work is removed from the bath and rinsed, therefore, such addition agents are removed from the solution at a more rapid rate, relatively, than are the other constituents of the plating bath. Accordingly, in order to compensate for the drag-out in the maintenance of the bath in such cases, it is necessary to add relatively larger proportions of the "catalyst" and promoter in respect to the other materials, than are used in making up a new solution or bath. The correct proportions may be found by chemical analysis or other suitable tests, and will vary with the amount of solution drag-out per ampere hour of plating.

The plating baths containing the addition agents or "catalysts" herein referred to have better throwing power than the same solutions not containing them; that is, such baths produce upon an irregularly shaped article a plate of more nearly uniform thickness than do baths not containing them.

The use of the organic compounds hereinabove specifically named, as addition agents in plating baths, is believed to be broadly novel irrespective of the quantity or concentration thereof in such baths or of the other operating conditions under which such baths are employed.

The deposits obtained when using cadmium or zinc in conjunction with a sulfonic addition agent or "catalyst" as in Example 7 hereinabove, are found upon analysis to contain carbon and sulphur, together with either cadmium or zinc as the case may be. In typical instances, where zinc is used as the promoter, the nickel deposit contains about 4.3 per cent zinc; and where cadmium

is the promoter, the deposit may contain around 0.8 per cent cadmium. In both cases, the nickel deposit also contains on the average in the neighborhood of 0.08 per cent carbon and 0.04 sulphur. Electrodeposits of nickel or other metal thus characterized are believed to be novel in the art.

What is claimed is:

1. An electroplating bath for producing a bright deposit of a nickel group metal which comprises an aqueous solution of an inorganic salt of a nickel group metal, together with a sulfonic acid compound of an organic radical whose concentration is relatively low as compared to that of the metal salt, said solution having a pH value not exceeding 5.5, and no substantial proportion of the amount of plating metal in the bath being in chemical combination with said sulfonic acid compound, said sulfonic acid compound being selected from the group consisting of the following: naphthalene monosulfonic acid, 1.5 and 2.7 naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid, products resulting from mild chlorination thereof, and salts of the foregoing.

2. An electroplating bath as defined in claim 1, wherein the plating metal is nickel, and the pH value of the solution is between 1.5 and 5.5.

3. An electroplating bath for producing a bright deposit of a nickel group metal of substantial thickness (i. e. more than 0.0002 inch) and characterized by good adherence and substantial freedom from cracking or curling, which comprises an aqueous solution of a compound of a nickel group metal, together with a sulfonated aryl compound brightening agent, and a small quantity of a promoter metal added to the bath to enhance the brightness of the electrodeposit obtainable therefrom, the concentration of said promoter metal not substantially exceeding one-tenth normal

$$\left(\frac{N}{10}\right)$$

4. An electroplating bath for producing bright nickel plating of substantial thickness (i. e., more than 0.0002 inch) and characterized by good adherence and substantial freedom from cracking or curling, which comprises an aqueous solution having an acid reaction and containing nickel mainly in the form of an inorganic salt, together with a sulfonated aryl compound brightening agent in quantity too small to bind chemically more than a small proportion of the nickel present in the bath, and a promoter metal adapted to cooperate with said sulfonated compound to enhance the brightening effect and employed at a concentration not substantially exceeding one-tenth normal

$$\left(\frac{N}{10}\right)$$

5. An electroplating bath for producing bright nickel plating of substantial thickness (i. e. more than 0.0002 inch) and characterized by good adherence and substantial freedom from cracking or curling, which comprises an aqueous solution having an acid reaction and containing nickel mainly in the form of an inorganic salt, together with a sulfonated naphthalene compound brightening agent in quantity too small to bind chemically more than a small proportion of the nickel present in the bath, and a promoter metal adapted to cooperate with said sulfonated compound to enhance the brightening effect and

employed at a concentration not substantially exceeding one-tenth normal

$$\left(\frac{N}{10}\right)$$

5 6. An electroplating bath as defined in claim 5, wherein said sulfonated naphthalene compound as selected from the group consisting of the following: alpha and beta naphthalene monosulfonic acids, 1.5 and 2.7 naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid, products resulting from mild chlorination thereof, and salts of the foregoing, the pH of said bath not exceeding 5.5.

15 7. An electroplating bath as defined in claim 3, wherein the plating metal is nickel and the sulfonated aryl compound is selected from the group consisting of the following: alpha and beta naphthalene monosulfonic acids, the 1.5 and 2.7 naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid, products resulting from mild chlorination thereof, and salts of the foregoing; the promoter metal being selected from the group consisting of cadmium and zinc.

25 8. The process of producing bright or mirror-like deposits of a nickel group metal which comprises electrodepositing such metal from an acid bath containing the same mainly in the form of an inorganic salt, with the aid of an assisting agent acting as a brightener and selected from the group consisting of the following: naphthalene monosulfonic acid, 1.5 and 2.7 naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid, products resulting from mild chlorination thereof, and salts of the foregoing, the quantity of such assisting agent employed being too small to bind chemically more than a small proportion of the nickel group metal present in the bath.

40 9. The process defined in claim 8, wherein the plating bath is maintained at a temperature between 35° and 60°, C., most desirably between 40° and 50° C., and at a pH between 5.5 and 1.5, most desirably at about 2.5, and is operated at a cathode current density of between 10 and 100 amperes, most desirably between 30 and 50 amperes, per square foot.

50 10. The process of producing bright or mirror-like deposits of nickel which comprises electrodepositing nickel from an acid bath containing the same mainly in the form of an inorganic salt, with the aid of an assisting agent acting as a brightener and selected from the group consisting of the following: naphthalene monosulfonic acid, 1.5 and 2.7 naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid, products resulting from mild chlorination thereof, and salts of the foregoing, the quantity of such assisting agent employed being too small to bind chemically more than a small proportion of the nickel present in the bath.

65 11. The process of producing bright or mirror-like deposits of nickel, characterized by good adherence and substantially free from cracking or curling, from an acid bath containing nickel mainly in the form of an inorganic salt, with the aid of a brightener comprising naphthalene monosulfonic acid, in quantity too small to bind chemically more than a small proportion of the nickel present in the bath.

75 12. The process of producing bright or mirror-like deposits of nickel, characterized by good adherence and substantially free from cracking or curling, from an acid bath containing nickel mainly in the form of an inorganic salt, with

the aid of a brightener comprising beta naphthalene monosulfonic acid in quantity too small to bind chemically more than a small proportion of the nickel present in the bath.

13. The process of producing bright or mirror-like deposits of nickel, characterized by good adherence and substantially free from cracking or curling, from an acid bath containing nickel mainly in the form of an inorganic salt, with the aid of a brightener comprising 1.5 naphthalene disulfonic acid in quantity too small to bind chemically more than a small proportion of the nickel present in the bath.

14. The process of producing bright or mirror-like deposits of nickel, characterized by good adherence and substantially free from cracking or curling, from an acid bath containing nickel mainly in the form of an inorganic salt, with the aid of a brightener comprising 2.7 naphthalene disulfonic acid, in quantity too small to bind chemically more than a small proportion of the nickel present in the bath.

15. The process of producing bright or mirror-like nickel plating of substantial thickness (i. e. more than 0.0002 inch) and characterized by good adherence and substantial freedom from cracking or curling, which comprises electrodepositing nickel from a plating bath containing it in the form of an inorganic salt, together with a sulfonated aryl compound brightening agent in quantity too small to bind chemically more than a small proportion of the nickel present in the bath, and a promoter metal capable of cooperating with said sulfonated compound to enhance the brightening effect and employed at a concentration not substantially exceeding one-tenth normal

$$\left(\frac{N}{10}\right)$$

the pH of said bath not exceeding 5.5.

16. The process of producing bright or mirror-like nickel plating of substantial thickness (i. e., more than 0.0002 inch) and characterized by good adherence and substantial freedom from cracking or curling, which comprises electrodepositing nickel from a plating bath containing it in the form of an inorganic salt, together with a sulfonated naphthalene compound brightening agent in quantity too small to bind chemically more than a small proportion of the nickel present in the bath, and a promoter metal capable of cooperating with said sulfonated compound to enhance the brightening effect and employed at a concentration not substantially exceeding one-tenth normal

$$\left(\frac{N}{10}\right)$$

the pH of said bath not exceeding 5.5.

17. The process of producing bright or mirror-like nickel plating of substantial thickness (i. e. more than 0.0002 inch) and characterized by good adherence and substantial freedom from cracking or curling, which comprises electrodepositing nickel from an acid plating bath containing it in the form of an inorganic salt, together with an organic brightening agent selected from the group consisting of the following: alpha and beta naphthalene monosulfonic acids, 1.5 and 2.7 naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid, products resulting from mild chlorination thereof, and salts of the foregoing, the quantity of such brightening agent employed being too small to bind chemically more

than a small proportion of the nickel present in the bath; and a promoter metal cooperating therewith to enhance the brightening effect and employed at a concentration not substantially
5 exceeding one-tenth normal

$$\left(\frac{N}{10}\right)$$

18. The process defined in claim 8, further
10 characterized by the fact that a small quantity

of a promoter metal, selected from the group consisting of cadmium and zinc, is added to the bath to enhance the brightness of the electrodeposit.

19. The process defined in claim 10, further characterized by the fact that a small quantity
5 of a promoter metal, selected from the group consisting of cadmium and zinc, is added to the bath to enhance the brightness of the electrodeposit.

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