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ART OF ELECTROPLATING

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This invention relates to art of electroplating; and it relates more particularly to electroplating baths and processes characterized by the employment of a water-soluble compound comprising an acid derivative, such as an acid ester, of an aliphatic alcohol containing at least three and most desirably eight or more carbon atoms in the molecule, especially an alkali-metal salt of such derivative, as an addition agent for preventing or substantially reducing pitting in electrodeposits of metals, more particularly nickel, which in acid baths normally tend to give deposits that are pitted.

The subject of pitting, which occurs frequently in electrodeposits of nickel and of zinc also to some extent, has been investigated to a considerable extent in the past, largely from a theoretical point of view in an effort to determine the underlying causes. Comparatively little has been accomplished, however, in the way of providing preventive methods that are entirely satisfactory or of general application in practical electroplating work under varying conditions of operation. The pitting here referred to its what is commonly known as gas pitting, and is to be distinguished from the pitting caused by the removal, through buffing, of foreign particles that are sometimes occluded in the metal deposit. Gas pitting is caused mainly by the retention of bubbles of hydrogen on the surface of the cathode. Metal deposition fails to take place at the point of contact between the bubble and the cathode, with the result that a minute depression appears on the cathode surface. This same type of pitting may also be caused by air, dissolved in the solution or bath when cold, becoming liberated when the solution is warmed by being electrolyzed; or by oxygen evolved at the anode, dissolved in the solution and eventually released at the cathode.

For a number of years it has been virtually universal practice to employ in nickel plating solutions a small amount of hydrogen peroxide to prevent or reduce pitting. Although undoubtedly the best material heretofore proposed for this purpose, hydrogen peroxide has several disadvantages. In the first place, it decomposes spontaneously in a nickel bath so that the concentration decreases whether the bath is being operated or not. It also lowers the cathode efficiency of nickel deposition. Moreover, where the nickel or other metal plating bath contains an organic agent added to insure production of a "bright" nickel or other metal deposit from the bath, the hydrogen peroxide rapidly destroys the brightening agent. Other oxidizing agents, such as free chlorine, nitrates, perborates and permanganates, which are among the various anti-pitting agents heretofore proposed, are even less suitable for the purpose than hydrogen peroxide.

The present invention is based upon the discovery that water-soluble compounds comprising acid derivatives of the higher aliphatic or fatty alcohols, such as acid esters thereof, when added in small amounts to nickel or other metal plating baths, are very effective in reducing pitting, and that the use of these materials does not unfavorably affect the cathode efficiency, nor does it cause decomposition of organic brightening agents if these latter be present. Moreover these anti-pitting materials are stable in nickel and other plating solutions under all conditions of operation and suffer no decomposition when the plating bath is idle. In the practice of the invention, the acid derivatives of higher fatty alcohols most desirable to employ are sulphuric acid derivatives, more particularly alcohol sulphates but not excluding sulphonates or mixtures of sulphates and sulphonates; and they are most conveniently and effectively employed in the form of alkali metal salts, especially the sodium salts. By higher aliphatic or fatty alcohols is here meant broadly those having three or more carbon atoms in the molecule, those containing eight or more being particularly useful in the practice of the invention.

Higher fatty alcohol acid deriavtives especially suitable for use as anti-pitting agents in accordance with the principles of the invention are derived from monohydric or polyhydric primary fatty alcohols, containing from eight to eighteen carbon atoms in the molecule. Such fatty alcohols, both saturated and unsaturated, may be produced by various known methods such, for example, as reduction of an alkyl ester of a fatty acid by sodium in the presence of a lower aliphatic alcohol. Where it is desired to produce alcohols that are for the most part saturated, this can be done by catalytic hydrogenation of fatty acids or of fatty acid esters such as fats, waxes, etc. Thus, the hydrogenation of cocoanut oil or its characteristic free fatty acids produces a product containing all the even-numbered saturated fatty alcohols from C_8 to C_{18}, the main constituent of the product being the alcohol C_{12} known as lauryl or dodecyl alcohol which usually constitutes around 60% of the mixture. Hydrogenation of stearine produces a mixture of cetyl (C_{16}) or stearyl (C_{18}) alcohols, principally

the latter, the mixture being known as Lanette wax or stearine alcohol. The unsaturated oleyl alcohol corresponds to and can be prepared from oleic acid; i. e. it is a C_{18} alcohol containing one double bond.

The sulphates or sulphuric acid esters of such higher fatty alcohols may be prepared by heating the corresponding alcohol with sulphuric acid at 100° C. in the presence of a dehydrating agent such as acetic anhydride, or by treating with chloro-sulphonic acid at lower temperatures. Neutralization with alkali produces the corresponding alkali metal salt or soap. Production of the sulphuric acid esters or sulphates may be and usually is accompanied by production of more or less of the sulphonates, the proportion of sulphonates increasing with the strength of the sulphuric acid or other sulphating or sulphonating agent employed and with the temperature at which the reaction is carried out. It is to be understood that anti-pitting agents characterizing the practice of the present invention may comprise either sulphates or sulphonates, or mixtures of both, all of which may be generically termed sulphuric reaction products or derivatives of the higher fatty alcohols. Such products or derivatives are to be distinguished from products, such as Turkey red oil, which are sulphonated carboxylic acid compounds and which are not suitable for use in practicing the present invention. The products or derivatives whose use as anti-pitting addition agents is here concerned are characterized by substantial absence of any free or esterifiable carboxylic groups.

The use of the foregoing and other sulphated fatty alcohols and mixtures thereof as detergents, wetting-out and softening agents has been proposed heretofore in the textile and metal-cleaning industries, where they replace soaps of the ordinary type. A number of them, all of which are suitable for use in the practice of the present invention, are described in the United States patents to Bertsch Nos. 1,968,793–4–5–6–7; but while the use of sulphated fatty alcohols referred to in said patents, and particularly certain of them to be more especially mentioned hereinafter, is highly effective in preventing or greatly reducing pitting in electrodeposits of nickel or other metal in accordance with the principles of the invention, it is not to be inferred that the invention is confined to the employment of the specific sulphated fatty alcohols disclosed in said patents. On the contrary, it appears that virtually all members of the class of compounds which can be generically designated as water-soluble derivatives or compounds of higher fatty or aliphatic alcohols with an acid are effective to a substantial extent, although in varying degree, as anti-pitting agents for the purposes of the present invention.

Among typical higher fatty alcohol derivatives of the character above described that have been found particularly useful in practicing the invention for preventing or greatly reducing pitting in the electrodeposition of nickel especially, may be mentioned the following: the sodium salt of the sulphuric acid ester of technical lauryl or lauric alcohol; the sodium salts of the sulphuric acid esters of a technical mixture of C_{12} to C_{18} alcohols, mainly lauric, myristic, cetyl and stearic alcohols; the sodium salt of the sulphuric acid ester of technical oleyl alcohol; the sodium salts of the sulphuric acid esters of a technical mixture of alcohols of the series $C_nH_{2n+1}OH$, having boiling points higher than that of lauric alcohol and comprising in a typical instance myristic, cetyl and stearic alcohols, or some one or more of them. Although sometimes referred to as alcohol soaps, they are not soaps, strictly speaking, but may be generically designated as sulphuric esters of normal primary aliphatic alcohols. They are effective to prevent or suppress pitting in both dull and bright plating solutions, especially nickel plating solutions. They do not themselves function as brightening agents.

In order to further illustrate the underlying principles of the invention, specific examples of typical electroplating solutions or baths and their operation, embodying the principles of the invention, will now be given. Although in these examples the electroplating baths are in each case for electrodeposition of nickel, and although the greatest present utility of the invention is in the field of nickel plating, it is to be understood that the invention is not limited to this field but extends also to the electrodeposition of any other metal, e. g. cobalt or zinc, in which the difficulty of pitting is encountered when employing an acid solution or bath.

In the following specific illustrative examples, the use of "single nickel salts" is mentioned in making up the various plating solutions or baths. This is the usual trade designation of the commercial grade of nickel sulphate crystals containing approximately 22% of nickel and consisting of a mixture of $NiSO_4.6H_2O$ and $NiSO_4.7H_2O$, with the $6H_2O$ crystal in predominating proportion. The designation "single" is used to distinguish this material from nickel ammonium sulphate containing approximately 14% nickel and known in the trade as "double" nickel salts. This latter, or any other compound of nickel suitable for use in nickel plating could be used in place of the "single nickel salts" which are hereinafter specified merely to illustrate the scope of the invention.

Example 1

A nickel plating solution containing in each gallon

	Ounces
Single nickel salts	53
Sodium chloride	2
Ammonium chloride	2
Boric acid	4
Technical sodium lauryl sulphate	0.067

is adjusted in the customary manner to a pH value of 5.25. Deposits made from this bath at a temperature of 105° F. are substantially free from pitting at all cathode current densities from 5 to 200 amperes per square foot. Deposits made under the same conditions from a bath of the same composition except for omission of the sodium lauryl sulphate are pitted at all current densities within the range specified. One form in which technical sodium lauryl sulphate is conveniently available is a preparation sold commercially under the trade-name "Gardinol WA"; but it is not essential, of course, that the sodium lauryl sulphate used in practicing this invention be in this form or prepared in the same manner.

Example 2

The nickel bath has the same composition as in Example 1 except that it contains 0.26 ounce of technical sodium lauryl sulphate per gallon of solution. Operating at a cathode current density of 50 amperes per square foot and a temperature of 105° F., deposits free from pitting are obtained at all pH values from 2.0 to 6.0;

while under the same conditions, a bath not containing the sodium lauryl sulphate but otherwise identical in composition gives pitted deposits at all pH values within the range specified.

Example 3

A solution containing in each gallon

	Ounces
Single nickel salts	40
Nickel chloride	4
Boric acid	4
Technical sodium lauryl sulphate	0.067

and adjusted to a pH value of 2.5 is operated at 105° F. and at cathode current densities ranging from 5 to 200 amperes per square foot. Nickel deposits free from pitting are obtained at all current densities within the specified range; whereas, using exactly the same bath except for the anti-pitting agent and operating under the same conditions, the deposits obtained were noticeably pitted.

Example 4

In this case the nickel bath is constituted as in Example 2, but its content of technical sodium lauryl sulphate is varied by small increments from 0.033 ounce to 2.5 ounces per gallon of solution, the bath being operated at pH 2.5, temperature 105° F. and cathode current density of 50 amperes per square foot. Under these operating conditions, nickel deposits free from pitting are obtained for all the various quantities of sodium lauryl sulphate used within the specified range; while under the same operating conditions and with the same bath except for omission of the sodium lauryl sulphate, pitted deposits are obtained.

Example 5

A nickel plating solution is used having the same composition as that specified in Example 3 except that it contains, as anti-pitting agent, from 0.26 to 3.0 ounces of the sodium salts of the sulphuric acid esters of a mixture of two or more aliphatic alcohols containing from twelve to eighteen carbon atoms in the molecule (mainly lauric, myristic, cetyl and stearic alcohols). A suitable mixture of this kind is conveniently available commercially under the trade-name "Gardinol LS," although it can be prepared in other forms by known methods. It is also practical to use any of the specified higher alcohol derivatives singly, in accordance with the invention, for preventing pitting. Operating at a pH value of 2.5, temperature 105° F. and 50 amperes per square foot cathode current density, nickel deposits free from pitting are obtained at all concentrations of the specified pitting agent within the specified range; whereas under the same operating conditions and with the same solution except for omission of the specified anti-pitting agent, pitting of the resultant nickel deposits is marked.

Example 6

A solution containing in each gallon

	Ounces
Single nickel salts	16
Nickel chloride	4
Boric acid	2
Technical sodium lauryl sulphate	0.133

gives pit-free deposits of nickel, operating at pH 5.5 and temperature 70° F., with cathode current densities ranging from 10 to 20 amperes per square foot. If the sodium lauryl sulphate addition is omitted, the solution gives deposits which are badly pitted under otherwise identical operating conditions.

Example 7

A bright nickel plating solution is prepared containing in each gallon

	Ounces
Single nickel salts	40
Nickel chloride	4
Boric acid	4
Beta naphthalene monosulphonic acid	0.26
Technical sodium lauryl sulphate	0.26

The beta naphthalene monosulphonic acid serves as the brightening agent in this bath. Operating at pH 2.5, cathode current density of 50 amperes per square foot and temperature 105° F., deposits made from this bath are bright and entirely free from pitting; whereas under the same conditions, but omitting the sodium lauryl sulphate, the resultant deposits, although bright, contain pits.

Example 8

Replacing the sulphated alcohol used in Example 7 by 0.26 ounce of the sodium salt of the sulphuric acid ester of technical oleyl alcohol, and maintaining the operating conditions the same, also results in production of bright nickel deposits free from pitting. While the oleyl alcohol derivative employed as anti-pitting agent may be in any suitable form and prepared in any suitable manner, one form in which it is conveniently available commercially is a preparation sold under the trade-name "Gardinol CA." Using 0.26 ounce of the sodium salts of the sulphuric acid esters of a mixture of fatty alcohols containing from twelve to eighteen carbon atoms as the anti-pitting agent, also gives excellent results.

Example 9

The sulphated alcohol used in Example 7 is replaced in the same bath by 0.26 ounce of a commercial sulphated alcohol preparation sold under the trade-name "Avirol L 142" and comprising the sodium salt of the sulphuric acid ester of one or more of the higher aliphatic alcohols including myristic, cetyl and stearic alcohols. Operating under the same conditions specified in Example 7, bright nickel deposits free from pits are obtained. Other forms of similarly constituted preparations sold under the trade-names "Avirol L 168" and "L 144," each employed in about the quantity per gallon above specified, give similarly satisfactory results as anti-pitting agents. Although it is convenient to use the materials commercially available under these trade-names, the above-mentioned alcohol derivatives may be obtained otherwise and employed singly or in mixture of two or more.

Example 10

In this case the bath is the same as in Example 7 except that 0.8 ounce of naphthalene 1.5 disulphonic acid is used as the brightening agent and 0.133 ounce of technical sodium lauryl sulphate is used as the anti-pitting agent, per gallon of solution. Operating at cathode current densities ranging from 20 to 200 amperes per square foot and maintaining the other operating conditions as specified in Example 7, pit-free bright nickel deposits are obtained; while omission of the sodium lauryl sulphate results in somewhat pitted deposits. The use of 0.133 ounce of sodium salts of two or more of the sulphuric acid esters

of a mixture of fatty alcohols containing from twelve to eighteen carbon atoms of the molecule, in place of the sodium lauryl sulphate, is equally effective in preventing pitting in the resultant bright nickel deposits under the same conditions of operation.

Example 11

A bright nickel plating solution is prepared having the same composition with respect to nickel salts and boric acid as the solution of Example 10; but in this case the brightening agent employed is 0.8 ounce naphthalene 1.6 disulphonic acid (instead of the 1.5 acid), per gallon, while the anti-pitting agent is 0.067 ounce of technical sodium lauryl sulphate per gallon. Operating at pH 2.5, temperature of 105° F. and cathode current density 50 amperes per square foot, bright nickel deposits free from pitting are obtained. Under the same conditions of operation and with the same bath except for omission of the sodium lauryl sulphate, deposits of excellent brightness are obtained, but they are pitted. Substituting alpha naphthalene monosulphonic acid as the brightening agent gives similar results, bright deposits free from pitting being obtained when the sodium lauryl sulphate addition is also used, but pitted deposits being obtained when it is omitted.

Example 12

In this example, the advantage of using alcohol soaps of the character hereinabove described over hydrogen peroxide for elimination of pitting in bright nickel plating is demonstrated. Two bright nickel plating baths are prepared, each containing per gallon

	Ounces
Single nickel salts	40
Nickel chloride	4
Boric acid	4
Beta naphthalene monosulphonic acid	0.133

To one bath hydrogen peroxide is added to eliminate pitting, while to the other bath technical sodium lauryl sulphate is added for the same purpose. After operating both solutions until 40 ampere hours per liter have passed, deposits from the bath to which peroxide was added are no longer bright, while deposits from the bath containing the alcohol soap (sodium lauryl sulphate) are uniformly bright. Upon continuing operation of the latter solution until 90 ampere hours or more per liter have passed, it still gives uniformly bright (i. e. lustrous or mirror-like) deposits.

The same absence of destructive action upon organic brightening agents added to the plating bath, referred to in Example 12 and elsewhere hereinabove, is invariably characteristic of the use of high molecular alkyl esters as anti-pitting agents in accordance with the principles of the invention. This contrasts markedly with the destructive action of hydrogen peroxide upon such brightening agents in bright plating baths, whereby not only is the cost of materials for maintenance increased through reduction in the useful life of the brightening agent used, but also there is made necessary very careful supervision to keep the bath in good condition at all times. The advantage over the use of hydrogen peroxide afforded by the present invention holds true not only for the specific brightening agents hereinabove mentioned, which are compounds of the aryl sulphonic acid type and are referred to hereby way of illustrating desirable practice in the use of brighteners, but also for organic brightening agents generally. When anti-pitting agents of the character herein recommended are used, bright plating baths operate for long periods of time without impairment of the brightening agent and without any special attention.

Of the various high molecular alkyl esters whose use as anti-pitting agents in accordance with the invention has been referred to hereinabove and illustrated by specific examples, it is found that, in general, technical sodium lauryl sulphate (obtainable commercially, as already stated, under the trade-name Gardinol WA) and mixed sulphates of fatty alcohols containing twelve to eighteen carbon atoms in the molecule (obtainable commercially under the trade-name Gardinol LS) are to be particularly recommended as effective in the elimination of pitting in both dull and bright nickel or other plating solutions. This is because they are notable for their effectiveness over particularly broad ranges of operating conditions especially favorable from a practical standpoint. The other available compounds of this class are effective over favorable operating ranges which, in general, are not so broad.

The concentration of fatty alcohol derivatives employed as anti-pitting agents in the solution or bath may vary considerably as indicated in the examples hereinabove given. Generally speaking, it is necessary to use only a very small quantity per gallon, on the order of the minimum concentrations mentioned hereinabove. The use of larger quantities, even exceeding the maximum quantities hereinabove indicated, is ordinarily unobjectionable but unnecessary. It will of course be further understood that, as regards concentration of plating metal in the baths specified in the foregoing examples, as well as the particular salt or salts of the metal employed and the other constituents of the bath, and other specific operating conditions recited in the above examples, such as pH values, temperatures, cathode current densities, and the like, all these merely represent typical good practice in using the invention and that they may all be varied widely while still realizing the benefits of the invention in substantial degree.

What is claimed is:

1. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a sulphuric ester of a normal primary aliphatic alcohol having from eight to eighteen carbon atoms in the molecule.

2. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a mixture of sulphuric esters of normal primary aliphatic alcohols having from eight to eighteen carbon atoms in the molecule.

3. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a sulphuric ester of a normal primary aliphatic alcohol having at least eight carbon atoms in the molecule.

4. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising an alkali metal salt of a sulphuric derivative of lauric alcohol.

5. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising an alkali metal salt of a sulphuric derivative of at least one of the following alcohols: myristic, cetyl, stearic.

6. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a sulphuric ester of a normal primary aliphatic alcohol having at least eight carbon atoms in the molecule, and an organic brightener of the aryl sulphonic acid type.

7. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a sulphuric ester of a normal primary aliphatic alcohol having at least eight carbon atoms in the molecule, and an organic brightener comprising an aryl sulphonic acid selected from the group consisting of alpha and beta naphthalene monosulphonic acids, naphthalene 1.5 disulphonic acid, naphthalene 1.6 disulphonic acid.

8. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a mixture of sulphuric esters of normal primary aliphatic alcohols having from eight to eighteen carbon atoms in the molecule, and an organic brightener comprising beta naphthalene monosulphonic acid.

9. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a mixture of sulphuric esters of normal primary aliphatic alcohols having from eight to eighteen carbon atoms in the molecule, and an organic brightener comprising naphthalene 1.5 disulphonic acid.

10. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a mixture of sulphuric esters of normal primary aliphatic alcohols having from eight to eighteen carbon atoms in the molecule, and an organic brightener comprising naphthalene 1.6 disulphonic acid.

11. A nickel electroplating solution containing, in addition to a suitable nickel compound, a compound comprising a sulphuric ester of a normal primary aliphatic alcohol having at least eight carbon atoms in the molecules.

12. A nickel electroplating solution containing, in addition to a suitable nickel compound, a mixture of sulphuric esters of normal primary aliphatic alcohols having from eight to eighteen carbon atoms in the molecule.

13. A nickel electroplating solution containing, in addition to a suitable nickel compound, a relatively small amount of an alkali metal salt of a sulphuric derivative of lauric alcohol.

14. A nickel electroplating solution containing, in addition to a suitable nickel compound, a relatively small amount of an alkali metal salt of a sulphuric derivative of at least one of the following alcohols: myristic, cetyl, stearic.

15. A bright nickel electroplating solution containing, in addition to the components specified in claim 11, an organic brightener of the aryl sulphonic acid type.

16. A bright nickel electroplating solution containing, in addition to the components specified in claim 11, an organic brightener comprising an aryl sulphonic acid selected from the group consisting of alpha and beta naphthalene monosulphonic acids, naphthalene 1.5 disulphonic acid, naphthalene 1.6 disulphonic acid.

17. A bright nickel electroplating solution containing, in addition to the components specified in claim 11, an organic brightener comprising beta naphthalene monosulphonic acid.

18. A bright nickel electroplating solution containing, in addition to the components specified in claim 11, an organic brightener comprising naphthalene 1.5 disulphonic acid.

19. A bright nickel electroplating solution containing, in addition to the components specified in claim 11, an organic brightener comprising naphthalene 1.6 disulphonic acid.

20. An electro-depositing bath comprising an aqueous acid solution of a compound of nickel, in which solution the solvent is preponderantly water, and a minor amount of a sulphate of lauryl alcohol.

21. In the art of electroplating, the process which comprises electrodepositing nickel from a plating solution containing a compound thereof in association with an addition agent comprising a sulphuric ester of a normal primary aliphatic alcohol having at least eight carbon atoms in the molecule, and an organic brightener comprising a naphthalene sulphonic acid.

22. A bright nickel electroplating solution containing, in addition to the components specified in claim 11, an organic brightener comprising a naphthalene sulphonic acid.

23. A bright nickel electroplating solution containing, in addition to a mineral acid salt of nickel, a relatively small amount of an alkali metal salt of a sulphuric derivative of at least one of the following alcohols: lauric, myristic, cetyl, stearic; together with an organic brightener of the aryl sulphonic acid type.

24. An electrodepositing bath comprising an aqueous acid solution of a compound of nickel, in which solution the solvent is preponderantly water, and a minor amount of a sulphate of lauryl alcohol; together with an organic brightener of the aryl sulphonic acid type.

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