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ELECTROFORMING METALS AND ELECTROLYTES THEREFOR

Peter Spiro, London, England, assignor to S. A. Vickers Limited, London, England

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ABSTRACT OF THE DISCLOSURE

In an electrolytic bath for use in the electro-forming of a base metal such as iron, cobalt, nickel, tin, zinc, manganese and copper, or a combination of two or more of these, the improvement which comprises that the bath contains at least one acetylenic compound devoid of amino groups in an amount within the range of 0.1 to 10 g./l., at least one α,β-unsaturated aromatic compound selected from the group consisting of cinnamic acid, cinnamaldehyde, 1,2-benzopyrone and phthalylacrylic acid, in an amount within the range of 0.1 to 50 g./l. and at least one difunctional aromatic acid containing in the molecule at least one carboxylic acid group and at least one sulphonic acid group and selected from the group consisting of sulphophthalic acid, sulphoisophthalic acid and sulphosalicylic acid, the difunctional aromatic acid being present in the bath in an amount within the range of 0.1 to 100 g./l.

CROSS-REFERENCE TO PRIOR APPLICATION

This invention is a continuation-in-part of my application Ser. No. 530,779 filed Mar. 1, 1966, now abandoned.

This invention is concerned with improvements in the electroforming of base metals and is particularly directed to the inclusion in electrolytic bath solutions of certain groups of additives, which have been found to have certain beneficial effects, as described in detail below.

BACKGROUND INFORMATION AND PRIOR ART

One base metal which is included in the invention is nickel, which is commonly applied to substrates by electrolytic processes. Nickel plating baths usually consist of aqueous solutions of nickel chloride and/or nickel sulphate, with various additives found to offer various advantageous effects. A particularly improved form of nickel plating bath is described and claimed in United States patent specification No. 2,802,779 dated Aug. 13, 1957; this improved bath contains a nickel salt, typically the chloride and/or sulphate, and sodium or potassium chloride; the presence of sodium or potassium chloride in nickel plating baths is known, but the aforementioned specification relates essentially to the inclusion of sodium or potassium chloride in an amount in relation to the amount of nickel present in the nickel salt by weight, namely from seven to twelve times that amount, which was much higher than had previously been used or proposed. This high-chloride nickel plating bath described in the aforesaid specification has the considerable advantage over other nickel baths of a much improved throwing power. The bath of the aforementioned invention is used particularly for the electro-deposition of nickel (and its alloys) for electro-forming purposes, though it

can naturally be used for any electro-deposition application, being especially advantageous where maximum throwing power, high hardness, low stress and other good physical properties of the resultant deposit are of importance.

It has now been discovered that the performance of a high-chloride nickel electroforming bath can be still further improved by the inclusion of a combination of additives, as specified below. The chief improvement in properties afforded by the present invention concerns the mechanical strength of the deposit, particularly at or adjacent angular portions of the substrate on which the deposit is formed. This enables the defect usually referred to as "corner weakness" to be largely minimised or even eliminated.

It has also been discovered that the same beneficial improvement in the mechanical properties of the deposit can be obtained if the combination of additives according to the invention is included in other kinds of nickel bath besides the high-chloride type according to the aforesaid U.S. specification No. 2,802,779, such as in the conventional Watts and "all-chloride" baths; moreover, the present invention is not restricted to nickel electroforming, but can also be employed with advantage with plating baths based upon other base metals, including iron, cobalt, tin, zinc, copper and manganese; in the case of copper plating, the additives of the invention are not appreciably useful inclusions in cyanide-based copper plating baths, but they are of utility in acid copper plating baths.

As mentioned above in connection with U.S. specification No. 2,802,779, a particularly useful application of a high-chloride bath according to that patent is in the manufacture of nickel articles by electroforming, where accuracy of shape of the electrodeposit is of more importance than brightness. Likewise, the present invention is also concerned with electroforming in other base metals than nickel, e.g. iron, cobalt, tin, zinc, manganese and copper, or a combination of two or more of such base metals.

There have been many proposals relating to the inclusion of additives in electrodeposition baths and research into this subject has been particularly widespread in connection with nickel electrodeposition. One class of compounds which has been investigated widely consists of acetylenic compounds, i.e. organic substances containing the —C≡C— structure, and particularly acetylenic alcohols, esters and ethers, which have the advantage of generally being adequately soluble in water for ready inclusion in aqueous baths. These acetylenic compounds are used primarily as brighteners in nickel plating baths. Another group of compounds which have useful properties as plating bath additives consist of ethylenically-unsaturated aromatic carboxylic acids and their derivatives, such as cinnamic acid, cinnamaldehyde, phthalylacetic acid and 1,2-benzopyrone. Such compounds can be prepared by the Perkin reaction, using an aromatic aldehyde and an aliphatic aldehyde to produce an α,β,-unsaturated aromatic carboxylic acid, which can be further modified if desired. It is known that compounds of this second class have use as additives which improve the resistance to corrosion of the ultimate plate. British patent specification No. 900,554 filed Dec. 23, 1959, in the name of Kemiska AB Candor relates to the inclusion in a nickel plating bath either of coumarin and an acetylenic alcohol, ester or ether or of an acetylenic derivative of a coumarin compound, thus using two additives selected respectively from the second and first classes of compounds as defined above; according to British patent specification No. 900,554, the use of these two additives in conjunction gives improved chemical resistance to the resultant nickel deposit. A third known class of plating bath additives, which contains an extremely large number of compounds, consists of what are often referred to as sulpho-oxygen compounds. Sulphonic acids are known as brighteners, particularly as so-called secondary brighteners, to be used in conjunction with other, primary brighteners, such as acetylenic compounds. The aforesaid British patent specification No. 900,554 describes the use, in order to obtain corrosion-resistant nickel deposits which are also perfectly bright, of an aromatic sulphonic acid, such as naphthalene trisulphonate.

SUMMARY OF THE INVENTION

It has now been discovered that superior properties of the resultant deposit are given, in the electroforming of iron, cobalt, tin, zinc, copper, manganese or, particularly, nickel, or a combination of two or more of such metals, by the inclusion of at least one of each of three different classes of additive in the bath.

According to this invention, an electrolytic bath for use in the electroforming of an article from a base metal includes at least one water-soluble acetylenic compound devoid of amino groups, at least one α,β-unsaturated aromatic compound selected from the group consisting of cinnamic acid, cinnamaldehyde, 1,2-benzopyrone and phthalylacrylic acid and at least one difunctional sulphonic-carboxylic acid selected from the group consisting of sulphophthalic acid, sulphoisophthalic acid and sulphosalicylic acid. In this bath, the first-mentioned additive, viz, the acetylenic compound free from amino groups, is present in an amount within the range of 0.1 to 10 g./l.; the second-mentioned additive, viz, the carboxylic acid or derivative of the stated group, is present in an amount within the range of 0.1 to 50 g./l.; the third-mentioned additive, viz, the difunctional organic acid, is present in an amount within the range of 0.1 to 100 g./l.

The invention is based upon the discovery that a combination of the three different classes of additive in the stated amounts gives a stronger deposit, particularly as regards low corner weakness of electroformed deposits, if the sulpho-oxygen compound is selected from the small group of aromatic compounds which contain in the molecule both a carboxylic acid group and a sulphonic acid group represented by the compounds specified above. High-chloride plating baths of this invention also exhibit the satisfactory throwing power characteristic of the high-chloride nickel baths of the aforesaid U.S. patent specification No. 2,802,779.

While the precise mechanism which is responsible for the benefits of the improved forms of base metal electroforming baths is not fully understood and must remain a matter of theory, at least to some extent, it is believed that the strengthening effect of the combinations of additives found to be effective is connected with their usefulness as deposit levellers, as distinct from additives which act mainly as brighteners. This is not to be taken as indicating that any additives known to effect a levelling function are useful as strengtheners according to the invention and many other combinations of additives, including a known leveller and one or two but not all three kinds of additive according to this invention have been investigated and have not given the improvements in corner weakness and other mechanical properties obtainable by carrying out the invention.

Examples of compounds which fall within each of the class of additives consisting of acetylenic compounds free from amino groups are given below, in order more particularly to illustrate the choice available in carrying out the invention; it is to be noted, however, that the following list is not exhaustive and that other compounds can

be used which are not specifically named, but are comprehended by the general definition given above.

Water-soluble acetylenic compounds, devoid of amino group:

3-butyn-1-ol
1-pentyn-3-ol
2-butyne-1,4-diol
3-hexyne-2,5-diol
4-octyne-3,6-diol
3-pentyn-1-ol
2,4-hexadiyne-1,6-diol
propargyl alcohol (2-propyn-1-ol)
propargyl acrylate
4-halo-2-butyn-1-ols
4-methoxy-2-butyn-1-ol
1-acyloxy-2-butynes
3-ethyl-1-heptyn-3-ol
propargyl acetate
1,4-di-(β-hydroxyethoxy)-2-butyne

In addition to a water-soluble source of the base metal in question and the one or more additives of each of the three classes defined, baths according to the invention will naturally be made up with other components in most instances, in order to impart a desired pH to the bath, for instance, and also to include other components found to be desirable for various reasons, concerned both with function of the bath and with properties of the deposits.

As indicated above, the respective amounts of the three additives can vary over wide limits; the full ranges of these amounts and the preferred amounts within those ranges may be summarized as follows:

Additives	Range, g./l.	Preferred, g./l.
Acetylenic compound	0.1–10	0.1–1.0
Aromatic carboxylic acid or derivative	0.1–50	0.1–1.0
Difunctional acid	0.1–100	0.1–1.0

The relative proportions of the three additives can also vary, but optimum results have been obtained with a particular ratio of their individual amounts, in concentration terms. Broadly speaking, the separate effects of acetylenic compounds and the group consisting of the stated α,β-unsaturated compounds in solution are similar; therefore, the ratio of their respective amounts can vary widely, because any reduction of effect caused by using a minor amount of one, toward the lower end of its range, can be compensated by using a correspondingly larger amount of the other. It is more important to ensure that the particular selection of additives in use preserves a reasonable balance between the first two taken together and the third additive. It has been found desirable, in fact, for the sum of the amounts of the acetylenic compound and of the α,β-unsaturated compound to be related to the amount of the difunctional acid by being in a ratio, by weight, within the range from 1:10 to 10:1; a 1:1 ratio often proves satisfactory in this regard, that is to say the amount of the difunctional acid present equals the sum of the amounts of the other two additives, the respective amounts of which can vary over wide limits provided each is present at least in the minimum amount of 0.1 g./l. which applies to each of the three additives.

In order that the invention may be readily understood, the following specific examples are given, by way of illustration. In these examples, references to concentrations in oz. per gal. mean ounces avoirdupois in imperial gallons; the equivalent concentration in g./l. is obtainable by division by 6.25, as 1 oz./gal.=6.25 g./l.

EXAMPLE 1

Electroforming of nickel

The following nickel plating baths were made up and used for electroforming:

(a)

	Oz. per gal.
Nickel sulphate	[1]3–4
Sodium chloride	30–35
Boric acid	Up to 5
Paratoluene sulphonamide	3–4
Propargyl alcohol	⅛
1,2-benzopyrone	⅛
Sulphophthalic acid	¼
Water to make 1 gallon.	

[1] As nickel.

(b)

	G./l.
Nickel sulphate	300
Sodium chloride	1200
Propargyl acrylate	0.2
Cinnamaldehyde	1.0
Sulphoisophthalic acid	1.0
Saccharin	10
Boric acid	40

(c)

Nickel chloride	50
Nickel sulphate	250
1,2-benzopyrone	1
Sulphosalicylic acid	2
4-chloro-2-butyn-1-ol	1
Boric acid	35
Saccharin	5

(d)

Nickel sulphate	300
Sodium chloride	1000
2-butyne-1,4-diol	1
1,2-benzopyrone	0.5
Sulphosalicylic acid	1.5
Boric acid	400

These plating baths had pH's in the range of 3–6 and are preferably operated at a current density of 1 to 10 a./dm.^{2} and a temperature from room temperature up to 80° C.

EXAMPLE 2

Electroforming of copper

The following is a typical acid copper bath for use under the conditions stated:

Copper (as $CuSO_4.5H_2O$)	oz./gal.	8
Free sulphuric acid	oz./gal.	6
Ammonium sulphate	oz./gal.	1
Gelatin	oz./gal.	0.25
Sulphosalicylic acid	oz./gal.	1
3-hexyn-2,5-diol	oz./gal.	0.5
Cinnamaldehyde	oz./gal.	1
Wetting agent (e.g., magnesium lauryl ether sulphate)	oz./gal.	0.025
pH		3–4.5
Current density	a./dm.^{2}	2–8
Temperature	° C.	55–75

EXAMPLE 3

Electroforming of iron

A typical bath is produced by formulating and using a bath of the kind specified in Example 2, with the exception that the copper is replaced by an equal amount of iron, provided for instance as ferrous ammonium sulphate.

EXAMPLE 4

Electroforming of zinc

This can be carried out readily by including in a conventional acid zinc plating bath the selection of additives according to the invention; one such bath is as follows:

	Oz./gal.
Zn (as $ZnSO_4 \cdot 6H_2O$)	10
Free H_2SO_4	6
Saccharin	1
Wetting agent	0.05
Sulphophthalic acid	0.5
2-butynol	0.5
Cinnamaldehyde	0.5
NH_4SO_4	0.5

Similar bath formulations to those illustrated in the above examples for nickel, copper, iron and zinc can also be made for tin, e.g. based on the fluoborate, manganese, e.g. based on the sulphate, and cobalt, e.g. based upon the chloride or sulphate. In use, it is found that there is a significant improvement in the mechanical properties of the resultant deposit and virtual elimination of corner weakness. This occurs where an electrodeposit is to be made on to a substrate having angularly-disposed surfaces; in using conventional baths, a discontinuity in the deposit is often formed approximately in a plane bisecting the angle between the two surfaces; this discontinuity is substantially eliminated in electroformed deposits made with the same baths, except that they are modified by inclusion of at least one each of the three classes of additive according to the invention. Apart from this significant improvement in relation to corner weakness, there is a marked increase in the hardness of the deposits which can amount to an increase in hardness, compared with deposits made using baths without the three essential additives, of up to 100 Vickers.

I claim:

1. In an aqueous acidic electrolytic bath for use in the electroforming of a base metal being iron, cobalt, nickel, tin, zinc, manganese or copper and combinations of two or more thereof, the improvement which comprises that the bath contains at least one acetylenic compound devoid of amino groups in an amount within the range of 0.1 to 10 g./l. at least one α,β-unsaturated aromatic compound selected from the group consisting of cinnamic acid, cinnamaldehyde, 1,2 - benzopyrone and phthalylacrylic acid, in an amount within the range of 0.1 to 50 g./l. and at least one difunctional aromatic acid containing in the molecule at least one carboxylic acid group and at least one sulphonic acid group and selected from the group consisting of sulphophthalic acid, sulphoisophthalic acid, and sulphosalicylic acid, the difunctional aromatic acid being present in the bath in an amount within the range of 0.1 to 100 g./l.

2. An electrolytic bath according to claim **1**, in which the sum of the amount of the first and second additives relative to the amount of the difunctional aromatic acid form a weight ratio in the range of 1:10 to 10:1.

3. A process of electroforming an article of a base metal selected from the group consisting of iron, cobalt, nickel, tin, zinc, copper and manganese and combinations of two or more of such metals, which comprises electrolysing the electrolytic bath of claim **1**.

4. A process according to claim **3**, wherein the bath contains 2-butyne-1,4 - diol as the first additive, 1,2-benzopyrone as the second additive and sulphosalicylic acid as the third additive.

5. A process of manufacture of a metal article which comprises electroforming the article upon a substrate by subjecting the substrate to electrolytic deposition of nickel by immersing it in a bath which consists essentially of an aqueous acidic solution containing a source of nickel ions and a three-component additive system comprising at least one acetylenic compound in an amount within the range of 0.1 to 10 g./l., at least one α,β-unsaturated aromatic compound selected from the group consisting of cinnamic acid, cinnamaldehyde, 1,2-benzopyrone and phthalylacrylic acid, said compound being present in an amount within the range of 0.1 to 50 g./l., and at least one difunctional aromatic acid selected from the group consisting of sulphosalicylic acid, sulphophthalic acid and sulphoisophthalic acid, said aromatic acid being present in an amount within the range of 0.1 to 100 g./l., and thereafter separating the resulting electroformed nickel article from the substrate.

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GERALD L. KAPLAN, Primary Examiner

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