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ELECTRODEPOSITION OF BRIGHT NICKEL, COBALT, AND ALLOYS THEREOF

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4 Claims. (Cl. 204—49)

1

This invention relates to the electrodeposition of bright plate from aqueous acidic cobalt and nickel baths.

One object of this invention is to plate bright cobalt plate over a very wide current density range.

Another object of this invention is to plate bright nickel and bright nickel-cobalt alloy plate over the entire concentration range of substantially zero nickel to 100% cobalt, and zero cobalt to 100% nickel.

A third object is to provide means to increase the tolerance of cobalt and nickel plating baths to larger concentrations of many inorganic and organic substances.

These objects and others can be accomplished by the use of small percentages of a salt of a sulfinic acid, preferably an aryl sulfinic acid, such as benzene or toluene sulfiinates (see Table II) in acidic cobalt and nickel baths (see Table I).

To cause the plate to be bright from an acidic cobalt bath (sulfate, chloride, fluoborate, sulfamate or mixtures) only about 0.1 to 0.5 g./l. (the saturation concentration is around 1 g./l.) is usually needed of the benzene or toluene sulfinate in the bath. The same is true for corresponding acidic nickel baths or for mixtures of acidic cobalt and nickel baths.

To prevent peeling (poor adhesion) or misplating or dark deposits in low current density areas in nickel plating or cobalt plating which might be caused by excessive quantities of inorganic or organic impurities it is necessary to use only as little as 0.005 to 0.03 g./l. to overcome these difficulties, especially in bright plating baths using o-benzoyl sulfimide. It is at the low current density areas (recesses) where the first excesses of materials like lead, zinc, copper, chromic acid and certain organic compounds which plate out or are reduced preferentially to nickel first show up. That is, the aryl sulfinates increase to a remarkable extent the tolerance of bright nickel baths to larger concentrations of zinc, thallium, lead, copper, iron cobalt, chloride ion, and a very large number of active organic compounds than could otherwise be tolerated in bright plating baths themselves without obtaining either dark or brittle plate or poorly adherent or both. Thus, these aryl sulfinates are effective when used in very small amounts .005–.03 gram per liter even when they are not the main brightening agent of the bath, that is, the aryl sulfinates in low concentration (0.005–.03 g./l.) used in conjunction with other brightener systems such as benzene sulfonic acids, naphthalene sulfonic acids,

2

benzene sulfonamides and sulfonimides extends the useful bright plate range of these materials to the very lowest current densities (where the cathode current density is around 1 amp./sq. ft. and less). This is very important in many commercial installations, especially in the plating of brass plumbing goods and of copper plated zinc-base die-castings where many articles have deep recesses (low current density areas) which must be plated bright to receive the subsequent chromium plate, or where no "rack marks" (dull low current density areas under the hooks of racks or under wires) must show.

However, evidently for the same reason that the aryl sulfinates are much more effective in increasing the tolerance of the nickel plating bath to much larger concentrations of impurities, they do not produce as high a rate of brightening or degree of lustre in conjunction with such brighteners as zinc, phenosafranine, etc. as do the benzene and naphthalene sulfonic acids in Watts type baths. However, while the latter give bright plate in Watts baths, they do not cause bright plate in the high chloride baths (over 150 g./l. nickel chloride) but yield dull gray plate instead. Whereas the benzene and toluene sulfinates yield bright plate in high nickel chloride content baths and in cobalt baths such as specified herein, the benzene and naphthalene sulfonic acids do not cause bright cobalt plate from such baths.

Furthermore, when ferrous sulphate (or its equivalent in ferrous chloride) is added in high concentrations to a Watts type nickel bath, for example, 75 g./l. $FeSO_4.7H_2O$ and higher, the sulfiinates will still make possible completely bright plate whereas with the benzene and naphthalene sulfonates the plates are dulled and embrittled by these high concentrations of iron. In the case of cobalt baths, the aryl sulfinates also increase the tolerance to ferrous iron, zinc and cadmium salts remarkably. These sulfiinates function in this manner evidently by retarding the rate of deposition of the iron, zinc, cadmium, etc. with respect to nickel and cobalt, and of cobalt with respect to nickel.

A useful application of the aryl sulfinates in acidic baths containing iron group metals is to give very fine grained, hard, adherent nickel or cobalt or binary and ternary alloys of nickel, cobalt, and iron plate which can be used where wear is an important factor, as on certain gauges where chromium is too difficult to apply and where the extreme hardness of electroplated chromium is not necessary.

Another useful application of the aryl sul-

finates is: when too much of an active material is accidentally added to the bath, then the addition of the aryl sulfinate will tend to counteract the harmful effects (peeling or dark deposits) immediately. The excess of harmful material can then later be removed if necessary for best results, at a more convenient time.

In Table II are listed a number of suitable sulfinates. It is preferred to use the p-toluene sulfinic acid (preferably in the form of the nickel or sodium salt, though other salts such as the zinc salt can be used) because it is most readily prepared.

The plate obtained with the aryl sulfinates alone in the nickel bath is very fine-grained, of good color, hard, adherent, and when deposited on a smooth or buffed surface is bright. After a concentration of about 0.5 g./l. is reached further additions up to saturation do not materially increase the brightness of the plate nor lessen the adhesion or affect the color.

The aryl sulfinates are effective in other nickel baths besides those of Table I, for example, in nickel baths containing nickel sulfamate: in the acidic nickel baths such as those used in plating zinc-base die casting directly with nickel and which baths often have high concentrations of sodium sulfate, or citrate, acetate, formate, or fluoborate. The sulfinates always tend to act to prevent dark plate, peeling, and defective low current density plate, in all these types of acidic nickel baths (pH=1.5–6.0).

Even very small concentrations of only 5 mg./l. are effective in the very low C. D. areas, though usually around 20 mg./l. is needed for the general amount of impurities encountered during plating. If the aryl sulfinates are used in concentrations as high as 0.5 g./l. or up to saturation, the bath will tolerate at least 2 g./l. of zinc or more and still obtain no streaked or dark plate, in fact adherent, hard bright plate will be obtained.

It was also noted that aryl sulfinates repressed pitting a remarkable extent even when no wetting agents were in the baths.

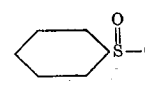
Representative cobalt baths

1. $CoSO_4.7H_2O$ ..... g/l 100–200
   $CoCl_2.6H_2O$ ..... g/l 10–50
   H_3BO_3 ..... g/l 20–40
   pH=2.5–5.5.
   Temperature=room to 60° C.
   C. D. up to 150 amps./sq. ft. (15 amps./sq. dm.).
2. $CoCl_2.6H_2O$ ..... g/l 100–200
   H_3BO_3 ..... g/l 20–40
   pH=2.5–5.5.
   Temperature=room to 60° C.
   C. D.=up to 150 amps./sq. ft. (15 amps. sq. dm.).
3. $CoSO_4.7H_2O$ ..... g/l 100–200
   H_3BO_3 ..... g/l 40
   NaF ..... g/l 6–15
   $CoCl_2.6H_2O$ ..... g/l 10–40
   pH=2.5–5.5.
   Temperature=room to 60° C.
   C. D.=up to 150 amps./sq. ft. (15 amps./sq. dm.).
4. $Co(NH_4)_2(SO_4)_2.6H_2O$ ..... g/l 100–200
   pH=4.5–5.5.
   Temperature=room to 60° C.
   C. D.=up to 40 amps./sq. ft. (4.5 amps./sq. dm.).
5. $Co(BF)_4$ ..... g/l 100–200
   $CoCl_2.6H_2O$ ..... g/l 0–40
   pH=2.5–5.5.
   Temperature=room to 60° C.
   C. D.=up to 200 amps./sq. ft. (20 amps./sq. dm.).

Representative cobalt-nickel baths

1. $CoSO_4.7H_2O$ ..... g/l 50–100
   $NiSO_4.6H_2O$ ..... g/l 100
   $NiCl_2.6H_2O$ ..... g/l 100
   H_3BO_3 ..... g/l 40
   pH=2.5–5.5.
   Temperature=room to 60° C.
   C. D.=up to 150 amps./sq. ft. (15 amps./sq. dm.).
2. Any one of the above listed cobalt baths with 50–200 g/l of either or both $NiSO4.6H_2ONiCl2.6H_2O$.

TABLE II

	Aryl Sulfinates and Aliphatic Sulfinates	Conc. in Bath (g./l.)
1	benzene sulfinic acid  (Na, K, Mg, Zn, Ni, Co salt, etc.)	.005–1
2	p-toluene sulfinic acid	.005–1
3	p-chlor benzene sulfinic acid	.005–1
4	o, m, p-xylene sulfinates	.005–1
5	α-naphthalene sulfinic acid	.005–1
6	β-naphthalene sulfinic acid	.005–1
7	m-benzene disulfinic acid	.005–1
8	ethane sulfinic acid (Na, Mg or Ni salt)	.005–1
9	ethane-1,2-disulfinic acid (Na, Mg or Ni salt)	.005–1
10	allyl sulfinic acid	.005–1
11	vinyl sulfinic acid	.005–1

In bright nickel plating baths one of the best uses of the aryl sulfinates is in low concentrations (.005–.02 gram per liter) in conjunction with o-benzoyl sulfimide. In bright cobalt plating larger concentrations up to saturation (1 g./l.) can be used with beneficial effects in conjunction with o-benzoyl sulfimide.

The sulfinic acids are not as stable as their salts the sulfinates, therefore they are preferably used in the sulfinate form. Of course, when added to the acidic baths they form the sulfinic acid and hence tend to oxidize rather readily in the baths and it is necessary to replenish the

TABLE I

Representative nickel baths

Bath No.	$NiSO_4.7H_2O$, g./l.	$NiCl_2.6H_2O$, g./l.	Buffer Formula	g./l.	Other Salts Formula	g./l.	Temp., °F.	pH	Current Density, amps./sq. ft.
1	300	45	H_3BO_3 (boric acid)	40			75–160	2–6	10–75
2		300	H_3BO_3	30			75–160	1–5	10–100
3	75	225	H_3BO_3	35			75–160	2–6	10–85
4	300	45	H.COOH (formic acid)	35			75–140	3–6	10–60
5	200 to 300	45	H_3BO_3 / NiF_2 or HF	40 / 4 to 8 / 2 to 4			75–140	2–6	10–60
6	300	45	Citric Acid (nickel salt)	30			75–140	3–6	10–60
7	300	45	H_3BO_3	40	$MgSO_4.7H_2O$	125	75–160	2–6	10–60
8	75		H_3BO_3 / Ni-citrate	15 / 8	NaCl	40	75	5.5	10–25
9	75		H_3BO_3	15	NH_4Cl / Na_2SO_4	15 / 75	75	5.5	10–25
10	100		H_3BO_3	15	NH_4Cl		75	5.3	5–20

small concentrations of sulfinate at a greater rate than their rate of reduction at the cathode. When the very low concentrations are used in nickel baths, the replenishment may be necessary every day, but this is not a great drawback as only very small concentrations are used.

This application is a continuation-in-part of my copending application Serial No. 600,212, filed June 18, 1945, which is a continuation-in-part of my application Serial No. 366,386, filed November 20, 1940, which applications are now abandoned.

I claim:

1. A bath for electrodepositing fine-grained, bright metal selected from the group consisting of nickel, cobalt, and alloys thereof, comprising an aqueous acid solution of a salt selected from the group consisting of the chloride, sulfate, and fluoborate salts of the metal to be deposited and mixtures of at least two of said salts, said metal being selected from the group consisting of nickel, cobalt, and mixtures thereof, said solution having dissolved therein an organic sulfinate in an

amount falling within a range from about .005 gram per liter of solution to saturation.

2. The bath defined in claim 1 wherein the organic sulfinate is an aryl sulfinate.

3. The bath defined in claim 2 wherein the aryl sulfinate is a benzene sulfinate.

4. The bath defined in claim 2 wherein the aryl sulfinate is toluene sulfinate.

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