

[54] **CHROMIUM PLATING ELECTROLYTE AND METHOD**

[75] Inventors: **Joseph Thomas Jordan; John Joseph Bernard Ward**, both of Wantage; **Clive Barnes**, West Hanney, all of England

[73] Assignee: **International Lead Zinc Research Organization, Inc.**, New York, N.Y.

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Primary Examiner—G. L. Kaplan

Attorney, Agent, or Firm—Brumbaugh, Graves, Donohue & Raymond

[57] **ABSTRACT**

An electrolyte bath and a method for using such a bath comprising trivalent chromium ions dissolved in an aqueous solution containing hypophosphite ions. The bath may also contain ammonium ions and an organic aprotic buffer such as dimethylformamide. The electrolyte according to the invention permits the uniform electrodeposition of chromium onto irregularly shaped objects such that adequate coverage is obtained at points of low current density and at the same time burning is avoided at points of high current density.

13 Claims, No Drawings

CHROMIUM PLATING ELECTROLYTE AND METHOD

The present invention relates to electroplating baths containing trivalent chromium ions and to methods of electrodepositing chromium from such baths.

Conventional chromium electroplating baths use solutions of hexavalent chromium as the electrolyte. The disadvantages of such solutions are well known and in recent years the possibilities of trivalent chromium plating baths have been investigated as an alternative to hexavalent chromium baths. One line of development has involved the inclusion of an organic and preferably aprotic buffer particularly dimethylformamide (DMF) into the trivalent chromium plating baths. Some aspects of this development are illustrated in U.S. Pat. No. 3,772,170. Although the incorporation of these buffers into trivalent chromium electroplating baths provides considerable improvements over previous attempts, the technique has disadvantages which detract from commercial exploitation. The buffers used tend to be rather expensive and thus improved performance has to be offset against higher material costs. Furthermore being preferably aprotic the buffers may cause a reduction in the conductivity of the bath. Also since many of the common ion supplying materials (added, among other reasons, to increase the conductivity) are less soluble in buffer/water mixtures than in buffer free systems, the conductivity increase afforded by the inclusion of these materials may be limited. Decreased conductivity leads to increased heat production. At high buffer concentrations the bath may need to be cooled under operating conditions. In addition the buffered trivalent chromium electrolytes may suffer from a relatively restricted plating range and have a relatively low covering power. These deficiencies are associated with the pH at which the buffered solutions are operable. It is known that to obtain a good plating range it is preferable to have the pH as high as possible. Unfortunately, unless the pH is kept relatively low the chromium precipitates out.

It has been found that the addition of hypophosphite ion to trivalent chromium plating baths, either as a supplement to an organic buffer or as a replacement for it, provides an electrolyte which mitigates or overcomes many of these disadvantages.

The present invention accordingly provides an aqueous chromium electroplating bath containing dissolved trivalent chromium ions and hypophosphite ions, preferably in a concentration of at least about 0.08 molar. It is also preferred that ammonium ions be present in a concentration of at least 0.2 molar.

The invention also provides a method of electrodepositing chromium-containing deposits onto a substrate which process comprises providing an anode and a cathode in a chromium electroplating bath according to the invention and passing an electric current between the anode and cathode so as to deposit chromium upon the cathode.

The precise limits of concentration of hypophosphite ion which are useful have not yet been evaluated but up to about 2 molar, improvements are noticeable. At higher concentrations the improvement with increasing concentration is small and also normal hypophosphite salts are not usually sufficiently soluble. The preferred range is from 0.5 to 2.0 molar in respect of hypophosphite ion. The source of hypophosphite ion is not believed to be critical provided the ion is not associated

with materials which would have a deleterious effect on the performance of the plating bath. Sodium hypophosphite e.g. as the monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) and hypophosphorous acid are possible sources. When using sodium hypophosphite the molar concentration limits on the hypophosphite ion represent from about 10 to 200 g/l with a preferred range of about 50 to 150 g/l.

The inclusion of hypophosphite ion in trivalent chromium electrolytes results in a remarkable increase in the plating range and particularly the bright plating range of the electrolyte. Previous DMF buffered trivalent chromium plating baths have typical bright plating ranges of 125 to 3000 Amps/meter². The use of hypophosphite either additionally to, or as a replacement for the DMF or other organic buffer can produce electrolytes with bright plating ranges of from 30 to 10,000 Amps/meter². The extension of plating range is a substantial advance over prior trivalent chromium baths.

A further effect on the electrolyte is that in the presence of hypophosphite ion the deposition of chromium at low current densities takes place at relatively high efficiency and at high current densities at relatively low efficiency. This effect can be such that in the electrolytic plating of chromium onto objects shaped so as to produce a wide range of current densities, the deposition rate may be very nearly uniform and independent of current density. The actual deposition efficiency is a complex function of many parameters both of the electrolyte and of the operating conditions. Typical figures, based on trivalent chromium, are 2.5% at 5000 Amps/meter² and 8% at 500 Amps/meter², but these figures can be varied widely by adjustment of the hypophosphite concentration or the concentration of other electrolyte constituents. With hypophosphite electrolytes overall efficiencies typically in the range from 3 to 16% based on the trivalent chromium ion can be obtained. These efficiencies produce plating rates as good as those obtainable from the best available hexavalent chromium systems. The efficiencies are rather lower than those which can be obtained with the addition of high levels of DMF (or other organic buffer), but this is more than offset by the improvement in plating performance obtained. It should be noted in this regard that when comparing current efficiencies it is important to correct for the valency of the ion being deposited to obtain a true comparison.

The degree to which the improved plating performance is realized depends inter alia on the concentration of hypophosphite ion. As indicated above at concentrations less than about 0.08 molar the improvements are scarcely noticeable, at concentrations up to about 0.5 molar a shift of the chromium threshold current density to lower values (from a zero concentration figure of about 125 Amps/meter²) to about 90 Amps/meter² is observed. Further increases of the hypophosphite concentration extend the plating range to even lower current densities (optimally as low as 30 Amps/meter²). As a result of reduced efficiency at high current densities, and a subsequent reduction of the deleterious high deposition rate at high current densities, the tendency of the deposit to burn is also reduced. This latter effect is more pronounced at the high values of pH produced in the electrolyte by the buffering action of the hypophosphite. The operation of the invention as a function or derivative of pH is discussed below. Burning can be prevented entirely when chromium concentrations of less than about 0.9 molar are employed in the presence of optimum concentrations

of hypophosphite.

The mechanism by which hypophosphite produces so significant an improvement in the deposition of chromium is not clearly understood. At present it is thought probable that three separate but inter-related effects are present. Hypophosphorous acid is a weak acid and so the presence of hypophosphite ion increases the pH of the electrolyte. Increasing electrolyte pH is known from previous experience to be beneficial. However, previously, with DMF baths, such an increase of pH would have resulted in the precipitation of chromium, as complex hydroxides, from the solution. The presence of hypophosphite ion very surprisingly prevents this. The conclusion from this is that some form of complex is formed between the trivalent chromium ion and the hypophosphite ion which is stable at relatively high pH's (up to pH 7). The stabilizing effect is also apparent from a subsequent observation that chromic salts, which are normally dissolved only with difficulty, can be dissolved in water at nearly neutral pH in the presence of hypophosphite ion. Usually to effect solution the pH must be substantially acid. Further, in dissolving chromic sulphate in water (or even aqueous acid) it is usually necessary to heat the mixture to effect reasonably rapid dissolution. In the presence of hypophosphite ion chromic sulphate will dissolve readily without heating.

The third way in which it seems that hypophosphite may be affecting chromium deposition is concerned with the actual electrode processes which are thought to be involved in the electrolytic deposition of chromium. The deposition of chromium metal from trivalent chromium solutions is thought to be a two stage process. The trivalent chromium ion is first reduced to the divalent state and subsequently to metallic chromium. The rate and ease of chromium deposition is thought to be determined by concentration of divalent chromium ions. In normal circumstances there is a tendency for divalent chromium to revert by oxidation to trivalent chromium thus slowing the overall reaction. The presence of hypophosphite seems to stabilize divalent chromium in relation to trivalent chromium and also to make the formation of divalent chromium from trivalent chromium by electrons in the solution more rapid. It is thought that this is associated with the activity of hypophosphite as a reducing agent although it seems that there is no net consumption of hypophosphite during electrolysis. It seems from this that not only does the hypophosphite ion stabilize trivalent chromium against high pH and divalent chromium against oxidative reversion, but also that in the presumptive trivalent chromium-hypophosphite complex the trivalent chromium is also acting to stabilize the hypophosphite against oxidation.

As mentioned above, hypophosphite-containing trivalent chromium electrolytes can be employed at rather higher pH's than were previously possible with DMF baths. The electrolytes of the present invention are operable to give electrodeposits of chromium or chromium alloys within the pH range of from 0.5 to 7, the preferred range being for chromium from 1.5 to 3.5. Previous baths were substantially restricted to a pH of from 1 to 3. This improvement in the operable pH range is important because it allows an increase in the plating range and also it can be useful in reducing the acidic attack on the substrate at the start of electroplating.

The concentration of trivalent chromium ions in the electrolyte is less critical than in previous systems. Typically, the chromium ion concentration will be from 0.5 to 1.75 molar, preferably from 0.7 to 1.3 molar. In practice since chromium salts are relatively expensive the chromium concentration will be kept as low as conveniently possible to minimize the capital cost of making up the bath and to reduce dragout on workpieces. The reduction in dragout loss is particularly important in making decorative chromium plating since dragout can amount to as much as five times the weight of metal deposited. The presence of hypophosphite ions tends to make the rate of deposition of metallic chromium relatively independent of trivalent chromium ion concentration. This is important when considering the electrode-position of alloys or mixed deposits from electrolyte containing mixed cations.

The particular source of chromium ions is not critical provided, of course, that adequate solubility can be attained and that other components which have deleterious effects on the electrolyte are not introduced. Typically the chromium may be used in the form of its chloride, other halide salts, sulphate, phosphorous oxy acid salts, salts with organic acids or salts or complexes with other anions. The salts may be normal, complex or basic, noting that pH adjustment may be necessary. The trivalent chromium ions may be generated in situ by the action of acid (e.g. hydrochloric, sulphuric or phosphoric acids) on the metal, its oxides (other than CrO_3) or hydroxides.

Other sources of chromic ion include (1) chromic acid reduced by hydrogen peroxide, (2) a 57% basic solid salt (i.e. a solid salt containing 57% by weight Cr_2O_3 and the remainder a neutral salt such as CrCl_3) or (3) a basic salt such as a 57% basic solid salt in a sufficient amount of acid to yield a solution of the neutral salt (e.g. a 57% basic solid salt in sufficient hydrochloric acid to yield a solution of CrCl_3). In general, basic salts can contain from 0% to 57% basic solids.

The preferred and optimum ranges of hypophosphite and trivalent chromium concentrations generally correspond so that for a relatively small concentration of trivalent chromium ions a low level of hypophosphite is desirable and similarly for large concentrations of trivalent chromium ions a high level of hypophosphite is appropriate. Molar ratios of trivalent chromium to hypophosphite in the range of from 0.16 to 5 are useful but ratios in the range of 0.7 to 1.7 are preferred.

As was indicated above, the anions present in the electrolyte are not critical. Since the bath does not require DMF or similar buffers the range of anions possible is widened somewhat. However, because hypophosphite is a moderately powerful reducing agent, anions with strongly oxidizing properties are thought to have deleterious effects. Thus among common anions nitrate and nitrite are not preferred anions. Among preferred anions are halide, especially chloride, bromide and iodide, sulphate and phosphate anions of various types. Minor proportions of other anions may also be present as a result of the inclusion of various additives as is discussed below. In contrast to DMF baths, which are preferably operated with a substantially common anion, hypophosphite baths can tolerate mixtures of anions easily. It is believed that use of a common anion in hypophosphite baths does not give any substantial advantage from a technical point of view.

The hypophosphite baths of the present invention can advantageously include organic buffers. As is the

case in prior trivalent chromium plating baths, the preferred organic buffers are those with a highly electro-negative oxygen atom and are also preferably aprotic. The most preferred is dimethylformamide. The organic buffers usable in the present invention are those described and defined in U.S. Pat. No. 3,772,170. DMF (or other buffer) is an optional component of the baths of the present invention and is usefully present in concentrations of up to about 95% by volume of the electrolyte. However, the concentration should not be so high as to restrict the solubility of other components of the electrolyte to give inoperable concentrations. Since these organic buffers are relatively expensive it is preferred to minimize the concentration. The need for the buffers depends upon the relative purity of the starting materials, particularly the source of chromium ions. If the starting materials are relatively impure and contain materials which could otherwise have a deleterious effect upon the performance of the electrolyte, than an organic buffer, particularly DMF may be useful in preventing substantial degradation of the performance of the electrolyte. Presently available commercial purity chromic chloride does contain fairly high levels of impurity and accordingly DMF may be included in the bath to improve performance, or rather to prevent a deterioration in performance. The concentration necessary to achieve this clearly depends upon the amount and nature of the impurities but for commercial grades of chromic chloride typically from 1% to 40% and preferably 20 to 35% by volume of DMF of the total electrolyte is useful. Chromic sulphate is available at the present time in a form sufficiently pure that no organic buffer may be necessary in the electrolyte to make operation feasible. However, such buffers are optional components of sulphate baths.

In operation, the electrolytes of this invention tend to produce rather larger quantities of gaseous hydrogen than the previous DMF type systems. This is particularly true in electrolytes containing little or no organic buffer. Inclusion of ammonium ion improves the stability and conductivity of the electrolyte. In order to have a significant effect a concentration of about 0.2 molar ammonium ion is necessary. The concentration can be increased up to about 6 molar to increase the effect and a preferred range of concentration is from 1 to 4 molar. The ammonium ion may be added as a halide or sulphate salt or as a mixture of salts or by reaction of ammonia with acid in situ.

Because the efficiency of deposition at high current densities is low it will usually be advantageous to include boric acid or a borate in the electrolyte. In the absence of boric acid or borate the efficiency at high current densities may fall to nearly zero giving rise to the possibility of bare spots at high current densities. Boric acid or borate increases the overall efficiency of deposition so as to avoid this possibility. The minimum concentration to have any noticeable effect is about 0.03 molar and useful improvements are obtained up to about 1 molar. A preferred range of 0.5 to 1 molar and particularly about 0.75 molar. Boric acid is a normal component of commercial electrolytes because of its ability to improve deposition efficiency. In the present invention, rather higher concentrations of boric acid or borate are possible than previously because of the increased pH.

As is usual in the prior art trivalent chromium baths, salts, particularly halides and especially chlorides of alkali and alkali earth metals, e.g. sodium and calcium,

may be included in the electrolyte of the present invention. Such additives improve bath performance with respect to plating range, current efficiency and covering power. Typically the concentration of this component will be 0.5 molar or higher. Because of the relatively small benefits from the presence of these compounds compared with the effect of hypophosphite these additives are regarded as being optional rather than specifically preferable.

Additions of surface active agents may be beneficial in the present invention. Previously the main type of surfactants employed in trivalent chromium baths were of the cationic type, other types not being preferred because of the tendency to produce dull deposits or black specks. The present electrolytes are much less sensitive in this respect and cationic, amphoteric and non-ionic types of surfactant are applicable. Present indications are that the former disadvantage of anionic agents may well be overcome in the present invention. This increased tolerance is believed to be a result of the higher possible pH's available with the present invention.

Examples of suitable surfactants are:

Cationic type — cetyl trimethylammonium bromide, substituted unidiazolines, etc.

Anionic type — sodium lauryl sulphate, sulphonated castor oils, etc.

Non-ionic type — higher fatty alcohols, ethers and epoxides.

Amphoteric type — higher fatty amino acids.

Typical levels of addition of surfactants are from 5 to 50 ppm. A possible further benefit which can be obtained from the inclusion of a suitable surfactant is that it may be useful in reducing spray from the bath resulting from the increased evolution of hydrogen mentioned above.

Other levellers and brighteners can be included in the electrolyte of the present invention but their presence is not critical and the benefits obtained are rather less than with previous systems.

The inclusion of certain phthalate esters in the electrolyte can have beneficial effects especially in mixed cation deposition systems. Di-n-alkyl phthalates, e.g. di-n-pentyl phthalate and di-n-butyl phthalate improve the current density range over which chromium alloys (especially Cr/Fe, Cr/Ni and Cr/Fe/Ni alloys), which are non-rusting, can be deposited from mixed electrolytes. Of particular usefulness is di-n-pentyl phthalate (DPP). The role of phthalate esters is uncertain but in the deposition of chromium/iron co-deposits they increase the non-rusting range of deposits. There does not seem to be a particular lower limit of concentration effective in the electrolytes of the present invention and improvements are found up to saturation. It is convenient to use a saturated solution in the presence of a small quantity of liquid phthalate ester to ensure continuing saturation. Various other additives such as cetyltrimethylammonium bromide can also be beneficial when used together with hypophosphite.

The temperature range over which the present invention is operable is similar to that for previous trivalent chromium electrolytes. Operation is preferred at or near ambient temperature, say in the range $25^{\circ} \pm 5^{\circ}\text{C}$. The practical maximum temperature depends upon the anions present in the bath. With chloride baths about 35°C is the operational maximum but with sulphate baths operation up to 55°C is possible. In general organic buffer (DMF) free systems are operable at higher temperatures than those including organic buffers. The

electrolytes of the present invention typically have substantially higher conductivities than the prior (DMF) type electrolytes and this has the dual advantage of reducing the voltage requirements and reducing the heating due to electrical resistance for a given overall current level. The best electrolytes of the present invention can operate substantially at thermal equilibrium at ambient or near ambient temperatures. Thus, to a large extent there is no longer any requirement for deliberate external cooling of the system.

The present electrolyte also permits the direct chromium plating on reactive substrates such as zinc, aluminum and brass without first plating the substrate with copper or nickel as is required with conventional hexavalent chromium baths. Because of their higher typical operating pH, hypophosphite baths are superior to prior trivalent chromium direct plating systems in that the substrate is less subject to acidic attack. However, some acidic attack will take place unless a thin protective layer of chromium is struck on the substrate. This can be ensured by immersing the substrate live in the bath, and/or by using a high initial current density.

An important subsidiary feature of the present invention is the possibility of forming co-deposits or alloys by employing a suitable mixture of cations in the electrolyte. Of particular interest are chromium-iron, chromium-nickel and chromium-iron-nickel systems. The dynamics of such binary and ternary systems are complex and are not fully understood. However, insofar as they affect the composition of the deposit formed on the cathode, the following factors appear to be relevant. With hypophosphite concentrations of similar molarity to the chromic ion and with concentrations of chromic ion above 0.8 molar, the rate of deposition of chromium from an electrolyte of constant composition is virtually independent of current density and also of any other cations which may be being co-deposited on the cathode. Thus, in a given time, the actual amount of chromium metal deposited on the cathode is constant. This is not true of either iron or nickel, the rate of deposition of both metals being a function of concentration. The functions connecting concentration and rate of deposition are direct but not linear. By varying the concentrations of iron and/or nickel in mixed plating baths substrates can be plated with a deposit of predetermined composition. With hypophosphite baths the dependency of the rate of deposition of iron and/or nickel upon current density is considerably reduced compared with previous systems. Thus, it is possible to plate approximately constant composition irrespective of current density. This leveling effect is not, however, so prominent with iron and nickel as it is with chromium and thus there is some variation of deposit composition with current density.

In binary, e.g. chromium-iron or chromium-nickel, systems in general, the chromium content of the alloy deposit increases at the expense of the other component with increasing current densities. In ternary, i.e. chromium-iron-nickel systems the situation is more complex but present results indicate that the chromium content increases with increasing current density largely at the expense of the iron; the proportion of nickel in the final deposit, expressed as a fraction of the total deposit, remaining roughly constant. The data available is not unequivocal because of the relatively high deposition rates of iron apparent. Higher nickel deposition rates may well reveal much more intense replacement of nickel by chromium.

One feature of binary and ternary deposition systems in hypophosphite electrolytes is that local variations in composition are diminished and thus nonrusting deposits containing iron can be formed over a much wider range of current densities. Non-rusting plate has been produced at current densities as low as 50 Amps/meter², but it is expected that this range will be extended with further work. The precise reasons for this improvement are not known but may be a result of the evening up of the deposition rate vs. current density function in the presence of hypophosphite. The improvement in non-rusting plating range can be augmented by the inclusion of phthalate esters particularly DPP.

Since ferric ion is an oxidizing agent it interferes with the deposition of chromium metal from chromic ion solution. Further any ferric ion would tend to oxidize the hypophosphite. It is thus preferred that any iron supplied to the electroplating bath of the invention be in a lower valency state. Usually the iron will be supplied as a ferrous salt.

Typically the concentration of iron, if present, will be from 0.05 M to 2.5 M, preferably 0.1 M to 1 M, and the concentration of nickel, if present, from 0.05 M to 1 M, preferably 0.1 M to 0.5 M. The precise concentration of iron and/or nickel is dependent upon the desired composition of the alloy to be deposited.

As with prior trivalent chromium systems, the present electrolyte can be used to produce coatings containing inert particulate material. The material in the form of particles usually 5 μ m diameter or smaller or whiskers usually from 3 to 6 mm. long and up to 100 μ m in diameter is suspended in the electrolyte during electroplating by air agitation or the like. The cathode is thus provided with a chromium deposit (or co-deposit with other metal) in which the particles or whiskers are embedded. The sizes of particles or whiskers used can be larger than the values indicated if suitably strong solution agitation is used. Typical inert materials useful in this application include alumina, yttria, zirconium diboride, molybdenum disulphide and tungsten carbide. Incorporation of such materials makes the electroplated layer much harder and wear resistant than would otherwise be the case.

The electrolytes of the invention can be made by admixture of the components and then adjusting the pH. Starting with normal chromic salts, sodium hypophosphite and preferably ammonium salts of mineral acids, together with, as desired, boric acid, a surfactant or other additive discussed above, and dissolving them in water or aqueous/organic buffer mixtures will in general produce an electrolyte whose natural pH is in the preferred range of pH for plating. However, the pH of any mixture will depend upon the precise nature of the starting materials. The pH may be adjusted simply by adding mineral acid or caustic alkali (or ammonia) as appropriate. One surprising observation is that with hypophosphite concentrations greater than about 1 M and with trivalent chromium concentrations at or above about 0.8 M, increasing the pH of the solution to greater than 7 results in solidification or gelling of the mixture. The tarry material so produced can be broken up into fine granules which can be redissolved in calculated quantities of acid to regenerate the plating electrolyte. This tarry solid is a convenient way of transporting and storing the electrolyte and constitutes an additional feature of the invention. As yet the precise nature of this solid is not known although it is presumed

that its overall composition can be determined.

In addition to this gel, the invention also provides a composition comprising a mixture of the components of the electrolyte which, when dissolved in water, aqueous acid or alkali or in mixtures of these with an organic buffer, will produce a solution suitable for use as an electrolyte according to the invention. Typically the mixture will have the following composition:

trivalent chromium ion (Cr^{+++}) — 25 to 100, preferably 35 to 70, parts by weight.

hypophosphite ion (H_2PO_2^-) — 5 to 130, preferably 40 to 100, parts by weight.

ammonium ion (NH_4^+) — 3 to 100, preferably 20 to 70, parts by weight.

The weight ratio of chromium ion to hypophosphite ion should be from 0.16 to 4, preferably from 0.6 to 1.4, and the weight ratio of chromium ion to ammonium ion should be from 0.5 to 7, preferably 1 to 4. The chromium hypophosphite and ammonium ion concentrations are here expressed in terms of the ions and not, of course, as the sort of materials which would actually be used. The following are the types of composition which would actually be used.

chromic chloride hexahydrate $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	150 to 500, preferably 200 to 400, parts by weight.
Sodium hypophosphite monohydrate $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	10 to 200, preferably 50 to 150, parts by weight.
Ammonium chloride NH_4Cl	30 to 170, preferably 55 to 110, parts by weight.
Boric acid $\text{B}(\text{OH})_3$	up to 65, preferably 30 to 65, parts by weight.
Surfactant Cetyl trimethylammonium bromide (Cetavlon)	up to 0.5 parts by weight.

The ratios of trivalent chromium ion to hypophosphite ion and trivalent chromium ion to ammonium ion should be within the ranges stated above.

chromic sulphate nonahydrate $\text{Cr}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	100 to 400, preferably 150 to 300, parts by weight.
Sodium hypophosphite as $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	10 to 200, preferably 50 to 150, parts by weight.
Ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$	30 to 200, preferably 50 to 150, parts by weight.
Boric acid as $\text{B}(\text{OH})_3$	up to 65, preferably 30 to 65, parts by weight.
Surfactant (Cetavlon)	up to 0.5 parts by weight.

Again, the ratios of trivalent chromium ion to hypophosphite ion and trivalent chromium ion to ammonium ion should be within the ranges stated above.

Dissolving these quantities in water or in water/DMF mixture (for example 50:50 by volume water:DMF) to a volume of 1000 parts will produce a chromium electroplating bath according to the invention.

The electrolytes of the invention seem to possess substantial operational stability over extended periods of time. Baths have been operating satisfactorily over 30 Ampere hours/litre. The electrolyte solutions are not entirely stable under all storage conditions. At storage

pH's lower than 1.5 current efficiency tends to rise, and at pH's higher than 3.5 efficiency tends to fall. The solid formulations discussed above are believed to be stable over indefinite periods.

The long term operational stability of the electrolytes is a further indication that the hypophosphite is not either rapidly consumed during electrolysis or that the decomposition products of hypophosphite that may be produced are not deleterious. The electrolytes of the present invention are operable over long periods by simply providing more trivalent chromium ions (and other deposit forming species) to the electrolyte together with water as appropriate and, when necessary small quantities of acid or alkali to maintain the pH. Dragout losses are replaced by addition of bath constituents.

The deposits produced from the electrolyte and by the process of the present invention are darker in hue than hexavalent chromium bath deposits. They appear to be slightly darker than is normal for prior trivalent chromium systems. Dupernell testing at $0.25 \mu\text{m}$ has shown the deposit to be intensely microporous. Chromium and chromium-iron, chromium-nickel and chromium-iron-nickel deposits produced by the invention are extremely resistant to concentrated hydrochloric acid and the complete dissolution of even a $0.25 \mu\text{m}$ coating may take up to $\frac{1}{2}$ hour. With alloy coatings, heating may be necessary to effect complete dissolution. Thicker deposits progressively darken in color as plating time increases and eventually become black. The method of the invention can be used to plate chromium and chromium alloys onto all conventional substrates such as iron, steel nickel, as well as more difficult substrates such as aluminum, copper, brass and zinc. Adhesion failure of chromium on overbrightened or imperfectly activated nickels has been observed. This sort of adhesion failure can be overcome, e.g. by a brief cathodic treatment at 1500 Amps/meter² in 10% sodium cyanide followed by a good rinsing before deposition of the chromium.

The present electrolyte and method of electroplating avoid the difficulties previously associated with anodic chlorine production. There is now no need to select special anodes or separate anolyte or catholyte. According to the present invention, the anode can conveniently be made of graphite. One feature which is more apparent with this bath than previous trivalent chromium systems is that more hydrogen is evolved at the cathode, especially at low or zero organic buffer concentrations. This is an inconvenience rather than a disadvantage as the production of gaseous hydrogen does not seem to have any effect on plating characteristics or on the deposit formed. The surface spray produced by the evolution of hydrogen can be overcome by including a surface active agent in the electrolyte as is indicated above.

The invention may be illustrated by the following Examples.

EXAMPLE I

An electroplating bath having the following composition was made up:

1 mole $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
1 mole NH_4Cl
1 mole $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$
1 mole $\text{B}(\text{OH})_3$
300 g DMF

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and made up to 1 liter with water.

The electrolyte had the following properties:

pH = 3

plating range 75 to 6000 Amps/meter²

Hull cell voltage = 18V

Hull cell current = 10A

Samples were plated in a bath containing the electrolyte for 2 minutes at 25°C giving the following deposits:

Current Density Amps/meter ²	100	450	800	1500	2500	4000	6000
Thickness μm	0.1	0.28	0.25	0.24	0.30	0.25	0.20

The results show a thickness distribution almost independent of current density.

EXAMPLE II

An electrolyte was made up as follows:

0.8 mole $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

1.5 mole NH_4Cl

0.75 mole $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$

0.75 mole $\text{B}(\text{OH})_3$

200 g DMF

and made up to 1 liter with water.

The electrolyte had the following properties:

pH = 2.5 plating range = 50 to 10,000 Amps/meter²

Hull cell voltage = 13V

Hull cell current = 10A

Samples were plated for 2 minutes at 25°C giving the following results:

Current density Amps/meter ²	100	450	800	1250	2400	5000
Thickness μm	0.15	0.30	0.35	0.33	0.30	0.20

These results show that the bath had a rather higher efficiency than that of Example I but still produced a substantially uniform deposit.

EXAMPLE III

Electrolyte composition:

0.8 mole $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

1.5 mole NH_4Cl

0.75 mole $\text{B}(\text{OH})_3$

0.75 mole $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$

150 g DMF

and made up to 1 liter with water plus 10 ppm cetyl trimethylammonium bromide.

This gave a bath having the following properties:

pH = 1.8

plating range 60 to 5000 Amps/meter²

Hull cell voltage = 12V

Hull cell current = 10A

Samples were plated for 2 minutes at 25°C giving the following results:

Current Density Amps/meter ²	150	300	600	1000	2000	4000
Thickness μm	0.1	0.15	0.25	0.25	0.20	0.15

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EXAMPLE IV

A wholly aqueous sulphate bath was tested as follows:

0.5 mole $\text{Cr}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (1M Cr^{+++})

2moles $(\text{NH}_4)_2\text{SO}_4$ (4M NH_4^+)

1 mole $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$

0.5 mole $\text{B}(\text{OH})_3$

were supplemented with water to a total volume of 1 liter.

This yielded a bath with the following properties:

PH = 2.5

plating range = 80 to 5000 Amps/meter²

Hull cell voltage = 10V

Hull cell current = 10A

Samples were plated for 2 minutes at 25°C to give a deposit having the following properties:

Current Density Amps/meter ²	100	400	1000	3000	5000
Thickness μm	0.1	0.28	0.33	0.30	0.20

EXAMPLE V

An electrolyte having no boric acid was made up according to the invention as follows:

0.8 mole $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

1.5 mole NH_4Cl

0.8 mole $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$

200 g DMF

water to a total volume of 1 liter.

This gave a bath having the following properties:

pH = 2.0

plating range 60 to 5000 Amps/meter²

Hull cell voltage = 12V

Hull cell current = 10A

Samples were plated for 2 minutes at 25°C giving the following results:

Current Density Amps/meter ²	100	250	600	1000	2000	4000
Thickness μm	0.1	0.12	0.24	0.24	0.15	0.06

The thickness were determined coulometrically by stripping the chromium to the nickel substrate.

EXAMPLE VI

The following wholly aqueous chloride electrolyte composition was tested:

0.8 mole $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

1.5 mole NH_4Cl

0.8 mole $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$

0.8 mole $\text{B}(\text{OH})_3$

water to a total volume of 1 liter.

The bath was adjusted with ammonia to pH = 2.5 and possessed a plating range on a nickel coated Hull cell plate of 60 to 4800 Amps/meter². Hull cell voltage and current were 10V and 10A coulometrically.

Current Density Amps/meter ²	150	250	500	1000	3000	4500
Thickness μ m	0.15	0.16	0.20	0.20	0.25	0.20

EXAMPLE VII

An electrolyte having the following composition was made up:

CrCl ₃ .6H ₂ O	370 g
FeCl ₂ .4H ₂ O	50 g
NH ₄ Cl	50 g
B(OH) ₃	2 g
H ₂ O	500 g
DMF	500 g
DPP	sat ^d
NaH ₂ PO ₂ .H ₂ O	varies

The pH of this solution was 1.5. **Electroplating tests were done at 25°C** to see how increasing amounts of NaH₂PO₂ affected deposition efficiencies and deposit compositions. The results are given in Table 1.

Table 1

NaH ₂ PO ₂ g/l	C.D. Amps/ meter ²	Time Sec.	Composition %		Efficiency %		
			Fe	Cr	Fe	Cr	Fe+Cr
0	300	300	80.0	20.0	23.0	9.0	32.0
0	1500	150	42.0	58.0	13.5	30.5	44.0
10	300	300	91.0	9.0	18.0	4.5	22.5
10	1500	150	44.0	56.0	11.5	23.0	34.5
50	300	300	76.0	24.0	15.0	8.0	23.5
50	1500	150	52.5	47.5	11.5	16.5	28.0
125	300	300	62.5	37.5	11.5	11.0	22.5
125	1500	150	70.5	29.5	12.0	8.5	20.5

As can be seen from these results, increasing the concentration of sodium hypophosphite has the effect of increasing the chromium efficiency at low current densities and decreasing the chromium efficiency at high current densities. The overall effect is that the metal deposition rates are almost constant as the current density is varied and the composition of the co-deposit is substantially uniform over the plating range.

EXAMPLE VIII

Example VII was repeated omitting DPP from the electrolyte and using 400 g DMF and 600 g H₂O. The pH was 1.5. The results are given in Table 2.

Table 2

NaH ₂ PO ₂ g/l	C.D. Amps/ meter ²	Time Sec.	Composition %		Efficiency %		
			Fe	Cr	Fe	Cr	Fe+Cr
0	300	300	81.0	9.0	7.0	1.0	8.0
0	1500	150	68.5	31.5	20.0	12.0	32.0

5	300	300	97.0	3.0	8.0	0.5	8.5
5	1500	180	69.0	31.0	16.5	12.0	28.5
10	300	300	95.5	4.5	11.0	0.5	11.5
10	1500	150	71.6	28.4	13.5	8.5	22.0
50	300	300	77.0	23.0	8.0	4.0	12.0
50	1500	150	43.0	57.0	7.0	15.5	22.5

Table 2-continued

NaH ₂ PO ₂ g/l	C.D. Amps/ meter ²	Time Sec.	Composition %			Efficiency %		
			Fe	Cr		Fe	Cr	Fe+Cr
100	300	300	62.5	37.5		7.0	8.5	15.5
100	1500	150	41.5	58.5		8.0	18.0	26.0

It will thus be appreciated that with this electrolyte an increasing hypophosphite concentration increases the chromium content of the deposit at both high and low current densities.

EXAMPLE IX

Electrolytes according to the present invention for the deposition of chromium-nickel and chromium-nickel-iron alloys were tested by formulating the following:

CrCl ₃ .6H ₂ O	370 g
NiCl ₂ .6H ₂ O	100 g
NH ₄ Cl	50 g
B(OH) ₃	2 g
H ₂ O	500 g
DMF	500 g

After 4 Ampere hours of plating operation, a Hull cell panel was plated. The quality of the deposit was poor with numerous black streaks in the deposit and there were two distinct regions: at high current densities, a chromium rich region and at low current densities, a nickel rich region.

The addition of 25 g/l sodium hypophosphite resulted in a marked improvement of the appearance of the deposit. The deposit was of good quality and homogeneous but of limited range, metal deposition occurring above 500 Amps/meter². Increase of the hypophosphite concentration lowered this threshold current until at a concentration of 100 g/l deposition was obtained at 150 Amps/meter². The addition of 15 ppm of cetyl trimethylammonium bromide further reduced the threshold current density to below 100 Amps/meter².

Table 3 shows the metal deposition efficiencies and deposit composition from this electrolyte. While overall efficiency is low (i.e. less than 15%), the composition shows little variation with current density.

Table 3 also records the effect of adding 100 g/l of FeCl₂.4H₂O to the electrolyte to produce a ternary system. Good quality deposits were obtained and the non-rusting range extended to 50 Amps/meter². This electrolyte has metal deposition efficiencies approaching 50%. Although the deposit is predominantly iron, it is contemplated that by adjusting the formulation, a deposit of composition similar to 18/8 stainless steel could be obtained.

Table 3

FeCl ₂ g/l	C.D. Amps/ meter ²	Time Sec.	Composition %			Efficiency %			
			Fe	Ni	Cr	Fe	Ni	Cr	Fe+Ni+Cr
0	300	300	—	27.0	73.0	—	2.5	12.0	14.5
0	1500	150	—	23.5	76.5	—	2.0	10.5	12.5
100	300	300	86.0	5.0	9.0	32.0	2.0	5.5	39.5
100	1500	150	75.5	3.5	21.0	36.0	1.5	14.5	52.0

We claim:

1. An electrolyte solution for electrodeposition of chromium on a substrate, said solution comprising hypophosphite ions in a concentration of at least about

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0.08 M, trivalent chromium ions in a concentration of at least about 0.5 M, and ammonium ions in a concentration of at least 0.2 M.

2. An electrolyte solution according to claim 1 containing ammonium ions in a concentration of from about 1 M to about 4 M.

3. An electrolyte solution for electrodeposition of chromium on a substrate, said solution comprising hypophosphite ions in a concentration of at least about 0.08 M, trivalent chromium ions in a concentration of at least about 0.5 M, and boric acid in a concentration of at least 0.03 M.

4. An electrolyte solution according to claim 3 containing boric acid in a concentration of from about 0.5 M to 1.0 M.

5. An electrolyte solution for electrodeposition of chromium on a substrate, said solution comprising hypophosphite ions in a concentration of at least about 0.08 M, trivalent chromium ions in a concentration of at least about 0.5 M, and containing at least 1% dimethylformamide.

6. A method of electrodepositing a chromium coating on a substrate which comprises immersing said substrate in an electrolyte solution comprising water, hypophosphite ions in a concentration of at least about 0.8 M and trivalent chromium ions in a concentration of at least 0.5 M, maintaining the temperature below about 55°C and passing an electric current through said

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solution thereby to deposit said trivalent chromium ions on a substrate.

7. A method according to claim 6 for the electrodeposition of chromium-nickel alloys wherein said solution contains nickel ions in a concentration of from about 0.05 M to about 1.0 M.

8. A method according to claim 7 for the electrodeposition of chromium-nickel alloys wherein said solution contains nickel ions in a concentration of from about 0.1 M to about 0.5 M.

9. A method according to claim 7 for the electrodeposition of chromium-iron-nickel alloys wherein said solution contains ferrous ions in a concentration of from about 0.05 M to about 2.5 M.

10. A method according to claim 6 for the electrodeposition of chromium-iron alloys wherein said solution contains additionally ferrous ions in a concentration of from about 0.05 M to about 2.5 M.

11. A method according to claim 10 for the electrodeposition of chromium-iron alloys wherein said solution contains ferrous ions in a concentration of from about 0.1 M to about 1.0 M.

12. A method according to claim 6 including the step of maintaining the temperature below about 35°C.

13. A method according to claim 6 including the step of maintaining the temperature between about 20°C and 30°C.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,917,517

DATED : November 4, 1975

INVENTOR(S) : Joseph Thomas Jordan, John Joseph Bernard Ward
and Clive Barnes

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 42, after "has" insert --now--. Column 3, line 51, "ph" should be --pH--. Column 4, line 16, "electrode-position" should be --electro-deposition--; line 57, "expecially" should be --especially--; line 58, "varrious" should be --various--. Column 5, line 4, "in" should be --is--; line 19, "than" should be --then--; line 59, "of" should be --is--; line 68, "alkali earth metals" should be --alkaline earth metals--. Column 7, line 65, "is" should be --are--. Column 9, line 9, "CR+++" should be --Cr+++--; line 19, after "mium" insert --,--. Column 10, line 3, "the" should be --be--; line 21, "Dupernell" should be --Dubpernell--; line 33, after "steel" insert --and--. Column 12, line 15, "PH" should be --pH--; line 52, "thickness" should be --thicknesses-- and "coulormetrically" should be --coulometrically--; line 68, "coulormetrically" should be --respectively--. Column 13, line 22, "HaH₂PO₂" should be --NaH₂PO₂--; line 31, "23.5" in column titled Fe+Cr should be --23.0--; line 53, "9.0" in column titled Cr under Composition % should be --19.0--; line 66, "180" in column titled Time Sec. should be --150--.

Signed and Sealed this

twenty-third Day of March 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks