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"TRIVALENT CHROMIUM ELECTROLYTE AND PROCESS
EMPLOYING VANADIUM REDUCING AGENT"

The present invention relates to chromium plating baths and processes for electroplating using such baths.

Chromium electroplating baths are in widespread commercial use for applying protective and decorative

5. platings to metal substrates. For the most part, commercial chromium plating solutions heretofore used employ hexavalent chromium derived from compounds such as, for example, chromic acid, as the source of the chromium constituent. Such hexavalent chromium electro-
10. plating solutions have long been characterised as having limited covering power and excessive gassing particularly around apertures in the parts being plated which can result in incomplete coverage. Such hexavalent chromium plating solutions are also quite
15. sensitive to current interruptions resulting in so-called "whitewashing" of the deposit.

Because of these and other problems including the relative toxicity of hexavalent chromium, and associated waste disposal problems, extensive work has

20. been conducted in recent years to develop chromium electrolytes incorporating trivalent chromium providing numerous benefits over the hexavalent chromium electrolytes heretofore known. According to the present invention a novel trivalent chromium electro-

25. lyte and process for depositing chromium platings has been discovered by which bright chromium deposits are produced having a colour equivalent to that obtained from hexavalent chromium baths. The electrolyte and process of the present invention further provide an

30. electroplating process which can employ current

- densities which can vary over a wide range without producing the burning associated with deposits plated from hexavalent chromium plating baths; in which the electrolyte composition minimizes or eliminates the evolution of mist or noxious odours during the plating process; the electrolyte and process provides for excellent coverage of the substrate and good throwing power; current interruptions during the electroplating cycle do not adversely affect the chromium deposit
5. enabling parts to be withdrawn from the electrolyte, inspected, and thereafter returned to the bath for continuation of the electroplating cycle; the electrolyte employs low concentrations of chromium thereby reducing the loss of chromium due to drag-out; and
10. waste disposal of the chromium is facilitated in that the trivalent chromium can readily be precipitated from the waste solutions by the addition of alkaline substances to raise the pH to about 8 or above.
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- The electrolyte of the present invention also
20. incorporates a reducing agent to prevent the formation of detrimental concentrations of hexavalent chromium during operation of the bath which heretofore has interfered with the efficient electrodeposition of chromium from trivalent chromium plating baths and
25. has tended to reduce the efficiency and covering power of the bath. In some instances, the buildup of detrimental hexavalent chromium has occurred to the extent that a cessation of electrodeposition of chromium has occurred necessitating dumping and
30. replacement of the electrolyte. In accordance with a

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- further aspect of the present invention, it has been found that the addition of the reducing agent defined to an electrolyte bath contaminated with excessive hexavalent chromium rejuvenates the bath and restores its plating efficiency and throwing power and avoids the costly and time consuming step of dumping and replacing the electrolyte.

10. According to the present invention, there is provided an additive composition suitable for use in an aqueous acidic trivalent chromium electroplating electrolyte comprising (a) a reducing agent comprising vanadium ions, (b) a complexing agent adapted to maintain trivalent chromium ions in solution in an aqueous acidic system, (c) halide ions, and (d) ammonium ions, optionally (e) conductivity salts and optionally borate ions.

15. The benefits and advantages of the compositions according to the present invention are achieved by an aqueous acidic electrolyte containing as its essential constituents, controlled amounts of trivalent chromium, a complexing agent present in an amount sufficient to form a chromium complex, halide ions, ammonium ions and a reducing agent comprising vanadium ions present in an amount effective to prevent the concentration of hexavalent chromium ions rising above a level at which continued optimum efficiency and throwing power of the electroplating bath ceases to be maintained. More particularly, the electrolyte can broadly contain 0.2 to 0.8 molar trivalent chromium ions, a complexing agent comprising a formate or an acetate or mixtures thereof present in an amount in relationship to the concentration of the chromium constituent and typically present in a molar ratio of complexing agent to chromium ions of 1:1 to 3:1, a bath soluble and bath compatible vanadium salt present in a concentration to provide a vanadium ion concentration of at least 0.015 grams per litre (g/l) up to about 6.3 g/l as a reducing agent for any hexavalent chromium formed during the electroplating process, ammonium ions as

- a secondary complexing agent present in a molar ratio of ammonium to chromium of 2.0:1 to 11:1, halide ions, preferably chloride and bromide ions, present in a molar ratio of halide ions to chromium ions of 0.8:1 to 10:1; one or more bath soluble salts to increase bath conductivity comprising compatible simple salts of strong acids such as hydrochloric or sulphuric acid or alkaline earth metal, alkali metal or ammonium salts thereof, of which sodium fluoborate comprises a preferred conductivity salt, and hydrogen ions present to provide an acidic electrolyte having a pH on the acid side i.e. of below 7 e.g. less than 6.5 or 6.0 and especially of 2.5 to 5.5.
5. The electrolyte may optionally, but preferably, also contain a buffering agent such as boric acid typically present in a concentration up to about 1 molar, a wetting agent present in small but effective amounts of the types conventionally employed in chromium or nickel plating baths as well as controlled effective amounts of anti-foaming agents. Additionally, the bath may incorporate other dissolved metals as optional constituents such as iron, cobalt, nickel, manganese or tungsten in such instances in which a chromium alloy deposit is desired.
10. In accordance with the process aspects of the present invention, the electrodeposition of chromium on a conductive substrate is performed employing an electrolyte bath in accordance with the present invention at a temperature ranging from about 15° to about 45°C. The substrate is cathodically charged and
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the chromium is deposited at current densities ranging from about 50 to about 250 amperes per square foot (ASF) (5.4 to 27 amperes per square decimetre (ASD)) usually employing insoluble anodes such as

5. carbon, platinized titanium or platinum. The substrate, prior to chromium plating, is subjected to conventional pretreatments and preferably is provided with a nickel plate over which the chromium deposit is applied.

10. In accordance with a further process aspect of the present invention, electrolytes of the trivalent chromium type which have been rendered inoperative or inefficient due to accumulation of hexavalent chromium ions, may be rejuvenated by the addition of controlled

15. effective amounts of the vanadium reducing agent to reduce the hexavalent chromium concentration to levels below about 100 parts per million (ppm), and preferably below 50 ppm at which efficient chromium plating can be resumed.

20. In accordance with the composition aspects of the present invention, the trivalent chromium electrolyte contains, as one of its essential constituents, trivalent chromium ions which may broadly range from 0.2 to 0.8 molar, and preferably from 0.4 to 0.6 molar.

25. Concentrations of trivalent chromium below about 0.2 molar have been found to provide poor throwing power and poor coverage in some instances, where concentrations in excess of about 0.8 molar have in some instances resulted in precipitation of the chromium

30. constituent in the form of complex compounds. For



this reason it is preferred to maintain the trivalent chromium ion concentration within a range of 0.2 to 0.8 molar, and preferably from 0.4 to 0.6 molar. The trivalent chromium ions can be introduced in the form of any simple aqueous soluble and compatible salt such as chromium chloride hexahydrate, or chromium sulphate. Preferably, the chromium ions are introduced as chromium sulphate for economic considerations.

A second essential constituent of the electrolyte is a complexing agent for complexing the chromium constituent present thus maintaining it in solution. The complexing agent employed should be sufficiently stable and bound to the chromium ions to permit electro-deposition thereof as well as to allow precipitation of the chromium during waste treatment of the effluents. The complexing agent may comprise formate ions, acetate ions or mixtures of the two, the formate ion being preferred. The complexing agent may be employed in concentrations ranging from 0.2 up to 2.4 molar as a function of the trivalent chromium ions present. The complexing agent is normally employed in a molar ratio of complexing agent to chromium ions of from 1:1 up to 3:1 with ratios of 1.5:1 to 2:1 being preferred. Excessive amounts of the complexing agent, for example formate ions, is undesirable since such excesses have been found in some instances to cause precipitation of the chromium constituent as complex compounds.

A third essential constituent of the electrolyte comprises a reducing agent in the form of one or more

bath soluble and compatible vanadium salts present in an amount to provide a vanadium ion concentration of at least 0.015 g/l up to 6.3 g/l. Excess amounts of vanadium appear to adversely effect the operation of

5. the electrolyte, in some instances causing dark striations in the plate deposit and a reduction in the plating rate. Typically and preferably, vanadium concentrations of from 0.2 up to 1 g/l are satisfactory to maintain the hexavalent chromium concentration in the electrolyte below about 100 ppm, and more preferably from about 0 up to about 50 ppm at which optimum efficiency of the bath is attained.

The vanadium reducing agent may be introduced into the electrolyte as any one of a variety of

15. vanadium salts including those of only minimal solubility in which event mixtures of such salts are employed to achieve the required concentration. The vanadium salt may comprise any one of a variety of salts which do not adversely effect the chromium
20. deposit and include, for example, sodium metavanadate (NaVO_3); sodium orthovanadate (Na_3VO_4 , $\text{Na}_3\text{VO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{VO}_4 \cdot 16\text{H}_2\text{O}$); sodium pyrovanadate ($\text{Na}_4\text{V}_2\text{O}_7$); vanadium pentoxide (V_2O_5); vanadyl sulphate (VOSO_4); vanadium trioxide (V_2O_3); vanadium di-, tri- or tetrachloride (VCl_2 , VCl_3 , VCl_4); vanadium trifluoride ($\text{VF}_3 \cdot 3\text{H}_2\text{O}$); vanadium tetrafluoride (VF_4); vanadium pentafluoride (VF_5); vanadium oxy bromide (VOBr); vanadium oxy di-, or tribromide (VOBr_2 , VOBr_3); vanadium tribromide (VBr_3); ammonium metavanadate (NH_4VO_3); ammonium vanadium sulphate ($\text{NH}_4\text{V}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$); lithium metavanadate
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($\text{LiVO}_3 \cdot 2\text{H}_2\text{O}$); potassium metavanadate (KVO_3); thallium pyrovanadate (Tl_4VO_7); thallium metavanadate (TlVO_3), as well as mixtures thereof.

- To the extent that the trivalent chromium salts, complexing agent, and vanadium salts do not provide adequate bath conductivity by themselves, it is preferred to further incorporate in the electrolyte controlled amounts of conductivity salts which typically comprise salts of alkali metal or alkaline earth metals and strong acids such as hydrochloric acid and sulphuric acid. The inclusion of such conductivity salts is well known in the art and their use minimizes power dissipation during the electroplating operation. Typical conductivity salts include potassium and sodium sulphates and chlorides as well as ammonium chloride and ammonium sulphate. A particularly satisfactory conductivity salt is fluoboric acid and the alkali metal, alkaline earth metal and ammonium bath soluble fluoborate salts which introduce the fluoborate ion in the bath and which has been found to further enhance the chromium deposit. Such fluoborate additives are preferably employed to provide a fluoborate ion concentration of from 4 to 300 g/l. The metal salts of sulphamic and methane sulphonic acid may also be employed as conductivity salts either alone or in combination with inorganic conductivity salts. Such conductivity salts or mixtures thereof are usually employed in amounts up to about 300 g/l or higher to achieve the requisite electrolyte conductivity and optimum chromium deposition.
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It has also been observed that the ammonium ions in the electrolyte enhance the reducing efficiency of the vanadium constituent for converting any hexavalent chromium formed to the tri-

5. valent state. Particularly satisfactory results are achieved at molar ratios of total ammonium ion to chromium ion ranging from 2.0:1 up to 11:1, and preferably, from 3:1 to 7:1. The ammonium ions can in part be introduced as the ammonium salt of the complexing agent such as ammonium formate, for example, as well as in the form of supplemental conductivity salts.

10. The effectiveness of the vanadium reducing agent in controlling hexavalent chromium formation is also enhanced by the presence of the halide ions in the bath of which chloride and bromide ions are preferred. The use of a combination of chloride and bromide ions also inhibits the evolution of chlorine at the anode.
15. While iodides can also be employed as the halide constituent, their relatively higher cost and low solubility render them less desirable than chlorides or bromides. Generally, halide concentrations of at least about 15 g/l are preferred to achieve sustained efficient electrolyte operation.
20. More particularly, the halide concentration is preferably controlled in relationship to the chromium concentration present and is controlled at a molar ratio of 0.8:1 up to 10:1 halide to chromium, with a molar ratio of 2:1 to 4:1 being preferred.
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In addition to the foregoing constituents, the bath optionally but preferably also contains a

- buffering agent in an amount of about 0.15 molar up to bath solubility, which amounts typically range up to about 1 molar. Preferably the concentration of the buffering agent is controlled from 0.45 to 0.75 molar calculated as boric acid. The use of boric acid as well as the alkali metal and ammonium salts thereof as the buffering agent also is effective to introduce borate ions into the electrolyte and these have been found to improve the covering power of the electrolyte.
5. In accordance with a preferred practice, the borate ion concentration in the bath is controlled at a level of at least about 10 g/l. The upper level is not critical and concentrations as high as 60 g/l or higher can be employed without any apparent harmful effect.
10. The bath further may also incorporate as an optional but preferred constituent, a wetting agent or mixture of wetting agents of any of the types conventionally employed in nickel and hexavalent chromium electrolytes. Such wetting agents or surfactants may be anionic or cationic and are selected from those which are compatible with the electrolyte and which do not adversely affect the electrodeposition performance of the chromium constituent.
15. Typically, wetting agents which can be satisfactorily employed include sulphosuccinates or sodium lauryl sulphate and alkyl ether sulphates alone or in combination with other compatible anti-foaming agents such as, for example, octyl alcohol. The presence of such wetting agents has been found to produce a
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clear chromium deposit avoiding the production of dark mottled deposits and providing for improved coverage in low current density areas. While relatively high concentrations of such wetting agents are not particularly harmful, concentrations greater than about 1 gram per litre have been found in some instances to produce a hazy deposit. Accordingly, the wetting agent, when employed, is usually controlled at concentrations less than about 1 g/l, with amounts of 0.05 to 1 g/l being typical.

It is also contemplated that the electrolyte can contain other metals including for example iron or manganese in concentrations of from 0 up to saturation or at levels below saturation at which no adverse effect on the electrolyte occurs in such instances in which it is desired to deposit chromium alloy platings. When iron is employed, it is usually preferred to maintain the concentration of iron at levels below about 0.5 g/l.

The electrolyte preferably further contains a hydrogen ion concentration sufficient to render the electrolyte acidic. The concentration of the hydrogen ions is broadly controlled to provide a pH of from about 2.5 up to about 5.5 while a pH range of 3.5 to 4.0 is particularly satisfactory. The initial adjustment of the electrolyte to within the desired pH range can be achieved by the addition of any suitable acid or base compatible with the bath constituents; hydrochloric or sulphuric acids or ammonium or sodium carbonate or hydroxide are

preferred. During the use of the plating solution, the electrolyte has a tendency to become more acidic and appropriate pH adjustments may be effected by the addition of bases such as alkali metal or ammonium hydroxides or carbonates, of which the ammonium salts are preferred in that they simultaneously replenish the ammonium constituent in the bath.

5. In accordance with the process aspects of the present invention, the electrolyte as hereinabove described is employed at an operating temperature ranging from about 15 to about 45°C, preferably 20° to 35°C. Current densities during electroplating can range from about 50 to 250 ASF (5.4 to 27 ASD) with densities of 75 to 125 ASF (8.1 to 13.5 ASD) being preferred. The electrolyte can be employed to plate chromium on conventional ferrous or nickel substrates or on stainless steel as well as on nonferrous substrates such as aluminium or zinc. The electrolyte can also be employed for chromium plating plastic substrates which have been subjected to a suitable pretreatment according to well-known techniques to provide an electrically conductive coating thereover such as a nickel or copper layer. Such plastics includes ABS, polyolefin, PVC, and phenol-formaldehyde polymers. The work pieces to be plated are subjected to conventional pretreatments in accordance with prior art practices and the process is particularly effective to deposit chromium platings on conductive substrates which have been subjected to a prior nickel plating operation.
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- During the electroplating operation, the work pieces are cathodically charged and the bath incorporates a suitable anode of a material which will not adversely affect, and which is compatible with, the electrolyte composition. For this purpose anodes of an inert material such as, for example, carbon, are preferred although other inert anodes of platinized titanium or platinum can also be employed. When a chromium-iron alloy is to be deposited, the anode may suitably be comprised of iron which itself will serve as a source of iron ions in the bath.
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- In accordance with a further aspect of the process of the present invention, a rejuvenation of a trivalent chromium electrolyte which has been rendered ineffective or inoperative due to a high concentration of hexavalent chromium ions may be achieved by the addition of a controlled effective amount of vanadium reducing agent or an additive composition as described above. Depending upon the specific composition of the trivalent electrolyte, it may also be necessary to add the other constituents of the additive composition or adjust their concentrations in the bath within the broad usable or preferred ranges as hereinbefore specified to achieve optimum plating performance. For example, the rejuvenant may comprise a concentrate containing suitable vanadium salt in further combination with halide salts, ammonium salts, borates, and conductivity salts as may be desired or required.
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- mixing. The time necessary to restore the electrolyte to efficient operation will vary depending upon the concentration of the detrimental hexavalent chromium present and will usually range from a period of only five minutes up to about two or more hours. The rejuvenation treatment can also advantageously involve an electrolytic treatment of the bath following addition of the rejuvenant by subjecting the bath to a low current density of 10 to 30 ASF (1.1 to 3.2 ASD) for a period of about 30 minutes to about 24 hours to effect a conditioning or so-called "dummying" of the bath before commercial plating operations are resumed. The concentration of the vanadium ions to achieve rejuvenation can range within the same limits as previously defined for the operating electrolyte.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying Examples.

20. EXAMPLES 1 to 36

A series of trivalent chromium electrolytes were prepared having compositions as set forth in Tables 1A to 1C.

TABLE 1A

Example No. 1 2 3 4 5 6 7 8 9 10 11 12

INGREDIENT	CONCENTRATION, G/L											
	1	2	3	4	5	6	7	8	9	10	11	12
Cr ⁺³ ions	20	20	26	20	20	20	26	20	20	26	20	20
Ammonium Formate	40	40	50	40	40	40	50	40	40	50	40	40
Potassium Formate	-	-	-	-	-	-	-	-	-	-	-	-
Vanadyl Sulphate	2	2	2	2	2	2	2	2	2	2	2	2
Sodium Sulphate	142	-	-	-	-	142	76	142	142	76	142	142
Ammonium Sulphate	-	132	-	-	-	132	-	-	-	66	132	132
Sodium Chloride	-	-	-	-	-	-	-	-	-	-	-	-
Potassium Chloride	-	-	-	-	-	-	-	-	-	-	-	-
Ammonium Chloride	25	25	90	90	90	25	90	25	25	90	25	25
Ammonium Bromide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sodium Fluoborate	-	-	110	-	-	-	110	-	-	110	-	-
Ammonium Sulphamate	-	-	-	114	-	-	-	114	-	-	114	-
Ammonium Methane Sulphonate	-	-	-	-	113	-	-	-	113	-	-	113
Boric Acid	45	45	45	45	45	45	45	45	45	45	45	45
Surfactant	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1
pH	2.5-4.0	2.5-4.0	2.5-5.5	2.5-4.0	2.5-4.0	2.5-4.5	2.5-5.2	2.5-4.0	2.5-4.0	2.5-5.2	2.5-4.0	2.5-4.0

TABLE 1B

Example No.

13 14 15 16 17 18 19 20 21 22 23 24

INGREDIENT

CONCENTRATION, G/L

Cr ⁺³ ions	26	26	20	26	26	26	20	26	20	26	20	26	20	26
Ammonium Formate	50	50	40	50	50	50	40	50	40	50	40	50	40	50
Potassium Formate	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Vanadyl Sulphate	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Sodium Sulphate	76	76	142	76	76	76	-	-	-	-	-	-	-	-
Ammonium Sulphate	-	-	-	66	66	132	132	66	132	66	132	66	132	66
Sodium Chloride	-	-	-	-	-	-	-	-	-	-	25	25	25	25
Potassium Chloride	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ammonium Chloride	90	90	25	90	90	90	25	90	-	-	-	-	-	-
Ammonium Bromide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sodium Fluoborate	110	110	-	110	110	110	-	110	-	110	-	110	-	110
Ammonium Sulphamate	114	-	114	60	60	60	-	114	114	-	-	-	114	55
Ammonium Methane Sulphonate	-	113	113	-	55	55	-	-	-	113	113	113	113	55
Boric Acid	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Surfactant	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1	.1
pH	2.5-5.5	2.5-5.5	2.5-4.0	2.5-5.5	2.5-5.5	2.5-5.5	2.5-4.0	2.5-5.5	2.5-4.0	2.5-5.5	2.5-4.0	2.5-5.5	2.5-4.0	2.5-5.5

- The particular sequence of addition of the bath constituents during bath make-up is not critical in achieving satisfactory performance. In all of the examples with the exception of Examples 34 and 35, the
5. trivalent chromium ions were introduced in the form of chromium sulphate. In Examples 34 and 35, the trivalent chromium constituent was introduced as chromium chloride hexahydrate. In each of the examples, the surfactant employed comprised a mixture of dihexyl
10. ester of sodium sulpho succinic acid and sodium sulphate derivative of 2-ethyl-1-hexanol. Nickel plated mild steel J-type test panels were immersed in the above described baths as the cathodes and were plated at operating temperatures of from 70 to about 80°F (21-27°C) at
15. cathode current densities of from about 100 to about 250 ASF (10.8 to 27 ASD) and an anode current density of about 50 ASF (5.4 ASD). A graphite anode was used at an anode to cathode ratio of about 2:1. Mild air and/or mechanical agitation was used. Subjecting the
20. bath to an electrolytic preconditioning at a low current density, e.g. about 10 to about 30 ASF (1.1 to 3.2 ASD) for a period up to about 24 hours can be advantageous in helping to achieve satisfactory plating performance at the higher operating current
25. densities.

- The plated J-type test panels produced by Examples 1-36 had full bright and uniform chromium deposits having good to excellent coverage over the current density ranges employed including good
30. coverage in the deep recess areas.

EXAMPLES 37A to 37D and 38A to 38C

Examples 37A to D are comparison examples and Example 38 demonstrates the effectiveness of the vanadium compound for rejuvenating trivalent chromium electrolytes which have been rendered unacceptable or inoperative because of an increase in hexavalent chromium concentration to an undesirable level. It has been found by tests that the progressive build-up of hexavalent chromium concentration will eventually produce skipping of the chromium plate and ultimately will result in the prevention of any chromium plate deposit. Such tests employing typical trivalent chromium electrolytes to which hexavalent chromium is intentionally added have shown that a concentration of about 0.47 g/l of hexavalent chromium results in plating deposits having large patches of dark chromium plate and smaller areas which are entirely unplated. As the hexavalent chromium concentration is further increased to about 0.55 g/l in such tests, further deposition of chromium on the substrate is completely prevented. The hexavalent chromium concentration at which plating ceases will vary somewhat depending upon the specific composition of the electrolyte.

In order to demonstrate a rejuvenation of a hexavalent chromium contaminated electrolyte, a trivalent chromium bath was prepared having the following composition:

<u>Ingredient</u>	<u>Concentration, g/l</u>
Sodium fluoborate	110
Ammonium Chloride	90
Boric Acid	50

Ammonium formate	50
Cr ⁺³ ions	26
Surfactant	0.1

5. The bath was adjusted to a pH between about 3.5 and 4.0 at a temperature of about 80 to about 90°F (27 to 32°C). S-shaped nickel plated test panels were plated in the bath at a current density of about 100 ASF (10.8 ASD).

EXAMPLE 37B

10. After each test run, the concentration of hexavalent chromium ions was increased from substantially 0 in the original bath by increments of about 0.1 g/l by the addition of chromic acid. No detrimental effects in the chromium plating of the test panels was
15. observed in the range of hexavalent chromium concentration of from 0.1 up to 0.4 g/l.

EXAMPLE 37C

- However, as the hexavalent chromium concentration was increased above 0.4 g/l large dark chromium
20. deposits along with small areas devoid of any chromium deposit were observed on the test panels.

EXAMPLE 37D

- As the concentration of hexavalent chromium attained a level of 0.55 g/l no further chromium
25. deposit could be plated on the test panel.

- Under such circumstances, it has heretofore been common practice to dump the bath containing such high amounts of hexavalent chromium and make up a new bath which constitutes a costly and time consuming
30. operation.

EXAMPLE 38A

To demonstrate the rejuvenation aspects of the present invention, vanadium ions were added in increments of about 0.55 g/l to the bath of Example 37D containing 0.55 g/l hexavalent chromium ions and plating of the test panels were resumed under the conditions described in Example 37A. The addition of 0.55 g/l of vanadium ions corresponds to 2.6 g/l of vanadyl sulphate and corresponds to an incremental weight ratio addition of vanadium ions to hexavalent chromium ions of about 1:1.

The initial addition of 0.55 g/l vanadium ions to the bath contaminated with 0.55 g/l hexavalent chromium ions (Example 37D) resulted in restoration of the efficiency of the chromium plating bath producing a good chromium deposit of good colour and coverage although hexavalent chromium ions were still detected as being present in the bath.

EXAMPLE 38B

The further addition of 0.55 g/l vanadium ions to the bath of Example 38A produced a further improvement in the chromium deposit and analysis indicated the presence of a small amount of hexavalent chromium in the bath.

EXAMPLE 38C

Finally, the addition of a further 0.55 g/l vanadium ions to the bath of Example 38B giving a total of 1.65 g/l vanadium ions in the bath resulted in an excellent chromium deposit and an analysis for hexavalent chromium was negative. These test results

of Examples 38A to 38C clearly demonstrate the efficacy of vanadium as a rejuvenating agent for contaminated trivalent chromium plating baths.

EXAMPLES 39A to 39F

5. In order to further demonstrate the process for rejuvenating trivalent chromium baths contaminated with hexavalent chromium, a trivalent chromium plating bath was prepared having the composition as described in Example 37A and 1.65 g/l of hexavalent chromium
10. were added corresponding to a concentration approximately three times the amount at which the tests described in Example 37D indicated deposition of chromium ceased.

EXAMPLE 39A

15. A test panel was plated under conditions as previously described in Example 37D clearly showing complete failure to deposit any chromium on the test panel.

EXAMPLE 39B

20. Thereafter, 4.95 g/l of vanadium ions corresponding to 23.5 g/l of vanadyl sulphate were added to the bath of Example 39A which was calculated to reduce all of the hexavalent chromium present to the trivalent state.
25. Following the addition of the vanadium rejuvenation agent, the bath under agitation was permitted to stand for approximately ten minutes after which a test panel was plated under the conditions as previously described in Example 37A. It was observed that the
30. test panel exhibited a trace of chromium plate on the surface thereof.

EXAMPLE 39C

- After waiting a total of forty-five minutes following the vanadium addition to the bath, a second test panel was plated and this showed improved chromium plating with an increase in thickness and better appearance.
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EXAMPLE 39D

- The bath was thereafter electrolyzed at a low current density of about 30 ASF (3.2 ASD) for an additional three hours and then a third test panel was plated. The chromium deposit was observed to be fully bright, of good colour, with some thin deposit in low current density areas.
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EXAMPLE 39E

- The bath was further electrolyzed at a low current density of 30 ASF (3.2 ASD) for an additional seventeen hour period after which a fourth test panel was plated resulting in a chromium deposit of good thickness, fully bright with thin areas in the low current densities.
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EXAMPLE 39F

- The test solution was replenished to return the concentration of the constituents to that originally provided in Example 37A prior to the hexavalent chromium and vanadium addition including the addition of 3 g/l of trivalent chromium ions and a fifth test panel was plated. The resultant panel was observed to have a fully bright chromium plating of good colour with substantially complete coverage over the entire surface thereof including low current density areas.
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- It should be appreciated that the efficacy of the vanadium compound to rejuvenate trivalent chromium baths contaminated with hexavalent chromium is applicable for a wide variety of such trivalent chromium electrolytes and is not specifically restricted to the electrolyte as set forth in Examples 37, 38 and 39.
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CLAIMS

1. An additive composition suitable for use in an aqueous acidic trivalent chromium electroplating electrolyte comprising (a) a reducing agent comprising vanadium ions, (b) a complexing agent adapted to maintain trivalent chromium ions in solution in an aqueous acidic system, (c) halide ions and (d) ammonium ions, optionally (e) conductivity salts and optionally borate ions.
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10. 2. An additive as claimed in Claim 1 in which the said vanadium ions are present in an amount of 0.015 to 6.3 g/l.
15. 3. An additive as claimed in Claim 1 in which the said vanadium ions are present in an amount of 0.2 to 1 g/l.
20. 4. An additive as claimed in Claim 1, 2 or 3 ~~containing halide ions~~ ^{in which} the said halide ions comprising chloride ions or bromide ions, or mixtures thereof present in an amount of at least about 15 g/l.
25. 5. An additive as claimed in any one of Claims 1 to 4 which contains conductivity salts.
6. An additive as claimed in Claim 5 in which the said conductivity salts are present in an amount up to about 300 g/l.



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7. An additive as claimed in any one of Claims 1 to 6 which contains borate ions.

8. An additive as claimed in Claim 7 in which the said borate ions are present in an amount of at least about 10 g/l.

9. An additive as claimed in Claim 8 in which the said borate ions are present in an amount up to about 60 g/l.

10. An additive as claimed in any one of Claims 1 to 9 further containing a buffering agent in an amount of about 0.15 molar up to bath solubility.

11. An additive as claimed in Claim 10 in which the said buffering agent is present in an amount of 0.45 to 0.75 molar.

12. An additive as claimed in Claim 10 or Claim 11 in which the buffering agent comprises boric acid or the alkali metal or ammonium salts thereof or mixtures thereof.

13. An additive as claimed in any one of Claims 1 to 12 further containing a surfactant.

14. An additive as claimed in Claim 13 in which the said surfactant is present in an amount of 0.05 to 1 g/l.

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27.

15. An aqueous acidic trivalent chromium electroplating electrolyte containing trivalent chromium ions and an additive as claimed in any one of Claims 1 to 14, ingredient (a) being present in an amount effective to prevent the concentration of hexavalent chromium rising, in use of the bath, above a level at which satisfactory chromium deposits are obtained.
- 5.
10. 16. An aqueous acidic trivalent chromium electroplating electrolyte containing trivalent chromium ions, a complexing agent adapted to maintain the trivalent chromium ions in solution, halide ions, ammonium ions, hydrogen ions to provide a pH on the acid side, and a reducing agent comprising vanadium ions present in an amount effective to maintain the concentration of hexavalent chromium ions at a level at which satisfactory chromium electrodeposits are obtained.
- 15.
20. 17. An electrolyte as claimed in Claim 15 or Claim 16 in which the said trivalent chromium ions are present in an amount of about 0.2 to 0.8 molar.
25. 18. An electrolyte as claimed in Claim 17 in which the said trivalent chromium ions are present in an amount of about 0.4 to about 0.6 molar.
30. 19. An electrolyte as claimed in any one of Claims 15 to 18 in which the said complexing agent is present in a molar ratio of complexing agent to chromium ions of from 1:1 to 3:1.



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20. An electrolyte as claimed in Claim 19 in which the said complexing agent is present in a molar ratio of complexing agent to chromium ions of from 1.5:1 to 2:1.
5. 21. An electrolyte as claimed in any one of Claims 15 to 20 in which the said vanadium ions are present in an amount of 0.015 to 6.3 g/l.
10. 22. An electrolyte as claimed in Claim 21 in which the said vanadium ions are present in an amount of 0.2 to 1 g/l.
15. 23. An electrolyte as claimed in any one of Claims 15 to 22 in which the said ammonium ions are present in an amount to provide a molar ratio of ammonium ions to chromium ions ranging from 2.0:1 to 11:1.
20. 24. An electrolyte as claimed in Claim 23 in which the said ammonium ions are present in an amount to provide a molar ratio of ammonium ions to chromium ions ranging from 3:1 to 7:1.
25. 25. An electrolyte as claimed in any one of Claims 15 to 24 in which the said halide ions are present in an amount to provide a molar ratio of halide ions to chromium ions of from 0.8:1 to 10:1.
30. 26. An electrolyte as claimed in Claim 25 in which the said halide ions are present in an amount to

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provide a molar ratio of halide ions to chromium ions of from 2:1 to 4:1.

27. An electrolyte as claimed in any one of
5. Claims 15 to 26 in which the said halide ions comprise chloride ions, bromide ions, or mixtures thereof present in an amount of at least about 15 g/l.

28. An electrolyte as claimed in any one of
10. Claims 15 to 27 further containing conductivity salts.

29. An electrolyte as claimed in Claim 28 in which the said conductivity salts are present in
15. an amount up to about 300 g/l.

30. An electrolyte as claimed in any one of Claims 15 to 29 further containing borate ions.

20. 31. An electrolyte as claimed in Claim 30 in which the said borate ions are present in an amount of at least about 10 g/l.

32. An electrolyte as claimed in Claim ³¹~~30~~ in which the said borate ions are present in an amount
25. up to about 60 g/l.

33. An electrolyte as claimed in any one of Claims 15 to 32 further containing a buffering agent in an amount of about 0.15 molar up to bath
30. solubility.



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34. An electrolyte as claimed in Claim 33 in which the buffering agent comprises boric acid or the alkali metal or ammonium salts thereof or mixtures thereof.

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35. An electrolyte as claimed in Claim ³⁴~~33~~ in which the said buffering agent is present in an amount of 0.45 to 0.75 molar calculated as boric acid.

10.

36. An electrolyte as claimed in any one of Claims 15 to 35 further containing a surfactant.

15.

37. An electrolyte as claimed in Claim 36 in which the said surfactant is present in an amount of 0.05 to 1 g/l.

20.

38. An electrolyte as claimed in any one of Claims 16 to 37 in which hydrogen ions are present to provide a pH of 2.5 to 5.5.

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39. An electrolyte as claimed in Claim 38 in which the said hydrogen ions are present in an amount to provide a pH of 3.5 to 4.0.

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40. An electrolyte as claimed in any one of Claims 16 to 39 in which the said trivalent chromium ions are present in an amount of about 0.2 to about 0.8 molar, the said complexing agent is present in a molar ratio of complexing agent to chromium ions of about 1:1 to about 3:1, the said halide ions are

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5. present in a molar ratio of halide ions to chromium ions of about 0.8:1 to about 10:1, the said ammonium ions are present in a molar ratio of ammonium ions to chromium ions of about 2.0:1 to about 11:1, hydrogen ions are present in an amount to provide a pH of about 2.5 to about 5.5, and the said vanadium ions are present in an amount of about 0.015 to about 6.3 g/l.

10. 41. An electrolyte as claimed in any one of Claims 16 to 39 in which the said trivalent chromium ions are present in an amount of about 0.4 to about 0.6 molar, the said complexing agent is present in a molar ratio of complexing agent to chromium ions of about 1.5:1 to about 2:1, the said halide ions comprise chloride, or bromide ions or mixtures thereof present in an amount to provide a molar ratio of halide ions to chromium ions of about 2:1 to about 4:1, the said ammonium ions are present in an amount to provide a molar ratio of ammonium ions to chromium ions of about 3:1 to about 7:1, hydrogen ions are present to provide a pH of about 3.5 to about 4.0 and the said vanadium ions are present in an amount of about 0.2 to about 1 g/l.

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42. An electrolyte as claimed in Claim 16 substantially as specifically described herein with reference to any one of Examples 1 to 36, 38A, 38B or 38C, 39C, 39D, 39E, or 39F.



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43. A process for electroplating a chromium deposit on an electrically conductive substrate comprising the steps of immersing the substrate in an aqueous acidic trivalent chromium electrolyte as claimed in any one of Claims 15 to 42, applying a cathodic charge to the said substrate to effect a progressive deposition of a chromium electrodeposit thereon, and continuing the electrodeposition of the said chromium electrodeposit until the desired thickness is obtained.

44. A process for rejuvenating an aqueous acidic trivalent chromium electrolyte which has been impaired in effectiveness due to contamination by excessive quantities of hexavalent chromium, the said electrolyte containing trivalent chromium ions, a complexing agent for maintaining the trivalent chromium ions in solution, halide ions, ammonium ions and hydrogen ions to provide a pH on the acid side, the said process comprising adding to the said electrolyte a reducing agent comprising vanadium ions or an additive as claimed in any one of Claims 1 to 14 whereby the amount of vanadium added is an amount sufficient to reduce the concentration of hexavalent chromium ions to a level at which the effectiveness of the electrolyte to deposit satisfactory chromium deposits is restored.

45. A process as claimed in Claim 44 in which the said vanadium ions added are in a valency state of 4^{+} .

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46. A process as claimed in Claim 44 or Claim 45 in which the said vanadium ions are added in an amount of 0.015 to 6.3 g/l.

5. 47. A process as claimed in Claim 46 in which the said vanadium ions are added in an amount of 0.2 to 1 g/l.

10. 48. A process as claimed in any one of Claims 44 to 47 in which the said vanadium ions are added in an amount reduce the hexavalent chromium ion concentration to a level below about 100 ppm.

15. 49. A process as claimed in Claim 48 in which the said vanadium ions are added in an amount to reduce the hexavalent chromium ion concentration to a level below about 50 ppm.

20. 50. A process as claimed in any one of Claims 44 to 49 in which the said vanadium ions are introduced in the form of electrolyte soluble and compatible vanadium salts.

25. 51. A process as claimed in any one of Claims 44 to 50 including the further step of electrolyzing the electrolyte following the addition of the said vanadium ions at a moderate current density optionally in the range 10 to 30 ASF or 1.1 to 3.2 ASD to accelerate reduction of the said hexavalent chromium ions by the said vanadium ions.

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52. A process as claimed in Claim 44 substantially



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as specifically described herein with reference to any one of Examples 38A, 38B, 38C, 39C, 39D, 39E or 39F.

5. 53. An aqueous acidic trivalent chromium electrolyte whenever rejuvenated by a process as claimed in any one of Claims 44 to 51.
10. 54. A substrate carrying a chromium or chromium alloy electrodeposit whenever made by a process as claimed in Claim 43.

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