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3,203,811

**MOLTEN TRANSITION METAL PLATING BATHS  
CONTAINING ZINC AMMINE CHLORIDES****Ernest R. Boller, Marion, Ind., assignor to The Boller  
Development Corporation, Marion, Ind., a corporation  
of Indiana****No Drawing. Filed Oct. 20, 1960, Ser. No. 63,720****11 Claims. (Cl. 106-1)**

This invention concerns a bath for the rapid galvanic deposition of a transition element, or metal, as a continuous and coherent plate on another metal having a significant component which stands higher in the Electromotive Series for this bath. More particularly, this invention relates to an anhydrous bath consisting essentially of a chloride of the transition metal being deposited, ammonia, added to the bath as ammonium chloride or as a zinc ammine chloride, and one or more metal chlorides selected from the group consisting of the alkali metal chlorides, the alkaline earth metal chlorides and zinc chloride. Inevitably, such a bath, once it has been put into use, will contain also a chloride of the metal on which the plate is being deposited. Still more particularly this invention relates to such a bath in which the transition metal chloride is present at a concentration between 0.1% and 5%, and the ammonia is present at a concentration of 0.05% to 18% of the total mass of the bath.

A transition metal is defined as one having a normal atom in which the two outermost electron quantum groups, or the three outermost electron quantum groups, are incomplete. In the usual American periodic classification of elements, the transition elements, or metals, are those in the "B" subgroups of groups III to VII and in group VIII of the four long periods. By virtue of their electronic configurations these elements exhibit many similarities in their chemical properties. All are metallic in their elemental state. They form a variety of stable complex compounds, due to formation of coordinate covalent bonds with electron donor molecules or groups. They can be plated galvanically from ordinary aqueous solutions only with difficulty or not at all, especially on ferrous surfaces. Thus chemically they constitute a definite group of elements, or metals.

The expressions "galvanic deposit," or "plate," are used in this specification to mean a solid, continuous and coherent film firmly adherent to the base metal. Deposits which consist of a finely divided powder or slime are excluded; they cannot logically be considered plates.

Galvanic deposition of a metal, of course, refers to its displacement from a solution of one of its salts by another metal having a greater solution potential with this solution. This deposition is obtained by mere immersion of the second metal in a suitable solution of a salt of the first metal. This phenomenon is sometimes designated chemical deposition.

It must be noted that with the fused salt baths of this disclosure the relative positions of many metals in the Electromotive Series are different from the commonly accepted version, which is for aqueous solutions. The relative positions of some metals will also vary with the composition of the fused chloride baths covered in this specification.

The above specification of the composition of the plating bath means that more than 95% of the bath consists of the ingredients recited. A small proportion, less than 5%, of one or more special addition agents may be added if desired. Such agents are frequently useful in the case of specific metals for improving the physical properties of the plate, increasing the rate of deposition, and so on.

In specifying a rapid deposit of the metallic plate, it is meant that the plate is formed within a few seconds.

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This is necessary if the invention is to have commercially acceptable utility. A plate whose deposition requires a matter of hours would possess little practical significance.

There are few references in the prior art relating to the galvanic deposition of transition metals from fused chloride baths. In the instances with which I am familiar a true plate is not obtained, but rather a spongy deposition of finely divided metal. Furthermore, the character of the salt baths of the prior art is essentially different from those defined in this specification. The fundamental role of ammonia derivatives in such plating baths has not heretofore been discovered, nor has the necessity for controlling the concentration of the chloride of the metal to be deposited within relatively low and narrow limits.

Very few of the transition metals can be plated galvanically from an aqueous solution, and then only with some difficulty. Possibly this may be attributed to the fact that the metals of this group form stable coordination complexes with water. In addition, any plates obtained from aqueous solutions are different in character from those obtained with the baths of this invention. With any plate deposited from an aqueous solution, there is almost invariably an oxide film between the base metal and the plated metal due to the action of water, or of oxygen dissolved in the water, on the base metal. When such plates are exposed to corrosive conditions, further chemical reaction occurs along this boundary and the plate peels, or flakes. With the plating baths of this invention such oxidation of the base metal cannot occur. The ammonia content of the bath exerts a powerful reducing action, and this with the elevated temperature required precludes the presence of any reactive oxygen-containing compounds. In fact any thin film of oxide formed on the base metal prior to introduction into the plating bath is immediately dissolved by the bath. Because of this, articles plated from these baths will not under any condition be susceptible to corrosion or chemical attack along the boundary between the base metal and the plated metal.

Many uses for this invention will suggest themselves to those familiar with the field. It is of especial importance that the galvanic plates from these baths may be applied to a variety of base metals easily, quickly and economically. In particular, the properties of the specific transition metal in the plate will determine its possible applications.

For example, titanium and molybdenum in contact with air develop surface oxide coatings which are not wetted by many molten metals and to which such molten metals will not adhere upon cooling. Chromium will develop a similarly acting oxide coating upon heating. Thus galvanic plates of such metals can be used as stop-off agents in hot-dip metal coating to prevent coating certain areas of metal being dipped. Such plates can also be employed to protect low cost iron and steel pots in melting and holding furnaces from attack by molten aluminum or zinc, as well as to protect other iron or steel equipment coming in contact with these molten metals. Another application is preventing adhesion of splatter metal in areas adjacent to a fusion weld. A further application is in foil welding. The requirement here is for foil which is a good conductor, to which the metal being welded will not adhere and which is reasonable in cost. Carbon steel foil galvanically plated with titanium in the bath described above will meet these requirements.

It is obvious that these galvanically plated metals will be useful in minimizing or eliminating corrosion. The chromium plate from these baths will prevent corrosion of carbon steel or cast iron in typical industrial atmospheres for a considerable time. Because of their inherent

adherence, these galvanic plates are of especial interest in combating high temperature corrosion. They afford, for example, an easy and economical method for preventing scaling and discoloration of ferrous materials during heat treatment.

Another important application for galvanic plates of most of the transition metals, with proper control of their deposition from baths of this invention, is as a blocking layer in connection with hot-dip aluminum coating of ferrous surfaces. This use of certain specified metals is described in my copending application, Serial No. 597,576, filed July 13, 1956 (now patent No. 2,957,782). These plates could also be used in a similar manner as a blocking layer in application of hot-dip zinc coatings to ferrous surfaces, serving to prevent reaction between the zinc and iron with consequent elimination of deleterious effects of the zinc-iron intermetallic compound on the properties of the zinc coating.

A preferred plating bath of this invention may be described in detail as follows:

4 parts by weight of a transition metal chloride and 6 parts of ammonium chloride are added to 90 parts of molten zinc chloride. In this are dissolved in order 12 parts of lithium chloride, 28 parts of potassium chloride, 23 parts of sodium chloride and 27 parts of calcium chloride. The final temperature is adjusted to a value between 750° and 800° F.

This bath is suitable for the application of galvanic transition metal plates to ferrous surfaces. The plating is accomplished by immersing the ferrous material in this bath for the requisite time. This time, measuring from when the salt initially frozen on the ferrous surface upon immersion is remelted, will vary from 2 to 10 seconds for cast iron or carbon steel to as much as 60 seconds for some of the more refractory ferrous alloys. The transition metal plates obtained from this bath under these conditions are very thin, but are smooth, continuous, coherent and, in effect, integral with the base metal.

There are many possible variations from the bath composition given above. The plating baths covered by this specification may be regarded as consisting of a solvent, which consists of one or more of the alkali metal chlorides, or of alkaline earth metal chlorides, or of zinc chloride, or of any mixture of such chlorides, the solvent being acidified with ammonia, added to the bath as ammonium chloride or a zinc ammine chloride, and containing as an essential solute a chloride of the transition metal being plated. After such a bath has been put into use it will unavoidably contain as a further solute a chloride of the metal on which the plate is deposited. From an industrial viewpoint, only lithium, sodium and potassium among the alkali metals and magnesium, calcium, strontium and barium among the alkaline earth metals are probably practical for consideration in the above definition.

On this basis the solvent may be defined as consisting of 0% to 95% of one or more of the following: zinc chloride, lithium chloride, potassium chloride, sodium chloride, calcium chloride, magnesium chloride, barium chloride, strontium chloride. The salt or combination of salts used in any particular instance will depend for most part on required melting point, fluidity, solvent power for the transition metal chloride and for ammonia, and upon cost considerations.

Commercial zinc chloride in anhydrous form contains basic zinc chloride, this usually being equivalent to 2 to 8% zinc oxide. When ammonium chloride is added to this fused zinc chloride, or to one of the above-defined solvents containing zinc chloride, it reacts immediately with the basic chloride, or zinc oxide, to form zinc diammine chloride. A certain amount of ammonium chloride is soluble in molten zinc chloride as such or as an addition compound with zinc chloride. This solubility falls rapidly with increase in temperature, and even more rapidly upon dilution of the zinc chloride with alkali or alkaline

earth chlorides. Ammonium chloride is eliminated from the system through decomposition into ammonia and hydrogen chloride, the evolved gases recombining above the surface of the liquid to form an ammonium chloride smoke. A small proportion of the free ammonia thus momentarily present in the system will coordinate with the zinc chloride to form zinc mono- or diammine chloride. From these considerations it is obvious that the addition of ammonium chloride to such a solvent containing zinc chloride automatically results in formation of a zinc ammine chloride.

Alternatively, a zinc ammine chloride may be added directly in place of or in addition to ammonium chloride. Practically the diammine would be used since it could be manufactured easily and cheaply by the chemical industry if there were a demand for it. In a limiting case, zinc diammine chloride itself would be the major constituent of the bath, which would be of interest because of its low melting point. Zinc diammine chloride melts without decomposition at about 300° F. At higher temperatures it is in equilibrium with the monoammine, the proportion of the monoammine rising with the temperature. The behavior of the diammine is similar when dissolved in a solvent consisting entirely or mostly of zinc chloride. When held for a considerable time at high temperatures some of the monoammine changes to ammono-basic zinc chloride. Since this is slightly volatile I have been able to isolate and identify it. There is also a further change to other ammonia derivatives. These are definite compounds, as indicated by X-ray diffraction studies, but their identity has not been established. Ammonium chloride is unstable in those of the above-defined solvents which contain no, or only a small proportion of, zinc chloride. Zinc ammine chloride is soluble in all these solvents, but when zinc chloride is absent, or is present only in small amounts, such solvents will retain ammonia in solution only for several minutes. In those cases where the required concentration of ammonia cannot be maintained it is necessary to resort to localized and fleeting supersaturation.

It should be noted that many of the transition metal chlorides form amines and other ammonia derivatives. These are pretty much analogous to the zinc-ammonia derivatives, but are generally less stable under the above-defined conditions. In any case their concentration is so low that they could not hold very much ammonia.

The alkali metal chlorides do not form stable ammonia derivatives at room temperature or above. Some of the alkaline earth metal chlorides form amines stable at room temperature, but unstable at temperatures with which the present invention is concerned.

It has been ascertained that the ammonia content of the bath should be between 0.05% and 18%, based on total mass of the bath. This amount of ammonia is essential for proper functioning of the bath. The ammonia, present in the forms indicated, is a major factor in determining the reactivity of the bath, that is, the rate at which the transition metal plate is deposited. This is due to ammonia acting as an acid, being an electron acceptor in this environment. Ammonia concentrations in the lower end of the range are suitable when the bath is used at high temperatures. In case the solubility of ammonia in a particular solvent composition at the temperature being employed is below the indicated limit, temporary local supersaturation of the solvent at the surface of the metal being plated will suffice. Ammonia concentrations at the upper end of the range are suitable for low temperature baths. For example, with a bath operable at 300° to 350° F. it is necessary that the major constituent of the bath be zinc diammine chloride, which might be described as zinc chloride saturated at high temperature with ammonia added as ammonium chloride.

It should be noted that under the conditions existing in these baths the zinc ammine chloride would be present as the diammine, the monoammine or both and that the

monoammine would be in equilibrium with a small amount of ammonio-basic zinc chloride and possibly with other ammonia derivatives of zinc chloride. As used in this specification, the term zinc ammine chloride refers to all such ammonia derivatives. The usual analytical method for estimation of ammonia will include all such ammonia residues.

Empirically, I have established the fact that these ammonia derivatives have a pronounced effect in promoting the deposition of the transition metal as a continuous and coherent plate. At present, I am unable to state a reason for this effect, but can only point out the fact that both continuity and coherence of the deposited film or plate are significantly improved by the presence of such ammonia derivatives in the bath.

It has also been ascertained that the concentration of the chloride of the transition metal being plated should be between 0.1% and 5%, on basis of weight of the bath. The concentration chosen in any particular instance will depend upon reactivity desired from this source. Generally the higher the concentration of the metal being plated, the higher its rate of deposition. At values below the indicated range, the rate of deposition is too slow to be of practical interest. At values slightly above the indicated limit the deposit becomes rough, and at still higher values the deposit is a sponge or slime of finely divided metal crystals.

Since in the galvanic deposit of a metal the stoichiometric equivalent of the metal on which the deposit is formed goes into solution, it is inevitable that these baths, once put into use, will contain the chloride of the metal on which the transition metal is plated. The concentration of this metal chloride will depend upon the amount of plating which has been done in the bath, upon the solubility of this metal chloride in the bath and upon the relative amounts of drag-out and make-up in the operation.

It is apparent from the foregoing that the activity of these plating baths, defined as the rate of deposition of the transition metal plate, is their most critical property, and that this must be controlled. This activity is affected by a number of factors, including temperature of the bath, concentration of ammonia, concentration of the transition metal chloride. The solvent is also a factor if it contains zinc chloride or lithium chloride, both these compounds increasing activity. All these factors are inter-related. A change in one must be accompanied by corresponding changes in one or more of the others to preserve optimum plating conditions. In practice some of these variables may be fixed by the nature of the operation. For example, if a plating operation must be carried out at a specified temperature, this fixes the composition of the solvent within fairly definite limits on bases of melting point, fluidity and the like. The required activity must then be obtained by adjustment of ammonia concentration and transition metal chloride concentration.

The transition metal may be added to the bath as a chloride, or as a compound which will react with constituents of the bath to give the chloride and other products which will volatilize from the bath or which are already present in the bath. Thus, if desirable for cost or other reasons, the transition metal oxides, hydroxides, nitrates, organic acid salts or transition metal oxy-acid salts of metal already in the bath may be used. These plating baths are strongly reducing in character, and the transition metal will be quickly reduced to its lowest stable valence state; and in that state will react with other chlorides in the bath to produce the corresponding transition metal chlorides.

The method by which a specific bath may best be formed and maintained in service will depend upon the identity and proportions of constituents, particularly of the solvent. In any case, a suitable procedure will be

apparent to anyone familiar with the chemistry of these fused salts.

Throughout the above disclosure, I have spoken of depositing a single transition metal on a "pure" metallic base. The process of the present invention is adaptable, however, for depositing a homogeneous mixture (which probably may properly be called an alloy) of transition metals on a suitable base, and for depositing a selected plate on a base which may be an alloy. The composition of the deposited plate will, of course, depend upon the composition of the bath; and if two or more transition metals are present in the bath, the resultant plate will consist of the several transition metals, usually substantially in the proportions in which they are present in the bath. If a plate is to be deposited on an alloy, it is necessary that at least one ingredient of the alloy shall be a significant amount (probably not less than 5%) of a metal which stands above all of the transition metals to be deposited, in the applicable Electromotive Series.

Thus, it will be understood that, in the claims appended hereto, the expression "a transition metal" is to be understood to include a mixture of a plurality of transition elements, while the expression "a base metal" is to be understood to include an alloy, and that the expression "a single transition metal" or the expression "an elemental base metal" will be used when it is intended to exclude such mixtures or alloys.

The following examples are given in order that this invention may be more fully understood:

#### Example No. 1

2 parts by weight of ammonium chloride and 2 parts of potassium dichromate were added to a molten solvent consisting of 150 parts of zinc chloride and 25 parts of a mixture consisting of 53% potassium chloride, 5% sodium chloride and 42% lithium chloride, which will be recognized as a triple eutectic mixture of these chlorides. The dichromate was immediately reduced to trivalent chromium and resulting water volatilized. This bath was adjusted to 750° F., and a specimen of carbon steel immersed in it for 10 sec. A smooth coherent plate of chromium was obtained. Its identity was established by spectrographic examination and by chemical analysis.

#### Example No. 2

2 parts by weight of ammonium chloride and 8 parts of cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , were added to same molten solvent as used in Example No. 1. After water had been expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth coherent plate of cobalt was obtained. Its identity was confirmed by spectrographic examination.

#### Example No. 3

2 parts by weight of ammonium chloride and 4.5 parts of ammonium vanadate,  $\text{NH}_4\text{VO}_3$ , were added to the same molten solvent used in Example No. 1. The vanadate was immediately reduced and resulting water volatilized. The bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth coherent plate of vanadium was obtained. Its identity was confirmed by spectrographic examination.

#### Example No. 4

2 parts by weight of ammonium chloride and 4.75 parts of thorium nitrate,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , were added to the same molten solvent used in Example No. 1. After the water and nitrogen oxides were expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth coherent plate of thorium was obtained. Its identity was confirmed by spectrographic examination.

#### Example No. 5

2 parts by weight of ammonium chloride and 3.3 parts of uranyl acetate,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ , were added to the

same molten solvent used in Example No. 1. After water and carbon dioxide were expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth coherent plate of uranium was obtained. Its identity was confirmed by spectrographic examination.

#### Example No. 6

2 parts by weight of ammonium chloride and 5.7 parts of potassium permanganate were added to the same molten solvent used in Example No. 1. The permanganate was immediately reduced. After resulting water was expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth coherent plate of manganese was obtained. Its identity was confirmed by spectrographic examination and by chemical analysis.

#### Example No. 7

2 parts by weight of ammonium chloride and 3.7 parts of sodium tungstate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , were added to the same solvent used in Example No. 1. The tungstate was quickly reduced. After the water was expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent plate of tungsten was obtained. Its identity was confirmed by spectrographic examination.

#### Example No. 8

2 parts by weight of ammonium chloride and 2 parts of rare earth metal chlorides,  $\text{RCl}_3 \cdot 6\text{H}_2\text{O}$ , were added to the same molten solvent used in Example No. 1. After the water was expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed for 10 sec. A smooth and coherent metallic plate was obtained. Spectrographic examination showed presence of rare metals in essentially the same proportion as in the original salt mixture.

#### Example No. 9

2 parts by weight of ammonium chloride and 2 parts of didymium chloride,  $\text{DiCl}_3 \cdot 6\text{H}_2\text{O}$ , were added to the same molten solvent used in Example No. 1. After the water was expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent metallic plate was obtained. Spectrographic examination showed presence of rare earth metals in essentially the same proportion as in the salt mixture added.

#### Example No. 10

2 parts by weight of ammonium chloride and 3.3 parts of titanium dioxide were added to the same molten solvent used in Example No. 1. The titania was dissolved slowly with evolution of water. After reaction was complete, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent metallic plate was obtained. Its identity as titanium was indicated by spectrographic examination.

#### Example No. 11

2 parts by weight of ammonium chloride and 5 parts of zirconyl nitrate,  $\text{ZrO}(\text{NO}_3)_2$ , were added to the same molten solvent used in Example No. 1. After water and nitrogen oxides were expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent plate of zirconium was obtained. Its identity was confirmed by spectrographic examination.

#### Example No. 12

2 parts by weight of ammonium chloride and 3 parts of ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , were added to the same molten solvent used in Example No. 1. The molybdate was immediately reduced and water volatilized. The bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A very

smooth and coherent plate of molybdenum was obtained. Its identity was confirmed by chemical analysis.

#### Example No. 13

2 parts by weight of ammonium chloride and 2 parts of nickel chloride,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , were added to the same molten solvent used in Example No. 1. After water was expelled, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent plate of nickel was obtained. Its identity was confirmed by chemical analysis.

#### Example No. 14

2 parts by weight of ammonium chloride and 2 parts of mixed niobium and tantalum oxides were added to the same molten solvent used in Example No. 1. After reaction was complete, the bath was adjusted to 750° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent metallic plate was obtained. Spectrographic examination indicated niobium and tantalum in essentially the same proportion as in oxide added.

#### Example No. 15

1.7 parts by weight of potassium dichromate were added to a bath prepared by fusing together 65 parts of zinc chloride, 10 parts of ammonium chloride and 25 parts of a mixture consisting of 53% potassium chloride, 5% sodium chloride and 42% lithium chloride. After water and excess ammonium chloride were expelled, the bath was adjusted to 600° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent chromium plate was obtained. Its identity was confirmed by chemical analysis.

#### Example No. 16

1.7 parts by weight of potassium dichromate were added to a bath prepared by fusing together 50 parts of zinc chloride, 5 parts of ammonium chloride and 45 parts of a mixture consisting of 53% potassium chloride, 5% sodium chloride and 42% lithium chloride. After water and excess ammonium chloride were expelled, the bath was adjusted to 625° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent chromium plate was obtained. Its identity was confirmed by chemical analysis.

#### Example No. 17

1.7 parts by weight of potassium dichromate were added to a bath prepared by fusing together 25 parts of zinc chloride, 2.5 parts of ammonium chloride and 72.5 parts of a mixture consisting of 53% potassium chloride, 5% sodium chloride and 42% lithium chloride. After water and excess ammonium chloride were expelled, the bath was adjusted to 650° F., and a specimen of carbon steel immersed in it for 15 sec. A smooth and coherent chromium plate was obtained. Its identity was confirmed by chemical analysis.

#### Example No. 18

2 parts by weight of ammonium chloride and 2 parts of potassium dichromate were added to a molten solvent consisting of 25 parts of zinc chloride, 20 parts of potassium chloride, 20 parts of sodium chloride, 9 parts of lithium chloride and 21 parts of calcium chloride. After reaction was complete, the bath was adjusted to 900° F. and a specimen of carbon steel was immersed in it for 10 sec. A smooth and coherent chromium plate was obtained. Its identity was confirmed by chemical analysis.

#### Example No. 19

2 parts by weight of potassium dichromate and 2 parts of ammonium chloride were added to a molten solvent consisting of 10 parts of zinc chloride, 27 parts of potassium chloride, 23 parts of sodium chloride, 12 parts of lithium chloride and 28 parts of calcium chloride. After

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water was expelled, the bath was adjusted to 950° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent plate of chromium was obtained. Its identity was confirmed by chemical analysis.

*Example No. 20*

1.5 parts by weight of sodium dichromate and 1.5 parts of ammonium chloride were added to a molten solvent consisting of 8 parts of zinc chloride, 17 parts of potassium chloride, 17 parts of sodium chloride, 8 parts of lithium chloride, 18 parts of calcium chloride and 15 parts of magnesium chloride. After water was expelled, the bath was adjusted to 1100° F. and a specimen of chromium plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 21*

1.5 parts by weight of sodium dichromate were added to a molten bath prepared by fusing together 10 parts of zinc chloride, 5 parts of zinc diammine chloride, 50 parts of potassium chloride, 6 parts of sodium chloride, 5 parts of lithium chloride and 24 parts of calcium chloride. After water was expelled, the bath was adjusted to 1100° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent plate of chromium was obtained. Its identity was confirmed by chemical analysis.

*Example No. 22*

2 parts by weight of potassium dichromate were added to a molten bath prepared by fusing together 95 parts of zinc chloride and 5 parts of ammonium chloride. After reaction ceased, the bath was adjusted to 600° F. and a specimen of carbon steel immersed in it for 10 sec. A smooth and coherent chromium plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 23*

2 parts by weight of titanium dioxide and 4 parts of ammonium chloride were added to a molten solvent consisting of 53 parts of potassium chloride, 5 parts of sodium chloride and 42 parts of lithium chloride. After reaction was completed, the bath was adjusted to 700° F., a pellet of ammonium chloride held beneath the surface of the bath and a specimen of carbon steel immersed in it for 20 sec. A smooth and coherent titanium plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 24*

6 parts by weight of ammonium molybdate and 6 parts of ammonium chloride were added to a molten bath containing 200 parts of zinc diammine chloride and 10 parts of lithium chloride. After reaction was completed the bath was adjusted to 400° F. and a specimen of carbon steel immersed in it for 20 sec. A smooth and coherent molybdenum plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 25*

1.5 parts by weight of potassium dichromate and 3 parts of ammonium chloride were added to a molten bath prepared by fusing together 75 parts of zinc diammine chloride and 25 parts of a mixture consisting of 53% potassium chloride, 5% sodium chloride and 42% lithium chloride. After reaction was completed the bath was adjusted to 500° F. and a specimen of carbon steel immersed in it for 20 sec. A smooth and coherent plate of chromium was obtained. Its identity was confirmed by chemical analysis.

*Example No. 26*

2 parts by weight of potassium dichromate and 2 parts of ammonium chloride were added to a molten solvent containing 75 parts of zinc chloride and 25 parts of a mixture consisting of 53% potassium chloride, 5% sodium chloride and 42% lithium chloride. After reaction

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ceased the bath was adjusted to 700° F. and a specimen of cast iron immersed in it for 30 sec. A continuous and coherent plate of chromium was obtained. Its identity was confirmed by chemical analysis. Specimens plated in this way could be immersed in 35% nitric acid without any detectable reaction.

*Example No. 27*

2 parts by weight of nickel chloride hexahydrate and 2 parts of ammonium chloride were added to the same molten solvent used in Example No. 26. After water was expelled the bath was adjusted to 700° F. and a specimen of type 410 stainless steel immersed in it for 20 sec. A smooth and coherent nickel plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 28*

3 parts by weight of ammonium molybdate and 3 parts of ammonium chloride were added to the same molten solvent used in Example No. 26. After reaction was completed the bath was adjusted to 700° F. and a specimen of type 410 stainless steel immersed in it for 20 sec. A smooth and coherent molybdenum plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 29*

3 parts by weight of ammonium molybdate and 3 parts of ammonium chloride were added to the same molten solvent used in Example No. 26. After reaction was completed the bath was adjusted to 700° F. and a specimen of type 310 stainless steel immersed in it for 30 sec. A smooth and coherent molybdenum plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 30*

2 parts by weight of potassium dichromate and 2 parts of ammonium chloride were added to the same molten solvent used in Example No. 26. After reaction was completed the bath was adjusted to 800° F. and a specimen of Inconel was immersed in it for 45 sec. A smooth and coherent chromium plate was obtained. This plated specimen was heated in air at 1750° F. for 8 hours without the surface oxidation and discoloration shown by the control specimen of the unplated Inconel.

*Example No. 31*

2 parts by weight of ferric chloride and 2 parts of ammonium chloride were added to a molten solvent consisting of 53 parts of potassium chloride, 5 parts of sodium chloride and 42 parts of lithium chloride. The bath was adjusted to 700° F. While excess ammonium chloride was still being evolved, a specimen of commercially pure aluminum sheet was immersed in the bath for 4 sec. A smooth and coherent iron plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 32*

2 parts by weight of potassium dichromate and 2 parts of ammonium chloride were added to the same molten solvent used in Example No. 31. The bath was adjusted to 700° F. While excess ammonium chloride was still being evolved, a specimen of commercially pure aluminum sheet was immersed in the bath for 4 sec. A smooth and coherent chromium plate was obtained. Its identity was confirmed by chemical analysis.

*Example No. 33*

3 parts by weight of ammonium molybdate and 3 parts of ammonium chloride were added to the same molten solvent used in Example No. 31. The bath was adjusted to 700° F. While excess ammonium chloride was still being evolved, a specimen of commercially pure aluminum sheet was immersed in the bath for 4 sec. A smooth and coherent molybdenum plate was obtained. Its identity was confirmed by chemical analysis.

## Example No. 34

2 parts by weight of potassium dichromate and 2 parts of ammonium chloride were added to a molten solvent containing 75 parts of zinc chloride and 25 parts of a mixture consisting of 53% potassium chloride, 5% sodium chloride and 42% lithium chloride. After reaction was complete, the bath was adjusted to 700° F. and a specimen of titanium immersed in it for 10 sec. A smooth and continuous chromium plate was obtained. Its identity was confirmed by chemical analysis.

## Example No. 35

2 parts by weight of potassium dichromate and 2 parts of ammonium chloride were added to same molten solvent used in Example 34. After reaction was complete, the bath was adjusted to 700° F. A specimen of pure molybdenum was anodically cleaned in a fused alkali metal chloride bath. It was immediately immersed in the plating bath for 20 sec. A smooth and coherent plate of chromium was obtained. Its identity was confirmed by chemical analysis.

I claim as my invention:

1. A molten, anhydrous bath for the rapid galvanic deposition of a continuous and coherent plate of a transition metal on another metal which includes an element which stands above the selected transition metal in the applicable Electromotive Series, said bath consisting essentially of from 0.1% to 5% of a chloride of the selected transition metal, an ammonia derivative of a constituent of the bath in an amount equivalent to 0.05% to 18% ammonia, and the balance of the bath being a solvent consisting essentially of at least two metal chlorides selected from the group consisting of the alkali metal chlorides, the alkaline earth metal chlorides and zinc chloride, no one of the components of such solvent constituting more than 90% by weight of the solvent.

2. A molten, anhydrous bath for the rapid galvanic deposition of a continuous and coherent plate of a transition metal on another metal which includes an element which stands above the selected transition metal in the applicable Electromotive Series, said bath being made up essentially from a reducible compound of the selected transition metal, an ammonia derivative in an amount exceeding that required to reduce said transition metal compound to its lowest stable valency but insufficient to cause dissolution of the selected transition metal, and at least two metal chlorides selected from the group consisting of the alkali metal chlorides, the alkaline earth metal chlorides and zinc chloride in an amount sufficient to convert the transition metal to a chloride.

3. A molten, anhydrous bath for the rapid galvanic deposition of a continuous and coherent plate of a transition metal on another metal which includes an element which stands above the selected transition metal in the applicable Electromotive Series, said bath consisting essentially of from 0.1% to 5% a chloride of the selected transition metal, 0.05% to 18% ammonia, and a significant quantity of a triple eutectic mixture of the chlorides of lithium, potassium and sodium.

4. The bath of claim 3 including zinc chloride.

5. A molten, anhydrous bath for the rapid galvanic deposition of a continuous and coherent plate of a transition metal on another metal which includes an element which stands above the selected transition metal in the applicable Electromotive Series, said bath consisting essentially of a reducible compound of the selected transi-

tion metal, an ammonia derivative in an amount exceeding that required to reduce said transition metal compound to its lowest stable valency but insufficient to cause dissolution of the selected transition metal, a compound including zinc and chlorine, lithium chloride, potassium chloride and sodium chloride.

6. The bath of claim 5 including calcium chloride.

7. The bath of claim 5 in which said compound including zinc and chlorine is a zinc chloride ammonia derivative.

8. A molten, anhydrous bath for the rapid galvanic deposition of a continuous and coherent plate of a transition metal on another metal which includes an element which stands above the selected transition metal in the applicable Electromotive Series, said bath being made up essentially from (1) a reducible compound of the selected transition metal, (2) ammonia derivative in an amount exceeding that required to reduce said transition metal compound to its lowest stable valency but insufficient to cause dissolution of the transition metal, said onium compounds to its lowest stable valency but insufficient to cause dissolution of the transition metal, said ammonia derivatives including a zinc ammine chloride and (3) zinc chloride, lithium chloride, potassium chloride and sodium chloride.

9. A molten, anhydrous bath for the rapid galvanic deposition of a continuous and coherent plate of a transition metal on another metal which includes an element which stands above the selected transition metal in the applicable Electromotive Series, said bath consisting essentially of a reducible compound of the selected transition metal, ammonia derivatives in an amount exceeding that required to reduce said transition metal compound to its lowest stable valency but insufficient to cause dissolution of the selected transition metal, a compound including zinc and chlorine, and at least one metal chloride selected from the group consisting of the alkali metal chlorides and the alkaline earth metal chlorides.

10. The bath of claim 9 in which said compound including zinc and chlorine is a zinc ammine chloride.

11. A molten, anhydrous bath for the rapid galvanic deposition of a continuous and coherent plate of a transition metal on another metal which includes an element which stands above the selected transition metal in the applicable Electromotive Series, said bath consisting essentially of (1) a reducible compound of the selected transition metal, (2) an ammonia derivatives in an amount exceeding that required to reduce said transition metal compound to its lowest stable valency but insufficient to cause dissolution of the selected transition metal, said ammonia derivatives including a zinc ammine chloride, and (3) at least two metal chlorides selected from the group consisting of zinc chloride, the alkali metal chlorides and the alkaline earth metal chlorides.

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*Examiners.*

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,203,811

August 31, 1965

Ernest R. Boller

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 48, for "logically" read -- logically --;  
column 2, line 69, for "eleminating" read -- eliminating --;  
column 3, line 7, for "transistion" read -- transition --; line  
10, for "ferous" read -- ferrous --; line 16, before "iron"  
insert -- the --; line 33, for "very" read -- vary --; column  
4, line 38, for "con-" read -- can- --; column 5, line 60,  
for "togive" read -- to give --; column 6, line 37, for  
"imediately" read -- immediately --; line 43, for "spectoro-  
graphic" read -- spectrographic --; line 57, for "imediately"  
read -- immediately --; column 7, line 36, before "metals"  
insert -- earth --; column 9, line 55, for "identify" read --  
identity --; column 12, line 17, for "derivative" read --  
derivatives --; lines 21 and 22, strike out "onium compounds  
to its lowest stable valency but insufficient to cause dissolu-  
tion of the transition metal, said"; line 31, for "seleceted"  
read -- selected --; line 41, for "galvinc" read -- galvanic  
--; line 47, strike out "an", first occurrence.

Signed and sealed this 15th day of March 1966.

(SEAL)  
Attest:

ERNEST W. SWIDER  
Attesting Officer

EDWARD J. BRENNER  
Commissioner of Patents