

## UNITED STATES PATENT OFFICE

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## PROCESS FOR THE PRODUCTION OF ELECTROLYTIC DEPOSITS

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It is known that certain metals, for instance tin or zinc, the salts of which melt at relatively low temperatures, may be precipitated by electrolysis from a molten mass, on certain other substances with a higher point of fusion, such as steel, iron and aluminium. The utilization of such known processes is however extremely limited in practice, as there is only a relatively small number of metal salts of a sufficiently low point of fusion, such as are required for the formation of the melts. Accordingly, the well known process can be used only for the electrolytic production of tin or zinc deposits.

The object of the invention is to use a molten mass for the separation or precipitation of any metals or alloys, more particularly of metals which have hardening and improving properties, such as more particularly chromium, nickel, molybdenum, tungsten, manganese, etc., which are deposited alone, or simultaneously with one or more other metals, on other metals, more particularly on iron. According to the invention, this problem is solved by choosing as the electrolyte a composition whose point of fusion differs by at least 100° C., preferably by several hundred degrees, from the point of fusion of the metal or alloy to be deposited. The metals or alloys to be deposited are introduced into the melt in any desired form, for instance in the form of one of their salts. As suitable materials for the fluxing composition can be chiefly used boron compounds, and sulphates, bisulphates, silicates or cyanides. Suitable boron compounds are for instance metaborates and borates of the alkalis, of the alkaline earths, of magnesium, and in certain cases also of zinc and of manganese. As a rule it is preferable to use a mixture of several of the substances mentioned.

If it is desired for instance to provide a metal, say iron, with a coating of chromium, oxide of chromium ( $\text{Cr}_2\text{O}_3$ ) is dissolved in a mass of borates, for instance in a mixture of meta- and tetra-borates. For the purpose in question there could be used for instance 40 parts of borax, 50 parts of sodium metaborate and 15 parts of chromium oxide, in which case good chromium coating will be obtained

as shown by experiments, by using a current density of about 1000 amperes per square meter. The temperature of the molten mass is about 950° C., so that practically all kinds of iron can be coated in this way with chromium.

If in addition to chromium, some other metal is to be deposited or precipitated, the "separation potential" of which is close to that of chromium, for instance, nickel, in the above mentioned mass of boron compounds, there are dissolved for instance 8 parts of chromium oxide and 8 parts of nickel compound, such as nickel oxide, and the electrolysis is again effected with a current density of about 1000 amperes per square meter.

With the new process it is also possible to deposit metals, the separation potential of which is higher than that of chromium, for instance the boron contained in the mass, by increasing the current density to a sufficient extent. In that case, chromium is also separated in addition to boron. The composition of the mass need not be modified in this case. The current density amounts in this case to about 4000 amperes per square meter. The temperature remains the same as that stated above. If the molten mass does not contain any heavy metal, for instance if it contains only sodium borate, it will be possible, with the current density mentioned to separate on the cathode boron alone.

A still better technical effect is obtained with the new process by using direct current of a non-uniform or irregular strength. This ensures a finer grain in the metal deposits. The reason for this result is that the process of crystallization during the depositing of the metal is disturbed. In most cases the metal coating deposited on a polished cathode surface will be therefore still smooth and bright even with a great thickness of deposit. This is an advantage as it saves the cost of polishing, which is of special importance in the case of hard metals such as chromium. The action could be still further improved, for instance by reversing the direction of the current in the intervals between two current impulses depositing metal.

The new process offers substantial advantages.

tages for instance in the manufacture of boron-containing chromium coating by electrolysis of a molten mass containing boron compounds.

As already stated, the best density of current for the precipitation of metallic chromium is materially smaller than the density of current at which boron chromide is obtained. If the current density is increased to such an extent as to separate boron chromide, it will be difficult to obtain the deposit in a compact form, as a powdery deposit is easily produced. This difficulty is overcome by electrolyzing with a uniform current density which gives an irreproachable metallic chromium deposit, and by increasing the current density at regular intervals and for a short period of time to such an extent as to produce separation of boron chromide which is embedded in the subsequently precipitated deposit of metallic chromium. If however for instance an iron surface is to be hardened merely by an electrolytic "borating" in the molten mass, it is preferable to work with a non-uniform direct current, in order to give time for the boron separated by one current impulse, to diffuse into the iron surface before the next current impulse is sent.

According to the results to be obtained, the current is either sent in the same direction, reversed or broken between two precipitating current impulses.

The non-uniform electric current for the purpose in question can be generated in various ways, to suit the special requirements. For instance, into the direct current circuit can be switched in a source of alternating current, for instance the secondary winding of a transformer, or the armature of the current generator can be provided with two separate windings, one of which supplies alternating current, and the other one direct current, these two windings being connected together in series. The separate excitation of the direct current generator could also be periodically modified in the required manner. Further, the electrolytic bath can be switched in and out at regular intervals, or two different sources of currents could be connected to the bath, or an auxiliary resistance could be short circuited.

*Example of carrying into practical effect.*—Into a mass constituted by 20 parts borax, 40 parts magnesium metaborate, 20 parts sodium metaborate and 15 parts chromium oxide and melted for instance by heating with gas, in a carbon crucible which at the same time constitutes the anode, is dipped an iron sheet or plate, the surface of which is 1 square decimeter, and connected as the cathode. First, the plate is exposed to 10 amperes, that is to say to 1000 amperes per square meter, for a period of 5 minutes, then for two minutes the strength of current is maintained at 40 amperes=4000 amperes per

square meter. This operation can be repeated as many times as desired.

In some cases it is advisable first to form a suitable mixture of foreign substances, for instance alkali metal salts, and to introduce the substance (metal or alloy) to be deposited only into the molten mixture. As solvents for the metals to be separated sulphates, bisulphates or cyanides, alone or mixed together, have proved particularly suitable. Two examples for carrying the invention into practical effect are given in the following:—

*First example.*—1000 parts by weight of potassium cyanide are melted, and to the molten mass are added 120 parts by weight of chromium oxide, a portion of which becomes dissolved in the molten mass. The molten bath is thereupon brought to a temperature of about 590° C., and the object to be coated, for instance a sheet or plate of iron, is dipped into the bath and connected as the cathode. The anode could be formed for instance by the melting crucible of graphite. By using a current density of about 2000 amperes per square meter at the cathode, there will be separated on the iron plate a dense deposit of chromium which combines with the surface of the iron plate to form a firmly adhering coating.

*Second example.*—If it is desired to obtain a silicon containing metal coating, suitable quantities of silicates are also introduced into the mass. The composition of the mass is made for instance as above, of 1000 parts by weight of potassium cyanide and 120 parts by weight of chromium oxide, and as addition—150 parts by weight of sodium silicate. The electrolysis of the molten mass is carried out preferably at a temperature of about 540° C. and with a current density of 3000–4000 amperes per square meter at the cathode. In the example, there is produced a silicon containing chromium coating which has a still greater resistance to oxidizing influences and to acids as well as a greater hardness than a pure chromium coating.

Any desired other metals or their alloys can be deposited in a similar manner in the form of practically useful coating. Instead of using alkali metal compounds as solvents, there could also be used for the purpose compounds of alkaline earths and of magnesium, either alone or as an addition to alkaline compounds. If desired, hydroxides or carbonates could also be introduced as addition into the above mentioned masses forming solvents.

It is frequently difficult to cover with chromium hollow bodies as well as the interior of relatively narrow bores and holes in general, and an auxiliary anode becomes necessary as in many aqueous galvanic processes. As the supply electrodes for such holes there are preferably used, as auxiliary anodes, rods or wires of some other metal, such as for in-

stances copper, covered with a thick deposit of chromium by strongly aqueous electrolysis or by molten mass electrolysis. Carbon or solid chromium is too brittle to be used as anode material for the purpose in question.

The carbon (or graphite) used as the crucible and eventually at the same time also as an electrode, is liable to wear, and is protected from burning and other chemical action by coating it with a thin and strongly adhering layer of boron carbide or silicium carbide. This coating is obtained by exposing the carbon as cathode to the action of electric current in the molten boric acid or silicic acid which contains an addition of suitable metals for the purpose of increasing its conductivity.

*Example.*—The carbon crucible to be protected, connected as cathode, is filled with molten boric acid to which has been added 10% borax, whilst a carbon rod, connected as anode, is introduced into the centre of the crucible. The temperature is about 950° C. The electrolysis is continued for a short time, about 10 minutes, with a current density of 5000 amperes per square meter. The boron separated combines in nascent state, owing to the heat, with the carbon and forms boron carbide.

What we claim and desire to secure by Letters Patent of the United States is:—

1. A process for the production of solid, adherent coatings of metals which comprises electrolytically depositing the metals at a temperature below the melting point thereof from a fused bath the point of fusion of which is at least 100° C. lower than the melting point of the metals to be deposited, said bath containing a boron compound and a compound of the metal to be deposited.

2. A process for the production of solid, adherent coatings of metals which comprises electrolytically depositing the metals at a temperature below the melting point thereof from a fused bath the point of fusion of which is at least 100° C. lower than the melting point of the metals to be deposited, said bath containing a borate and a compound of the metal to be deposited.

3. A process for the production of solid, adherent metallic coatings containing chromium which comprises electrically depositing the chromium at a temperature below the melting point thereof from a fused bath the point of fusion of which is at least 100° C. lower than the melting point of the chromium, said bath containing a borate and a compound of chromium.

4. A process for the production of solid, adherent metallic coatings containing chromium and boron which comprises electrically depositing the chromium at a temperature below the melting point thereof from a fused bath the point of fusion of which is at least 100° C. lower than the melting point of the

chromium, said bath containing a borate and a compound of chromium.

5. A process for the production of solid, adherent metallic coatings containing chromium which comprises electrolytically depositing the chromium at a temperature below the melting point thereof from a fused bath comprising a borate and a compound of chromium.

6. A process for the production of solid, adherent metallic coatings containing chromium which comprises electrolytically depositing the chromium at a temperature below the melting point thereof from a fused bath comprising a borate, an alkaline earth metal salt, and a compound of chromium.

7. A process for the production of solid, adherent metallic coatings containing chromium which comprises electrolytically depositing the chromium from a fused bath comprising a borate and a compound of chromium and during said deposition periodically varying the current density.

8. A process for the production of solid, adherent metallic coatings containing chromium which comprises electrolytically depositing the chromium from a fused bath comprising a borate and a compound of chromium and during said deposition periodically varying the current density by the superposition of an alternating current.

9. A process for the production of solid, adherent metallic coatings containing chromium which comprises electrolytically depositing the chromium at a temperature below the melting point thereof from a fused bath containing at least one borate, and chromium oxide.

In testimony whereof we affix our signatures.

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