Patented June 10, 1924. 1,497,417

UNITED STATES PATENT OFFICE.

HENRY C. P. WEBER, OF EDGEWOOD PARK, PENNSYLVANIA.

PROCESS OF COATING METALS.

No Drawing. Original application filed March 31, 1919, Serial No. 286,415. Divided and this application filed March 31, 1920. Serial No. 370,237.

To all whom it may concern:

Be it known that I, HENRY C. P. WEBER, a citizen of the United States, and a resident of Edgewood Park, in the county of Allegheny and State of Pennsylvania, have invented a new and useful Improvement in Processes of Coating Metals, of which the following is a specification, this application being a division of my application Serial No. 286,415, filed Mar. 31, 1919, now Patent No. 1,373,038.

My invention relates to a process of applying metallic coatings and it has, for its primary object, the provision of a process by means of which it is possible to employ, as coating metals, numerous metals which previously it has been impossible to employ satisfactorily for such purpose. Although my process may be utilized for applying metallic coatings to various metals, it is particularly useful for applying coatings to iron, steel and other ferrous metals.

Heretofore, it has been commercially impossible to provide ferrous alloys with metallic coatings of metals which are reducible only with great difficulty, such as chromium, tungsten, molybdenum, uranium, titanium, columbium, zirconium, cerium, thorium, vanadium, beryllium and the like.

One object of my invention, therefore, resides in the provision of a process by which uniform coatings may be readily obtained, not only by means of the above mentioned metals, but also by means of the more readily reducible metals.

I am aware that certain electrochemical processes have been utilized for providing metallic coatings for certain metals upon certain other metals. The success with which the metal may be deposited depends upon the position of the metal in the electrochemical series. The electropositive metals, such as silver, gold and nickel are deposited without difficulty. The more electropositive metals, such, for example, as sodium, cannot be deposited because they immediately react with the liquids utilized in electrolysis, while the less positive metals, such, for instance, as those above mentioned, do not form adherent or coherent coats even from fused electrolytes. As will be later pointed out, my process is not limited in any such manner, being entirely independent of the relative positions of the utilized metals in the electrochemical series. For example, I may cause the replacement of a more positive metal by a less positive metal.

In fact, my improved process differs fundamentally from any of the prior processes because it does not depend upon a reaction between a liquid (fused solid) and a solid or between two liquids (fused solids), nor does it depend essentially upon the heats of formation of the substances or compounds participating in the reaction, nor upon the positions in the electrochemical series of the metals concerned.

The reaction upon which my process depends is that between a vapor, which is a compound of the metal being reduced and another metal in a solid condition which is, itself, capable of being converted, in part, at least, into a volatile compound during the process. The availability of my process for coating one metal with another, or with an alloy of other metals, depends chiefly upon the relative volatilities of the gaseous compounds originally present, or produced, and those formed during the reaction. It is, also, in part, dependent upon the relative quantities of the volatile compounds and, in part, upon the duration of the reaction, both of these conditions being readily controllable.

Broadly speaking, my invention comprehends the heating of the metal to be coated to a suitable temperature below its melting point, in the presence of a vapor or gas of a compound of the metal which is to form the coat. Obviously, various metals may be coated and any one of various salts of numerous metals may be employed as the coating agent. It is essential, however, that the metal compound employed as the coating agent shall be at least slightly volatile and that the metal to be coated shall be capable of combining with the volatilized compound to replace the molecules of metal contained therein with the formation of a second volatile compound, which should preferably be more volatile than the first. Furthermore, it is advisable to exclude all oxygen or oxide-forming material during the process which should, therefore, either be performed in a partial vacuum or in the presence of an inert gas, such as nitrogen, or in the presence of a reducing gas.

Although, as will be later pointed out, my process is susceptible of general application, it may well be illustrated by certain specific

examples. I will, therefore, explain the practicing of my process for producing a chromium coating upon another metal such, for example, as iron.

More specifically, my invention comprises the reduction of a halide by a metal also forming a volatile halide. By this, I mean to include all halogen compounds, mixed halides, and also what, for the purpose of my present process, are their equivalents; namely, cyanides and carbonyls of any metal, alloy or metalloid capable of forming halogen compounds.

When a coating of chromium on iron or a ferrous alloy is to be formed, the article upon which the chromium is to be deposited may be first cleaned and dried in any suitable and well known manner and it may then be placed in a receptacle to be evacuated. While in the receptacle, it may be covered with a layer of chromium chloride, after which the receptacle may be evacuated and gradually heated. By a chemical interaction, according to the general formula, $A+BCl_n=ACl_n+B$, in which A is the metal being coated and B is the chromium or other metal forming the coat, the chromium is deposited upon the ferrous article while ferric chloride is driven off.

The depth of the coating may be regulated by properly controlling the temperature and the length of time during which the reaction is permitted to proceed. For example, I have found that chromium coatings of about 0.2 mm. in depth may be obtained by heating to approximately 1000° C. while coatings of above 0.35 mm. in depth may be obtained by heating to substantially 1200° C. The heating should be continued for a number of hours, although, after a certain length of time, the thickness of the coating cannot be further appreciably increased in a reasonable period of time without increasing the temperature. At the temperatures above indicated, I have found it advisable to heat the receptacle and enclosed agents for approximately five hours.

The process may be started at room temperature and completed at a higher temperature, as seems desirable.

While it is preferable to perform the process in a vacuum in order to insure the removal of the ferrous chloride produced from the vicinity of the ferrous body being coated and to thus facilitate and hasten the reaction and to also prevent any possible oxidization, it is not absolutely essential that the vacuum be maintained. For example, I may practice my process in the presence of an inert gas, such as nitrogen, or in the presence of a reducing gas.

I am well aware that processes, such as sherardizing, have been devised in which the metal (zinc) to be applied as the coating is sufficiently volatile and may be made to diffuse directly into other metals, or may be reduced from its oxide by more electropositive metals. Such processes, however, cannot be applied to the formation of coatings of chromium. In my process, the reaction is driven by the relative volatility of the chloride or other halides and their quantity and not by the relative electrical potentials or by heats of formation of the oxides. Being, in fact, a gas reaction, the production of the desired coating is bound to occur, to a certain extent, at least, the extent and direction of the reaction depending upon the relative concentrations of the halide in which the metal is heated and of the halide produced by the reaction. It is thus possible to plate or coat a more positive metal, such as chromium, upon a less positive one, such as iron, or even nickel.

I do not limit myself to the employment of chlorides in practising my process since I have obtained similar results with other halogens, carbonyl compounds and various volatile metal salts in general. Furthermore, while I have employed chromium as a specific example of the metal forming the coating, my process is applicable to numerous other metals which form volatile halogen compounds, such as molybdenum, tungsten, columbium, tantalum, cobalt, nickel and the like, or to volatile mixtures of these compounds if it is desired to obtain a coating in the nature of an alloy.

A chromium coating upon a ferrous metal obtained by the above described process is highly resistant to oxidization both at normal temperatures and at relatively high temperatures. The coating has a bright silvery color, is very hard and assumes a high polish. It is extremely resistant to atmospheric corrosion, either moist or dry, and concentrated nitric and sulphuric acids do not attack it readily, nor do dilute nitric or hydrochloric acids affect it. Iron, coated with chromium, according to my process, resisted oxidization at 1000°C. for five hours in the air with only the formation of a very slight coating of chromium oxide. The coating actually alloys with the iron and is very tenacious. For example, a chromium-coated iron rod may be bent at right angles without breaking the coating, or it may be elongated by as much as 100%, by any of the usual methods, before cracking occurs. For this reason, coated articles may be readily rolled, swaged or otherwise worked without injury to the coating.

From the foregoing explanation, it will be appreciated that my process is general and may be utilized for the production of coatings of any of the metals previously designated; that is, metals capable of forming volatile compounds upon any metals capable of combining with such compounds to produce metallic halides. In other words, the

reducing agent need not be iron but may be any metallic substance capable of forming a volatile compound during the reaction such, for instance, as tin, zinc, lead and the like which act as catalyzers. Furthermore, coatings in the nature of alloys may be provided by heating the metal to be coated in the presence of a mixture of halides of the desired metals.

It is not essential to the process that the volatile substance or compound from which the metal to provide the coating is to be produced, or deposited, be originally present at the start of the process. For example, the chromium chloride may be produced during the process by any of the well known methods of forming it and it will immediately react to provide a coating of such metal.

Furthermore, the process may be made continuous, if desired. In fact, the process possesses all of the desirable features fully pointed out in a copending application filed by me March 31, 1919, Serial No. 286,415, of which this application is a division. I reserve the right, therefore, to make any changes in the practice of my process or in the apparatus employed therein which may come within the scope of my invention as set forth, either in the original application above referred to or in this application, and my invention is to be limited only as indicated by the appended claims.

I claim as my invention:—

1. The process of coating metals or metalloids that comprises heating the metal or metalloid to be coated in a vacuum with a vaporizable compound of the metal or metalloid which is to form the coating.

2. The process of coating metals or metalloids that comprises heating the metal or metalloid to be coated at a temperature below the melting point of the metal or metalloid to be applied in a vacuum with a vapor of a compound of the metal or metalloid which is to form the coating.

3. The process of coating metals that comprises disposing the metal to be coated in a receptacle, creating a vacuum in the receptacle, depositing a quantity of a chloride of the metal which is to form the coating upon the metal and applying heat thereto.

4. The process of coating metals or metalloids that comprises heating the metal or metalloid to be coated in the presence of a powder consisting of a compound of the metal or metalloid which is to form the coating at such temperature that a vapor is formed and the coating is deposited by chemical interaction of the vapor with the metal or metalloid to be coated.

5. The process of coating metals that comprises disposing the metal to be coated in intimate relation with a powder consisting of a volatile compound of the metal to be deposited and raising the temperature until the powder interacts with the metal to be coated and a second volatile compound is formed which may subsequently be removed.

6. The process of coating metals that comprises disposing the metal to be coated in intimate relation with a powder consisting of a volatile halogen compound of the metal to be deposited and applying heat until the powder interacts with the metal to be coated and a second volatile compound is formed which may subsequently be removed.

7. The process of coating metals or metalloids that comprises effecting the chemical interaction with the metal or metalloid to be coated of a sublimable compound of a metal or metalloid which is to form the coating.

8. The process of coating a metal or metalloid that comprises effecting the chemical interaction with the metal or metalloid to be coated of a sublimable compound of a metal or metalloid and producing a second sublimable compound with the metal or metalloid to be coated.

9. The process of coating metals that comprises effecting the chemical interaction with the metal to be coated of a plurality of powders comprising volatile compounds of metals which are to form the coating.

10. The process of coating metals and metalloids that comprises forming a vapor compound of the metal to be deposited and reducing such vapor compound by another metallic substance to be coated capable of also forming a volatile compound during the reaction.

11. The process of coating metals and metalloids that comprises forming a vapor compound of the metal to be deposited and heating the vapor compound in contact with a metal to be coated which is capable of also forming a volatile compound and thereby reducing the metal of the first named vapor compound.

In testimony whereof, I have hereunto subscribed my name this 24th day of March 1920.

HENRY C. P. WEBER.