

# UNITED STATES PATENT OFFICE.

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## IMPROVEMENT IN THE ELECTRO-DEPOSITION OF NICKEL.

Specification forming part of Letters Patent No. **93,157**, dated August 3, 1869.

### *To all whom it may concern:*

Be it known that I, ISAAC ADAMS, JR., of Boston, in the State of Massachusetts, have invented or discovered certain new and useful Improvements in the Electro-Deposition of Nickel, of which the following is a specification.

It has long been well known that nickel possesses certain qualities which would render it of great value in the arts if it could be readily and surely deposited by the battery in such a manner as to make these qualities available. These qualities are, first, its infusibility; second, its color, which is nearly that of silver; third, its hardness, which is nearly equal to that of steel, and by reason of which it resists wear and abrasion to a much greater degree than silver; fourth, its power of resisting oxidation and the tarnishing and corrosive effects of many gases and liquids.

The two last-named qualities render it for many purposes greatly superior to silver, which it much resembles in appearance, for electroplating other metals, and for making articles of solid metal. To these advantages should be added its cheapness as compared with silver.

It has long been known that nickel could be deposited from certain solutions by electricity; but the character of the deposits has been such that the valuable qualities of the metal could not be secured to such an extent as to render it practically useful for general purposes.

The difficulties in the way of its deposition have arisen mainly from the character of the solutions employed and the nature of the nickel used for anodes in the depositing-cell.

I have discovered the causes of certain difficulties in the practical deposition of this metal, and am able to remove them and to point out methods of preparing solutions and the conditions which they must satisfy and under which they must be used, so that solid coherent tenacious and flexible nickel can be deposited to any desired amount. I can thus render the electro-deposition of nickel practically valuable not only for electroplating other metals, but for that branch of the art of electro-deposition known as "electrotyping"—that is, the deposition of nickel upon a surface not to remain upon it as a permanent coating, but to be removed and used independently of it.

My improvements relate, first, to the method of preparing certain solutions from which the nickel is to be deposited and to the properties and conditions which such solutions must possess; second, to a method of preparing nickel plates for the anode of the depositing-cell; third, to the character of the deposits obtained.

In order to explain fully the nature of my invention, it is necessary to refer to certain facts relating to the electro-deposition of metals generally which have been long known.

It is well known that metals are deposited in three conditions—viz., first, as a black powder; second, in a state called "reguline metal"—that is, in a condition which exhibits the ordinary qualities of the metal; third, in a hard crystalline condition.

For most purposes in the arts it is necessary that the metals should be deposited in the reguline state, the applications which are made of the powdery or crystalline deposits being very few.

There are two applications of the art of electro-deposition which are usually recognized as two distinct branches of the art, and which embrace nearly all its practical uses. One is called "electroplating," and consists in depositing a coating of one metal upon another metal to remain upon it as a permanent coating. The other application is called "electrotyping," and consists in depositing one metal upon another, or upon a prepared surface of some other substance, from which it is to be removed to be used separately from the surface upon which the deposit is made. For each of these purposes the metal must be deposited in the reguline state.

It has long been known that the metals differ greatly in the facility with which they can be deposited by the electric current, especially in the reguline form. So, also, different solutions of the same metal differ greatly in respect to the deposits which may be obtained from them. With some solutions it is difficult, if not impossible, to obtain a deposit of reguline metal under any circumstances. The difficulty seems in some cases to be inherent in the character of the solution itself. In other cases it is due to the presence of foreign elements, or to the density or temperature of the solution, or to the density of the current employed.

Different solutions also differ greatly in the amount of metal which can be deposited with

a given strength of current. Some solutions give a deposit of metal which is the full chemical equivalent of the electricity passing through the solution, while others fall far below it. Solutions also differ within wide limits in respect to the intensity and density of the current required to give a reguline deposit. The differences in solution in these respects are of great importance with reference to the cost of depositing the metals. The higher the intensity required to effect the deposition of the metal the greater the cost, and it is obvious that the cost of the deposit will increase in proportion as it falls short of the full amount due to the electricity passing through the solution.

Another circumstance is of great importance in the depositing of metals. It often happens that a thin film may be obtained of one metal upon another, but that the process of deposition cannot be carried on to such an extent as to obtain a coating of any appreciable thickness. As soon as the metal to be coated has received a mere film, the conditions are so changed that the deposit is practically stopped.

A characteristic of this filmy deposit is that, though the particles of the metal adhere separately to the metal on which the deposit is made, the deposit is so thin that the particles of the deposit have no such coherence among themselves as will allow the deposit to be removed from the surface on which it is deposited, nor will such a deposit afford any substantial protection against abrasion in the ordinary wear to which most plated articles are subjected, or to the action of corrosive agents. It is obvious, therefore, that it is impossible to make electrotype-plates from such deposits, and that such deposits are practically useless for most purposes to which electroplating, is applied.

Although it has long been known that nickel could be deposited to some extent from various solutions, yet I believe that prior to my improvements it has not been practicable to obtain deposits of such character and thickness as are required for electrotyping or even for most of the purposes of electroplating.

The solutions from which nickel has been heretofore most successfully deposited are, I believe, the chloride of nickel, the cyanide of nickel and potassium, the double sulphate of nickel and ammonia, and the double chloride of nickel and ammonium. Of these solutions as heretofore prepared I believe the chloride is the best; but the deposits obtained from it are very far from what are required for the general purposes to which the electro-deposition of metal may be applied.

As this solution is ordinarily prepared, it is a good conductor of electricity as compared with most liquids, and the nickel is deposited from it freely, but in a spongy, brittle condition, and more or less mixed with the peroxide of nickel, which gives it a brownish appearance. The deposit has also a great tendency

to accumulate on the edges of the plate on which it is made in nodules or warty protuberances. Therefore, although the deposits may be obtained of considerable thickness, they are practically useless for electrotyping or electroplating. Moreover, a portion of the electricity is expended in forming a subchloride of nickel, which falls to the bottom of the vessel as an insoluble precipitate. In consequence of this the solution is soon exhausted both of nickel and chlorine and the process of deposition stops. Even when this solution is formed in the best-known manner by subliming a pure nickel chloride, the deposited metal, though free from the oxide, and therefore white, is deposited in the brittle warty condition, accompanied with the precipitation of the subchloride.

The double cyanide of nickel and potassium is a poor conductor of electricity, and requires a high battery-power. With a low battery-power very little metal can be deposited, and that little is accompanied with the deposition of peroxide of nickel to such an extent as to be black or nearly black. With a high battery-power a film of white nickel may be obtained, but not thick enough to satisfy the ordinary requirements of electroplating. Neither of these solutions, so far as I have seen them used, gives for any great length of time the full equivalent of metal for the electricity employed, and so far as I have been able to discover these two solutions are inherently incapable of giving a coherent tenacious flexible metal such as is required in the arts for electrotyping and electroplating.

Of the other two solutions named I believe that before my improvements the best results were obtained from the double chloride of nickel and ammonium; but the metal deposited from it is of such a character as to be worthless when deposited to any appreciable thickness. It is accompanied with the deposit of peroxide, and is therefore black or brown. It is extremely liable to split up into thin scales, which may be rubbed off even with the hand. This want of coherence and tenacity unfits it for the requirements of the arts. The metal deposited from the double sulphate of nickel and ammonia is substantially the same as the above, but it is not so easily obtained. If with these solutions a battery-power is used of an intensity of two Grove cells, or thereabout, a white deposit may be obtained of considerable thickness, but still with such a tendency to split up in scales that it is practically useless, and neither solution gives the full equivalent due to the current. I have discovered, however, that the difficulties attending the use of these last-named solutions and the character of their deposits are not inherent in the nature of the solutions, but are due to the modes of preparing them, or to the presence in minute quantities of certain substance, which are generally, and, I believe, universally, employed in making them, or in the reduction of the nickel used in making them.

In order, therefore, to prepare these solutions in such a manner as to give the results I have reached, it is necessary to adopt processes in their preparation and observe precautions which shall either dispense with the use of these substances altogether or shall effectually remove them if they are employed, and which are wholly unnecessary in their preparation for any other use with which I am acquainted.

In preparing my solution I prefer to use pure nickel; but commercial nickel may be used. Commercial nickel almost always contains more or less of the reagents employed in the purification or manufacture of the metal, such as sulphate of lime, sulphide of calcium, sulphide of sodium or potassium, chloride of sodium, and alumina. When any of these substances are present, it is necessary to remove them. This can be done by melting the nickel or by boiling it in water containing at least one per cent. of hydrochloric acid.

The boilings must be repeated with fresh acid and water until the wash-waters give no indication of the presence of lime when treated with oxalate of ammonia.

When the metal is purified by melting, the foreign substances collect on the top of the melted nickel in the form of a slag, which can be removed mechanically.

If the nickel contains zinc, it should be melted in order to volatilize the zinc and drive it off.

The crucible in such case must not be closed so tightly as to prevent the escape of the zinc fumes.

If copper, arsenic, or antimony is present in the nickel, it can be removed after the nickel is dissolved by passing sulphureted hydrogen through the solution.

The acid to be used in dissolving the metal consists of one part strong nitric acid, six parts muriatic acid, and one part water.

Nitric acid or muriatic acid may be used separately; but the above mixture is preferred. A quantity of this acid is taken sufficient to dissolve any given amount of the metal with as little excess of the former as possible. A gentle heat is all that is required. The resulting solution is then filtered, and to prepare the solution of the double sulphate of nickel and ammonia a quantity of strong sulphuric acid sufficient to convert all the metal into sulphate is added, and the solution is then evaporated to dryness. The mass is then again dissolved in water and a much smaller quantity than before of sulphuric acid is added, and the whole again evaporated to dryness, the temperature being raised finally to a point not to exceed 650° Fahrenheit. This temperature is to be sustained until no more vapors of sulphuric acid can be detected. The resulting sulphate of nickel is pulverized and thoroughly mixed with about one-fiftieth ( $\frac{1}{50}$ ) of its weight of carbonate of ammonia,

and the mass again subjected to a gradually-increasing temperature, not to exceed 650° Fahrenheit, until the carbonate of ammonia is entirely volatilized.

If any iron is present, the most of it will be converted into an insoluble salt, which may be removed by filtration. The resulting dry and neutral sulphate of nickel is then dissolved in water by boiling, and if any insoluble residue remains the solution is filtered.

From the weight of the nickel used before solution the amount of sulphuric acid in the dry sulphate can be calculated. This amount of sulphuric acid is weighed out, diluted with four times its weight of water, and saturated with pure ammonia or carbonate of ammonia. I prefer the former. This solution, if it is at all alkaline, should be evaporated until it becomes neutral to test-paper.

The sulphate of ammonia of commerce may likewise be used; but pure sulphate of ammonia is to be preferred. The two solutions of the sulphate of nickel and sulphate of ammonia are then united and diluted with sufficient water to leave one and a half to two ounces of nickel to each gallon of solution and the solution is ready for use.

The object of twice evaporating to dryness and raising the temperature to so high a degree is, in the first place, to drive off the excess of sulphuric acid, and, secondly, to convert the sulphate of iron, if it exists, into basic sulphate, which is quite insoluble in water.

In order to give the best results, it is necessary that the solution should be as nearly neutral as possible, and it should in no case be acid. I prefer to use the solution of a specific gravity of about 1,052°, (water 1,000°,) though a much weaker or a still stronger solution may be used.

At temperatures above the ordinary the solution still gives good results, but is liable to be slowly decomposed.

An excess of sulphate of ammonia may be used to dilute the solution in cases where it is desirable to have it contain much less than an ounce of nickel to the gallon.

In preparing the solution of the double chloride of nickel and ammonium the nickel is to be purified and dissolved in the same manner as is described for the previous solution; and it is to be freed from copper and other foreign matters in the same manner. The solution is then to be evaporated to dryness. It should be made as nearly anhydrous as possible. The salt is then placed in a retort and heated to a bright-red heat. The salt sublimes and is collected in a suitable receiver, the earthy matter being left behind. The salt thus purified is dissolved in water, and to the solution is added an equivalent quantity of pure chloride of ammonium. The solution is then ready for use. It may have a specific gravity of 1,050° to 1,100°.

Of these two solutions I much prefer the double sulphate, as it gives a softer metal,

which can be polished or otherwise worked more readily than that obtained from the double-chloride solution.

The double-sulphate solution has this important advantage over any other solution with which I am acquainted, that it gives a deposit with a smooth surface which can be polished with comparatively little labor.

When the process is properly conducted, the deposit can be made much thicker than is ordinarily required for plating other metals before it acquires a rough or matted surface. With a metal so hard as nickel this is a matter of great importance.

Another important part of my invention is the preparation of the nickel plates to be used as anodes in the depositing-cells. Almost all commercial nickel contains more or less copper, zinc, and arsenic, and the complete removal of all these metals would be a matter of great difficulty and expense, and yet it is necessary to remove them or in some way counteract or neutralize their influence. When these metals are present, they are to some extent deposited with the nickel and seriously affect the character of the deposited nickel. Copper impairs its color and has a tendency to produce a gray hard deposit, less tenacious and coherent than pure nickel, more easily tarnished, and hard to polish. A very small amount of arsenic makes the nickel tarnish readily in the air. Zinc affects the deposited metal in much the same way as copper, and it also tends to cause the evolution of hydrogen at the cathode or negative pole, and thus interferes with the deposition of the nickel.

I have discovered that in my improved solutions the depositions of copper and arsenic when present with the nickel may be effectually prevented by combining iron with the nickel. The iron itself is almost wholly precipitated as a peroxide, and is not deposited with the nickel to a sufficient extent to injure the character of the deposit; neither does it injuriously affect the solution.

The effect of the iron upon the copper is either to prevent it from being dissolved, or, if dissolved, to immediately reduce it upon the anode, where it forms a coating which may be removed from time to time by scraping. The arsenic forms an insoluble precipitate with the persalt of iron. The amount of iron which should be combined with the nickel will vary with the amount of copper and arsenic present, and should be as nearly as possible the chemical equivalent of the amount present of those metals. It can be combined with the nickel by introducing the proper quantity in small fragments into the crucible in which the nickel is melted. Sometimes commercial nickel has sufficient iron present to counteract the influence of the copper and arsenic.

When copper and zinc are present to any considerable extent in nickel, it may be melted in a crucible and cast into plates for anodes without any serious difficulty, as it then melts at a temperature not much greater than the

melting-point of cast-iron. The presence of cast-iron also facilitates the melting of nickel. Pure nickel is very hard to melt; but it may be melted without much difficulty by introducing into the crucible carbon in a finely-divided state, or silica, or both, in the manner described in a patent granted to me May 25, 1869, and the presence of these substances in the nickel does not injure the solution. It is necessary to melt commercial nickel not only to cast it into plates for anodes and combine it with iron when copper and arsenic are present, but to remove any potash, soda, lime, or alumina left adhering to it in the process of eduction, these substances being removed, as before stated, as slag. When zinc is present, it will be removed to a great extent in the process of melting by volatilization unless the melting be done in a tight vessel.

Having prepared the solutions and anodes as herein described, nickel may be readily deposited; but in order to carry on the deposition continuously it is necessary to observe certain precautions.

First. The use of a battery of too high an intensity must be avoided. An intensity of two Smee cells is sufficient. A high intensity decomposes the solution and liberates free ammonia, thus rendering the solution alkaline and impairing its value. Whenever the smell of free ammonia arises from the decomposing-cell, the operator may be certain that the solution is being injured. It is important that the depositing shall not be forced by the use of too strong a current.

Second. It is important that great precautions should be used to prevent the introduction into the solution of even minute quantities of potash, soda, or nitric acid. When an article to be coated is cleaned in acid or alkaline water, or is introduced into it for any purpose, the greatest care must be taken to remove all traces of these substances before the article is introduced to the nickel solution, as the introduction of the most minute quantities of acids or alkalis will surely be injurious. It is important that the solution be kept free from all foreign substances; but its purity from those above named is especially important.

Third. The anode of the depositing-cell should present a surface to the action of the solution somewhat larger than the surface upon which the deposit is being made, particularly in the double-sulphate solution. The reason is that nickel dissolves so slowly that if the exposed surface is not larger than the surface on which the deposit is made the solution will not keep saturated. On the other hand, if the anode is very much larger than the positive pole, it tends to give a deposit of black powder.

Fourth. If zinc is to be coated, it should first be coated with copper, as it is difficult to make nickel adhere to zinc, and there is danger that the zinc may be acted on and injure the solution.

With solutions and anodes thus prepared and used the deposition of nickel can be carried on continuously and almost as surely and certainly as the deposition of copper from the common sulphate solution, though the limits of the battery-power which may be used are narrower.

The metal deposited is compact, cohesive, and tenacious. It may be deposited of nearly uniform thickness over any surface, however large. The deposited metal is capable of being annealed by a heat below a low-red heat. It then becomes flexible, malleable, and ductile. The deposit may be made of any required thickness, either to furnish effectual protection to the metal on which it is deposited, or to be removed and used separately from the surface on which it may be deposited. Thus electrotype-plates of nickel may be produced either as copies of irregular surfaces which it is desired to reproduce, or as plane sheets of nickel, which, after being annealed, may be rolled, hammered, or spun into a variety of forms or articles.

The solutions also give the full equivalent of nickel for the electricity employed. I believe deposits possessing these qualities were never produced except by means of my improvements.

I therefore claim—

1. The electro-deposition of nickel by means of a solution of the double sulphate of nickel

and ammonia, or a solution of the double chloride of nickel and ammonium, prepared and used in such a manner as to be free from the presence of potash, soda, alumina, lime, or nitric acid, or from any acid or alkaline reaction.

2. The use, for the anode of a depositing-cell, of nickel combined with iron to prevent the copper and arsenic which may be present from being deposited with the nickel or from injuring the solution.

3. The methods herein described for preparing the solution of the double sulphate of nickel and ammonia and the double chloride of nickel and ammonia.

4. The electroplating of metals with a coating of compact, coherent, tenacious, flexible nickel of sufficient thickness to protect the metal upon which the deposit is made from the action of corrosive agents with which the article may be brought in contact.

5. The deposition of electrotype-plates of nickel to be removed from the surface on which the deposit is made and used separately therefrom.

The above specification of my said invention signed and witnessed at Boston this 2d day of July, A. D. 1869.

ISAAC ADAMS, JR.

Witnesses:

CHAUNCEY SMITH,  
WILLIAM W. SWAN.