

## UNITED STATES PATENT OFFICE

2,430,581

## METALLIZING NONMETALLIC BODIES

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No Drawing. Application November 29, 1944,  
Serial No. 565,815

14 Claims. (Cl. 117-65)

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This invention relates to a method of metallizing non-metallic bodies, and more particularly to a method of chemically depositing metallic nickel, metallic cobalt or mixtures of these two metals on non-conductive surfaces whereby to provide firmly adherent, hard, tarnish resisting metallic films having good electrical conductivity.

In the metallization of non-metallic bodies, it has been customary, in the past, to first produce a metallic film thereon by one of several methods, such as evaporation, metal spraying or chemical deposition. The last named method has often been preferred because of the ease with which a large variety of non-metallic bodies can be metallized thereby. However, for all practical purposes, only silver has been used for such chemical deposition. Several methods of producing such silver films are available, among these being the Brashear method, the Rochelle Formula method, etc. These are all based on chemical reduction from an ammoniacal silver solution and are subject to certain shortcomings which are more or less common to all of them. For example, the solutions are light-sensitive and their performance is easily affected by the presence of certain impurities such as chlorides. Under certain conditions, they are prone to produce deposits of a silver-nitrogen compound which has explosive characteristics. The solutions cannot be stored indefinitely and, if stored at all, this must be done in cool, light protected places.

Other disadvantages pertain to the silver films produced by these methods. For one thing, the film is soft and does not show much resistance against abrasion. It is subject to tarnish which is particularly serious in an atmosphere containing sulphur compounds. This tarnish is often sufficiently heavy to offset the advantage of high electric conductivity which the films possess initially. Finally, under certain conditions, the silver film is subject to a form of dendritic growth which is particularly harmful in the case of quartz plate oscillators which are silver-plated by chemical deposition.

Films of other metals, particularly gold, copper, and the platinum metals, have also been produced by chemical reduction. In the case of copper, the tarnishing characteristics are even more pronounced than with silver, while gold is even softer than silver and the platinum metals. In any case, the depositions of the latter metals by chemical reduction to provide satisfactory films is a very expensive process.

I have found that satisfactory films consisting of metallic nickel, metallic cobalt, or mixtures

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of these two metals can be produced by chemical reduction and applied to non-metallic bodies or surfaces in a very effective manner and that the films produced according to my present invention will not only adhere firmly to such bodies or surfaces but will be hard and tarnish resistant and will have very good electrical conductivity. The process of my present invention readily lends itself to the chemical deposition of nickel, cobalt, and mixtures thereof on such non-metallic bodies as quartz, glass, ceramics, mica, plastics and the like.

Now, it has been known for some time that metallic nickel or cobalt can be obtained from an aqueous solution of their salts by the reducing action of a hypophosphite. It has also been proposed, heretofore, to reduce nickel and cobalt from salts thereof by hydrazine in the presence of palladium. However, prior art processes involving such reduction have had to be carried out at elevated temperatures, required a considerable period of time, and the deposits formed thereby contained considerable amounts of phosphide. These and other limitations have made the prior art processes of chemically depositing nickel and cobalt entirely impractical.

The primary object of my present invention is to provide an improved method of depositing metallic nickel, cobalt, and/or mixtures thereof upon non-metallic bodies, which method will be entirely free from the aforementioned limitations.

More particularly, it is an object of my present invention to provide an improved method of depositing the aforesaid metals which can be carried out rapidly and at room temperatures.

Another object of my present invention is to provide an improved method as aforesaid which will produce films of metallic nickel, cobalt and/or mixtures thereof which will be low in phosphide content and which will have good electrical conductivity.

Still another object of my present invention is to provide an improved method of depositing the aforesaid metals in a manner which will provide uniform films on the surface of any non-conductive object immersed in the plating solution from which the metal is deposited.

A further object of my present invention is to provide an improved method as aforesaid which will result in films upon which the same or other metals can be electrodeposited with great efficacy.

Still a further object of my present invention is to provide improved coatings of metallic nickel, cobalt and/or mixtures thereof upon non-metallic

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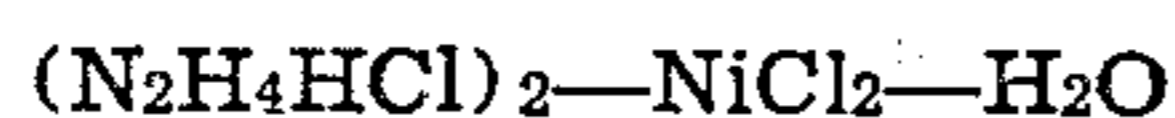
bodies, which coatings will have such properties from the standpoints of adhesion, hardness, tarnish-resistance and electrical conductivity as to render them useful in combination with such non-metallic bodies as piezo-electric quartz crystals, glass, mica, ceramics, plastics and other similar materials whereby to obtain novel forms of electrical and other useful articles, such as quartz plate oscillators, electric capacitors, electric contacts, matrix shells and many other devices.

Another object of my present invention is to provide on non-metallic surfaces adherent metal coatings or films as aforesaid to which solder joints may be readily made by hot-tinning or hot-soldering.

It is also an object of my present invention to provide an improved method of depositing metallic nickel, cobalt and/or mixtures thereof which can be readily carried out with great efficiency even by one not highly skilled in the art, and which is relatively inexpensive to practice.

In accordance with my present invention, I effect the deposition of the nickel, cobalt, or mixtures thereof chemically from a bath containing a hypophosphite, a hydrazine compound, and a noble metal catalyst. The resulting film or coating may be used directly as an electrical conductor or for any other suitable purpose, such as a base for a solder connection, as a base for subsequent electrodeposition of the same or other metals, or for other similar purposes, as may be desired.

The reduction of a nickel or cobalt salt by means of hypophosphite in the presence of a noble metal catalyst takes place rather slowly at room temperature. Hydrazine, too, in the presence of a similar catalyst, has an extremely slow reducing action at room temperature. I have found a surprising acceleration of the reducing action if the solutions, in addition to the catalyst, contain simultaneously a hypophosphite and a hydrazine compound. The acceleration is so great that reduction and film formation occur within a few minutes not only at room temperature, but even at lower temperatures down to the freezing point of the solutions. I have found it to be an advantage to work at such lower temperatures (preferably not exceeding 20° C.) because some film properties, such as adhesion, are improved thereby. I have also found that the films formed in this manner are low in phosphide and have good electric conductivity. Hydrazine, nickel and cobalt form a number of well characterized double salts, such as



$\text{NiSO}_4\text{—}3\text{N}_2\text{H}_4$ ,  $\text{CoCl}_2\cdot 2\text{N}_2\text{H}_4$ ,  $\text{CoSO}_4\text{—}3\text{N}_2\text{H}_4$ , etc. It is likely that the formation of such double salts or addition products contributes to the effect observed. In any case, this effect is very striking.

For instance, if, to the mixture No. 1 given below, 2 drops of a 0.1%  $\text{PdCl}_2$  solution are added, intensive reaction sets in at room temperature after several minutes. After 10 minutes, the reaction is practically completed and the walls of the glass vessel containing the mixture are covered with an opaque, nickel mirror having an electrical resistance of about 300 ohms between two points 1 cm. apart. However, if the hydrazine hydrate is left out of this mixture, the reaction is much slower at room temperature. After 10 minutes, no mirror is obtained but only a very faint dark film having an electrical resistance of the order of  $10^6$  ohms between two similar points.

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If the hypophosphite is left out of this mixture, leaving only the hydrazine hydrate and the  $\text{PdCl}_2$  to react with the nickel acetate, no reaction or film formation whatever is noted after 10 minutes at room temperature.

I have also found that not all nickel salts are reduced with the same rapidity and that there exists a definite influence of the anion upon the reducing action. Thus, the acetate appears to work better than the chloride, and the latter better than the sulphate. However, outstanding performance is obtained in the presence of the formate ion. This may be introduced either by using nickel formate, or by the addition of some other soluble formate, such as sodium formate. Good reduction is also obtained in the presence of ions of a hydroxy acid, other than tartaric acid, such as citric or lactic acid, or of a keto acid, such as levulinic acid. These ions may be introduced by the use of the corresponding nickel or cobalt salts, or by the addition of some soluble salt of these acids.

The electrical conductivity of the films obtained by the reaction depends partly upon the phosphite content of the deposits. The P content may be as high as 13–14%, resulting in relatively poor electrical conductivity. However, films obtained by the method described herein have a much lower P content, this being of the order of 3% or even less. Films of lower P content are obtained by increasing the alkalinity of the solutions, as by the addition of ammonia. However, even better results may be obtained by the use of organic nitrogen-containing bases with at least one C—N bond. Such bases may be of the amine type, such as monoethyl-amine or diethyl-amine; of the heterocyclic type, such as morpholine or pyridine; or of the quaternary ammonium base type, such as tetraethanol ammonium hydroxide or benzyl trimethyl ammonium hydroxide. An additional advantage of introducing such basic substances lies in their surface tension decreasing and detergent action which aids in the formation of more uniform films having improved adhesion.

In a similar manner, benefits may be obtained by the addition of other materials which, while not alkaline in nature, act as solvents or wetting agents. Such materials may be water soluble organic solvents, such as ethyl or methyl alcohol, acetone, dioxane, diethylene glycol, monoethyl ether acetate, acetonyl acetone, propylene oxide, glycol diformate, etc. They may also be high-molecular weight wetting agents, of which a large number are known. Characteristic examples are a sorbitan monolaurate polyoxyalkylene derivative made by the Atlas Powder Co., Wilmington, Del., an aryl alkyl polyether alcohol made by Rohm and Haas Co., Philadelphia, Pa., acetyl dimethyl benzyl ammonium chloride (also manufactured by Rohm and Haas Co.), etc. All of the wetting agents useful for this purpose have at least one chain of not less than 6 C atoms.

The improvements described above apply to the formation of both nickel and cobalt films. In addition, I have been able to obtain films containing both nickel and cobalt with a varying small amount of phosphorus. Metallic films containing both nickel and cobalt have been obtained previously by electrodeposition and such films are distinguished by superior hardness and corrosion resistance. The films obtained by the simultaneous chemical deposition of nickel and cobalt show the same advantages together with some additional ones based upon the extremely

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fine grain of chemically deposited layers and the small phosphide content. These factors are particularly important with respect to adhesion to certain non-metallic surfaces. I have preferred to use equal weight percentages of both nickel and cobalt salt in the reducing solution. However, other relative proportions may be used.

The solutions described may be prepared in any convenient manner and may be stored for considerable periods without deterioration, especially if kept in a refrigerator. However, it is advisable to prepare the hypophosphite solution separately and to add it to the mixture of the other ingredients shortly before the solution is to be used.

In order to start the reaction, addition of an accelerating catalyst is necessary. This catalyst is best chosen from the family of the platinum metals and may consist of a solution of a platinum salt, palladium salt, etc. The concentration of such a solution may be varied over a wide range, the reaction taking place more quickly if higher concentrations are used. I prefer to use a 0.1% solution of palladium chloride in water, of which I add 1 or 2 drops for each 10 cc. of reducing solution used.

The action of the catalyst is presumably due to the reducing action of nascent hydrogen adsorbed on the colloidal palladium. In order to obtain uniform film formation, it is important that the colloidal catalyst remain in contact with the surfaces to be metallized and that it be prevented from precipitating and settling prematurely to the bottom of the reaction vessel. I have found it advantageous to add a protective colloid to the solution of the catalyst. This may be done by adding a small percentage of a colloidal material such as polyvinyl alcohol, methyl cellulose, glue, etc. to the palladium solution. It is also advantageous to keep the solution in motion by mechanical stirring, or to introduce bubbles of air or some other gas while the film formation takes place.

In giving below a number of solutions representing various embodiments of my invention, I wish to emphasize that this invention resides principally in the qualitative composition of the solutions used. The quantitative relation, i. e., percentage of the various ingredients, may be varied over a wide range between extreme dilution and saturation of the solution with any particular ingredient. The actual quantity of the ingredients is thus a matter of choice governed by practical considerations, such as the preferred reaction speed, and by considerations of economy with respect to the cost of the ingredients contained in the spent solution. I have preferred to use solutions of the indicated concentrations, although higher or lower concentrations may be used. The solutions described are intended only as examples and illustrations of the principles of the invention but not as limitations as to quantitative composition. Neither should the description be construed as a limitation excluding the use of compounds of a closely related chemical nature.

The percentages indicated in the following illustrative compositions are based on weight in aqueous solution, while the figures indicate volume parts:

1

1% nickel acetate.....	10
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1

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1% nickel formate.....	10
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1

3

1% nickel levulinate.....	10
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1

4

1% nickel formate.....	10
Concentrated aqua ammonia.....	1
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1

5

1% nickel citrate.....	10
Saturated solution of sodium formate.....	1
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1

6

1% nickel formate.....	10
Saturated solution of sodium hypophosphite..	1
Concentrated aqua ammonia.....	3
Solid hydrazine sulfate.....	5% of total

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1% nickel acetate.....	10
Saturated solution of sodium hypophosphite..	1
85% of hydrazine hydrate.....	1
Methanol.....	3

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1% nickel acetate.....	10
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1
Sorbitan monolaurate polyoxyalkylene derivative.....	2% of total

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1% nickel formate.....	10
85% hydrazine hydrate.....	1
Saturated solution of sodium hypophosphite..	1
42% benzyltrimethyl ammonium hydroxide..	1

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1% cobalt acetate.....	10
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1

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1% cobalt acetate.....	10
Concentrated aqua ammonia.....	1
Saturated solution of sodium hypophosphite..	1
85% hydrazine hydrate.....	1

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1% cobalt acetate.....	10
1% nickel formate.....	10
Saturated solution of sodium hypophosphite..	2
85% hydrazine hydrate.....	2

In order to produce uniform and adhering films, the surfaces to be metallized should be cleaned by methods most suitable in any particular case. Organic solvents, alkaline cleaners, and wetting agents may be used followed by suitable rinsing. After immersing the objects to be metallized in the solution, the reaction is initiated by the addition of the catalyst. If foaming due to hydrogen evolution should be excessive, an antifoam agent, such as a small quantity of octyl alcohol, capryl alcohol, etc., may be added. At a certain stage of the reaction, when the film formation has taken

place and the remainder of the reaction consists primarily in hydrogen evolution, the objects may be removed, washed in water or any other desired medium and dried by any convenient method. On the other hand, if a thicker film is desired than can be obtained by one reaction stage, the bodies may be reimmersed into a second bath directly after removal from the first bath and the procedure repeated. This may be done any desired number of times.

I have also found that such films constitute an excellent electrically conductive base for the subsequent electrodeposition of other metals, such as copper, nickel, silver, gold, etc., and that the combination of such electrodeposited metals with chemically deposited nickel or cobalt possesses novel and meritorious qualities with respect to adhesion, electrical conductivity and other properties.

The films can be readily coated with molten tin, solder, or similar alloys by any of the customary soldering procedures and such a combination provides excellent means of making solder connections with the non-metallic base carrying the film. The hot-tinning operation may be carried out directly on the chemically deposited nickel or cobalt by the use of a special flux, such as an organic phosphate or pyrophosphate (for instance, isopropyl acid pyrophosphate in alcoholic solutions), or the chemically deposited film may be electroplated with an easily solderable metal such as copper, tin, silver, cadmium, etc. and the hot-tinning operation carried out without flux or with the aid of a mild flux, such as rosin. In some cases, particularly if the non-metallic base is heat sensitive, solder alloys of lower melting point, such as those containing lead and bismuth may be used.

The present invention has been utilized with particular success in the formation of metal electrodes on quartz oscillator plates useful in radio circuits. Such electrodes have heretofore been produced by chemically depositing silver films. Such silver films, however, are soft and subject to tarnishing and to a dendritic crystal growth under the influence of an applied D. C. potential tending to produce a short circuit around the edges of the oscillator plate. Nickel or cobalt films deposited by the method described herein were found to possess excellent adhesion to the quartz and to show considerable hardness and resistance against tarnishing. They were free from dendritic growth. Where the film formed in one plating step was of insufficient thickness, two such steps were used successively. Another type of electrode may be produced by first metallizing the oscillator plate with nickel, cobalt or both of these metals by chemical deposition according to the present invention and then applying a layer of electrodeposited nickel.

Another application of the invention lies in the formation of the conductive layers of condensers. The dielectric in this case may be mica, glass, paper, plastic material, ceramic material, etc. In this case, too, the chemically deposited film may be used alone or in combination with a subsequently electrodeposited metal.

Still another application lies in the metallization of materials such as wax, shellac, ethyl cellulose, cellulose acetate, etc. for the purpose of producing matrix shells by subsequent electrodeposition of copper or some other metal and separating the metallic layer from the non-metallic base.

Still another application lies in the metalliza-

tion of plastics such as Bakelite, methacrylate, polystyrene, etc. for the purpose of producing electrically conductive films or optically reflective mirrors. Many such applications in the field of electronics will suggest themselves.

Another application lies in the formation of hermetic seals joining non-metallic bodies, such as glass bushings, to metallic housings. For applications of this type, it is advantageous to heat the metallized body to an elevated temperature, preferably in a protective atmosphere such as hydrogen or nitrogen gas. The metallized glass bushing is heated to a temperature substantially above 100° C. but below the flow point of the glass. After cooling, the metallized layer may be hot-tinned and soldered by the method outlined above.

From the foregoing description, it will be manifest that I have provided not only an improved method of producing films of nickel, cobalt, and mixtures of these two metals by chemical deposition, but also novel combinations of such layers with metallic films produced by other methods and with non-metallic materials. Due to the unique microstructure and composition of the chemically deposited layers, the aforesaid combinations possess novel characteristics unobtained heretofore. It will be evident that many changes, modifications, and combinations of the matter described above can be made on the basis of the facts established, and it is therefore desired that the invention shall not be limited except insofar as is made necessary by the prior art and by the spirit of the appended claims.

What is claimed is:

1. The process of metallizing a non-metallic body which comprises immersing said body in a solution containing a salt of a metal selected from the group consisting of nickel and cobalt, a hypophosphite and a hydrazine compound.

2. The process of metallizing a non-metallic body which comprises immersing said body in a solution containing a salt of a metal selected from the group consisting of nickel and cobalt, a hypophosphite, a hydrazine compound, and a compound of a member of the group of platinum metals.

3. The process of metallizing a non-metallic body which comprises immersing said body in a solution containing a salt of a metal selected from the group consisting of nickel and cobalt, a hypophosphite, a hydrazine compound, ammonia, and a compound of a member of the group of platinum metals.

4. The process of metallizing a non-metallic body which comprises immersing said body in a solution containing a salt of a metal selected from the group consisting of nickel and cobalt, a hypophosphite, a hydrazine compound, an organic base containing a C—N bond, and a compound of a member of the group of platinum metals.

5. The process of metallizing a non-metallic body which comprises immersing said body in a solution containing a salt of a metal selected from the group consisting of nickel and cobalt, a hypophosphite, a hydrazine compound, anions of an acid selected from the group consisting of formic acid, keto acids and hydroxy acids other than tartaric acid, and a compound of a member of the group of platinum metals.

6. The process set forth in claim 1 characterized in that the solution also contains an organic compound selected from the group consisting of water-soluble alcohols, ketones, ethers and esters.

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7. The process of metallizing a non-metallic body with a film containing both nickel and cobalt which comprises immersing said body in a solution containing a nickel salt, a cobalt salt, and a reducing agent comprising a mixture of a hypophosphite and a hydrazine compound.

8. The process of metallizing a non-metallic body with a film containing both nickel and cobalt which comprises immersing said body in a solution containing a nickel salt, a cobalt salt, a hypophosphite, a hydrazine compound and a compound of a metal selected from the group of platinum metals.

9. The process set forth in claim 2 characterized in that said compound is one capable of precipitating out the platinum group metal to provide a colloidal suspension of said metal capable of acting as a catalyst, and characterized further in that said precipitated metal is maintained in suspension by mechanical agitation.

10. The process set forth in claim 2 characterized in that said compound is one capable of precipitating out the platinum group metal to provide a colloidal suspension of said metal capable of acting as a catalyst, and characterized further by the addition of a protective colloid capable of maintaining said platinum group metal in colloidal suspension.

11. The process set forth in claim 2 characterized by the additional step of passing bubbles of an external gas through said solution while said body is immersed therein.

12. The process set forth in claim 2 characterized in that said solution is maintained at a temperature not exceeding 20° C.

13. The process of metallizing a non-metallic

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body which comprises depositing on said body a metallic film by bringing it in contact with a solution containing the salt of a metal selected from the group comprising nickel and cobalt, a reducing agent comprising a mixture of a hydrazine compound and a hypophosphite, removing the metallized body from the solution, and heating said metallized body to a temperature above 100° C. but below the flow point of said body.

14. The process of establishing a solder connection to a non-metallic body which comprises bringing said body into contact with a solution containing the salt of a metal selected from the group comprising nickel and cobalt and a reducing agent comprising a mixture of a hydrazine compound and hypophosphite, maintaining said contact until a metallic film has been formed on said body, and thereafter applying a layer of molten solder to said metallic film.

LEOPOLD PESSEL.

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