June 20, 1950 C. C. MA ET AL 2,512,141

COATING ARTICLES WITH MOLYBDENUM

Filed June 14, 1945

Fig. 1.

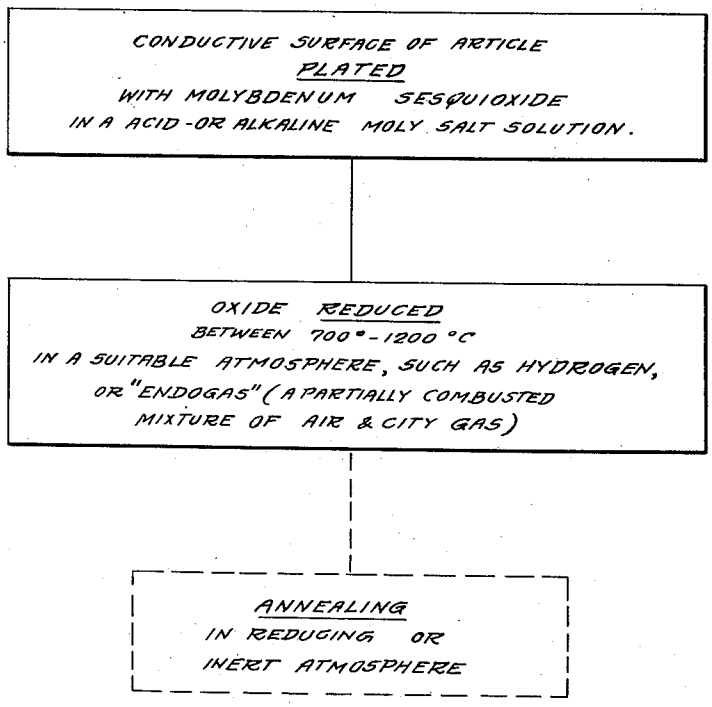
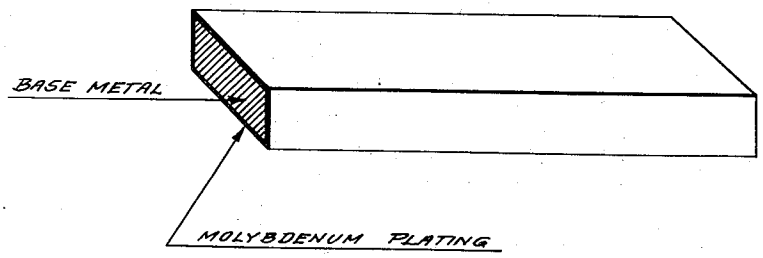


Fig. 2.



INVENTORS
C. C. MA
M. W. OFFINGER.
BY
ATTORNEY

Patented June 20, 1950

2,512,141

UNITED STATES PATENT OFFICE

2,512,141

COATING ARTICLES WITH MOLYBDENUM

Chuk Ching Ma, Orange, N. J., and Martin W. Offinger, Wilton, Conn., assignors to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

Application June 14, 1945, Serial No. 599,332

9 Claims. (Cl. 204—37)

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This invention relates to electroplating and more particularly to such a process for depositing molybdenum on articles formed of base metal.

The principal object of our invention, generally considered, is to deposit molybdenum from aqueous solutions on conductive surfaces of articles.

Another object of our invention is to provide metal articles coated with pure or uncontaminated molybdenum, by first plating hydrated molybdenum sesquioxide from a molybdenum salt solution, and then heating the plated article in a suitable atmosphere to reduce the plating to metallic molybdenum.

A further object of our invention is to provide a process for plating molybdenum throughout a wide range of molybdenum salt concentrations, pH, current densities, and bath temperatures.

A still further object of our invention is to electroplate metal articles with a coating consisting essentially of molybdenum sesquioxide and then reduce to metal said coating in hydrogen, carbon monoxide, or other reducing atmosphere, by heating therein to a temperature of between 700° C. and 1200° C.

An additional object of our invention is to provide a satisfactory bath from which a molybdenum compound may be deposited as a firmly-adherent film on the surface of a metal article.

Other objects and advantages of the invention will become apparent as the description proceeds.

Referring to the drawing:

Fig. 1 is a flow diagram illustrating how our invention may be practiced.

Fig. 2 is a perspective view of a product of our process.

As is generally known, molybdenum is not at room temperatures attacked by hydrochloric acid of almost any strength, dilute hydrofluoric acid, or dilute sulphuric acid. Although inferior to tungsten in hardness and resistance to chemical corrosion, it is superior in ductility and workability. On account of its several valuable characteristics from a standpoint of resistance to chemical corrosion, erosion, and abrasion, molybdenum is useful as a protective coating for base metals.

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It has been attempted to deposit molybdenum from aqueous salt solutions, but because of the chemical reactivity between the nascent molybdenum atoms and those of water, and the relative insolubility and stability of molybdenum sesquioxide, the latter in a hydrated condition ($Mo_2O_3.H_2O$) is deposited on a cathode from an aqueous molybdenum salt solution, rather than metallic molybdenum. We have found that this sesquioxide is deposited not only from alkaline molybdate solutions but also from weakly acid solutions, that is, within a pH range of 4 to 9.

Referring to the drawing in detail, and first considering Fig. 1, it will be seen that the ferrous or other base metal is plated with hydrated molybdenum sesquioxide ($Mo_2O_3.H_2O$) in an acid or alkaline molybdenum salt solution. Examples of such solutions which have been used, and the current employed, as well as the results obtained, are given in the following table:

Solution Used	No. of coatings	Current amps.	Base Metal Plated	Size of plate, inches	Thickness of the plate, inches
15% ammonium molybdate solution	5	2	Nickel	½ x 3	0.004 (approx.).
15% ammonium molybdate solution, modified by acetic acid to pH 5.	5	4	do	½ x 3	0.004 (approx.).
15% sodium molybdate solution	5	5	do	½ x 3	0.003 (approx.).
10% sodium molybdate solution, heated to 70° C. before electrolyzing.	4	5	Copper	1 x 3	0.003 (approx.).
20% sodium molybdate solution	5	5	do	1 x 3	0.003 (approx.).
10% sodium molybdate solution	5	4	Iron	½ x 3	0.003 (approx.).

It will therefore be seen that we may deposit the sesquioxide on almost any usual base metal, except one attacked by the solution used in the plating operation. Usable base metals, therefore, obviously include molybdenum. The solution may be from 10% to 20% of an alkali molybdate, or such solution may be acidulated at least up to pH 5 with a weak acid, such as acetic. We

may also plate the sesquioxide from an acid bath formed by dissolving molybdenum trioxide, say 100 grams, in a weak acid such as perchloric, or sulphuric or hydrochloric, diluted in the proportion of 50 to 75 grams of acid per liter of water, thereby obtaining the perchlorate, the sulphate or the chloride of molybdenum, as the case may be. Strong acid is to be avoided because of its attack on the metal to be plated. The current density, whether the bath be alkaline or acid, to produce an adherent coating is desirably low, that is, between .2 and 1 ampere per sq. inch of cathode surface.

When the surface of the cathode becomes completely coated with the black molybdenum sesquioxide, further plating appears to stop and hydrogen is evolved. This process has been found to take from 10 to 20 minutes depending on the current density employed. Thicker coatings are obtainable by dehydrating and reducing the sesquioxide to metallic molybdenum, by heating to between 700° and 1200° C. in a reducing atmosphere, such as hydrogen, carbon monoxide, water gas, or "Endogas," which is a partially combusted mixture of air and city gas, as defined in the Rennie application, Ser. No. 471,604, filed January 7, 1943, now Patent No. 2,402,084, dated June 11, 1946, before continuing the process.

If a strongly-reducing gas, such as hydrogen, is employed, the temperature for effecting the reduction may be lower, that is, between 700° and 1000° C. than if a more weakly reducing gas, such as "Endogas," is employed in which case a temperature between 1000° and 1200° C. is desirably employed. However, reduction starts to take place at temperatures above 600° C., but the higher the temperature the quicker the reducing action.

If the base metal on which the plating is applied is steel or other carbon-containing material, it is desirable to use a non-decarbonizing atmosphere, such as carbon monoxide, "Endogas," or other reducing atmosphere which is not too rich in hydrogen, as pure hydrogen and high concentrations thereof tend to decarbonize such material by combining with the carbon content thereof and producing hydrocarbons.

After the first oxide plating has been reduced to metal, the process of plating and reduction may be repeated any number of times to build up the plating to the desired thickness. In other words, the sesquioxide may be plated on metallic molybdenum, and if the base metal is all molybdenum the plated or built-up article, including the reduced sesquioxide, may then, of course, be handled like solid molybdenum produced in a customary manner. After the plating has been built up to the desired thickness, the article may, if desired, be annealed in a reducing or inert atmosphere. Fig. 2 illustrates such an article comprising a base metal having a plating of molybdenum on its surface.

From the foregoing disclosure, it will be seen that our invention involves two distinct discoveries, first a method for plating a firmly-adherent coating of molybdenum sesquioxide from an acid or alkaline molybdenum salt solution within a wide range of molybdenum concentrations, hydrogen ion concentrations, current densities, and bath temperatures and, second, how to change this sesquioxide coating to a likewise firmly-adherent coating of metallic molybdenum. Our process results in an adherent coating of molybdenum, and may be practiced using solutions of high conductivities at temperatures between

about 20° and 100° C. If a reducing atmosphere, in which hydrogen not too concentrated, is employed, the base metal is not decarburized.

A general schedule for the production of molybdenum plate would therefore be as follows:

1. Plate molybdenum sesquioxide on the metal or other article having a conductive surface, from an acid or alkaline solution, using a pH between 4 and 12. The temperature of the bath does not seem to matter, provided it is between usual room temperatures and 100° C.

2. The black sesquioxide on the surface is then reduced either in hydrogen between 700° and 1000° C., if there is no fear of decarburation, or in "Endogas" or other more weakly reducing agent between 1000° and 1200° C. The article after reduction is cooled below 100° C. before it is taken from the furnace in order to avoid subsequent reoxidation.

3. Plate another coating by repeating the processes of the preceding paragraphs 1 and 2.

4. Repeat the process of paragraphs 1 and 2 until the desired thickness of molybdenum plate is obtained.

5. Anneal, if desired, in a vacuum, an inert gas, or a reducing gas.

Although a preferred embodiment of our invention has been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

We claim:

1. The method of coating a conductive surface of an article of metal, not attacked by weak acids and alkalis, with metallic molybdenum, comprising forming a 10% to 20% aqueous solution, within a pH range of 4 to 12, of a compound of molybdenum selected from the group consisting of the alkali molybdates and the perchlorate, the sulphate, and the chloride of molybdenum, placing said article in said solution, depositing a plating consisting essentially of molybdenum sesquioxide thereon by making it the cathode, and then heating said plated article to a temperature above 600° C. in a gaseous reducing atmosphere to reduce the plated compound to metallic molybdenum.

2. The method of coating an article of metal, not attacked by weak acids and alkalis, with metallic molybdenum, comprising forming a 10% to 20% aqueous solution, within a pH range of 4 to 12, of a compound of molybdenum selected from the group consisting of the alkali molybdates and the perchlorate, the sulphate, and the chloride of molybdenum, placing said article therein, depositing a plating consisting essentially of molybdenum sesquioxide thereon by making it the cathode, and heating said plated article to a temperature between about 700° and 1200° C. in a gaseous reducing atmosphere to reduce the plating to metallic molybdenum.

3. The method of coating an article of metal, not attacked by weak acids and alkalis, with metallic molybdenum, comprising forming a from 10% to 20% alkali molybdate aqueous solution, within a pH range of 4 to 12, placing said article therein and depositing a plating consisting essentially of molybdenum sesquioxide thereon by passing a current between it as a cathode and an anode in said solution, with a current density between .2 and 1 ampere per sq. in., removing said article from said solution, and heating it to a temperature above 600° C. in a gaseous reducing atmosphere to reduce the plating to metallic molybdenum.

4. The method of coating an article of metal,

not attacked by weak acids and alkalis, with metallic molybdenum, comprising forming a 10% to 20% aqueous solution, within a pH range of 4 to 12, of a compound of molybdenum selected from the group consisting of the alkali molybdates and the perchlorate, the sulphate, and the chloride of molybdenum, placing said article in said solution, and depositing a plating consisting essentially of molybdenum sesquioxide thereon by making it the cathode therein, removing said article, heating it to a temperature above 600° C. in a gaseous reducing atmosphere to reduce the plating to metallic molybdenum, and annealing in a protective atmosphere.

5. The method of coating a carbon-containing article of metal, not attacked by weak acids and alkalis, in which decarburization is undesirable, with metallic molybdenum, comprising forming a 10% to 20% aqueous solution, within a pH range of 4 to 12, of a compound of molybdenum selected from the group consisting of the alkali molybdates and the perchlorate, the sulphate, and the chloride of molybdenum, placing said article in said solution, and depositing a plating of molybdenum sesquioxide thereon by making it the cathode therein, removing said article, heating it to a temperature above 600° C. in a gaseous reducing atmosphere not containing a large enough proportion of hydrogen to decarburize the metal article, to reduce the plating to metallic molybdenum, and annealing in a protective atmosphere to regain the desired properties of the original uncoated article.

6. The method of coating an article of metal, not attacked by weak acids and alkalis, with metallic molybdenum, comprising forming a 10% to 20% alkali molybdate aqueous solution, within a pH range of 4 to 12, placing said article therein, depositing a plating of hydrated molybdenum sesquioxide thereon by making it the cathode, and then heating said plated article to a temperature above 600° C. in a gaseous reducing atmosphere to remove the oxygen from the plating and leave metallic molybdenum.

7. The method of coating an article of metal, not attacked by weak acids and alkalis, with metallic molybdenum, comprising forming a 10% to 20% aqueous solution, within a pH range of 4 to 12, of an alkali molybdate, heating said solution, placing said article therein, depositing a plating of hydrated molybdenum sesquioxide thereon by making it the cathode, removing said article, and heating it to a temperature between about 700° and 1200° C. in a gaseous reducing atmosphere to dehydrate and remove the oxygen from said plating, leaving metallic molybdenum on said article.

8. The method of coating an article of metal, not attacked by weak acids and alkalis, with metallic molybdenum comprising forming a 10% to 20% alkali molybdate aqueous solution, within a pH range of 4 to 12, placing said article therein, depositing a plating consisting of hydrated molybdenum sesquioxide thereon by passing a current between it as a cathode and an anode in said solution, removing said article, and heating it in a hydrogen atmosphere between about 700° and 1000° C. to dehydrate and reduce the plating to metallic molybdenum.

9. The method of coating an article of metal, not attacked by weak acids and alkalis, with metallic molybdenum comprising forming a 10% to 20% alkali molybdate aqueous solution, within a pH range of 4 to 12, placing said article therein, depositing a plating of hydrated molybdenum sesquioxide thereon by causing a current to flow between it as a cathode and an anode in said solution, removing said article, and heating it in a gaseous reducing atmosphere relatively low in hydrogen to a temperature between about 1000° and 1200° C. to dehydrate and reduce the plating to metallic molybdenum.

CHUK CHING MA.
MARTIN WM. OFFINGER.

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