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ELECTROPLATING

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Our invention relates to the deposition of metallic rhenium and particularly to methods of procedure and suitable electrolytic baths for effecting such deposition and to articles of manufacture produced by the practice of our invention.

The element rhenium is a metal which bears the classification No. 75 in the Periodic Table. Unsuccessful efforts have been made heretofore to effect satisfactory electrolytic deposition of metallic rhenium from aqueous solutions and to produce a coating or plating of metal, see for example the articles by H. Holeman in Zeitschrift für Anorganische und Allgemeine Chemie, vol. 202 (1931) pages 277 to 291 and vol. 211 pages 195 to 206. The deposits obtained according to these investigations were altogether unsatisfactory for commercial purposes and were for the most part admixtures of the metal with the metallic oxide. In contrast with the results described in these articles, we have discovered that it is possible to obtain hard, bright, compact deposits of metallic rhenium within a very short period of time upon various metals and conducting surfaces by electrolytic deposition from aqueous solutions containing compounds of rhenium. The deposits produced have been found to be extremely resistant to the action of hydrochloric acid and are very hard, being much harder than rhodium and but little softer than chromium plate. These properties of the plating or deposits render our invention particularly suitable for use in producing hydrochloric acid resisting equipment, jewelry, tools, door handles and various other articles.

We have also discovered that in order to obtain the desired deposit of metallic rhenium the operation should be carried out with particular attention to conditions of operation. The most important factors which appear to influence the results obtained are the hydrogen ion concentration of the bath used, the temperature of the bath and the current density employed. We have discovered that the conditions under which the metal will deposit from various baths also depends upon the chemical composition of the bath and that these conditions may differ considerably when using baths having different chemical characteristics, although the procedure in each case is influenced by the same factors.

It is possible that the concentration of the rhenium compound in ionized form in the bath influences the results obtained. In any event, our work clearly indicates that the failure of previous investigators to control the above factors has largely been responsible for their failure to obtain satisfactory results. However, it is possible, of course, that other features of the procedure hereinafter described may also contribute to the success of the process.

One of the objects of our invention is to effect satisfactory deposition of metallic rhenium from baths containing a rhenium compound.

A further object of our invention is to control the conditions under which deposition of metallic rhenium takes place so as to obtain a deposit which is hard, bright and compact.

Another object of our invention is to produce articles of manufacture such as mirrors, reflectors, hydrochloric and other acid resisting apparatus, jewelry and the like provided with a hard, bright, compact deposit of metallic rhenium thereon.

Another object of our invention is to provide electrolytic baths adapted for use in the deposition of metallic rhenium.

These and other objects and features of our invention will appear from the following description thereof.

In effecting the electrodeposition of metallic rhenium we prefer to employ an aqueous solution of a rhenium compound, such as a rhenium oxide, for instance the heptoxide Re_2O_7 which is the best known of the oxides of rhenium, or potassium perrhenate ($KReO_4$) (also called potassium metaperrhenate) although salts such as the sulfoperrhenate, nitrate, oxalate, phosphate and ammonium perrhenate, or the like may also be used. The amount of rhenium compound in solution may vary considerably and in practice we have used both relatively dilute solutions and those which are substantially saturated with the rhenium compound.

Deposits have been obtained from both acid and alkaline baths as well as from substantially neutral solutions. However, the deposit is produced most satisfactory when the pH value of the bath is maintained within a rather limited range, which range in each case is dependent upon the nature of electrolytes other than the rhenium compound which are present in the bath. For example, when using a sulfate bath the best range for the pH value at temperatures of 25 to 45° C. is about .7 to 1.2. With a phosphate bath the range pH value giving best results is from about 1.7 to 2.3. With an oxalate bath we have obtained excellent results when the pH value is within the limits of about 1.2 to 1.5 and with an alkaline bath containing sodium bicarbonate and ammonium sulfate the preferred range of the pH value is about 9.0 to 7.5.

The ranges indicated above have been determined experimentally and when using other baths it is desirable to determine in a similar manner the limits of the range in pH value which will give the best results before proceeding with the operation.

The temperature of the bath influences to some extent the conditions giving the best results and in general it may be stated that the range of pH value used is higher when the temperature is increased. In the case of a rhenium containing sulfate bath the preferred pH value at 0° C. is about 0.3 to 0.9 while at temperatures of 90 to 100° C. the pH value should be kept within the limits of about 2.3 to 3.0.

The range of the pH value in the case of the phosphate bath varies in the same manner with the temperature but to a more limited extent whereas the range of pH value giving best results with an oxalate bath changes very little with change in temperature. In the case of the alkaline bath referred to above the change in pH value with temperature giving best results is about the same as for the phosphate bath.

In general the current density employed varies somewhat in the same manner as the pH value, being higher at high temperatures of the bath. However, the preferred current density in each case falls within the limits of about 8 to 17 amperes per square decimeter of the cathode surface. When operating with a sulfate bath at temperatures in the neighborhood of 0° C. the current density is preferably from about 8 to 14 amp. per dm^2 while at 80 to 90° C. the preferred current density is about 12 to 16 amperes. Similar, although limited variations may be made in the current density employed when using other baths. The voltage used is usually about 4 volts although higher voltage may, of course, be employed if desired. In this respect the current consumption in accordance with our invention is relatively small as compared with that of the methods described in the literature referred to above.

In order to illustrate typical methods of procedure in accordance with our invention when using various sulfate baths the following examples are cited.

Example 1

Potassium perrhenate ($KReO_4$), 11 grams per liter of solution.
Concentrated sulphuric acid (H_2SO_4) sp. gr. 1.84, 3.5 grams per liter of solution.
pH=0.9.
Temperature, 25° to 45° C. (77–113° F.).
Current density, 10 to 14 amp./dm^2 (92.9–113 amp./sq. ft.).

Example 2

Perrhenic acid ($HReO_4$), 20 grams per liter of solution.
Concentrated sulphuric acid (H_2SO_4) sp. gr. 1.84, 5 grams per liter of solution.
Temperature, 25–30° C. (77–86° F.).
Current density, 10 to 15 amp./dm^2 (92.9–140 amp./sq. ft.).
pH=.7 to 1.2.

Example 3

Potassium perrhenate ($KReO_4$), 10 to 25 grams per liter of solution.
Concentrated sulphuric acid (H_2SO_4) sp. gr. 1.84, 90 grams per liter of solution.
Ammonium hydroxide (of 28% of NH_3 content), 100 c. c.
pH=1.00–0.80.
Temperature, 25 to 45° C. (77–113° F.).
Current density, 10 to 16 amp./dm^2 (92.9–114.8 amp./sq. ft.).

In general we prefer to use a sulphate bath for practical operation due to the ease in handling such baths with standard and well known apparatus. The concentration of the rhenium compound in the above examples is also given as representing preferred practice although we have found results to be very satisfactory when the bath is either relatively dilute or substantially saturated with the rhenium compound.

Examples of typical phosphate and oxalate baths are as follows:

Example 4

Potasium perrhenate ($KReO_4$), 3.0 grams.
Phosphoric acid sp. gr. 1.7, 7.0 c. c.
Sodium phosphate (Na_2HPO_4), 16.5 grams.
Water, 250 c. c.
Current density, from 13 to 17 amp./dm^2.
Temperature, 80–90° C.
pH at 90° C., 2.282 (quinhydrone electrode).
pH at 30° C., 1.743 (quinhydrone electrode).

Example 5

Potassium perrhenate ($KReO_4$), 2.2 per 230 c. c. about 10 gr. per liter.
Oxalic acid, 8 gr. per liter.
Temperature, 80–90° C.
pH=1.438.
Current density, 12 amperes to 15 per dm^2.

As an example of a typical alkaline bath the following is cited:

Example 6

Perrhenic acid ($HReO_4$) or metaperrhenic, 10 c. c.
$NaHCO_3$ c. p., 10 grams.
Ammonium sulphate $(NH_4)_2SO_4$, 5 grams.
Water, 250 c. c.
Current density, 13–17 amp./dm^2.
Temperature, 80–90° C.
pH at 28° C., 8.647.

The process may be carried out very readily with any of the standard types of apparatus and it is unnecessary to employ a special form or shape of anode since the throwing power of the bath is very good. In fact the throwing power has in each case been found to be from about 75 to 90% of that of a nickel sulfate bath so that plating of the metal takes place substantially uniformly throughout the surface of the articles treated and within all the exposed interstices thereof.

In preparing the article for plating it may be treated in any suitable manner to clean the same. Ordinarily it is also desirable to polish the article before plating because of the hardness of the deposit produced. Cleaning may be effected by immersing the article in a sodium phosphate bath and passing a current therethrough with the article to be plated serving as the cathode as in the usual practice. Thereafter the article is washed and then immersed in the rhenium containing bath and the current turned on. It is preferable to turn on the current as soon as the article is placed in the bath in order to avoid the formation of sulphates or other reaction products on the surface of the article to be plated. After plating the article is washed and dried.

The length of time required to produce the desired deposit will, of course, vary with the nature of the plating desired, the concentration of the rhenium in the bath, as well as other factors but when applying a plating for use as a reflector on a polished brass surface excellent results are obtained in 90 seconds when using the sulphate bath of Example 1. In no case has the plating required more than a very few minutes.

The hardness of the plating when tested by the scratch method described by Fink and Lah in Trans. of the Electro-Chemical Society Vol. 58 (1930) pages 373–385 is about 33 which corresponds to a Brinell hardness of about 250. This compared with a scratch of 56.8 for a rhodium plating corresponding to a Brinell hardness of about 150, and with a recognized Brinell hardness of about 400 for chromium plating. This property of the plating renders it useful for the plating of handles for tools, the faces of golf clubs, and for other purposes wherein the article is subjected to wear.

In producing reflectors or other polished articles in accordance with this invention it is possible to obtain a very smooth, bright surface of high reflecting power by polishing the surface of the material on which the metal is to be plated before immersing it in the bath and it has been discovered that by so polishing the surface the resulting plated surface presents a smooth, bright deposit of the metal which requires little or no further polishing.

The resistance of platings of metallic rhenium to the action of hydrochloric acid in all concentrations is an important characteristic of articles of manufacture embodying our invention and renders the same applicable not only for use with acid resisting equipment and apparatus but also for the plating of jewelry such as bracelets, necklaces, wrist watches and wrist watch bands, door handles or other articles which are subjected to the action of hydrochloric acid present in perspiration.

In contrast with its resistance to the action of hydrochloric acid the plating is readily dissolved by nitric acid and may easily be stripped from surfaces by immersion in nitric acid.

We have also found that the process described herein lends itself well for use in the co-deposition of rhenium and other metals to produce a plating of an alloy of the metal, such as a rhenium-nickel alloy.

The foregoing description of our invention has been illustrated with reference to a number of typical baths containing electrolytes other than the rhenium. However, it should be understood that the invention is not limited to the use of these particular baths since similar results may be obtained by the use of any of a large number of electrolytic baths, it being necessary only to determine those factors such as the range of pH value which are characteristic of the bath it is desired to employ and thereafter to follow the procedure indicated above.

What is claimed is:

1. The method of effecting electro-deposition of rhenium which comprises the step of passing current through a sulphate solution containing a soluble rhenium compound, which solution has a hydrogen ion concentration of a pH from about 0.3 to about 3.0 while maintaining the current density between about 8 and 17 amperes per square decimeter of the cathode surface.

2. The method of effecting electro-deposition of rhenium which comprises the step of passing current through a solution of potassium perrhenate in the presence of a sulphate, which solution is maintained at 25 to 40° C. and has a hydrogen ion concentration of a pH from 0.7 to about 1.2.

3. The method of effecting electro-deposition of rhenium which comprises passing current at a density of from about 10 to 16 amperes per square decimeter of the cathode surface through a sulphate solution having a rhenium compound dissolved therein which solution has a hydrogen ion concentration of a pH about .9 while maintaining the temperature within the limits of about 25° to 45° C.

4. A bath for use in the electro-deposition of rhenium which comprises a solution of a rhenium compound having a sulphate dissolved therein, and having a hydrogen ion concentration of a pH from about 0.3 to 3.0.

5. A bath for use in the electro-deposition of rhenium comprising a solution of a sulphate and a perrhenate and having a hydrogen ion concentration of a pH 0.7 to 1.2.

6. The method of producing electrolytic deposits of metallic rhenium which comprises the steps of preparing a bath containing a rhenium compound and a sulphate, adjusting the pH value of the bath to within the limits of 0.3 and 3.0 and passing an electric current through the bath.

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