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VAPOR COATING PROCESS

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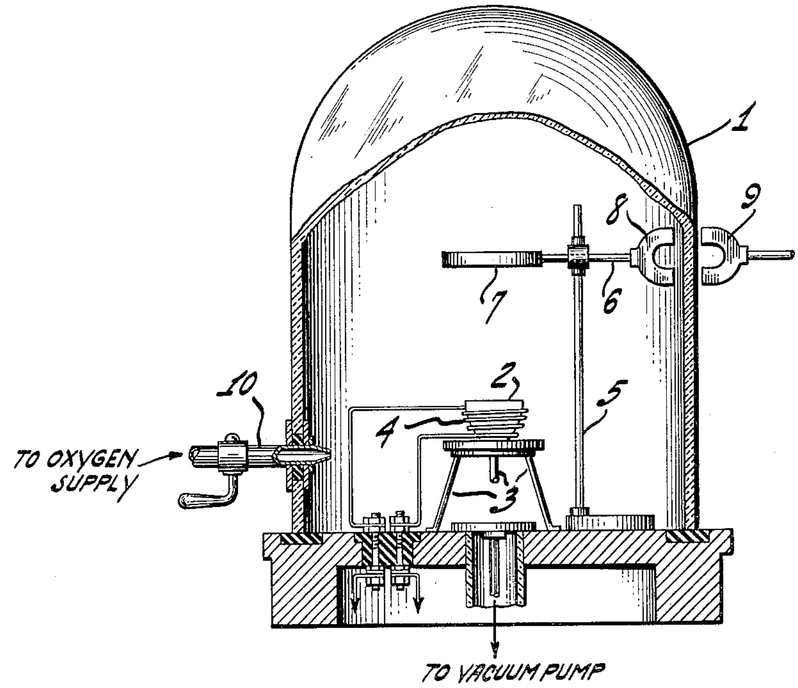

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VAPOR COATING PROCESS

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5 Claims. (Cl. 117—107)

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This application is a continuation-in-part of application, Serial No. 676,477 (now abandoned), filed June 13, 1946.

This invention relates to the art of vapor coating. More particularly, it relates to improvements in the art of depositing a hard, resistant, metallic coating, which is also a good conductor of electricity.

In general, the formation of metallic coatings on surfaces such as glass is done within a highly evacuated chamber. The metal to be deposited is placed in a coil of tungsten wire or a crucible located within the chamber and the chamber is evacuated down to a pressure at least as low as 10^{-3} mm. of mercury (see Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1944, page 176) in order to obtain good results. Somewhat higher pressures than this can be used but the results, in the ordinary process of vapor coating, become increasingly poor as the degree of evacuation becomes less. This is due to collisions of the metal molecules with residual gas molecules preventing metal from travelling to the surface to be coated. The metal to be deposited is heated to its vaporization temperature and the molecules of metal, if unhindered by intervening gas molecules, travel in straight lines to deposit on all relatively cooler opposing surfaces including the surface of the article which it is desired to coat.

In these previous processes of vapor coating, then, every effort has been made to use the highest possible vacuum and, in most cases, to prevent oxidation of the coating being deposited.

The present invention deals primarily with the deposition of a particular metal, namely, titanium. One object of the invention is to provide a method for the formation of a hard, resistant coating of this metal on any surface able to withstand the conditions existing during the evaporation process.

Another object is to provide a method of forming a hard, mirror-like coating of titanium.

Another object is to provide a very thin coating of titanium, which is a relatively good conductor of electricity.

Another object is to provide a thin, metallic coating having nearly the hardness of steel.

Another object is to provide a thin metallic coating highly resistant to ordinary inorganic acids and alkalies.

Still another object is to provide a coating of titanium which is so thin as to be light transmitting but which is electrically conductive.

These and other objects will become apparent and the invention will be better understood from the following description and the accompanying drawings which represent a side view of conventional vapor coating apparatus with an added inlet to admit a desired amount of oxygen.

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Referring to the figure, there is positioned within a vacuum chamber 1 a boat or crucible 2 on a holding stand 3 and adapted to be heated by a heating coil 4. On a holder 5 having an arm 6 of adjustable height, there is placed the article 7 to be coated. By means of magnet 8 on the end of the holding arm and a similarly shaped magnet 9 outside the vacuum chamber the article being coated may be turned over in order to coat its reverse side if desired. An inlet 10 in the wall of the vacuum chamber is for the purpose of admitting a desired amount of oxygen into the chamber.

The preparation of a coating of titanium according to the invention is as follows: titanium, either in the form of wire or powder, is placed in the boat which may be of tungsten. If desired, the boat may be omitted and a tungsten coil used instead. In this case, wires of titanium are preferable to use of powder. The chamber is exhausted to a high vacuum of about 0.1 to 0.01 micron of mercury. There is then admitted an amount of pure oxygen sufficient to bring the pressure up to from 1 to 50 microns. The amount of oxygen introduced will necessarily vary with the type of base to be coated, distance from evaporator to work surface, degree of hardness desired, etc. The exact upper limit of pressure is determined by the practical consideration of whether the mean free path of the titanium molecules is sufficient to allow their reaching the surface of the object being coated considering the distance between evaporator and work surface. If the oxygen pressure is too high, however, some of the titanium will be converted to the oxide and if the pressure is substantially lower than 1 micron the resulting coating will be too soft and have too low a degree of adherence.

Next, the evaporator is heated to melt the titanium and the temperature of the evaporator is then raised in order to evaporate the metal. This temperature is usually from 1800–2000° C. Time of evaporation will depend upon thickness of coating desired, temperature of evaporation, and amount of oxygen present.

Many different types of work surfaces are suitable to receive the titanium coating. Glass or other hard ceramics are preferred but metals can also be used equally well as can mica, mineral fibers, etc. Any base which is not adversely affected by the high evaporation temperatures may be utilized.

Even very thin coatings of titanium deposited according to the method of the present invention are relatively good electrical conductors. For example, a coating on glass of such thickness as to transmit 50 percent of the incident light had a resistance of 300 ohms between needle pointed electrodes spaced apart a distance of 2.5 inches. The glass was 0.5 inch in width. A titanium dioxide coating of comparable thickness has a resistance of the order of megohms.

On smooth surfaces such as glass or mica, bright mirror coatings can be deposited when made of sufficient thickness as to be opaque. Since the coatings are also very hard, they make excellent front surface reflectors. Their hardness being only slightly less than that of steel, these mirror surfaces are highly resistant to scratching and scuffing.

The adherence of a coating deposited as above described was tested as follows. The pressure under which evaporation and deposition took place was about 10 microns. A coating of rubber cement was placed on the titanium coating and then stripped off the surface. The metal coating was undamaged and the tweezers could not be made to scratch the coating. A similar titanium coating deposited under a high vacuum of 0.1 micron of ordinary atmosphere was covered with similar layer of rubber cement. When the rubber cement was stripped from the surface most of the metallic underlayer was stripped from the base.

Titanium coatings made according to the present invention were also subjected to the following abrasion test. A steel ball covered with linen and loaded with a 500 g. weight was subjected to a reciprocating motion across the surface of the coating. More than 200 cycles were required to completely remove the coating by this process whereas titanium deposited under high vacuum conditions could be completely removed during the first few strokes of the ball. (This testing method has been reported by Noel Scott, Engineering Board, Fort Belvoir, Virginia.)

In addition to their hardness characteristics, the titanium coatings which have been described are also almost completely insoluble in the inorganic acids and even resist the attack of hot alkali solutions. For this reason, they are little affected by the usual corrosive components of the atmosphere and can be used under conditions where other mirrors fail completely.

The unexpected improvements which result when a coating of titanium is deposited in an atmosphere of oxygen appear to be due to small amounts of oxygen dissolving in the metal coating. At the same time, some titanium dioxide is also formed but the percentage appears to be relatively minute and does not seem to be responsible for the improved properties. Just why the dissolved oxygen should improve the properties of the coating is not understood and it is not desired to be limited by the suggested theory. There is considerable evidence to support the conclusion that the oxygen present in the evaporation chamber becomes dissolved in or adsorbed by the titanium coating rather than uniting chemically with the metal to form oxides of titanium. One is that the resulting coating is metallic in luster. Another is that the coating is a much better electrical conductor than a titanium dioxide semiconductor would be. The coating also elliptically polarizes light on reflection, which is a characteristic of metals.

Further explanation of the ability of titanium to dissolve oxygen (and other gases) may be found in Transactions of the Electrochemical Society, vol. 87, 1945, pp. 289—. In an article entitled "Lowering of the Photoelectric Work Function of Zr, Ti, Th and Similar Metals by Dissolved Gases" by H. C. Rentschler and D. E. Henry, p. 290, is the statement:

"Zirconium, titanium and hafnium are unique in that oxygen, nitrogen and hydrogen form a solid solution in the metal; that is, the gas atoms are in the crystal lattice and not in the form of compounds in the grain boundaries."

Titanium coatings prepared according to the present invention have many uses. The formation of hard mirrors on optically smooth surfaces is one of the more important applications. Another is the formation of thin electrically conductive coatings for making sliding contacts. The formation of an adherent conductive coating on a ceramic surface to which a heavy metallic coating is subsequently to be applied by electrodeposition is still another important use. Also, the formation of electrically conductive coatings on transparent glass surfaces is important in many industries. One of these is in alarm systems which operate when a glass cover is broken.

There has thus been described a method of forming a hard chemically resistant coating by depositing titanium vapor in the presence of oxygen. Results are greatly improved over depositing the coating in an ordinary high vacuum with almost no oxygen present although the reasons for the difference are not fully understood. When deposited in a high vacuum, the coating is relatively soft and can easily be scratched off the coated surface. Deposition made according to the present method produces hard, chemically resistant coatings having a mirror-like luster. The coatings are also relatively good, electrical conductors.

I claim as my invention:

1. A method of forming an adherent, abrasion-resisting coating on a surface of a refractory material comprising positioning said material within an evacuated chamber, introducing into said evacuated chamber an amount of pure oxygen sufficient to provide a pressure of 1 to 50 microns therein, vaporizing titanium in vacuo, and exposing said surface to said vaporized titanium, while in the presence of said oxygen.

2. A method according to claim 1 in which said refractory material is glass and the thickness of coating material deposited is such that it transmits light.

3. An article comprising a base of refractory material having a coating of titanium thereon, said titanium having a small amount of oxygen dissolved therein and having been deposited by the process of claim 1.

4. An article according to claim 3 in which said material is glass and the thickness of coating material deposited is such that it transmits light.

5. An article according to claim 3 in which said material is glass and the thickness of coating material deposited is such that it is opaque to light.

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REFERENCES CITED

The following references are of record in the file of this patent:

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