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PRODUCING THIN FILM OF METAL OXIDE

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1 Claim. (Cl. 117-127)

1

This invention relates to an improved method of forming a metal oxide coating on a supporting base and more particularly to an improved method of forming a uniformly thin, adherent coating of uranium oxide on a polished metal surface. The method of the present invention is particularly well adapted for use in forming on a metal support a layer or coating of an oxide of a radioactive element of such a character that it may be advantageously employed in analytical procedures of the type referred to below. However, it will be apparent as the description proceeds that the method may also be used in forming thin layers of other metal oxides for other purposes as well.

Analytical techniques and procedures for determining the relative proportions of different isotopes of an element present in particular samples of the element have recently become increasingly important. Where it is desired to determine the proportions of different isotopes present in a radioactive element, an analysis may be made by measuring the intensity of the radiation given off by the element. In the case of uranium, for example, the proportion of the U^{235} isotope present in a mixture of U^{234} , U^{235} and U^{238} may be determined within a certain range of proportions by counting in a suitable counting apparatus the number of alpha particles emitted from a given weight of the material in a unit length of time and comparing this alpha particle count with that of a standard sample under the same conditions.

It has been found that the desired accuracy in counting the emission of alpha particles or otherwise determining the intensity of radiation may be best obtained by forming on a suitable support such as a metal disc a thin adherent layer of a compound of the radioactive element such as, for example, an oxide of the element. In order to obtain the desired accuracy in making such a count of alpha particles, it is necessary that the quantity of radioactive element or compound used as a sample be accurately determined, that the sample be spread out in a thin layer or film on a supporting base, and that the film be uniform in thickness, within relatively narrow tolerances, and firmly adherent to the support.

The problem of preparing such a film is a difficult one. Unless the metal oxide layer is firmly adherent, parts of the layer will tend to flake off and be removed when the disc is handled or while it is in the counting device, thus introducing errors into the analytical results obtained. It is not ordinarily possible to use many

2

of the various well-known binder materials which may frequently be used to improve the bonding characteristics of a metal oxide deposit because the metal compound forming the film must be pure and free from foreign matter in order to obtain the desired accurate analysis.

Since alpha particles emitted by the inner layers of the oxide film will be absorbed by the outer layers of the film in accordance with a definite relationship between particle energy and film thickness, it is desirable that the oxide film be relatively thin to minimize errors introduced by this absorption phenomenon. It is also desirable that the oxide layer be thin enough to reduce the rate at which alpha particles are emitted from a unit area of the film to the point at which the emission of individual particles may be adequately differentiated by existing types of counting apparatus.

The accuracy of the count made depends to some extent on the number of particles counted, that is, if a relatively large number of individual particles are counted, the probable error in the count is less than in cases where a small number of particles are counted. The oxide film should be thick enough so that a large number of individual particles, say half a million, may be counted within a reasonable time, say two hours. It is also desirable that the film be thick enough so that the total weight of oxide may be easily determined with satisfactory precision. Moreover, the oxide layer should be of uniform depth over the surface of the support, otherwise, unequal absorption of the alpha particles from the lower layer of the film will introduce an error into the analysis. Desirably the layer should adhere firmly to the supporting base and its thickness should not vary more than 5% over its entire area.

It is an object of the present invention to provide a method of forming on a supporting base an adherent, uniform, relatively thin layer of a metal oxide.

It is a further object of the invention to provide a method of forming on a smooth metal surface a relatively thin coating of a compound of a radioactive metal which is of uniform thickness within close limits.

It is still another object of the invention to provide a method of forming on a metal support a coating of a compound of a radioactive metal which may be used in a particle counting device to give an accurate count of the alpha, beta, or gamma radiation emitted from a unit quantity of the element.

3

Other objects of the invention will be in part obvious and will in part appear hereinafter.

The objects of the present invention may be attained in general by preparing a solution of a suitable metal salt in a volatile solvent, spraying the solution on a metal base having a smooth, polished surface, and subsequently heating the coating to a temperature sufficient to volatilize the solvent and convert the metal salt into an oxide of the metal. For purposes of clarity and simplicity, the method of the present invention will be described as applied to the formation of a uranium oxide layer on a polished platinum surface, although, as will be later pointed out, the method may equally well be applied to the formation of other types of metal oxide films on other supporting bases.

In accordance with a preferred embodiment of the present invention, a solution is prepared by dissolving a small quantity of a uranium salt, such as the chloride, in amyl acetate, spraying the solution on a polished platinum disc, and then heating the coating to a temperature sufficient to volatilize the amyl acetate and convert the uranium chloride into a uranium oxide. A binder such as "Zapon Aquanite A" lacquer is preferably added to the solution to assist in formation of a suitable coating of metal salt on the disc. Binders of this character are substantially completely removed from the coating at temperatures at which the conversion of the uranium salt to the oxide occurs. "Zapon" is the trade name of a solution of cellulose nitrate in amyl acetate manufactured by the Atlas Powder Company.

The method of application of the solution to the metal base is an important feature of the present invention. It has been found that a much more nearly uniform layer of the metal salt may be obtained when the solution is sprayed on the disc than when it is applied by other methods such as dipping or brushing. The spraying device used in applying the solution to the disc should be of a type that will finely atomize the solution. It has been found that an artist's air brush may be advantageously used in obtaining the desired fineness of atomization.

The coating is preferably built up by alternately spraying the disc with the solution and heating to convert the metal salt into an oxide, until an oxide layer of the desired thickness has been obtained. Satisfactory results with existing types of coating apparatus have been achieved by building up a layer containing of the order of 0.5 milligram of uranium oxide per square centimeter of the disc. It has been found that the adherence and coherence of the oxide layer are affected by the rate at which the oxide layer is built up. If an attempt is made to spray on too heavy a film in a single application, the resulting coating tends to peel or flake off. Hence, it is usually desirable to apply a relatively large number of thin coats rather than a smaller number of thicker coats. In practice it has been found that a satisfactory layer containing 0.5 milligram per square centimeter may be built up by the application of about 40 to 50 coats of the solution described in the specific example given below. The number of coats required to give a desired thickness and adherence will of course vary with the type of solvent used, the type of binder used, the chemical nature of the salt used, the fineness of atomization of the solution, and other related factors.

The following specific example is given to illus-

4

trate one mode of application of the present invention: A solution of uranyl chloride (UO_2Cl_2) in amyl acetate was prepared having a concentration of two milligrams of the chloride per milliliter of solvent. To this solution 8% by volume of "Zapon" lacquer was added. The resulting solution was applied to one surface of a smooth, highly polished platinum disc about 5 centimeters in diameter using an artist's air brush. The disc was mounted in a vertical position and the nozzle of the air brush was maintained at a distance of about 6 inches from the disc, the brush being adjusted to give a very fine spray. With this adjustment the angle of the spray cone was such that the spray did not impinge on the entire area of the disc at one time and the air brush was moved with a rotary motion to cause the solution to coat uniformly over the area of the disc. About 1 milliliter of solution was passed through the air brush for a single application, and the air brush was so adjusted that this quantity of solution was sprayed in about half a minute. Only a fraction of the metal salt sprayed (perhaps one eighth) was actually deposited on the disc. It was found that under the conditions described the solution reaching the disc was sufficiently fluid to coalesce to form a uniform layer and yet was not so fluid as to run down over the surface of the disc.

After application of the solution to the disc, the coating was heated at 600°C . to convert the uranyl chloride into uranium trioxide (U_2O_3). After ignition at 600°C . for about one minute, the surface of the disc was wiped to remove any loosely adherent material. A second coating of the solution was then applied to the disc and the disc again ignited at 600°C . The coating and ignition were repeated until 40 coats had been applied and a deposit of about 0.6 milligram per square centimeter had been built up. The resulting coating was firmly adherent to the disc and its thickness varied less than 5% over the entire area of the disc.

It is to be understood that the invention is not to be limited to the details set forth in the specific example and that other materials and conditions may be used in place of those specifically disclosed above. Thus the coating may be formed by heating salts of other metals than uranium to produce an oxide of the metal used, provided that the salt is of such a character that it will decompose to form an oxide upon heating. The supporting metal base need not be platinum but may be of any metal of the platinum-palladium group or may be gold, or in fact any metal that will maintain a high polish and not change weight during ignition. The ignition temperatures may vary between 500°C . and 1100°C . The supporting base need not be a disc but may have any desired shape or form.

In place of amyl acetate as the volatile solvent for the salt solution, any volatile solvent may be used that is capable of completely dissolving the salt to give a clear solution, and that will volatilize without residue, provided that the solvent will dissolve at least about 1 milligram of salt per milliliter of solvent. When a solvent of higher volatility, such as acetone, is used, it has been found that a larger number of coats are required to give a layer of desired thickness.

In place of the "Zapon," other binders may be used, such as cellulose acetate or butyrate dissolved in suitable solvents. Resins such as phenol formaldehyde resins, urea resins, methylmethacrylate resins, or styrene resins can also be used

5

with solvents producing clear solutions of reasonable concentration compatible with the solution of the salt. The binder may comprise from 2 to 20% by volume of the solution with the remainder being composed of the volatile solvent and the metal salt. The metal salt preferably comprises not more than 1% by weight of the solution.

From the above description it should be apparent that the present invention provides an improved method of forming a thin adherent coating of a metal oxide on a supporting base. Since many embodiments might be made of the present invention and since many changes might be made in the preferred embodiment described above, it is to be understood that the foregoing description is to be interpreted as illustrative only and not in a limiting sense, except as required by the appended claim.

I claim:

A method of forming a thin, smooth, adherent uranium oxide coating of substantially uniform thickness on a polished platinum disc which comprises preparing an amyl acetate solution of uranyl chloride containing about two milligrams of the chloride per milliliter of amyl acetate and

6

about 8% by volume of an organic solvent solution of a binder, spraying said solution in finely atomized condition onto said disc, heating said coating to a temperature of about 600° C. to convert said chloride into uranium triauroxide, and repeating said spraying and heating steps alternately until a coating has been built up containing approximately half a milligram of uranium triauroxide per square centimeter of said coating.

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