UNITED STATES PATENT OFFICE.

QUENTIN MARINO, OF LONDON, ENGLAND, ASSIGNOR OF THREE-FOURTHS TO EDWIN JOSEPH RICHARDSON, OF LONDON, ENGLAND.

METALLIZATION OF VITREOUS CERAMIC SURFACES.

No. 925,365. Specification of Letters Patent. Patented June 15, 1909.

Application filed July 31, 1908. Serial No. 446,337.

To all whom it may concern:

Be it known that I, QUENTIN MARINO, a citizen of Italy, and residing at 65 Wymering Mansions, Wymering Road, Elgin avenue, London, W., England, have invented certain new and useful Improvements in or Relating to the Metallization of Vitreous Ceramic Surfaces, of which the following is a specification.

This invention relates to the metallization of vitreous, porcelain, earthenware and the like surfaces, so that metal or metallic alloy may be electrolytically deposited upon such surfaces, and it has for its object to enable such metallization to be effected in a simple manner.

The metallization of the surface according to this invention is intended to be effected after said surface has been roughened or rendered matte, which operation may be accomplished in any well known manner, for instance, by the use of hydrofluoric acid, or by means of an emery wheel or sand blast.

My invention is carried out as follows. A cold solution is made by putting cuprous oxid into a solution of nitrate of silver whereby is quickly formed a gray substance consisting of filiform silver and basic nitrate of copper

$$6Ag+2Cu(NO_3)_2+Cu_4O_3(NO_3)_2;$$

the use of this substance enables the electrolytic metallization of the surface to be effected. This gray substance is then dissolved in hydrofluoric acid, and the solution so formed is applied, say, by means of a brush, to the roughened surface. In order to insure its adherence to such surface, I reduce the copper and the silver in the fluorid to a metallic state by eliminating the hydrofluoric acid. To effect this reduction, I dust the surface, while it is wet with the last-mentioned solution, with a mixture of metals, or with one metal only, in a finely-divided state and such as will reduce the silver on the one hand and the copper on the other, both of which latter are combined with the fluoric acid. For this purpose, I may use a mixture of powdered copper and zinc, or a powder of copper with either iron, nickel, cobalt, cadmium, lead or bismuth, the copper and zinc reducing the silver, while the zinc, iron, nickel, cobalt, cadmium, lead or bismuth reduces the copper. I may, however, use powdered zinc only, which reduces both the silver and the copper. Or I may use powdered zinc mixed with either iron, nickel, cobalt, cadmium, lead or bismuth to effect the reduction. In any case, when a mixture of metals is employed, the particles thereof must be intimately mixed together. The surface thus becomes coated with a mixture of silver and copper in the form of a very thin film sufficiently continuous for it to be electrically conducting for the purpose of having deposited thereon electrolytically the metal or metallic alloy desired. Instead of leaving the surface in this condition, I render it more conductive by rubbing it briskly, when dry, with a brush or the like, until it presents a polished and uniform appearance, thereby facilitating the passage of the electric current throughout the film. In some cases it may be desired to electrolytically deposit the metal or metallic alloy on portions only of the surface, for instance, when ornamenting a surface; in such cases, only those portions of the surface which are to be ornamented require to be roughened, and, as my solution, applied as above described, adheres only to the roughened portions, any solution which lies on the unroughened portions may be easily removed therefrom, by, say, wiping it off with a cloth or the like. The article with its surface treated as above described may now be placed as a cathode in a suitable electrolyte of gold, silver, nickel, copper, or other metal or metallic alloy of which a deposit is required, and electrical connection be made so as to cause the metal or alloy to be deposited thereon by electrolysis as usual.

I may use cupric hydrate instead of cuprous acid.

I claim,

1. Metallizing a roughened, vitreous, ceramic surface by applying thereto a solution resulting from dissolving in hydrofluoric acid a gray substance consisting of filiform silver and basic nitrate of copper, and then, while the surface is wet with the solution, dusting said surface with a metal in a finely divided state and such as will reduce the silver and copper in the fluorid to a metallic state, substantially as described.

2. The process of metallization of a roughened vitreous, ceramic surface, the step of preparing a gray substance consisting of filiform silver and basic nitrate of copper and dissolving the gray substance so formed

in hydrofluoric acid, substantially as described.

3. In the metallization of a roughened, vitreous, ceramic surface, preparing a gray substance consisting of filiform silver and nitrotetra cuprate of copper—

$$6Ag+2Cu(NO_3)_2+Cu_4O_3(NO_3)_2,$$

dissolving this substance in hydrofluoric acid, applying the resulting solution to said roughened surface, then while the surface is wet with the solution, dusting thereon a suitable powdered metal which will reduce the silver and the copper in the fluorid to a metallic state and when the surface is dry, rubbing said surface briskly until it presents a polished and uniform appearance, substantially as hereinbefore described.

4. The process of metallization of a roughened vitreous ceramic surface, the step of preparing a cold solution made by putting cuprous oxid into a solution of nitrate of silver.

5. Metallizing a roughened vitreous, ceramic surface by applying thereto a solution resulting from dissolving in hydrofluoric acid filiform silver and basic nitrate of copper and then while the surface is wet with the first mentioned solution, dusting said surface with a metal in a finely divided state such as will reduce the silver and the copper in fluorid to a metallic state and then electrically depositing upon said surface a metal or a metallic alloy of which a deposit is required.

6. In the metallization of a roughened vitreous, porcelain, earthenware surface, preparing a gray substance consisting of filiform silver and basic nitrate of copper—

$$6Ag+2Cu(NO_3)_2+Cu_4O_3(NO_3)_2,$$

dissolving this substance in hydrofluoric acid, applying the resulting solution to said roughened surface, then while the surface is wet with the last mentioned solution dusting thereon a suitable powdered metal which will reduce the silver and the copper in the fluorid to a metallic state and when the surface is dry, rubbing said surface briskly until it presents a polished and uniform appearance, and then electrically depositing upon said surface a metal or metallic alloy of which a deposit is required.

In witness whereof I have hereunto set my hand in presence of two witnesses.

QUENTIN MARINO.

Witnesses:
HARRY T. P. GEY,
JOHN NALLE SMITH.