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PRODUCTION OF METALLIC DESIGNS ON NONMETALLIC MATERIALS

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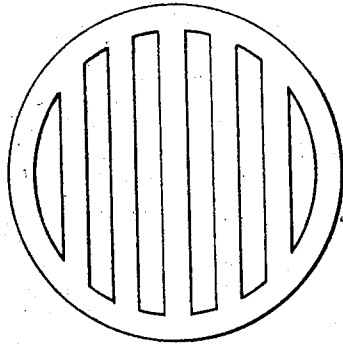


FIG. 1.

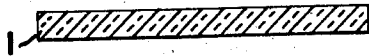


FIG. 2.



FIG. 3.

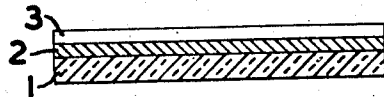


FIG. 4.

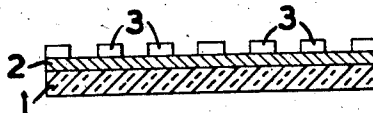


FIG. 5.

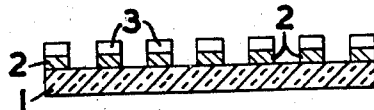


FIG. 6.

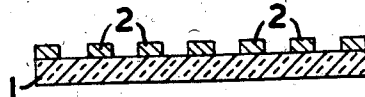


FIG. 7.

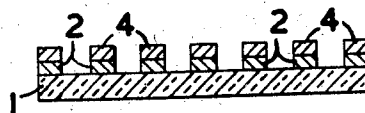


FIG. 8.

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PRODUCTION OF METALLIC DESIGNS ON NONMETALLIC MATERIALS

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6 Claims. (Cl. 41-42)

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This invention relates to the production of designs in gold, silver or palladium on non-metallic surfaces, as for example glass, glazed porcelain, glazed earthenware or other impervious non-metallic material which will withstand heating to a temperature of at least 500° C.

A particular object of the invention is to produce a design of fine lines in a geometrical pattern on a non-conducting transparent base, as for example glass, the said lines consisting of a metal of high electrical conductivity. The invention is, however, not limited to this particular application and may be used also for the production of decorative or other types of designs in metal on glass and non-porous ceramic or natural products.

According to this invention I produce a metallic design on a non-metallic material (which I will hereinafter call the base) by a process comprising the following steps, namely:

(a) Providing the base with a thin coating of silver, gold or palladium evenly distributed over its surface,

(b) Coating the resulting metal surface with a film of light-sensitised glue or gelatin which is then processed by photographic methods so as to take the form of a positive image of the desired design,

(c) Hardening the image in known manner to produce a resist,

(d) Removing the metal not covered by the resist by etching with a solution of bromine or iodine in a liquid alcohol or ester which is not readily attacked by these halogens, thus leaving the design in metal below the resist, and (e) firing the article at such a temperature, generally from 500° to 900° C., that the resist is burned away and the metallic design is caused to adhere firmly to the base.

If desired, the opacity and/or resistance to wear of the metallic design may be improved by:

(f) Applying an electroplated coating of the same or another metal. Since the additional metal is applied by electrodeposition, it is deposited only on the metallic design, the non-metallic surface remaining unaffected.

The thin coating of precious metal in step (a) may be produced by the known methods of sputtering or evaporation in a high vacuum. It may also be produced by the use of the materials known commercially as "liquid gold," "liquid silver" and "liquid palladium," which consist mainly of solutions of sulphoresinates or resinates of the metals in solvents, such as essential oils. When using "liquid metals," a suitable

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amount of the liquid is applied to the surface of the base and the latter is spun by rotating it at a high speed about a central axis in a horizontal plane so as to cause the liquid to spread evenly over the surface of the base and throw off any excess of liquid. The base is then fired at a temperature sufficiently high to decompose the organic constituents of the "liquid metal" but not high enough to cause the resulting metal film to adhere strongly to the base. A suitable temperature may be between 300° and 600° C.

Commercial "liquid metals" contain a considerable quantity of solvents of low boiling point, such as chloroform, or ethyl acetate, and the presence of these may cause deposition of moisture during the spinning operation due to the chilling caused by their rapid evaporation. It is therefore preferred to use in place of these solvents liquids such as cyclohexanol and benzyl alcohol which have a low rate of evaporation.

The glue or gelatin used in step (b) is preferably one of the glue preparations sold commercially for photo-engraving processes and is rendered light-sensitive by the addition of a soluble chromate or bichromate. A wetting agent may be added to assist in even distribution of the glue over the metal.

A suitable sensitised glue solution may be composed as follows:

Ammonium bichromate	grams	28
0.880 ammonia	cc	8
Distilled water	cc	660
Wetting agent	grams	8
Photoengraving glue	cc	200

This is filtered by vacuum through a retentive paper to remove suspended particles of dust and the like and applied to the metal coating by spinning in the same way as the "liquid metal" in step (a).

The glue film is then placed in close contact with a negative image of the desired design and exposed to light through this negative, the light thereby penetrating the transparent portions of the negative and producing an insoluble positive image of the design. The parts of the glue film which have remained soluble are then removed by washing in cold water and the whole is dried rapidly, whereby the desired design is left as a glue image on the surface of the metal coating.

This image is then converted into a resist (step (c)) for example by heating for 20 minutes at from 250° to 300° C. Alternatively, the hardening may be effected by treatment with chemical reagents, such as formaldehyde or chrome alum.

The removal of the metal not protected by the resist (step (d)) is effected by an etching process. The reagent used in this process must be such that it does not attack the resist or the underlying metal. The usual etching reagents for silver, gold and palladium consist of aqueous solutions of relatively strong acids with or without the addition of oxidising agents, or of alkaline solutions containing cyanides with or without oxidising agents such as hydrogen peroxide or ammonium persulphate. All these attack glass resists very readily so that it is difficult to remove the metal from the parts not covered by the resist without at the same time causing the resist, at least in part, to lift away from the base and thus expose part of the metallic design to the action of the etching reagent.

I have found that this difficulty can be overcome by using as etching reagents solutions of bromine or iodine in non-aqueous solvents which do not penetrate the resist and which are not themselves readily attacked by bromine or iodine. Such solvents are, for example, the lower aliphatic alcohols, such as methyl, ethyl, isopropyl, butyl and amyl alcohols, polyhydric alcohols, such as ethylene glycol, diethylene glycol and glycerol, or their esters, preferably their high boiling esters, such as ethyl lactate, butyl lactate, amyl lactate and the glycol and glycerol acetates.

As examples of suitable etching baths I may mention:

(1) 2 parts of iodine, 4 parts of potassium iodide and 100 parts of ethyl alcohol;

(2) 100 parts of ethylene glycol monoacetate, 10 parts of acetic acid and 2 parts of bromine; or

(3) 100 parts of ethyl lactate, 10 parts of lactic acid and 2 parts of bromine all parts being by weight.

Solutions containing bromine act more rapidly than those containing iodine.

The action of the etching reagent may be accelerated by suspending therein a solid, as, for example, fine sawdust or levigated alumina, which exerts a mild scouring action on the metal coating when the etching bath is gently agitated.

If the metal coating in step (a) is produced by the use of a "liquid metal," the adherence of the metal coating to the base is effected by including bismuth or other metal resinates in the liquid metal. In this case, when the metal is removed by etching in step (d), a thin film of bismuth, or other metal, oxide may remain adhering to the base. This may be removed by immersing the base in a dilute acid solution which does not attack the resist and in which the metal oxide is soluble, as for example tartaric acid or citric acid, preferably dissolved in a non-aqueous solvent, for the reasons given above. In some cases this acid may be added to the etching reagent, so that the metal and the metal oxide are removed at the same time.

The metal applied to the design in step (f) may be the same metal as the design, or a different metal. For example by electroplating a layer of rhodium or platinum on to a design in gold, silver or palladium, the design is rendered more resistant to wear, denser, and more opaque.

The metals may be applied from appropriate known plating baths, and I will describe the application of rhodium to a gold design on a glass surface. Other metals may be deposited in a similar manner.

The glass, with the gold design thereon, is first cleaned by immersing it for a few seconds in a hot solution of caustic soda and sodium phos-

phate. The design is then electroplated with rhodium in a plating bath containing, for example, rhodium sulphate, alkali or ammonium sulphate and sulphuric acid at a temperature of 30° C. at a voltage of 12 and a current density of from 0.1 to 0.8 ampere per square centimetre for from 10 to 60 seconds. In this way the design becomes thicker without the lines becoming appreciably wider. Since rhodium is a harder metal than gold, the design is more resistant to wear; it is also more opaque.

The way in which designs according to this invention may be built up is illustrated diagrammatically in the accompanying drawing in which the dimensions of the various layers are greatly exaggerated.

Figure 1 shows the shape of the desired design and Figures 2-8 are sections showing how the design is built up.

Figure 2 shows the base 1 on which it is desired to produce the design.

Figure 3 shows the base 1 with a coating 2 of metal produced by step (a) as hereinbefore described.

Figure 4 shows the film of glue or gelatin 3 applied to the metal coating 2, while Figure 5 shows the film 3 in the form of the design after exposure to light and removal of the unaffected glue or gelatin.

Figure 6 shows the article after etching by step (d), the metal not covered by the film 3 having been removed leaving the metal design 2 covered by the film design 3.

Figure 7 shows the metal design 2 on the base 1 after firing by step (e) the film 3 having been burned away.

Figure 8 shows the result of optional step (f) in which the design 2 is made thicker by electrodeposition thereon of the same or another metal 4 which also takes the form of the design.

I claim:

1. A process of producing metallic designs on non-metallic materials comprising the steps: (a) providing a non-metallic material with a thin coating of a precious metal selected from the group consisting of silver, gold and palladium evenly distributed over its surface, (b) coating the resulting metal surface with a film of light-sensitised colloid selected from the group consisting of glue and gelatin and processing said film by photographic methods to produce a positive image in said colloid of the desired design, (c) hardening said image to convert it into a resist, (d) removing the metal not covered by said resist by etching with a solution of a halogen selected from the group consisting of bromine and iodine in a solvent selected from the group consisting of the lower aliphatic alcohols and the esters thereof, thus leaving the design in metal below the resist, and (e) firing the article to burn away the resist and cause the metallic design to adhere firmly to the non-metallic material.

2. A process of producing metallic designs on non-metallic materials comprising the steps: (a) providing a non-metallic material with a thin coating of a precious metal selected from the group consisting of silver, gold and palladium evenly distributed over its surface by spinning a film of a composition selected from the group consisting of the resinates and sulphoresinates of the precious metals dissolved in a solvent therefor, onto the surface of the non-metallic article and thereafter firing to convert said film into a thin coating of the desired metal, (b) coat-

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ing the resulting metal surface with a film of light-sensitized colloid selected from the group consisting of glue and gelatin and processing said film by photographic methods to produce a positive image in said colloid of the desired design, (c) hardening said image to convert it into a resist, (d) removing the metal not covered by said resist by etching with a solution of halogen selected from the group consisting of bromine and iodine in a solvent selected from the group consisting of the lower aliphatic alcohols and the esters thereof, thus leaving the design in metal below the resist, and (e) firing the article to burn away the resist and cause the metallic design to adhere firmly to the non-metallic material.

3. A process as claimed in claim 2 in which the composition comprises a solute selected from the group consisting of resins and sulphoresins of a metal chosen from the group consisting of silver, gold and palladium in essential oils diluted with a solvent having a low rate of evaporation.

4. A process as claimed in claim 1 in which the solvent for the halogen in step (d) is selected from the group consisting of lower aliphatic monohydroxylic and polyhydroxylic alcohol and esters of the same.

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5. A process as claimed in claim 1 in which the etching bath used in step (d) is acidified with a weak organic acid.

6. A process as claimed in claim 1 in which the etching bath contains a suspended solid.

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