Patented Sept. 9, 1952

2,610,126

UNITED STATES PATENT OFFICE

2,610,126

DECORATION OF HEAT-RESISTING BASES, SUCH AS GLASS, EARTHENWARE, AND CHINA

Frank Enoch Kerridge and Cyril Stanley Couper, London, England, assignors to Johnson, Matthey & Company Limited, London, England, a British company

No Drawing. Application April 19, 1948, Serial No. 21,857. In Great Britain April 23, 1947

8 Claims. (Cl. 106—26)

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This invention relates to improvements in and relating to the decoration of heat-resisting bases, that is to say, bases capable of withstanding firing at a temperature of at least 400° C., such as glass, earthenware and china and is more particularly concerned with the decoration of such bases with a design or decoration in gold.

In the art of decorating glass, earthenware, or china with a design in gold, a variety of materials of different composition have heretofore been used and these have been applied to the ware in a variety of manners.

The materials hitherto used have usually consisted of the following:

1. A product known commercially as "liquid gold," consisting essentially of a solution of a sulphoresinate of gold in suitable solvents;

2. "Liquid burnish gold"—a suspension of gold powder in essential oils, with or without the addition of "liquid gold," and an adhesion promoting material, such as a lead borosilicate flux or a bismuth compound and an extender such as a mercury salt, and

3. A precipitated gold powder with or without a powdered mercury salt, plus an adhesion promoting agent, also in powder form.

In the decoration of articles with a single simple design each of the above materials may be applied by hand painting with subsequent firing, material 3, which is in powder form, being used in a resinous vehicle.

Where a repetitive design is required to be applied to the ware, however, it is usual to apply the decoration by a printing method.

The methods of printing hitherto generally employed have consisted of (*a*) applying the design by means of a rubber stamp and firing; (*b*) engraved plate printing, i. e. applying transfers printed from etched metal or glass plates and then firing; and (*c*) lithographic printing, i. e. applying lithographic transfers made with a transfer paper either of the collodion "slide off" type, or of the "stick down" type, and then firing. Methods (*a*) and (*b*) may be used with any of the materials referred to above, whilst method (*c*) is generally used only with material 3.

The rubber stamp method of applying a gold decoration is extensively employed owing to the rapidity with which it may be carried out by relatively unskilled operators and the fact that it does not require expensive equipment. The results obtainable by the use of this method, however, usually suffer from lack of richness and sharpness of outline; moreover, ceramic colours cannot be printed simultaneously in register with the gold.

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In carrying out the method (*b*) a transfer is prepared by engraving or etching a design on a metal or glass plate, filling the interstices or depressions so formed with the gold printing paste, applying a sheet of gummed tissue paper, gummed side downwards, to the coated plate and then removing the paper, which now carries the design. To decorate an article, the paper is applied, whilst the paste is still moist or sticky with the design-carrying side downwards, to the article. The tissue paper is then soaked off and the article fired.

This method, in the hands of a skilled operator, gives a decoration of good quality, but, as the design is applied to the ware in the moist state, it cannot be used for applying both gold and ceramic colour simultaneously in register. A further disadvantage is that transfers prepared by this method cannot normally be stored for future use.

With lithographic printing, transfers are prepared from a lithographic stone or plate, usually on "Duplex" type paper, which consists of a paper backing having a gummed sheet of tissue paper on one side thereof. To apply the transfer, the tissue paper, carrying the design, is stripped off the paper backing and pressed, design downwards, on to the surface of the article to be decorated, the latter having been previously treated with a size of a sticky nature. The tissue paper is then wetted to soften the gum and allow the tissue paper to be removed, leaving the design adhering to the article, which is then fired.

This method enables an article to be decorated with intricate designs in multi-colour, but, as the transfer bears only a very thin deposit of enamel or gold, the effect produced on a transparent base, such as glass, is poor. Better results can be obtained on opaque bases, such as earthenware, china and the like, but the effectiveness of the decoration is detrimentally influenced by the thinness of the deposit.

It is also known to decorate ware by applying directly to the article to be decorated a vitreous enamel paste by means of the silk-screen printing method. Such a method of decoration produces a heavier deposit of enamel than is possible with the lithographic transfer method and designs in multicolours can be readily applied. This method of decoration, however, can in general only be successfully employed to decorate substantially flat surfaces.

The materials referred to above as heretofore used for producing a gold decoration by the various methods outlined are quite unsuited for various reasons for use with the silk-screen

printing method and the principal object of this invention is to provide an improved gold paste suitable for direct application to an article to be decorated by the silk-screen printing method, or for the production, by the silk-screen printing method, of transfers intended for subsequent application to an article.

Another object of the invention is to provide an improved method of preparing a gold transfer or of decorating a heat-resisting base with a gold design or decoration by which the thickness of the deposit is readily controllable and tone effects from red-gold to green-gold may be obtained as desired.

With these and other objects in view, the invention, in its broadest aspect provides a silk-screen printing paste for the preparation of a gold transfer or for direct application to a heat-resisting base, as hereinbefore defined, said paste comprising a mixture of (1) gold powder, (2) mercuric aurate, (3) a low fusing flux and (4) a medium or vehicle consisting of a cellulose derivative, dissolved in a solvent or solvent mixture having a rate of evaporation suitable for silk-screen printing, in an amount to give the required viscosity; the proportion of medium (4) to solid substances (1, 2 and 3) being preferably substantially 1–4 parts of medium to 2 parts of solids.

The invention also provides a method of preparing a gold transfer which comprises applying to a transfer paper by the silk screen printing method a paste comprising a mixture of (1) gold powder, (2) mercuric aurate, (3) a low fusing flux and (4) a medium or vehicle consisting of a cellulose derivative, dissolved in a solvent or solvent mixture having a rate of evaporation suitable for silk-screen printing, in an amount to give the required viscosity; the proportion of medium (4) to solid substances (1, 2 and 3) being preferably substantially 1–4 parts of medium to 2 parts of solids.

The invention further provides a method of decorating a substantially flat heat-resisting base, as hereinbefore defined, which comprises applying to the base by the silk-screen printing method a gold printing paste prepared in accordance with the invention, and firing the coated base at a suitable temperature to burn away the organic matter and leave a firmly adherent coating of gold on the said base.

We have found that in practice the viscosity of the medium should preferably be from 1500–2500 centistokes.

The gold powder, mercuric aurate and flux may be present in the following proportions by weight of the total solids: namely (1) gold powder 50–90% by weight, (2) mercuric aurate 10–50% by weight and (3) low fusing flux 1–15% by weight.

Gold powder prepared either by precipitation or mechanically by comminution of the metal may be used.

If desired, up to 20%, determined on the weight of gold in the paste, of silver powder or of a silver compound, such as silver carbonate, may be included in order to give a more greenish tone to the ultimately fired film.

The low fusing flux employed is preferably a lead borosilicate flux or a bismuth compound, such as bismuth oxide or oxychloride.

If the paste is to be used to prepare a transfer, it will be found necessary to incorporate in the medium a suitable plasticizer or plasticisers, such as methyl abietate and/or castor oil, in an amount equal to 50–200% of the weight of cellulose derivative in the medium, for the purpose of preventing cracking of the decoration during transferring or firing.

A preferred composition of paste, formed in accordance with the invention and particularly suitable for preparing transfers for the decoration of glazed earthenware consists of the following:

	Per cent by weight
Gold powder	26
Mercuric aurate	22
Low fusing lead borosilicate flux	1
Plasticised nitrocellulose medium, viscosity 200 centistokes	51

the said constituents being ground together to form the paste.

This paste, whilst being particularly suitable for use in preparing a transfer by the silk-screen printing method for subsequent transfer to an article of pottery to be decorated, may also be used for direct silk-screen printing on to a substantially flat pottery article.

In the case of the decoration of a glass article, it will be found necessary to include a high percentage (preferably 3%) of flux in the paste owing to the lower firing temperatures employed.

The preferred composition of the individual constituents of the improved paste is as follows:

Flux or adhesion promoting constituent

Although any known lead borosilicate flux which melts at a temperature of 400–500° C. or a bismuth compound may be used, we have found that the most satisfactory results are obtained by using a flux having the following composition:

	Per cent by weight
Lead monoxide	80
Boric oxide	13
Silica	7

Medium or vehicle

	Per cent by weight
Amyl lactate	56
Ethyl lactate	20
Nitrocellulose (medium viscosity)	8
Methyl abietate	8
Castor oil	8

Mercuric aurate

	Per cent by weight
Gold	Approximately 55
Mercury	Approximately 33
Water and oxygen	Approximately 12

The mercuric aurate may be prepared by adding an aqueous solution of a gold halide e. g. the chloride, to an aqueous solution of a mercuric salt other than a halide in amounts to give the required proportions, both solutions being at or near their boiling points, filtering and washing the precipitated mercuric aurate and drying at a temperature below 100° C.

In the case where a thinner deposit is desired, than will be obtainable with the above composition, 1–10% (preferably 5%) by weight of anthracene may be included in the paste, the exact amount depending on the particular effect desired.

In the use of the improved paste for the decoration, for example, of a substantially flat article of glazed earthenware, the paste is applied to the article, so as to form any desired design thereon, by the silk-screen printing method, and allowed to dry. The coated article is then fired at a temperature within the range of 700–750° C. to burn

away the organic matter and cause the metallic gold to adhere firmly to the article.

If the base being decorated is of glass, the firing temperature should preferably be between 500° C. and 650° C., the exact temperature depending on the particular variety of glass under treatment.

The decoration, after firing, will present a matt surface, and may, if desired, be lightly scoured with sand or burnished with agate so as to produce a bright effect.

When the paste is to be used for preparing a gold transfer, the paste is applied, in any desired design, to a sheet of transfer paper by the silk-screen printing method and is again allowed to dry. To decorate an article, the transfer paper, with the design thereon, is applied to the article and the design transferred to the surface thereof by the well-known "slide off" method. The article is then fired at a suitable temperature, i. e. within the range of 500–650° C. in the case of a glass article and 650–800° C. in the case of pottery or earthenware.

The fired design may, in this case also, be lightly burnished.

What we claim is:

1. A silk-screen printing paste for use in the preparation of gold transfer or for direct application to an earthenware base, said paste comprising a mixture of the following constituents in the following proportions by weight, namely:

	Per cent
Gold powder	26
Mercuric aurate	22
Lead borosilicate flux	1
Solution of plasticised nitrocellulose medium	51

2. A gold silk-screen printing paste comprising a mixture of (1) mercuric aurate, (2) gold powder, (3) a flux chosen from the group consisting of lead borosilicate fluxes having a melting point no higher than 500° C., bismuth oxide and bismuth oxychloride and (4) a liquid vehicle comprising a solution of nitrocellulose; the mercuric aurate, gold powder and flux being present in the following proportions of the total solids, namely: mercuric aurate 10–50% by weight, gold powder 50–90% by weight and flux 1–15% by weight and the liquid vehicle being present in an amount to form with the solids a paste suitable for silk-screen printing, said gold powder, mercuric aurate and flux being always present and constituting together not more than 100% of the total solids.

3. A gold silk-screen printing paste comprising a mixture of (1) mercuric aurate, (2) gold powder, (3) a flux chosen from the group consisting of lead borosilicate fluxes having a melting point no higher than 500° C., bismuth oxide and bismuth oxychloride and (4) a liquid vehicle comprising a solution of nitrocellulose; the mercuric aurate, gold powder and flux being present in the following proportions of the total solids, namely: mercuric aurate 10–50% by weight, gold powder 50–90% by weight and flux 1–15% by weight; and from a trace up to 20%, determined on the weight of gold in the paste, of silver powder and the liquid vehicle being present in an amount to form with the solids a paste suitable for silk-screen printing, said gold powder, silver powder, mercuric aurate and flux constituting together not more than 100% of the total solids.

4. A silk-screen printing paste for use in the preparation of a gold transfer or for direct application to a heat-resisting base, said paste consisting essentially of a mixture of (1) gold powder, (2) mercuric aurate, (3) a flux selected from the group consisting of lead borosilicate fluxes having a melting point no greater than 500° C., bismuth oxide and bismuth oxychloride and (4) a liquid vehicle comprising a solution of nitrocellulose; the gold powder, mercuric aurate and flux being present in the following proportions of the total solids, namely: gold powder 50–90% by weight, mercuric aurate 10–50% by weight and flux 1–15% by weight; and from a trace up to 20%, determined on the weight of gold in the paste, of silver carbonate for the purpose specified and the liquid vehicle being present in an amount to form with the solids a paste suitable for silk-screen printing, said gold powder, silver carbonate, mercuric aurate and flux constituting together not more than 100% of the total solids.

5. A silk-screen printing paste for use in the preparation of a gold transfer or for direct application to a heat-resisting base, said paste consisting esssentially of a mixture of (1) gold powder, (2) mercuric aurate, (3) a flux consisting of 80% by weight of lead monoxide, 13% by weight of boric oxide and 7% of silica and (4) a liquid vehicle consisting of 56% by weight of amyl lactate, 20% of ethyl lactate, 8% of nitrocellulose, 8% castor oil and 8% methyl abietate, the mercuric aurate, gold powder and flux being present in the following proportions of the total solids, namely, mercuric aurate 10–50% by weight, gold powder 50–90% by weight and flux 1–15% by weight and the liquid vehicle being present in an amount to form with the solids a paste suitable for silk-screen printing, said gold powder, mercuric aurate and flux being always present and constituting together not more than 100% of the total solids.

6. A silk-screen printing paste for use in the preparation of a gold transfer or for direct application to a heat-resisting base, said paste consisting essentially of a mixture of (1) gold powder, (2) mercuric aurate, (3) a lead borosilicate flux and (4) a liquid vehicle consisting of nitrocellulose dissolved in a mixture of amyl lactate and ethyl lactate, the mercuric aurate, gold powder and flux being present in the following proportions of the total solids, namely, mercuric aurate 10–50% by weight, gold powder 50–90% by weight and flux 1–15% by weight and the liquid vehicle being present in an amount to form with the solids a paste suitable for silk-screen printing, said gold powder, mercuric aurate and flux being always present and constituting together not more than 100% of the total solids.

7. A gold silk-screen printing paste consisting essentially of a mixture of (1) mercuric aurate, (2) gold powder, (3) a flux chosen from the group consisting of lead borosilicate fluxes having a melting point no higher than 500° C., bismuth oxide and bismuth oxychloride, and (4) a liquid vehicle comprising a solution of nitrocellulose, said liquid vehicle also containing a small amount of a plasticiser selected from the group consisting of methyl abietate, castor oil and mixtures thereof and the mercuric aurate, gold powder and flux being present in the following proportions of the total solids, namely, mercuric aurate 10–50% by weight, gold powder 50–90% by weight and flux 1–15% by weight, and together constituting not more than 100% of the total solids, and the liquid vehicle being present in an amount to form with the solids a paste suitable for silk-screen printing.

8. A gold silk-screen printing paste consisting essentially of a mixture of (1) mercuric aurate, (2) gold powder, (3) a lead borosilicate flux having a melting point no higher than 500° C. and (4) a liquid vehicle comprising a solution of nitrocellulose, the mercuric aurate, gold powder and flux being present in the following proportions of the total solids, namely, mercuric aurate 10–50% by weight, gold powder 50–90% by weight and flux 1–15% by weight and constituting together not more than 100% of the total solids and the liquid vehicle being present in an amount to form with the solids a paste suitable for silk-screen printing.

FRANK ENOCH KERRIDGE.
CYRIL STANLEY COUPER.

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