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SILK-SCREEN PRINTING PASTE

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

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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. See also our co-
pending application 105,444, filed July 18, 1949.

Gold decorations on glass, china or earthenware have in general hitherto been produced by the use of:

(1) "Liquid gold," which consists essentially of a solution of a sulphoresinate of gold in suitable solvents, and

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

In the decoration of articles with a single simple design in gold, each of the above materials may be applied by hand painting with subsequent firing.

When, however, a repetitive design is required to be applied to the ware, it is usual to apply the decoration by a printing method, namely rubber stamp printing or engraved plate printing.

The rubber stamp method, whilst being simple and rapid in use, results in a design which is lacking in richness and sharpness of outline and, moreover, does not enable ceramic colours to be printed simultaneously in register with the gold.

With engraved plate or copper plate printing, a transfer is prepared by engraving or etching a design on a copper 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.

It is also known to decorate ware with a ceramic colour or vitreous enamel by applying directly to

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the ware a vitreous enamel or ceramic colour paste by means of the silk-screen printing method, and it has also been proposed to prepare a ceramic colour transfer by the silk-screen printing method.

Silk-screen printing, whether used for decorating an article by direct application or for the preparation of transfers, offers advantages over the other methods referred to in that the apparatus employed is inexpensive, a variety of decorative effects are obtainable and prints of high quality and well-defined outlines can be readily produced by relatively unskilled workers.

Pastes embodying the above-mentioned materials, as heretofore constituted for use with the rubber stamp or engraved plate printing methods are quite unsuited for use with the silk-screen printing method, particularly in the case of the preparation of transfers.

It will be appreciated from a consideration of the above that, if a gold paste were provided which could be satisfactorily applied by the silk-screen printing method, very considerable advantages would accrue both from the artistic and the commercial aspects. In the first place it would be possible to decorate an article with a design in gold which would have a more pleasing effect than those hitherto obtainable, owing to the improved definition of the outlines and the fact that it becomes possible to print a ceramic colour design in register with the gold, and secondly the process of decorating can be carried out relatively inexpensively.

Silk-screen printing, however, produces a very thick deposit and whilst this is, in many instances, particularly in the case of ceramic enamels, greatly to be desired, it may be that, in the case of a gold decoration, the cost of the gold may outweigh the advantages attainable by the use of this method. Attempts to produce a thinner deposit by employing a low gold: medium ratio in the paste, will result in unsatisfactory printing, owing to the low proportion of solid in the paste, and frequently in flowing of the prints and loss of sharpness of outline before drying.

An object of the invention, therefore, is to overcome the above disadvantages and to provide an improved gold paste consisting essentially of a metal powder-ceramic flux mixture containing gold powder or a mixture of gold powder and silver powder and suitable for direct application to an article to be decorated by the silk-screen printing method, or for the preparation, by the silk-screen printing method, of transfers intended for subsequent application to an article.

Another object is to enable a thin deposit of gold to be applied to a heat-resisting base by the silk-screen printing method.

A further object is to enable the thickness of the gold deposit to be readily controllable and tone-effects ranging from red-gold to green-gold to be obtained as desired.

Another object is to provide a gold silk-screen printing paste for the preparation of a transfer or for direct application to a heat-resisting base, said paste including a volatilisable solid, which will volatilise without carbonising during the subsequent firing of a heat-resistance base decorated with the paste.

A still further object is to provide a gold silk-screen printing paste comprising a mixture of gold powder, or a mixture of gold powder and silver powder, a volatilisable solid, a flux or adhesion promoting agent having a melting point no higher than 500° C. and an organic silk-screen printing medium or vehicle.

By including a volatilisable solid in the paste, the amount of gold present in the paste, and hence the thickness of the final gold film obtained after firing, may be varied as desired, since by suitably proportioning the amount of volatilisable solid included, the ratio of liquid to total solids in the paste may be maintained in the correct proportion to give good printing qualities.

The volatilisable solid may consist of any solid which volatilises completely at a low temperature, but we have found that certain organic materials, such as oxanilide, acetanilide or anthracene are more suitable than volatilisable inorganic materials, such as ammonium chloride. Of the organic materials mentioned, we prefer to use anthracene.

The proportion of medium to solid substances is preferably 1-4 parts of medium to 2 parts of solid, the exact proportions depending on the particle size of the solids and the viscosity of the medium.

The organic medium will comprise a film-forming ingredient dissolved in a solvent, for example it may be a cellulose derivative or a natural or synthetic resin or resins or a mixture thereof dissolved in a solvent or solvent mixture having a rate of evaporation suitable for silk-screen printing. For example, the medium may consist of nitrocellulose dissolved in amyl and/or ethyl lactate or of colophony dissolved in pine oil.

The gold powder employed may be of the kind produced by adding a reducing agent to a solution of a gold compound or a powder produced by mechanical comminution of the metal may be used.

The flux may be a lead borosilicate or a lead alkali borosilicate flux or a bismuth compound, such as bismuth oxide or oxychloride.

If desired, an extender, such as a mercury salt, may be included in the paste. In this case, we prefer to use mercurous chloride.

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

If the paste is to be used to prepare a transfer, it will be found desirable to include in the medium a suitable plasticiser or plasticisers, such as methyl abietate and/or castor oil for the purpose of preventing cracking of the decoration during transferring or firing.

The following are examples of pastes prepared in accordance with the invention, for the decoration

tion of earthenware, containing a cellulose derivative-based and a resinous medium respectively.

Per cent by weight

(1) Gold powder	40
Mercurous chloride	8
Low fusing lead borosilicate flux	2
Volatilisable solid (anthracene)	10
Plasticised nitrocellulose medium	40

the constituents being ground together to form a paste.

Per cent by weight

(2) Gold powder	40
Mercurous chloride	8
Low fusing lead borosilicate flux	2
Volatilisable solid	10
Plasticised resinous medium	40

the constituents being again ground together to form a paste.

In the case of the decoration of a glass article, owing to the lower firing temperature which is employed so as to avoid distortion of the glass, it will be found necessary to include a higher percentage of flux in the paste to ensure adequate adhesion.

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

Flux or adhesion promoting constituent

Although many lead borosilicate or lead alkali borosilicate fluxes, which melt at a temperature of 400-500° C. or bismuth compounds may be used, we have found the most satisfactory results are obtained by using a flux having the following composition:

Per cent by weight

Lead monoxide (PbO)	85.5
Boric oxide (B ₂ O ₃)	7.0
Silica (SiO ₂)	7.5

Medium

If a medium based on a cellulose derivative is employed, the following composition will be found suitable:

Per cent by weight

Amyl lactate	56
Ethyl lactate	20
Nitro cellulose (medium viscosity)	8
Methyl abietate	8
Castor oil	8

If a resinous medium is employed, the following composition will be found suitable:

Per cent by weight

Pine oil	70
Colophony	20
Methyl abietate	5
Castor oil	5

In the use of our 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 650-750° 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 is preferably between 500° C. and 650° C.

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.

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

It is to be understood that our improved gold paste may be printed so as to register with vitreous enamels or ceramic colours in a combined gold and enamel decoration.

What we claim is:

1. A silk-screen printing paste for the preparation of a transfer or for direct application to a heat-resisting base, said paste comprising a mixture of gold powder, anthracene, a ceramic flux and an organic vehicle consisting of 56% by weight of amyl lactate, 20% by weight of ethyl lactate, 8% by weight of nitrocellulose, 8% by weight of methyl abietate and 8% by weight of castor oil and the relative proportions of gold powder, ceramic flux and anthracene to liquid vehicle being always substantially 2 parts of solids to 1-4 parts of vehicle.

2. A silk-screen printing paste for the preparation of a 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:

	Percent
Gold powder	40
Mercurous chloride	8
Lead borosilicate flux	2
Anthracene	10
Solution containing plasticized nitrocellulose	40

3. A silk-screen printing paste for the preparation of a transfer or for direct application to a heat-resisting base, said paste consisting essentially of a metal powder-ceramic flux mixture, said metal powder being chosen from the group consisting of gold powder and a mixture of gold powder and silver powder, and anthracene, said metal powder-ceramic flux mixture and anthracene constituting solid ingredients, and an organic screening vehicle comprising nitrocellulose dissolved in a solvent selected from the group consisting of amyl lactate, ethyl lactate and mixtures thereof, and the relative proportion of the combined amounts of metal powder-ceramic flux mixture and anthracene to liquid vehicle being always substantially 2 parts of solids to 1-4 parts of vehicle.

4. A silk-screen printing paste for the preparation of a transfer or for direct application to a heat-resisting base, said paste consisting essentially of a gold powder-ceramic flux mixture and anthracene, said gold powder-ceramic

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flux mixture and anthracene constituting solid ingredients, and an organic screening vehicle comprising nitrocellulose dissolved in a solvent selected from the group consisting of amyl lactate, ethyl lactate and mixtures thereof and the relative proportion of the combined amounts of gold powder-ceramic flux mixture and anthracene to liquid vehicle being always substantially 2 parts of solids to 1-4 parts of vehicle.

5. A silk-screen printing paste for the preparation of a transfer or for direct application to a heat-resisting base, said paste consisting essentially of a gold powder-lead borosilicate flux mixture and anthracene, said gold powder-lead borosilicate flux mixture and anthracene constituting solid ingredients, and an organic screening vehicle comprising nitrocellulose dissolved in a solvent selected from the group consisting of amyl lactate, ethyl lactate and mixtures thereof and the relative proportion of the combined amounts of gold powder-lead borosilicate flux mixture and anthracene to liquid vehicle being always substantially 2 parts of solids to 1-4 parts of liquid vehicle.

6. A silk-screen printing paste for the preparation of a transfer or for direct application to a heat-resisting base, said paste consisting essentially of a gold powder-ceramic flux mixture, said flux being selected from the group consisting of bismuth oxide and bismuth oxychloride and anthracene, said gold powder-ceramic flux mixture and anthracene constituting solid ingredients, and an organic screening vehicle comprising nitrocellulose dissolved in a solvent selected from the group consisting of amyl lactate, ethyl lactate and mixtures thereof, and the relative proportion of the combined amounts of gold powder-ceramic flux mixture and anthracene to liquid vehicle being always substantially 2 parts of solids to 1-4 parts of vehicle.

FRANK ENOCH KERRIDGE.
CYRIL STANLEY COUPER.

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