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Lynch

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[54] **VITREOUS ENAMELLING**

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[51] **Int. Cl.²** **C23D 5/06**; C23D 08

[58] **Field of Search** ..... 117/40, 70 B, 94, 129, 117/45; 427/261, 279, 282, 287, 346, 376; 428/35, 210

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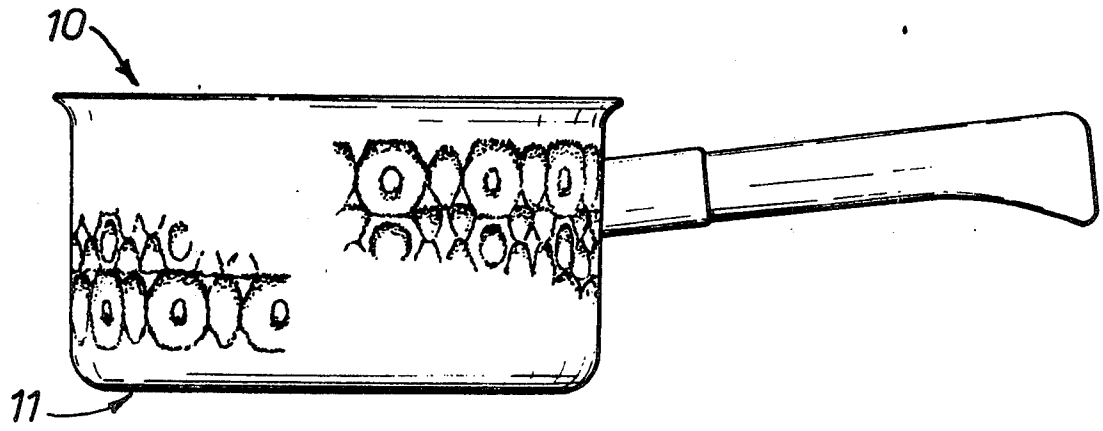
[57] **ABSTRACT**

A method of applying a decorative enamel surface to a steel article such as a cooking vessel in which a first layer of enamel is applied and fused at high temperature and a pattern of a second enamel or ceramic ink is applied and fused at high temperature, such that the two enamels react chemically and physically and some physical movement of the enamels occurs so that the base surface is partly exposed, thus providing an effect similar to glazed earthenware or pottery.

11 Claims, 5 Drawing Figures



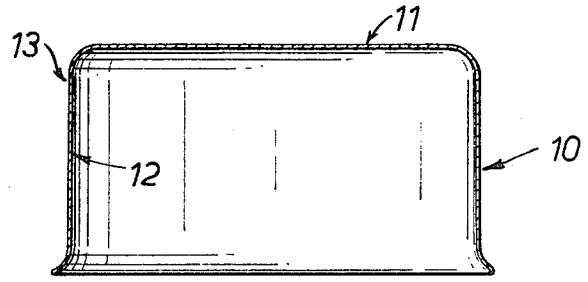


FIG. 1.

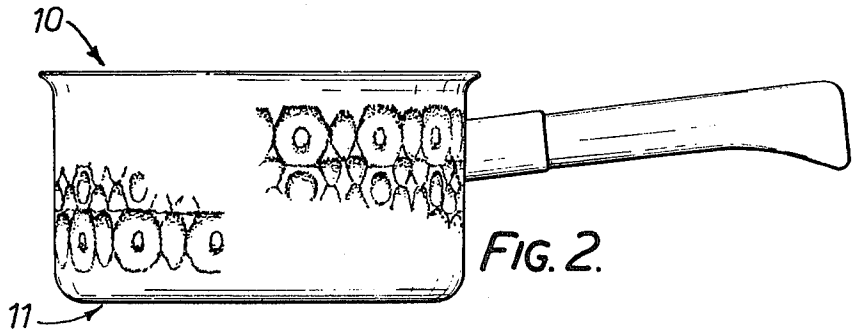


FIG. 2.

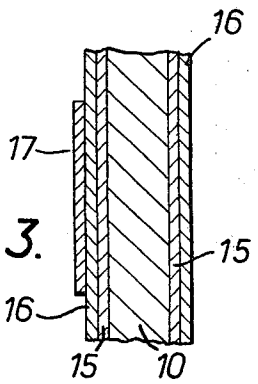


FIG. 3.

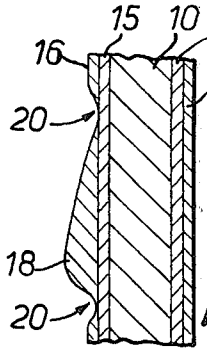


FIG. 4.

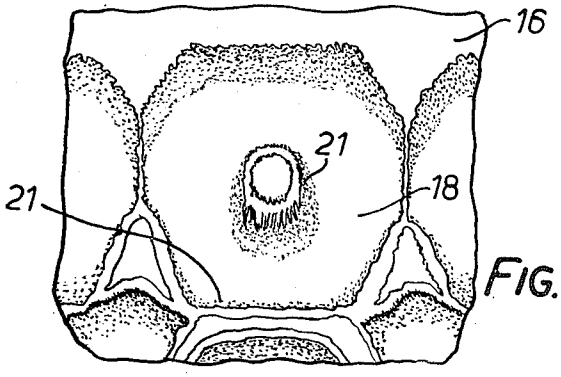


FIG. 5.

VITREOUS ENAMELLING

This invention relates to the decorating and coating of metallic surfaces by vitreous enamelling and the invention is particularly though not exclusively applicable to the enamelling of steel vessels or pans for domestic purposes.

It is known to decorate metallic houseware articles by vitreous enamelling and to obtain decorative effects by applying so-called enamelling or screening "inks" over the background enamel, the overlying "ink" (which normally consists of or contains a glass or other vitreous enamelling material) being then fired or fused to produce attractive colored enamel patterns on the base enamel.

The present invention by comparison is based on the discovery of a special enamelling process which can in some cases be made to resemble "decorated" earthenware or pottery, an effect which has hitherto been found impossible or extremely difficult to produce on an enamelled metal article.

Broadly stated from one aspect the invention consists in a method of decorating a metallic object by vitreous enamelling, in which two different enamels are applied, having different melting points, and the enamels are heated to a fusing temperature for long enough to cause reaction between the two enamels and some physical movement.

According to a preferred feature of the invention one of the two enamels is applied over the other and is of sufficient thickness to provide a relief or raised effect in the final product. Moreover it is important that the enamel materials should be such that the reaction product produced during the fusing process exhibits surface tension in relation to the underlying surface such that the body of material forming the reaction product tends to stand up proud of the surface.

In some embodiments of the invention the fusing process is continued for a period of at least 15 minutes and preferably approximately 30 minutes, but by suitable choice of enamel materials it may be possible to reduce the fusing period.

In any case it is important that sufficient quantities of the enamel materials should be applied to give the final raised relief effect and preferably the overlying enamel is applied as a relatively thick layer having a thickness of at least 0.005 inch.

Usually one of the two enamels will be an alkali-boro-silicate glass cover coat containing an oxide pigment and this is fused before the second enamel is applied, and preferably the second enamel applied over the first enamel has a softening point which is at least 50°C below the softening point of the underlying enamel.

In some preferred embodiments of the invention the two enamels are applied over an underlying enamel ground coat, conveniently formed of an alkali-boro-silicate glass, and preferably the second overlying enamel is a ceramic screening ink as used for decorating vitreous enamels, glass or pottery, consisting of finely ground glass with a pigment in a fluid medium such as pine oil. The second enamel may be of any colour but in some examples it is desirable that it should be of approximately the same color as the underlying enamel.

Particularly when the fusing process is of extended duration it is preferred that the metal article should be formed of de-carburized steel or low carbon steel containing not more than 0.005 percent carbon, and resistant to thermal distortion or sag at the fusing temperature of the enamels, i.e., up to about 750° to 800°C for an extended period.

According to another preferred feature of the invention the fusing operation is continued until portions of the underlying surface (e.g., the ground coat) become visible. Moreover in many cases the decorated surface is positioned in a vertical or inclined plane during fusing and fusing is continued until there is some downward flow of the reaction material.

The invention also consists in a metallic article such as a domestic cooking utensil having a decorative enamel surface produced by the process in any of the forms defined above. In other terms the invention consists in a metallic hollow-ware or houseware article such as a cooking pan having a decorative enamel surface comprising areas of a first enamel, areas of a second enamel consisting of the reaction product of the first enamel with the second enamel applied in localised areas, the surface having a relief or raised effect and parts of the underlying surface or ground coat being visible at the boundaries between the first and second enamel materials referred to.

The invention may be performed in various ways and one specific embodiment with various modifications will now be described by way of example with reference to the accompanying drawings, in which:

FIG. **1** is a sectional side elevation through a typical steel pan before enamelling, in an inverted position,

FIG. **2** is a side elevation illustrating the final decorated pan,

FIG. **3** is a diagrammatic sectional view on an enlarged scale through part of the side wall of the pan showing the decorative enamel layers before the final fusing operation,

FIG. **4** is a similar diagrammatic sectional view illustrating part of the surface of the side wall after the final fusing operation, and

FIG. **5** is a front view on an enlarged scale illustrating the final appearance of this portion of the enamelled side wall.

In this particular example the basic steel pan **10** illustrated in FIG. **1** is formed from a sheet steel blank, the steel preferably being decarburized low carbon steel containing not more than 0.005 percent carbon. This steel has the desirable property that at the fusing temperatures of the order of 850°C it is not subject to thermal distortion or sag which might result in an undesirable change of shape due to the relatively prolonged fusing process. In particular the base **11** of the pan will remain flat.

The first stage of the process is to apply a conventional enamel ground coat **15** to the internal and external surface **12, 13.** This is preferably an alkali-boro-silicate glass and may contain some cobalt. The alkali constituent may for example be sodium, and/or potassium, and/or lithium. The material is produced in conventional manner in the form of a "slip" by grinding the glass to a fine slurry and this is then applied by spraying or dipping, after which it is dried and then fused at a temperature of for example 840°C for a period of 4 to 6 minutes. This produces a blue-black enamel ground coat over the whole pan, inside and out.

The next stage is to apply an enamel cover coat **16** of the desired color. Again this enamel is an alkali-boro-silicate glass containing an oxide pigment which in the present example is preferably selected to produce an ochre or brown colour when fused. This cover coat **16**

is applied as a slip in the same way over the whole surface and is fused at a slightly lower temperature of between 780° and 840°C (preferably about 820°C) for 4 to 6 minutes.

When the cover coat is fused a further pattern of a second enamel **17** is then applied using a ceramic screening "ink" selected to have a melting or softening point which is preferably lower than that of the cover coat. For example if the softening point of the cover coat enamel **16** is 450°to 500°C the softening point of the screening ink enamel **17** would preferably be at least 50°C less (alternatively as mentioned below the softening point of the screening ink enamel may be greater than that of the cover coat). The screening "ink" is preferably a ceramic screening ink as used for decorating vitreous enamels, glass or pottery and consisting of very finely ground glass or frit, with a pigment, in a liquid medium such as pine oil. The term "screening ink" implies that the "ink" can pass through a silk screen and conventional silk screens have a mesh size of about 280 to 300 holes per linear inch.

It is desirable that the layer of screening ink **17** should be relatively thick in comparison with the normal thickness at which such inks are applied, which is conventionally of the order of 0.001 to 0.003 inch The screening ink layer in performing the present invention may have a thickness of about 0.005 to 0.008 inch or more. The thickness is important in providing sufficient material to react with the underlying cover coat **16** and also to provide sufficient material for the final desired relief or raised effect. The screening ink pattern may be applied in various different ways, for example through a stencil or by hand brushing or a wax-resist process, or by transfer, or more conveniently through a silk screen: in the latter case in order to provide sufficient thickness it is preferable to use an ink with a particle size designed for a 280 mesh screen but to use a coarse screen with a mesh size of about 50 holes per linear inch.

In this particular example the screening ink pigment is so chosen that the colour of the reaction product **18** (see FIG. **4**) with the cover coat is also brown and this gives a rustic pottery effect in the final product. However it will be understood that in general any color of screening ink may be used.

The screening ink pattern **17** is then dried, after which the final fusing operation is then performed. In the present example this is a heating process at a temperature of approximately 800°C for a period of about 30 minutes, considerably longer than in a conventional enamel fusing process of about 5 minutes for normal thin gauge metal as used in cookware, e.g. about 0.048 inch thickness or less. During this heating stage the screening ink **17** fuses and reacts and combines with the underlying cover coat **16** which it modifies, and the reaction product **18** becoming soft or molten tends to draw away from the adjacent areas **20** of cover coat where no screening ink is applied thus exposing bands of the dark undercoat **21** at the boundary of each screening ink area. The plastic or fluid reaction product material also tends to rise up clear of the surface as a result of surface tension and/or gravity and produces a relief pattern as illustrated in FIG. **4**. In addition the boundaries of the surrounding cover coat are blurred or "tattered" as shown in FIG. **5** and in some cases portions of the soft or molten reaction product tend to flow downwards over adjacent parts of the adjoining cover coat.

The duration of this fusing stage can be varied to some extent in accordance with the fusing temperature and the melting points of the materials. For example if the temperature is raised to about 840°C the time of the process may be reduced to about 15 minutes and by suitable choice of materials the time may be further reduced to 10 minutes or less. If the temperature does not exceed about 780°C the fusing time may have to be extended to about 45 minutes. With these prolonged heating processes it is of some importance that the base metal should be of de-carburized steel or other metal capable of standing up to these temperatures without distortion.

Full details of one particular example of the invention including specific compositions of the coating materials, are as follows:

Ground Coat

This consists of three different frits which are subsequently milled with additions to produce a final slurry for application to the basic metal. The composition of the three frits A, B, and C is as follows (parts by weight):

	FRIT A	FRIT B	FRIT C
Quartz	192	257	145
Dehydrated Borax	63	150	131
Granulated Borax	118	105	105
Soda Ash	41	35	47
Fluorspar	36	42	42
Sodium Nitrate	32	37	37
Manganese Dioxide	9	10	10
Cobalt Oxide	3	4.2	3.2
Nickel Oxide	3	4.2	3.2
Felspar	122	—	164

Each frit composition is placed separately in a furnace and smelted at about 1200° to 1300°C for approximately 1½ hours. The materials react and some gases are driven off, and the product is a molten glass like substance which is quenched by pouring into cold water, and shatters into very fine frit particles. The chemical analysis of these frit products is as follows (parts by weight):

	FRIT A	FRIT B	FRIT C
SiO_2	52.52	43.3	44.0
Al_2O_3	5.0	0.7	5.6
B_2O_3	16.5	25.6	21.6
Na_2O	15.0	17.8	17.8
K_2O	1.0	—	1.1
CaF_2	6.9	8.6	7.1
NiO	0.57	0.86	0.5
CoO	0.57	0.86	0.5
MnO_2	1.7	1.8	1.6

These three granular frit batches are dried and then mixed with additions in the following portions (parts by weight):

FRIT A	40
FRIT B	30
FRIT C	30
CLAY	7.0
SODIUM NITRITE	0.1
WATER	40.0

The mixture is then milled for about 8 hours to produce a fine slurry such that when a 50 cc sample is passed through a 200 mesh sieve (having 200 holes per linear inch) approximately 9 gms of the material will remain on the sieve. The resultant slurry is then applied to the base metal surface of the pan **10**, by dipping or

spraying. It is dried to remove water and then fired at 840°C for approximately 4 minutes.

Cover Coat

The cover coat enamel **16** is prepared as follows:

First the frit is prepared having the following composition in parts by weight.

Felspar	126
Quartz	205
Sodium Silico Fluoride	20
Dehydrated Borax	128
Titanium Dioxide	60
Potassium Carbonate	56
Sodium Nitrate	60

This composition is smelted as with the ground coat frit described above to produce a frit having the following chemical analysis:

SiO_2	49.2
B_2O_3	14.6
Al_2O_3	4.75
Na_2O	12.1
K_2O	7.25
TiO_2	10.0
F_2	2.0

This frit is dried and mixed with the following additions (parts by weight):

Frit	100
White Clay	5
Bentonite	0.25
Sodium Nitrite	0.1
Brown Oxide Pigment	5
Water	40

The mixture is milled to produce a fine slurry such that a 50 cc sample will pass through a 200 mesh sieve leaving 1 to 3 gms. on the sieve. The resultant slurry is then applied as the cover coat **16** over the ground coat **15**, for example by dipping or spraying. This is dried to remove the water and then fired at about 800°C for approximately 4 minutes.

Screening Enamel or Ink

First a frit is prepared having the following composition (parts by weight):

Red Lead	36
Quartz	45
Aluminium Oxide	5
Boric Acid	17.8
Sodium Nitrate	12

The materials are smelted in a furnace at about 1000° to about 1100°C and quenched in water to produce fine frit particles which have the following chemical analysis (parts by weight):

PbO	35
SiO_2	45
Al_2O_3	5
B_2O_3	10
Na_2O	5

The frit is dried and milled in a dry condition to a very fine powder which will pass through a 280 or 300 mesh sieve. 100 parts by weight of this powder are mixed with 40 parts of pine oil and 10 parts of an ochre oxide pigment which may contain a flux such as Borax so that the melting point of the pigment is close to the melting point of the screening enamel itself. The mixture is milled again to produce a pasty material which will pass through a 50 mesh screen. This paste is then applied in a pattern through a stencil or silk screen over the cover coat **16**.

It is then dried in a warm oven to remove the oil and then fired at about 800°C for about 30 minutes.

I claim:

1. A method of vitreous-enamel decorating of an object formed of de-carbonized or low carbon steel, comprising the steps of; applying a first coating of enamel having a first melting temperature, heating said first coating of enamel to said first melting temperature to fuse said enamel to the object, applying in a controlled pattern a second coating of enamel over said first coating, said second coating of enamel having a second melting temperature different from said first melting temperature, heating said second coating of enamel to a fusing temperature to cause said first and second coatings of enamel to become flowable and timing said fusing temperature until there is physical movement of the two enamels relative to the object being coated thereby forming a surface having a relief raised effect conforming substantially to said controlled pattern.

2. A method according to claim **1**, in which said two enamels, are such that the reaction product of said enamels produced during the fusing process exhibits surface tension in relation to the underlying surface, whereby the body of material forming the reaction product tends to rise up.

3. A method according to claim **1**, in which the said second enamel is applied as a relatively thick layer having a thickness of at least 0.005 inch.

4. A method according to claim **1**, in which said first enamel is an alkali-boro-silicate glass cover coat containing an oxide pigment.

5. A method according to claim **1** in which the said second enamel has a melting point which is at least 50°C below the melting point of said first enamel.

6. A method according to claim **1**, in which said two enamels are applied over an underlying enamel ground coat.

7. A method according to claim **1**, in which said second enamel is a ceramic screening ink consisting of finely ground glass with a pigment in a fluid medium.

8. A method according to claim **1**, in which said second enamel is of approximately the same color as the first enamel.

9. A method according to claim **1**, in which the fusing operation is continued until portions of the underlying surface become visible.

10. A method according to claim **1**, in which the decorated surface is positioned in a vertical or inclined plane during fusing and fusing is continued until there is some downward flow of the reaction material.

11. A metallic houseware article comprising; a body formed of decarbonized or low carbon sheet steel, a first coating of enamel formed on said body, a second coating of a different enamel over said first coating and applied thereto in a predetermined pattern, said first and second coatings of enamel being combined to form a surface having a relief raised effect corresponding to said predetermined pattern.

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