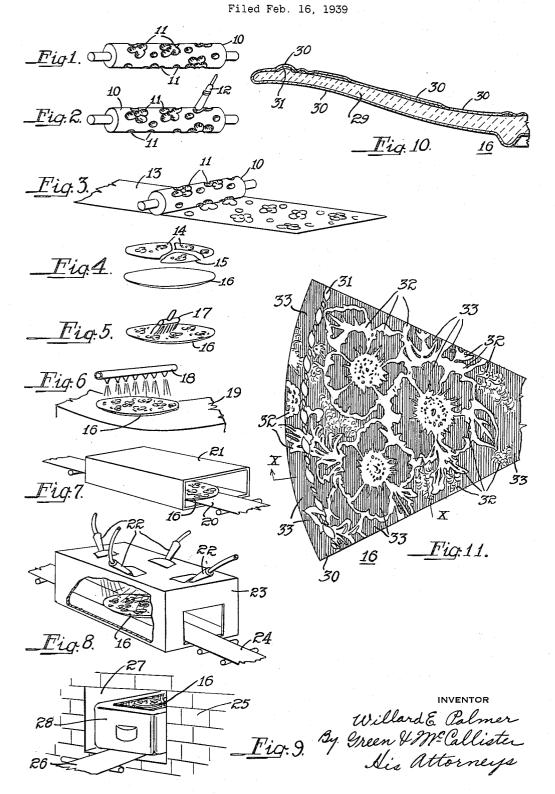
DECORATED CERAMIC WARE AND METHOD OF MAKING THE SAME



## UNITED STATES PATENT OFFICE

2,270,081

DECORATED CERAMIC WARE AND METHOD OF MAKING THE SAME

Willard E. Palmer, East Liverpool, Ohio, assignor to The Taylor, Smith & Taylor Company, a corporation of West Virginia

Application February 16, 1939, Serial No. 256,750

14 Claims. (Cl. 41-26)

The present invention relates to the production of ceramic ware such as plates, saucers and other items of dinnerware with an underglaze design or pattern; the invention comprehends both the finished ceramic articles and the method of 5 producing them.

Decorated dinnerware of ceramic material having designs or patterns either of the overglaze or underglaze type is extensively made and used all over the world. In the overglaze type the de- 10 sign of the underglaze type in the article. sign or pattern is on the top surface of the glaze which covers the more or less porous ceramic body of the article. In the underglaze type the design or pattern is applied to the ceramic body prior to glazing and thus lies beneath the subse- 15 quently applied and fused glaze. In the overglaze type the glaze may be opaque and colored but in the underglaze type the glaze must be transparent so that the design or pattern will show through. Overglaze designs are usually 20 thereby produced: short-lived as they are exposed to wear, alkalis, etc. and are ordinarily used on cheaper types of ware. Underglaze designs are limited to transparent glazes and thus suffer from the handicap of a relatively small range of color schemes or 25 designs. The production of ware having designs lighter in color than the balance of the ware is unsatisfactory for overglaze designs and difficult or impossible for underglaze designs.

As will be appreciated from the foregoing, the 30 to a ceramic article such as plate; industry has been somewhat hampered and restricted in the matter of glazes and designs and is desirous of extending the type and variety of product for commercial and economic reasons. Due to the exceedingly keen competition in this 35 field the industry is always particularly on the lookout to improve its products and, if possible, to cut down costs. The present invention represents a substantial improvement in both these respects.

It is, accordingly, one of the objects of the present invention to broaden the scope of the present underglaze and overglaze designs and to eliminate certain disadvantages inherent in and restricting the manufacture of both.

Another object of the invention is to produce ceramic articles of dinnerware such as plates of the underglaze type, wherein the glaze and hence the background of the plate is colored and opaque but wherein the design is in white, off-white or 50 light tones.

An additional object of the invention resides in the production of ceramic dinnerware having an opaque glazed surface of suitable color and a design of the underglaze type visible due to a 55 pyrochemical reaction between the material of the design and the glaze which occurs during firing and which produces a reaction product colored differently from the glaze itself.

producing a plate or other ceramic body in conventional manner, applying thereto a design motif composed of a special zinc oxide paste, covering the entire article including the design motif with an opaque colored glaze and subjecting the whole to firing in a kiln at a suitable temperature whereby the chemicals in the design decolorize corresponding portions of the glaze, thereby producing a white or light colored contrasting de-

Other and further objects and advantages reside in the various combinations, sub-combinations and details of structure and procedure hereinafter described and claimed and in such other and further matters as will be understood by those skilled in this art.

In the accompanying drawing wherein I have diagrammatically illustrated one mode of carrying out my present invention and the results

Fig. 1 illustrates in perspective a printing roll with an intaglio design formed in the surface thereof:

Fig. 2 indicates the application of zinc oxide paste composition to the printing roll;

Fig. 3 illustrates the application of the design to a paper base of the kind used for decalcomania transfers:

Fig. 4 indicates the application of the design

Fig. 5 illustrates the treating of the design on the plate with a lubricant and the elimination of wrinkles from the paper;

Fig. 6 illustrates how the paper base is hydraulically removed, leaving the design isolated on or transferred to the ceramic article;

Fig. 7 diagrammatically indicates the drying of the design on the article;

Fig. 8 illustrates the application of a colored 40 or opaque glaze to the ceramic article;

Fig. 9 diagrammatically illustrates the firing of the glazed article in a kiln;

Fig. 10 represents a cross section through a fragment of an article embodying the present 45 invention; and

Fig. 11 illustrates in plan view a segmental fragment of the ceramic article of Fig. 10.

Like numerals designate corresponding parts throughout the various views of the drawing which is intended as purely diagrammatic and exemplary to aid in an understanding of the invention.

In carrying out my present invention I first preliminarily prepare a suitable roll 10 preferably made of copper or other appropriate material, and in the cylindrical surface of this roll I produce in any known manner an intaglio design or pattern as at 11 or a plurality of design elements which may be employed to make up a suitable A further object of the invention resides in 60 pattern or other design motif, as is well under2 2,270,081

stood by those versed in these matters. In the recessed design I next apply a special composition in the form of a paste. This paste is composed of pure zinc oxide mixed with an oily material which is made up essentially of boiled linseed oil, Stockholm tar and a small amount of red lead, the proportions being adjusted so as to form a very thick and very viscous paste.

This paste is applied to the recessed designs or design elements in the roll in any suitable 10 way, as by an applicator 12. The roll 10 in this condition, is utilized to print the design, pattern, etc. over and over on a paper base 13 of the character commonly used in decalcomania transfers. While I have illustrated the roll 10 by itself, 15 this is for simplicity and convenience of illustration, but it will be understood that the roll forms a part of a suitable machine, the structural details of which are not pertinent to the present invention.

As illustrated in Fig. 3, the design or pattern may be printed over and over on a long continuous strip of paper although not necessarily so, and then from this paper pieces are cut which contain elements or portions of the design, or 25 entire groups or desired arrangements of design elements, of such size and shape as will give the desired pattern or decorative effect on the particular ceramic ware involved.

In Fig. 4 I have illustrated one mode of ac- 30 complishing this, and ordinarily one or more arcuate pieces 14 are cut and frequently a disklike portion 15 provided so that a plate 16, for example, can be provided along its outer upper surface with a design and usually with a central 35 design element or pattern, but it will be understood that no general rule can be laid down as to the size and shape of the pieces cut from the printed paper because this necessarily depends upon the size of the ware involved and the kind of design or pattern which is to be produced therein.

In the case of an allover design, one or more pieces can be cut, and whatever the precise paper portion may be, the same is laid upon the plate with the printed side down in contact with the ware. The next step is to apply a lubricant such as gelatin or soap, and this is brushed or rubbed on or over the paper by a brush or applicator as is diagrammatically indicated at 17 in Fig. 5. 50 limestone), approximately 1-3% chromium oxide This ensures close and smooth contact and eliminates wrinkles from the paper. I next pass the article in such condition beneath or through a water spray or bath is by hand or on a circular or other conveyor such as 19 diagrammatically indicated in Fig. 6, and this softens, loosens and disintegrates the paper base on which the design is printed, and since this paper may be of the so-called water soluble or disposable type the paper is removed by the water, leaving the 60 design on the comparatively porous ware, which is of the type known in the industry as bisque or semivitreous. Thus, as the paper floats away or disintegrates, the design is transferred to and isolated on the ware in the position or positions 65 determined by the size, shape and disposition of the design-carrying paper parts previously placed on such ware.

The next step in my procedure is to dry the ware with the design thereon, and this I accom- 70 plish by subjecting the now "printed" ware to a temperature between about 700° F. and 900° F. This may be done in any suitable way, such as is graphically illustrated in Fig. 7, by the passage of the plate 16 on a suitable conveyor 20 through 75

a chamber, oven, heating zone or the like 21 within which the desired temperature is maintained. At the temperature indicated, the paste above mentioned is subjected to some volatilization and oxidation, particularly insofar as the oily components of the paste are concerned, and this I have found to be important because all portions of the plate must be able to receive and retain equally well the glaze subsequently applied. If the decoration or inchoate design were in an oily, slippery or improperly treated condition the glaze would not "take" on the design itself. By the heat treatment just described I therefore convert the printed design into a condition in which it is capable of receiving glaze just as well as the comparatively more porous portions of the ware which carry no design. The chamber or the like 21 is of sufficient size or length so that the heating time is adequate to accomplish the 20 specified result.

The so-prepared ware is next provided with a fine, thin layer of liquid glaze, usually by spraying the same from nozzles 22 mounted in a booth 23 through which the ware passes on a suitable conveyor or the like 24, as schematically shown in Fig. 8 for illustrative purposes. This glaze is not of the ordinary clear or transparent type commonly employed in the past in connection with the production of dinnerware or the like having an underglaze type design, but the glaze utilized in connection with my present invention is a tinted or colored glaze which is opaque or substantially opaque.

Without being limited thereto, I have found that a glaze containing a chrome tin stain serves admirably for the purposes of the present invention where it is desired to produce dinnerware having a pink background with an underglaze type design which is cream colored. It is to be understood that the production of pink ware with a cream colored underglaze type design is only one example of results which can be accomplished by means of the present invention, and by suitably changing the paste and glaze, or the proportions of the components therein, other color combinations can be produced.

The chrome tin stain above mentioned is composed of approximately 50-70% tin oxide, approximately 20-30% calcium oxide (applied as (Cr2O3), a small percentage of lead antimonate, and minor percentages of other ingredients. The glaze made therefrom has a pink color and is applied preferably by spraying, as above indicated, to the ware with its heat-treated design thereon, and this glaze adheres equally well to the decorated portions of the ware as to the undecorated portions.

The entire article in this condition is then fired in a kiln of the usual type, diagrammatically indicated at 25, and this may be carried out on the usual kiln conveyor 26 which passes through the tunnel 27 of the kiln in a saggar 28 at a rate such that the ware is subjected to the kiln temperature for the requisite period of time. The usual temperature is approximately 2000° F. for the firing operation, but I may utilize any temperature between about 1800° F. and 2400° F. The temperature is usually determined by Standard or Henderson pyrometric cones and may range from cone 06 to cone 12. It is during this firing that one of the important steps of my invention is effected. Due to the composition of the paste from which the design is produced and also to the composition of the glaze contain-

3 2,270,081

ing the chrome tin stain above referred to, and the compositions of which have been particularly chosen for the purposes of the present invention, a pyrochemical action occurs at the high temperature which results in decolorizing the chrome tin stain at those locations—and only at those locations—where the two compositions are in contact.

While I am not prepared to state at this time exactly what does occur, chemically speaking, there is undoubtedly an interaction between the ingredients of the two compositions which produces glassy or fused reaction products reproducing the exact configurations of the zinc oxide Printed design or pattern but which is substantially cream colored, although within this term I wish to include white, off-white, ivory and similar shades. So faithfully and accurately does the action occur that even fine traceries or filamentary or feathery design elements can be re- 20 produced, and in one actual operation I have found that there is no difficulty in producing an allover flower spray design of petals, stems, leaves and feathery foliage, such as has been illustrated in Fig. 11, although it will be appreciated that a pen and ink drawing cannot bring cut all the minutiae of detail of a complex design. An attempt has been made to reproduce some of this in Fig. 11 for illustrative purposes.

In connection with the zinc oxide paste as above set forth, the composition thereof may be somewhat varied as above mentioned. For example, half of the zinc oxide can be replaced by zirconium oxide, or one-fourth of the zinc oxide can be replaced either by calcined English china 35 clay or hydrated alumina. Titania can be emplayed as a substitute for part or all of the zinc oxide. Such and other variations in the zinc oxide paste composition are intended to be within the present invention.

The chrome tin stain above set forth may likewise be somewhat varied in its percentage composition, although I have found that the composition set forth is entirely satisfactory where glaze referred to is made up as follows:

100 parts of base glaze, which itself is composed of approximately 44 parts of frit and 56 parts of lead, etc., are mixed with 6 parts of the chrome tin stain above set forth and with 6 parts of zir- 50 conium oxide. These ingredients are ground together to a very fine state of subdivision and applied preferably by spraying as above described, it being understood that dipping, brushing or sorted to in special circumstances or as required.

Referring particularly to Figs. 10 and 11 of the drawing, the numeral 29 indicates the body portion of the ware or plate i6 and the numeral upper surface of the glaze is shown as being irregular in Fig. 10 and this irregularity is caused by the fact that the zinc oxide paste forming the design has some thickness and therefore in those portions where the design occurs the pink glaze 65 rises and falls, accommodating itself to the contour of the surfaces which it covers. In some cases I produce a plate or the like with a raised bead-like design 31 near the peripheral edge and is not to be considered as constituting a limitation upon my invention but rather as showing what can be accomplished in accordance therewith.

The numeral 32 in Fig. 11 indicates some of 75

the cream colored design portions and the numeral 33 indicates some of the pink background portions. The unshaded or white portions of Fig. 11 are the cream colored or light colored portions of the design, and the shaded or darker portions of Fig. 11 are the pink portions of the background.

Summarizing for convenience, my present procedure comprises the application of designs by 10 means of decalcomania transfers to ceramic ware, such as dinnerware, the transfer of the design to the ware, the conditioning of the design so that it will receive glaze, the application of nontransparent glaze of suitable composition to the article, and the firing of the same in a kiln so as to bring about the pyrochemical action above referred to and which, in the case of the particular compositions above described, produces a cream colored underglaze design beneath a pink glaze but which in other cases and other color schemes produces black, red or other colored reaction products as determined by the chemical considerations involved, as will be understood by ceramic chemists.

I have explained above that I am not limited to the production of cream, white or off-white designs under a pink glaze. Many other color combinations are possible, and so long as they are produced in accordance with the principles of the present invention such are deemed to fall within the scope thereof. For example, reds, yellows and blues as background colors are specifically deemed as falling within the contemplation of my invention and these may be used in connection either with the cream, white or offwhite underglaze designs above referred to, or by utilizing appropriate or special compositions the underglaze design may be black, red (where a red background is not used) or a complementary. contrasting or harmonizing color or shade, and the variations required in my procedure to produce such are appropriate changes in the compositions of the paste and glaze.

While I have illustrated an allover type of dea pink background or glaze is desired. The pink 45 sign, it is to be understood that designs may be produced in accordance with this invention as only border designs, as only central designs, as a combination of a border and central design, or as regular or irregular patterns of many and varied kinds.

While my invention has been described more particularly in connection with ceramic dinnerware such as plates it is to be understood as applicable to all items of dinnerware and also to other modes of applying the glaze can be re- 55 numerous other similar, analogous or allied ceramic products such as vases, lamp bases, art objects, sinks, bathtubs and the like which involve a glazed ceramic body which is decorated or ornamented by a design, pattern, etc. of the 30 indicates the layer of glaze thereover. The 60 underglaze type. The invention also includes vitreous bodies or articles such as china ware which may be decorated in accordance herewith.

My invention also comprises dinnerware such as plates composed of a ceramic body covered by a colored opaque glaze, portions of which have been decolorized or changed in color by a pyrochemical reaction, and such constitute new articles of commerce insofar as I am aware.

Having thus described my invention, what I thereof, but this is purely a matter of design 70 claim as new and desire to secure by Letters Patent is:

> 1. As a new article of commerce ceramic ware which comprises a fired ceramic body, an opaque colored glaze on said ceramic body and a differently colored pyrochemical reaction product un

der and combined with portions of such glaze to form for such ware a design of the underglaze type.

2. As a new article of commerce ceramic dinnerware which comprises a semivitreous ceramic body, a thin fused layer of nontransparent pink glaze covering said ceramic body predetermined portions of which glaze are decolorized to produce in such dinnerware a design of the underglaze type.

3. As a new article of commerce ceramic ware which comprises a fired ceramic body of comparatively porous nature, a thin fused layer of opaque colored glaze covering said ceramic body and a design or pattern of the underglaze type 15 between portions of said ceramic body and said glaze, the said design or pattern being a pyrochemical reaction product resulting from high temperature interaction between said glaze and a zinc oxide paste composition which defines the 20 chemically develop the design or pattern. design or pattern.

4. A plate or other ceramic article which is made up of a ceramic body, a colored opaque glaze covering said ceramic body, and a pyro-chemical reaction product between said glaze 25 and said ceramic body which has different color characteristics than the glaze and which with such glaze defines a design of the underglaze

type.

5. A method of making decorated ceramic ar- 30 ticles of the kind described which comprises the steps of applying to such article a decalcomania transfer bearing a design printed thereon with a zinc oxide paste composition, transferring the design to the article, subjecting the article with 35 the design thereon to a heat treating operation of such nature as to convert the design to a condition in which it can receive and hold glaze, applying a colored opaque glaze to the thus treated article and firing the same at high tem- 40 perature to bring about a pyrochemical reaction between the design and the glaze whereby the glaze is altered in color where the design contacts the same by the formation of reaction products.

6. A method of making ceramic dinnerware which comprises printing a design on a paper base of the type commonly used for decalcomania transfers with a paste composition containing zinc oxide, applying one or more por- 50 tions of the thus printed paper to dinnerware printed side down, applying a lubricant to the paper base, removing the paper base to transfer the design to predetermined position on the dinnerware, heating the article in this condition to 55 approximately 700°-900° F. for a period of time sufficiently long to volatilize and oxidize those ingredients of the composition which are susceptible of such action, applying a colored opaque glaze to the dinnerware, and firing the same at 60 about 1800°-2400° F. to bring about a pyrochemical action between the zinc oxide composition and the glaze whereby a design of the underglaze type is defined on the dinnerware of different color characteristics than said glaze.

7. A method of making ceramic dinnerware of the kind described which comprises applying a zinc oxide paste composition in the form of a desired design or pattern to such dinnerware, subjecting the same to a drying heat treatment, 70 applying an opaque glaze of desired color characteristic to such dinnerware, and subjecting the same to a temperature sufficiently high to bring about a pyrochemical action between the zinc oxide composition and the glaze to develop a 15

design or pattern corresponding to that of the zinc oxide composition but of a different color characteristic.

8. A method of making a plate or other ceramic article of the character described which comprises applying a zinc oxide paste to a suitable intaglio design or pattern formed in a suitable printing roll, printing such design or pattern on a paper base of the kind commonly used 10 for decalcomania transfers, severing portions of such paper base containing desired design or pattern elements and predeterminedly applying the same paste side down to the ceramic plate, applying a lubricant to such paper base, disintegrating the paper base to transfer the design or pattern to the plate, drying the design or pattern at about 700° F., spraying the whole with a liquid pink opaque glaze, and firing the same at about 2000° F. to fuse the glaze and to pyro-

9. A method as defined in claim 8 wherein the glaze contains a chrome tin stain which is composed of approximately 50-70% tin oxide, approximately 20-30% calcium oxide, approximately 1-3% of chromium oxide, a small percentage of lead antimonate and minor amounts of other

ingredients.

10. A method as defined in claim 8 wherein the zinc oxide paste composition consists of substantially pure zinc oxide intermixed with an oily composition composed of boiled linseed oil, Stockholm tar and a small proportion of red lead.

11. In a method of making a ceramic article decorated with a design of the underglaze type the steps which comprise applying a chemical paste to a surface of the article to define the desired design, drying the paste under mild heat, covering the surface and design with a liquid opaque glaze and causing the paste pyrochemically to develop and fix a corresponding design in the glaze by firing the whole at a temperature of about 2000° F.

12. In a method of making a colored ceramic 45 article decorated with an uncolored design of the underglaze type the steps which comprise printing a design on a paper base with a paste composed of zinc oxide, linseed oil, Stockholm tar and red lead, transferring the design from the paper base to a surface of the ceramic article and heating the article and design at about 700°-900° F. for a time adequate to convert the design to a condition in which it is capable of receiving and retaining a thin covering of a liquid opaque glaze.

13. In a method of making a ceramic article decorated with a design of the underglaze type the step of altering the color characteristics of a colored opaque glaze in predetermined portions to develop and fix a design therein by heating the article and glaze to about 1800°-2400° F. in contact with a chemical paste capable of reacting with the glaze to produce pyrochemical reaction products having color characteristics dif-

65 ferent from said glaze. 14. In a method of making colored ceramic

ware decorated with a lighter colored design of the underglaze type, the step which comprises pyrochemically developing the design through interaction of a chemical paste of which the design is printed and contacting corresponding portions of an opaque glaze, which latter are lightened in color due to the interaction aforesaid.