Oct. 3, 1944. B. C. BRICKER 2,359,462

DECALCOMANIA

Filed Sept. 21, 1942

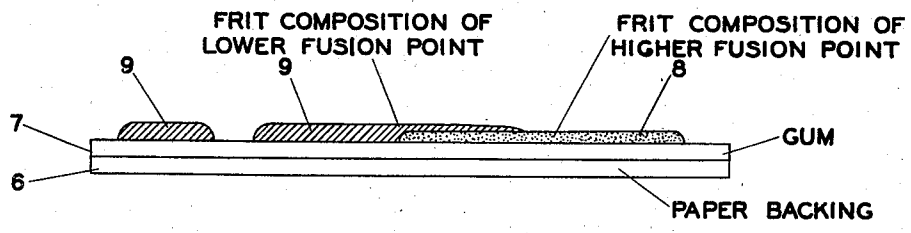


FIG. 1

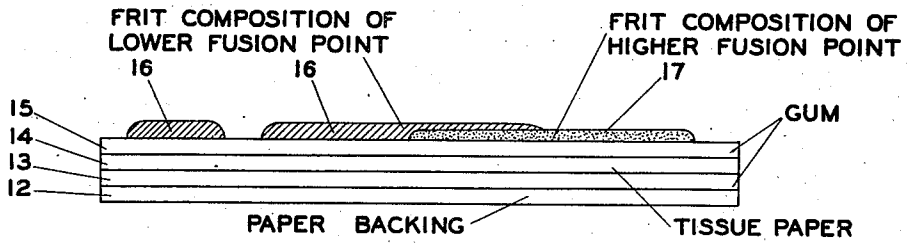


FIG. 2

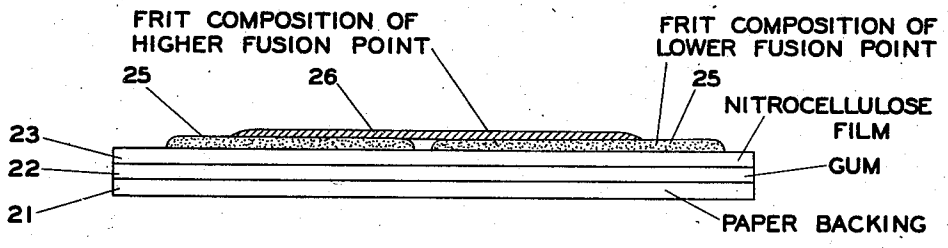


FIG. 3

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Patented Oct. 3, 1944

2,359,462

UNITED STATES PATENT OFFICE

2,359,462

DECALCOMANIA

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Application September 21, 1942, Serial No. 459,073

2 Claims. (Cl. 41—33)

This invention relates to the preparation of an improved decalcomania transfer capable of utilization in the production of multi-color designs upon ceramic objects such as articles made from glass or chinaware.

The production of designs by means of decalcomania transfers prepared with vitrifiable enamel colors has been known in the ceramic industry and practiced thereby for many years. The decalcomania consists essentially of a sheet of paper upon which the design is printed in one or more vitrifiable enamel colors. After the design has been printed on the backing sheet, it is transferred to the ceramic surface on which it is finally to appear, and is affixed thereto by means of a temporary binder in the position it is desired that is shall occupy. The ceramic article is then subjected to a firing operation which not only destroys the organic material present both in the ink or other vehicle used to bind the color on the paper as well as the bond which fastens it to the ware, but at the same time brings the vitrifiable enamel color compositions to their fusion points so that they melt and form a permanent bond with the ceramic surface.

Decalcomanias intended for application to ceramic objects, such as glass ware or chinaware articles, have generally been of two general types. In one type, the paper backing sheet carries a thin layer of a water soluble gum and it is upon this gummed surface that the design is imprinted. The paper may be either of a sufficient weight to handle in a printing operation, or it may be tissue paper, in the latter case the tissue being itself fastened to a heavier paper backing sheet by means of a second gummed layer. This latter modification of the first general type of decalcomania transfer is known in the industry as Duplex paper.

The second general type of decalcomania transfer is the so-called collodion or slip type. This consists of a backing sheet, a gummed coating on the backing sheet, and on top of the gum a thin film of nitrocellulose or other water insoluble film-forming material. With this type of transfer the design is printed on the nitrocellulose film surface.

Both single color designs and multi-color designs may be printed on either of these types of paper by lithography, letter press, intaglio or stencil printing according to the effect and specific characteristics desired. After completion of the printing operation there is produced a decalcomania sheet wherein the surface of the paper carries a hardened ink layer in which the particles of the vitrifiable enamel color compositions are bonded and held in position by means of the organic vehicle.

In applying the design to the ceramic ware or glass article to be decorated, in the case of the Duplex paper, there is first applied a tacky varnish size to the surface of the article and the decalcomania is affixed to this size layer. The backing paper is then ordinarily removed with water. When using decalcomania transfers of the second type, those in which the color design is imprinted on the collodion film surface, the design is affixed to the ware by immersing the paper in water. This dissolves the gum layer between collodion film and backing sheet, and the collodion film may be slid off onto the article to be decorated with the side which has been next to the backing sheet positioned against the surface of the ware. Ordinarily enough gum remains on the collodion layer to provide the necessary bond.

When preparing decalcomanias of the Duplex type, the design as it is affixed on the ware to be decorated is inverted, i. e. the vitrifiable enamel color which was printed last is closest to the surface of the ware. In the case of decalcomanias of the slip type the reverse is true, i. e. the sequence of vitrifiable enamel colors is the same as it appears on the original print.

My invention is concerned especially with the nature and formulation of the vitrifiable enamel colors which are employed in the manufacture of such decalcomanias. The essential or primary object of my invention is to provide an improved decalcomania sheet which, when the design is transferred from it and fired on the ceramic articles to be decorated, will result in freedom from blisters and other defects even when the firing is carried out rapidly or under other adverse conditions. Still another object of my invention is to provide groups of vitrifiable enamel colors which are especially suitable for use in the manufacture of decalcomania sheets of high quality. Another object is the provision of a procedure by which a great variety of vitrifiable enamel colors may be formulated, which colors have all the visual and optical properties necessary for design requirements, yet also possess those qualities necessary to insure uniform firing and freedom from defects even when the designs are fairly complicated.

One of the major defects with all decalcomania transfer work, a difficulty which has occasioned great loss in the ceramic decorating industry and which has heretofore been considered un-

solvable by any practical means, is the tendency of decalcomania designs to form blisters or cracks during the firing operation. This tendency is present and has caused serious financial loss in commercial application methods even though the design as printed on the paper may be perfect in every respect when subjected to the most critical examination.

In the past various procedures have been proposed in an effort to overcome this objectionable tendency. In one proposed method the decalcomania transfer is made up by imprinting the design in a series of colors, different percentages of flux being mixed with each color in order to produce a graded series of fusion temperatures with the color of lowest fusion point being next to the surface of the ceramic ware. Although this procedure was originally suggested almost a quarter of a century ago, it has not been found utilizable in practice, since the procedure of mixing flux with the various colors cannot be accomplished without destroying the useful coloring properties. This means that the design which it is desired to reproduce on the ceramic ware is not faithfully rendered, for the color values are changed by the necessity for admixing therewith various amounts of flux in order to secure fusion points for the various layers in accordance with the scheme previously referred to. Since the primary aim of decalcomania transfer methods is to produce a faithful and properly colored reproduction of the artist's design, it is obvious that unsatisfactory color reproduction destroys the principal advantage of this method.

I have now found that greatly improved decalcomania transfers can be produced, transfers having great freedom from blistering and other firing defects, if the decalcomanias are prepared utilizing a series of vitrifiable colors compounded in different fluxes, each color being in a different flux composition. The principal cause of the enormous losses resulting from employment of the decalcomania method in industry has been the use of a series of vitrifiable enamel colors made up, either influxes which are substantially identical in fusing point, or which are wrongly formulated as to fusion point with respect to each other, i. e. not formulated according to the position in which the vitrifiable color appears on the decalcomania print. In preparing decalcomanias of uniform quality and satisfactory firing characteristics, I have found it essential to formulate or select a set of colors in a series of fluxes, and to position them in sequence during the printing operation so that the colors made up from the respective fluxes constitute a sequence varying about 20 degrees (C.) in fusion points. The most fusible color is that at the bottom of the series of layers when the design is in place on the surface of the ware being decorated.

It is obvious that in some designs in which as many as twelve colors may perhaps be present it is not necessary to be concerned about the relative sequence of certain colors in the design when those colors do not overlap or come over or under another color. The position in sequence is important only with respect to those colors which appear in layers positioned one on top of the other, as it is in such layers that blistering invariably causes severe difficulty during the firing operation. In considering the relative order of fusibility desired, it is primarily the fusion point of the flux particle itself which is determinative, and not the fusion point of the complete vitrifiable color, containing pigment as well as vitrifiable enamel composition, in which from 5 to 40% of pigment may be present in addition to the frit or flux. In this respect my improved decalcomania transfers, suitable for use in ceramic decoration, are distinguished from previous efforts to overcome the disadvantages incident to their use in commercial decorating operations. In previous attempts the ratio of flux to pigment was controlled, greater or less amounts of flux being added to the pigmentary composition in order to secure the desired sequence of maturing temperatures. Such practice prevents accurate reproduction of the color values in the design, for the pigmentary shade cannot be accurately controlled. As contrasted with this, in my improved decalcomanias, the maturing temperatures of the flux formulations themselves are suitably determined and arranged in sequence, the pigment which is present in addition to the vitrifiable enamel composition having no appreciable effect on the maturing temperature of the color composition. In this way, it is possible accurately to predetermine the exact hue of the fired enamel thereby accurately reproducing the artist's design in the precise color values desired.

The absolute softening points of the vitrifiable color compositions themselves need not possess fixed values, but they may, for example, cover a range of from about 480° C. for the most fusible color to 680° C. for the least fusible color. The exact incipient softening points of vitrifiable colors or fluxes can be determined by means which are well known to the ceramic industry. No particular problem, therefore, exists in securing a set of fluxes which are in each case compatible with the pigments to be employed, which fluxes have various softening points, and then arranging these fluxes in printing sequence, so that in the final position of the colors on the ceramic ware the most fusible color is next to the ware and the colors are arranged in sequence as to fusibility, the least fusible being uppermost.

My improved decalcomanias are illustrated in the annexed drawing, wherein Figure 1 represents a ceramic decalcomania transfer of the simple type; Figure 2 represents one of the Duplex type; while Figure 3 represents one wherein the vitrifiable ceramic color layers are imprinted upon a nitrocellulose or similar film which serves as the impression receiving layer.

Referring specifically to Figure 1, 6 designates the paper backing strip, and 7 the adhering layer of gum or adhesive. Imprinted on the gum layer 7 are two layers of a vitrifiable color composition, 8 and 9. Since 8 and 9 overlap, or come into contact with each other at certain portions of the design, it is necessary that 8 be prepared from a pigment and frit or flux composition of relatively high fusion point, while 9 is prepared by admixing pigment with a flux of lower fusion point. In use, the backing strip is moistened and applied to the ceramic or glass ware article with the portion bearing the design close up against the surface to be decorated. Those portions of the design formed by means of color composition 9 accordingly must possess the lower fusion points, having fusion points at least 20° C. lower than the fusion point of layer 8.

In Figure 2, showing the Duplex type of decalcomania, 12 is the backing strip, 13 the first gummed layer, 14 the tissue paper strip, and 15

the gummed layer which serves as the impression receiving layer. On this are imprinted vitrifiable ceramic colors 16 and 17 forming different portions of the design. As 16 and 17 come into contact with each other, that portion of the design intended to be closest to the surface of the ceramic ware to be decorated, 16, is formed from a pigmentary material and ceramic flux of lower fusion point than the ceramic flux which, when mixed with a pigment, constitutes portion 17.

Referring now to Figure 3, 21 represents the paper backing, 22 the gum layer and 23 the nitrocellulose film. Imprinted on the nitrocellulose film is a design formed of two layers of vitrifiable color composition designated 25 and 26 respectively. In use, as previously stated, the paper backing is slipped off and the gummed layer applied close up against the surface of the ceramic ware to be decorated. Accordingly, that portion of the design rendered by vitrifiable color composition 25 is closer to the surface of the ware to be decorated than that portion formed by vitrifiable color composition 26. Layer 25 therefore comprises a pigment and a vitrifiable flux or frit having a lower melting point than the vitrifiable flux or frit which, when admixed with pigment, constitutes layer 26. As previously stated, especially where a great many colors are involved in the design, vitrifiable color layers 25 and 26 should differ in fusion points by at least 20° C.

In preparing decalcomanias in accordance with my invention, it is necessary only to utilize the usual and well-known printing techniques. Any satisfactory method for printing the vitrifiable color compositions on the decalcomania surface supporting the same may be adopted, it being understood, of course, that the set of vitrifiable color compositions employed is arranged in order of maturing temperatures as previously specified, in order that a decalcomania product will be secured which has the superior firing properties characteristic of my improved transfers.

It should be understood that various changes and modifications may be made from the embodiments given herein as illustrative of my preferred form, which changes would nevertheless fall within the scope of my invention. Accordingly, its scope is to be determined in accordance with prior art and appended claims, bearing in mind that it is my intention to comprehend within the scope of the invention various slight modifications from preferred form.

I claim:

1. A ceramic decalcomania for use in applying a multi-color design in vitrifiable enamel colors to the surface of ceramic ware which comprises a backing member, an impression receiving layer secured to said backing member, and a plurality of successively over-lapping vitrifiable colors constituting the design contained on said impression receiving layer, said colors each comprising a pigment and a frit, each color having the desired hue and depth and a fusing temperature higher than the color preceding it in the order in which the colors of the decalcomania will be positioned on the ceramic ware, the hue and depth, and the fusing temperature, of each color being determined by the proportion and composition of the frit contained therein, the composition of the frit of at least some of said colors differing from the composition of the frit of another color or colors.

2. A ceramic decalcomania as defined in claim 1 wherein the fusing temperatures of the succeeding colors differ from each other by at least 20° C.

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