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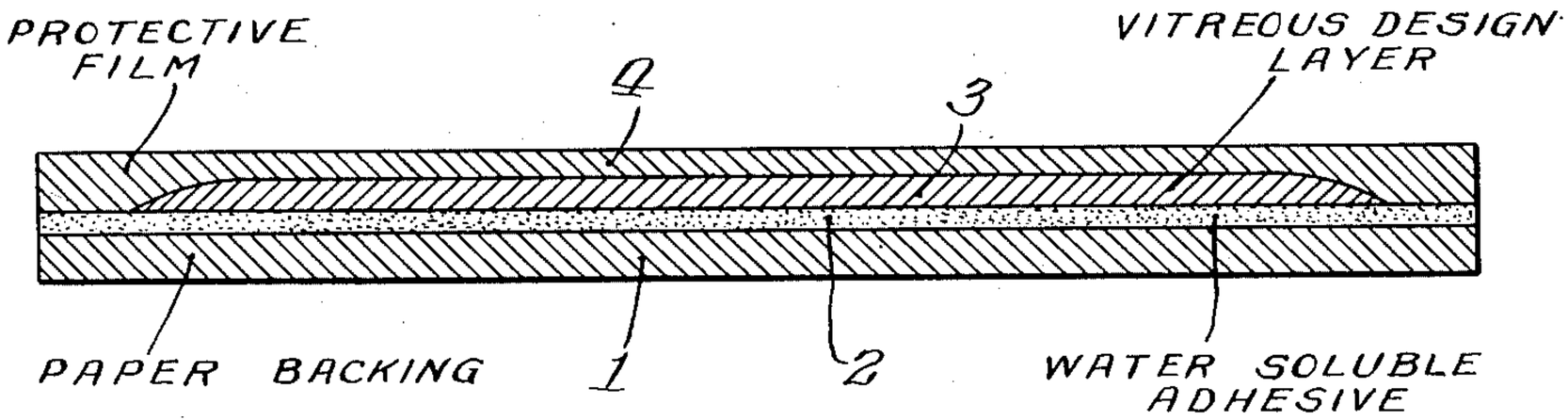

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VITREOUS DECALCOMANIA AND METHOD OF APPLYING THE SAME

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This invention relates to decalcomanias and more particularly to a vitreous type of decalcomania and a method of applying the same to glassware, chinaware, pottery or the like.

Heretofore, one of the principal difficulties in producing surface decorations on glassware, cinaware, pottery or the like by means of designs which are transferred from the decalcomania paper to a surface to be decorated and then fired, was the tendency of the material forming the design to improperly fuse to the surface and to form minute pits, bubbles, blisters or voids during the firing operation. These imperfections resulted primarily from the action of the gases of the solvents, binder and other consumable materials as they escaped or attempted to escape from the vitreous design as the firing temperatures were increased. Where the layers of vitreous design material were unduly thick or where no provision was made to facilitate their escape or release, the gases tended to concentrate in certain areas and forced their way up through the design to form pits or blow holes, thereby detracting from the appearance of the finished product and rendering it commercially unsalable.

Some attempts have been made to provide design structures of the foregoing character affording some escape or release means for the gases generated by the firing process in order to avoid surface disfiguration, but for the most part such attempts have not proven wholly satisfactory. One such attempt comprised printing the design on the transfer paper in the form of minute dots or lines which were placed in overlapping relationship in order to avoid an unduly thick blanket, the theory being that the gases could escape more readily so as to avoid blistering or other surface disfiguration. However, this method was difficult to control and the results therefrom were not always uniform nor successfully achieved.

It is, therefore, one of the principal objects of the present invention to provide an improved decalcomania adapted to be applied to glassware, chinaware, pottery or other vitreous surfaces and thereafter fired without formation of pits, blisters, blowholes or other surface disfigurations.

Another object of the invention is to provide an improved decalcomania of the foregoing character which inherently contains provision for facilitating the escape or release of the gas of solvents, binder or other consumable materials which are generated during firing in order to prevent surface disfiguration of the fused design.

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Still another object of the invention is to provide an improved design film of the foregoing character in which the vitrifiable material such as pulverized glass, is associated with two incompatible or immiscible substances which, when agitated, form minute, separate droplets, globules or units from and between which the gases generated upon firing may readily escape without causing surface disfiguration.

Another object of the present invention is to provide an improved film of the type defined in the preceding object in which the two incompatible or immiscible substances are ethyl cellulose and a polymethacrylate resin such as polymerized methyl-methacrylate resin in the proper proportions.

A further object of the invention is to provide an improved design film of the foregoing character containing vitrifiable material in which the surface and body thereof, while appearing homogeneous, are nevertheless actually heterogeneous so as to be, in effect, minutely granular or open, thus permitting the ready escape of gases when fired and facilitating the proper fusing of the vitrifiable material to the surface of the vitreous article.

A still further object is to provide an improved process for applying a design film of vitrifiable or ceramic material to articles of glassware, chinaware, pottery or the like in such a manner that the formation of blisters, pits, bubbles or blowholes in the surface of the design are eliminated by facilitating the ready escape of the gases generated from the consumable material therein when fired.

Another further object is to provide an improved process similar to that defined in the foregoing object in which a transferred design film of vitrifiable material is thoroughly softened or converted to a semi-fluid or paint-like consistency prior to firing, thus permitting the ready release of the gases generated during firing.

A still further object is to provide an improved process as above described in which the transferred design film containing vitrifiable material is thoroughly softened or converted to a semi-fluid or paint-like consistency prior to firing by the application of a mixture of a suitable solvent and a plasticizer to the under surface of the film or the surface to which the film is applied, followed by the application of the mixture to the outer surface of the film after application to the article.

Other objects and advantages of the present invention will become apparent as this description

progresses, particular reference being made to the drawing which is a schematic cross-sectional view on an exaggerated scale showing a decalcomania embodying the features of my invention.

The decalcomania of the present invention comprises a design film of vitrifiable or ceramic material applied to the water soluble adhesive coating of decalcomania paper of the conventional type, and an overlying protective film applied over the design film. The decalcomania, therefore, is, in the preferred embodiment, essentially a four layer structure, although the design film may be used in other layer combinations and may contain overlapping strata and areas and may comprise a plurality of colors arranged in the desired outline and design. The design film may be applied to the water soluble adhesive coating of the decalcomania paper by various methods including screen printing, lithograph, rotogravure and the like. Referring to the drawing, a decalcomania backing paper of a conventional type is designated at **1** and is provided with a water soluble gum or adhesive coating **2** for permitting ready release of the backing. The vitreous or ceramic design film is applied directly over the water soluble coating, as at **3**, and the protective outer layer is designated at **4**.

The material or ink used to print the design film, which comprises one of the novel features of the present invention, is composed of a quantity of pulverized glass and coloring material which is added to and thoroughly mixed in a flowable vehicle or binder containing solvents and at least two incompatible or immiscible substances. The resultant mixture is of such consistency that it may be screen printed or utilized with satisfactory results in other printing processes. When the above ingredients have been thoroughly stirred or otherwise agitated, the pulverized glass particles are believed to be contained in, on and between the minute droplets of the two incompatible substances so that the material is minutely heterogeneous rather than one homogeneous mass. The ink material is thus composed of individual, minute units or droplets of binder material separate from each other and containing quantities of vitrifiable material and solvent, these droplets not mixing with adjacent droplets.

After the design material has dried on the soluble adhesive layer, it still retains its heterogeneous internal and surface structure so that it may be termed granular or open rather than comprising a relatively solid, impervious blanket over its entire surface. It is, in effect, somewhat cellular or composed of independent particles so that, as the consumable substances are fired out, the gases generated therefrom readily pass up through the multiplicity of minute passageways between the particles and escape into the atmosphere. Thus the gases are readily released from the film over its entire area and they are not required to force their way out by relatively great expanding pressure so as to disturb the smooth surface configuration by forming therein pits, blisters and the like.

A specific embodiment of the vitrifiable ink composition employed in forming the design layer may be made in accordance with the example or formula now to be specifically set forth. A lead borosilicate base or flux comprising seventy per cent (70%) lead oxide, fifteen per cent (15%) silica and fifteen per cent (15%) boric oxide is thoroughly mixed and finely ground with coloring

metallic oxides or other metallic compounds, such as cadmium sulphoselenide and cadmium oxide (red), cadmium sulphide (yellow), chromium oxide, iron oxide and cobalt oxide (black), chromium oxide, cobalt oxide, antimony oxide and in admixture with these sometimes tin oxide (green), lead molybdate or titanium dioxide (white), lead molybdate plus a small percentage of cadmium sulphoselenide (pink), and chromium oxide, iron oxide and zinc oxide (brown). The lead borosilicate base or flux is mixed with the metallic oxides in a ratio of approximately one hundred (100) parts of flux to from twelve to twenty (12–20) parts of metallic oxides depending upon the density of color desired.

This finely ground mixture is then thoroughly mixed with a flowable vehicle in a ratio of approximately 4.75 parts of dry pulverized mixture to 1 part vehicle. The vehicle may be composed of sixty per cent (60%) butyl Cellosolve, nineteen per cent (19%) polymerized methyl-methacrylate resin which is a polymerized acrylic resin, nineteen per cent (19%) chlorinated biphenyl and two per cent (2%) lecithin. To this mixture of flux, coloring oxides and vehicle, there are then finally added a quantity of ethyl cellulose in an amount of fifteen per cent (15%) by volume and a quantity of finely ground clear flint glass also in an amount of fifteen per cent (15%) by volume. This final composition of ingredients is then thoroughly agitated in order to distribute the various ingredients as uniformly as possible throughout the mass, after which the final composition of ink is ready for printing on the soluble adhesive coating as above described.

However, in spite of a thorough agitation of the final composition of ingredients, the composition still remains to a certain degree a heterogeneous mass rather than a homogeneous one. This is due to the fact that two of the ingredients of the final composition, namely, the polymerized methyl-methacrylate resin and the ethyl cellulose, are incompatible or immiscible, with the result that the minute droplets of polymerized methyl-methacrylate resin are separately interspersed between separate minute droplets of ethyl cellulose. This forms a more or less globular structure of disunited, separate units or particles without any bonding medium to hold such droplets together. It is believed that the other ingredients of the final composition are distributed throughout the mass thereof as parts of each type of incompatible droplets and that the finely ground flux or glass particles are contained within, on the surface of and between each of said type of incompatible droplets.

However, whatever may be the minute character of the final composition, the two incompatible substances in the ink do provide a layer, which when dry is more or less granular or open and still in the form of separate units or particles as compared to an impervious surface. The layer is primarily heterogeneous in nature so that when the decalcomania film has been transferred and is being fired at relatively high temperatures, the gases generated by the decomposition of certain of the ingredients including the binder material may readily escape up between and from the minute particles into the atmosphere. Because the openings are minute and extend over the entire area, no large concentrations of gases are formed in pockets nor are the gases forced to push their way through a relatively impervious surface under relatively great pressure. They merely take the easiest avenues

of escape which are already provided between the minute divisions or particles.

The final protective coating 4 which is laid down over the design film 3 is composed of clear ethyl cellulose. As clearly seen in the drawing, this protective coating is of greater size and extent than the design film so as to extend somewhat beyond the outer edges thereof and to thus protect the design film when it is being pressed down during application to the article being decorated. The final coating also serves as a supporting film particularly when the design film has remote portions projecting from the main body of the design.

The final protective coating of ethyl cellulose and the binder materials of the design film, including the ethyl cellulose and the polymerized methyl-methacrylate resin, are of such nature as to entirely disappear or decompose during firing, thus leaving only the vitrifiable glass base design which becomes fused in the surface of the article as an integral part thereof. It is thus important in the selection of the two incompatible materials that they have the additional characteristic of entirely disappearing or firing out.

It is to be understood that equivalent materials may be substituted for the ethyl cellulose and the polymerized methyl-methacrylate resin with equally satisfactory results. For example, a cellulose ether such as benzyl cellulose may be substituted for the ethyl cellulose since it is likewise incompatible with polymerized methyl-methacrylate resins. Similarly, other types of polymerized acrylic resins may be substituted for the methyl-methacrylate resin.

Another important feature of the preesnt invention is the process by which the above described decalcomania is applied to the article to be decorated and is prepared for firing. As a first step in this process, the decalcomania is dipped in water for a sufficient period of time to soften the soluble adhesive and to permit the design film and the protective outer coating to be released therefrom. When these two layers have been released, a mixture containing a plasticizer and a solvent for the design and protective coatings is sprayed or wiped over the surface to be decorated, and immediately thereafter the transfer is applied to the wetted surface with the design film in contact therewith. Then the transfer is rubbed down with a squeegee or roller in the usual manner in order to eliminate all air bubbles and to insure intimate contact of the film with the wetted surface.

When the transfer has been rubbed down flat on the wetted surface, an additional quantity of the mixture of solvent and plasticizer is sprayed or wiped over the outer face of the protective coating. In connection with a transfer comprising the design film and the protective coating and composed of the materials of the specific formula above set forth, a mixture of dibutyl-phthalate, diethylene glycol and ethyl alcohol in equal parts has been found satisfactory. The mixture acts as a plasticizer and a solvent for the binder materials of the design film and for the ethyl cellulose coating, and by application of the mixture to the surface of the article and later to the outer face of the transfer after it has been applied to the wetted article surface, both sides of the transfer are wetted. Upon being wetted by the solvent plasticizer mixture, both the design film and the protective coating becomes quite soft and almost the consistency of paint. In fact, the design film and the coating closely

approach their wet or semi-fluid condition as when first applied to the decalcomania paper. In a sense they are almost the same consistency as if they had been screen printed directly onto the article.

The application of the solution and the consequent softening of the design and protective coating serve to open up the surfaces of the design and protective coatings and puts the same in a semi-fluid state at the very outset of the firing process. Thus, when the article is placed in a furnace immediately after the solution has been applied to the transfer, the gases may escape more readily than if the transfer were put into the furnace in a hard dry state. The binder materials are reduced to a semi-fluid state and the gases start forming and escaping at a much earlier stage. As a consequence, the binder materials and the protective coating are fired out in a very much shorter period of time thereby reducing the overall firing period and their ready escape prevents the formation of pits, blisters and blowholes. The use of a plasticizer as well as a solvent in the softening mixture has a definite purpose. The solvent tends to rapidly soften the films but being more volatile will evaporate quickly and at lower temperatures. However, the plasticizer is of lower volatility and will remain longer in the film until higher temperatures are reached thus affording a longer period of time for the escape of gases.

The decalcomania transfer above described in detail may be applied both to glassware and to chinaware with equally satisfactory results. When the design is being fused to a glass surface the firing temperature may range from 1030° F. to 1200° F. and when being applied to a chinaware surface the higher temperatures of from 1250° to 1650° F. may be employed. It has been found that a transfer containing the ingredients above described in detail and applied and prepared for firing in the manner above set forth, may be completely and perfectly fused to the surface of the article at such temperatures in one and one-half to two hours as compared with older types of decalcomanias fired dry, which have required from six to eight hours. Because the firing time has been materially reduced by the internal structure of the present decalcomania and by the novel manner of its preparation for application, the mass production of decorated glassware and chinaware is made feasible, thus considerably extending the potential field of vitreous decalcomanias and considerably reducing the cost of the finished articles.

By means of the present invention, the finished design is perfectly and smoothly fused in the surface of the article being decorated. When properly made and applied, it contains no pits, bubbles, blisters or blowholes so that articles bearing the same design will be readily salable and uniform in appearance. These satisfactory results are manifestly achieved because of two factors, one being the internal multi-particle or granular structure of the design layer of the transfer and the other being the application of the solvent plasticizer mixture to the transfer to soften the same prior to firing. Both of these factors contribute to providing a multiplicity of ready avenues throughout the entire area of the transfer for escape of the gases. As the gases escape and the binder material decomposes, the uniformly distributed, pulverized glass particles are melted down and fused into the surface being decorated.

Because of the advantageous results flowing from the novel type of vitreous ink above described, it is apparent that it may also be utilized in forming or printing the design film directly onto the surface of the article to be decorated rather than first preparing the same on a releasable backing. In this direct method of application, the gases generated by the decomposition of the incompatible binder materials and solvents freely escape upwardly and outwardly between and from the minute, separate droplets of binder materials. The pulverized glass fuses to the article surface and no blowholes or pits are formed as the gases are freely released.

Although there has been described above a specific embodiment of a vitreous type of decalcomania comprising the present invention and a process of preparing the same prior to firing, it will be understood that modifications in the structural details and composition of the vitreous film and in the details of the process may be effected without departing from the spirit and scope of the appended claims.

I claim:

1. In a decalcomania, a film comprising a pulverized vitrifiable material in a binder comprising ethyl cellulose and a polymerized methyl-methacrylate resin.

2. In a decalcomania, a design film comprising a pulverized vitrifiable material in a binder, said binder comprising two incompatible materials, one of said materials being ethyl cellulose and the other being a polymerized methyl-methacrylate resin.

3. In a decalcomania, a design film comprising a pulverized vitrifiable material in a binder, said binder comprising two incompatible materials, one of said materials being a cellulose ether and the other being a polymerized acrylic resin.

4. A decalcomania comprising a backing, a water soluble adhesive on said backing, and a design film over said adhesive, said film comprising a pulverized vitrifiable material in a binder and said binder comprising a cellulose ether and a polymerized acrylic resin.

5. In a decalcomania, a film comprising a pulverized vitrifiable material in a binder, said binder comprising two incompatible materials, one of said materials being a cellulose ether and the other being a polymerized acrylic resin.

6. In a decalcomania, a design film comprising a pulverized lead borosilicate glass material in a binder, said binder comprising ethyl cellulose and polymerized methyl-methacrylate resin divided up into minute, individual, incompatible particles interspersed with each other throughout said film.

7. The method of preparing a decalcomania which comprises adding a quantity of finely pulverized ceramic material to a vehicle containing a solvent and two incompatible binder materials, one of said materials being ethyl cellulose and the other being a polymerized methyl-methacrylate resin, agitating said composite of materials to distribute said ceramic material throughout the mass thereof and to divide up said incompatible binder materials into minute, individual and separate droplets, applying said agitated composite to a surface on a leasable backing in the form of a design and then drying the same.

8. The method of preparing a decalcomania which comprises agitating a composite of materials comprising a quantity of finely pulverized ceramic material, a solvent and a binder comprising two incompatible resinous film-forming combustible materials to distribute said ceramic material throughout the mass thereof and to divide up said incompatible binder materials into minute, individual and separate droplets, applying said agitated composite to a surface on a releasable backing and drying the same.

9. The method of preparing a decalcomania which comprises first mixing a quantity of pulverized ceramic material with a vehicle comprising a solvent and a binder material of polymerized methyl-methacrylate resin, then adding to said first mixture an additional quantity of pulverized ceramic material and a binder material of ethyl cellulose, said binder materials being incompatible with each other, agitating said composite of materials to distribute the ceramic material throughout the mass thereof and to divide up said incompatible binder materials into minute, individual and separate droplets, applying said agitated composite to a surface on a releasable backing and drying the same.

10. The method of applying a vitreous design film containing pulverized ceramic material and a binder material therefor for firing on the surface of an article to be decorated which comprises applying the film to said surface, applying a mixture containing a solvent and a plasticizer for the binder material to said film to convert the same to a softened, semi-fluid state, and then firing the same.

11. The method of applying a vitreous design film containing pulverized ceramic material and a binder material therefor for firing on the surface of an article to be decorated which comprises applying a mixture containing a solvent and a plasticizer for the binder material to the under surface of said film when said film is applied to the surface of the article, applying a quantity of said solution to the outer face of said film after application to said article surface, said solution serving to convert said film to a softened, semi-fluid state, and then firing the article and the attached film.

12. The method of applying to the surface of an article to be decorated a transfer portion of a decalcomania comprising a design film containing a ceramic material and a binder therefor and a supporting film for said design film, which comprises applying the transfer portion to said article surface, converting said transfer portion to a softened, semi-fluid state by the application of a solution containing a solvent and a plastizer for said binder material and said supporting film, and then firing the article and the attached film.

13. The method of decorating an article of glassware, chinaware and the like, which comprises applying directly to the surface of an article to be decorated a ceramic coating composition comprising a finely pulverized ceramic material, a solvent, and a binder comprising two incompatible resinous film-forming combustible materials, said ceramic material being distributed throughout the composition in suspension therein and said incompatible materials being dispersed into minute separate particles, and thereafter firing said article.

14. The method of applying a vitreous design film containing pulverized ceramic material and a binder including two incompatible resinous film-forming combustible materials, which comprises applying the film to the surface of an article to be decorated, converting said film to a softened semi-fluid condition, and then firing the same.

15. The method of applying a vitreous design

film containing pulverized ceramic material and a binder comprising ethyl cellulose and a polymerized methyl-methacrylate resin, which comprises applying the film to the surface of an article to be decorated, converting said film to a softened semi-fluid condition, and then firing the same.

16. The method of applying a vitreous design film containing pulverized ceramic material and a binder including two incompatible resinous film-forming combustible materials, which comprises applying the film to the surface of an article to be decorated, applying a mixture containing a solvent and a plasticizer for the binder to said film to convert the same to a softened semi-fluid condition, and then firing the same.

17. In a vitreous decalcomania, a film containing a pulverized vitrifiable material in a binder comprising interspersed discrete particles of two incompatible resinous film-forming combustible materials, the incompatibility of said particles providing a heterogeneous substantially pervious layer permitting ready escape and release of combustion gases during firing of the decalcomania whereby to avoid surface disfiguration of the film.

18. A ceramic coating composition for use in applying a design to an article of glassware, chinaware and the like comprising a finely pulverized ceramic material, a solvent, and a binder comprising two incompatible resinous film-forming combustible materials, said ceramic material being distributed throughout the composition in suspension therein and the incompatible binder materials being dispersed into minute, individual and separate droplets.

19. A decalcomania comprising a backing, a water soluble adhesive on said backing, and a design film over said adhesive, said film comprising a pulverized vitrifiable material in a binder and said binder comprising two incompatible resinous film-forming combustible materials separated into discrete particles interspersed with each other throughout said film.

20. The method of claim 8 further characterized in that said incompatible binder materials comprise a cellulose ether and a polymerized acrylic resin.

21. The composition of claim 18 further characterized in that said incompatible binder materials comprise a cellulose ether and a polymerized acrylic resin.

22. The method of claim 13 further characterized in that said incompatible binder materials comprise a cellulose ether and a polymerized acrylic resin.

23. The method of claim 14 further characterized in that said incompatible binder materials comprise a cellulose ether and a polymerized acrylic resin.

24. The method of claim 16 further characterized in that said incompatible binder materials comprise a cellulose ether and a polymerized acrylic resin.

25. The method of claim 10 further characterized in that said mixture comprises diethylene glycol, ethyl alcohol, and dibutyl phthalate.

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