Feb. 24, 1953 H. C. RATHKE 2,629,670

VITREOUS DECALCOMANIA

Filed July 23, 1948

Fig. 1.

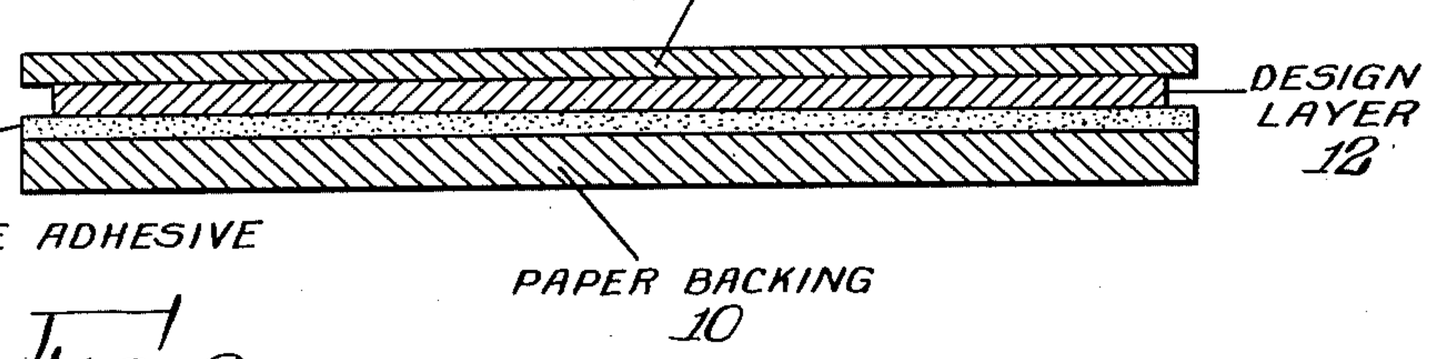


Fig. 2.

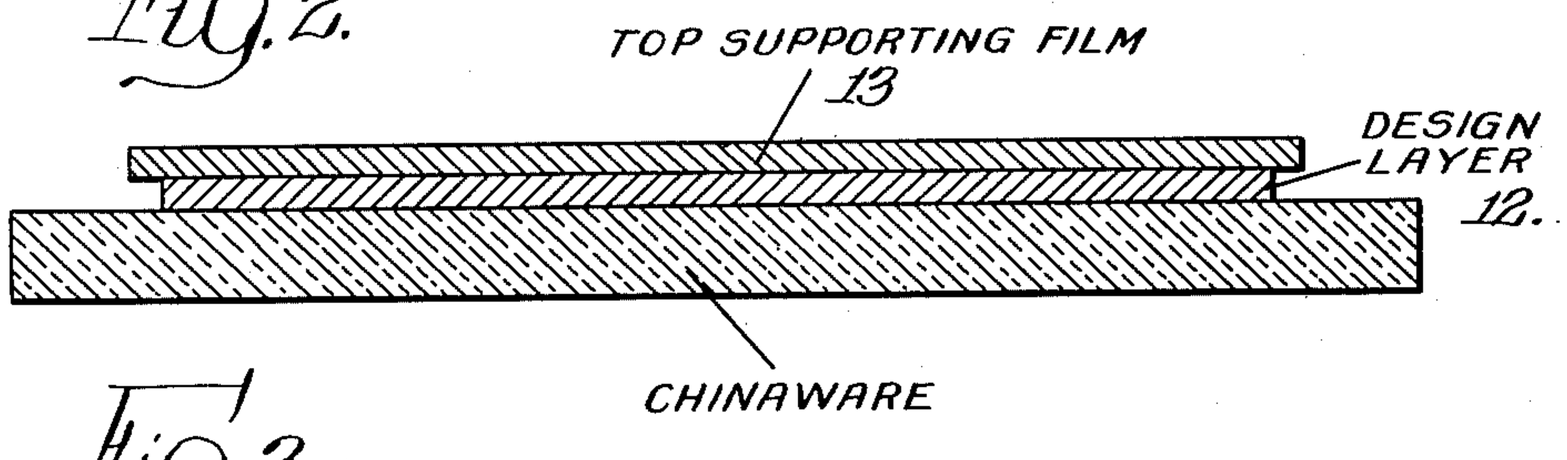


Fig. 3.

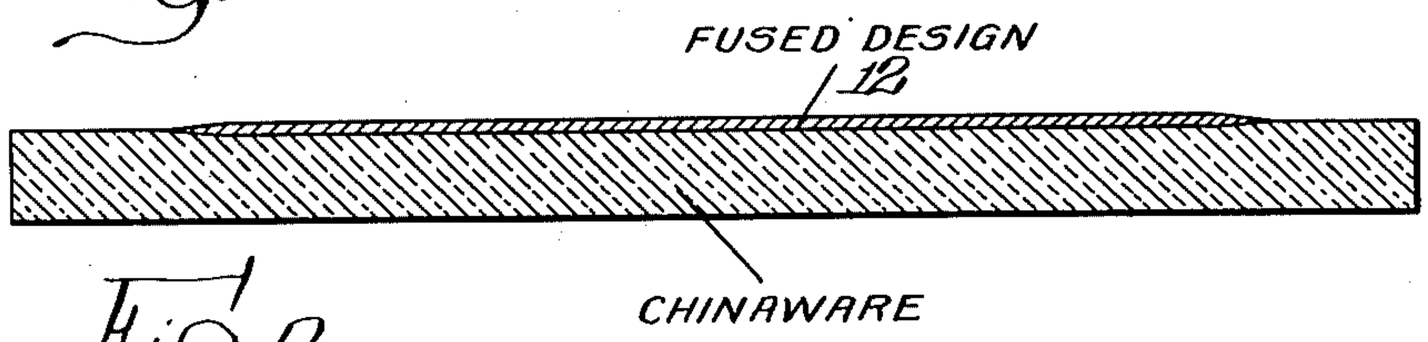


Fig. 4.

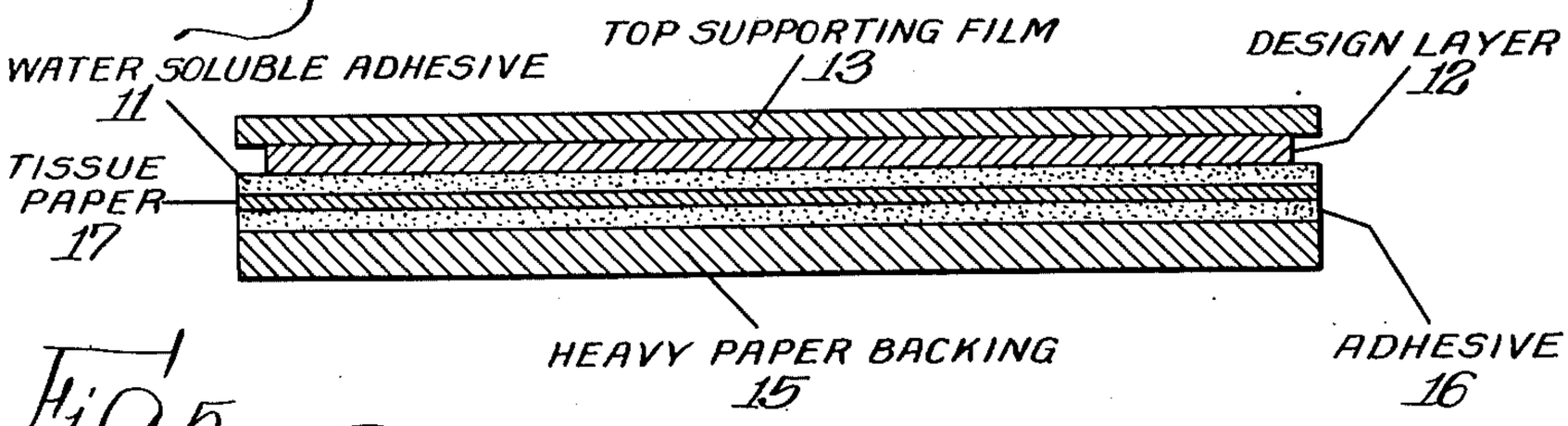
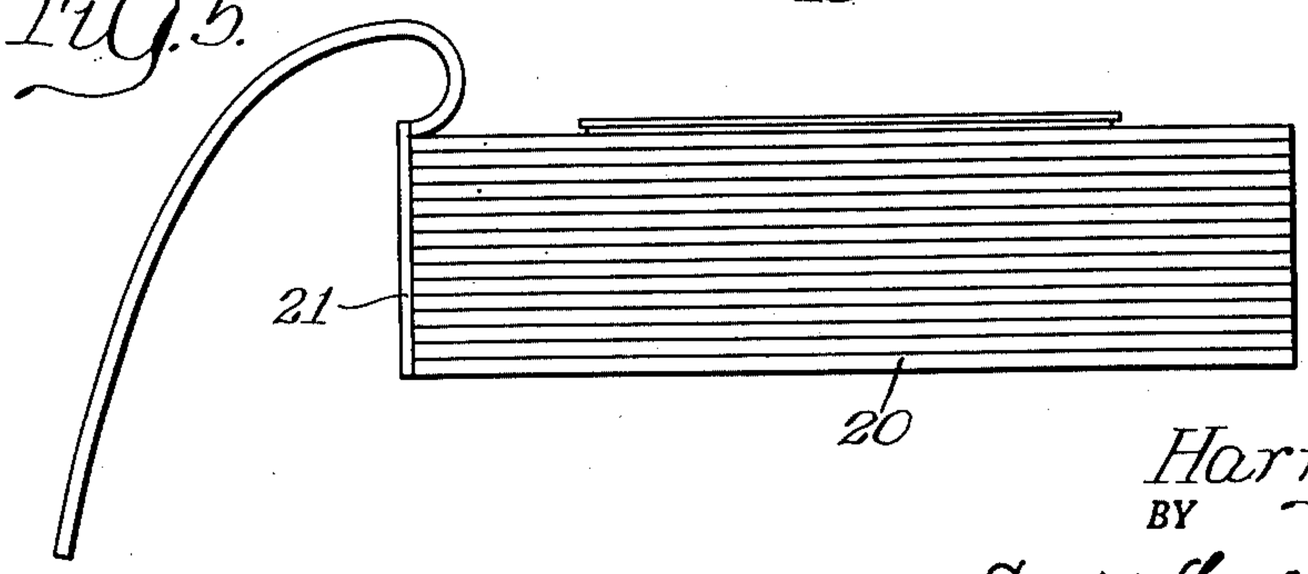


Fig. 5.



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VITREOUS DECALCOMANIA

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1 Claim. (Cl. 117—3.6)

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

Heretofore, one of the principal disadvantages in producing surface decorations on chinaware, pottery or the like by means of designs which are transferred from decalcomania paper to a surface to be decorated and then fired, was the tendency of the vitreous material forming the design to improperly fuse to the article surface and to form minute pits, bubbles, blisters or voids during the firing operation. These design imperfections resulted primarily from the action of the gases of the solvents, binder and other consumable material in the body of the transfer as they escaped or attempted to escape therefrom as the firing temperatures were increased.

In some instances the design layer or layers were formed on top of a supporting film which was relatively impervious like the design layer and which was placed against the surface to be decorated so as to underlie the design layer during firing. The disadvantage of this construction was that the gases which formed upon decomposition of the supporting film forced their way up through the design layer and caused imperfections therein. Moreover, because the design layer was separated by the supporting film from the article surface, the design layer did not fuse down properly into the surface of the article when fired. The formation of gases and the consequent boiling action of the under layer tended to hold the design material away from the article surface.

Such types of decalcomanias were also applied to the surface of an article by means of a special china cement or adhesive which was manually applied to the article surface by a brush after which the transfer portion of the decalcomania was applied thereagainst and rubbed down. However, it was quite difficult, if not impossible, to apply the special adhesive in a thin, smooth film due to the brush method of application and also to the fact that evaporation of solvents and changes of room temperature during use caused the consistency of the adhesive to thicken and the ingredients thereof to separate in the container. Furthermore, from day to day, the brushes and the adhesive were not properly sealed or protected from the air so that oxidation of the adhesive caused the formation of minute

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particles or solids. If the adhesive was applied in a thick, uneven coat or had oxidized particles therein, the finished fired product would be wholly unacceptable since the gases of these concentrations of adhesive would form eruptions and pits in the design surface.

Moreover, it has been found that even if the special adhesive, which usually comprised some sort of varnish containing a resin, was applied in a thin, smooth film nevertheless gases were formed and a boiling action took place under the design layer or under the supporting film and, in order to escape, the gases necessarily forced their way up through the design layer spoiling the appearance of the finished design.

Another disadvantage of the use of adhesive was the impossibility of correctly positioning the transfer once it had been applied thereto. Because the adhesive was sticky, the transfer could not be slid about into the desired position so that if proper positioning was not achieved on first contact, the transfer would have to be removed and rewashed along with the article surface. This constituted a loss of labor as well as materials thereby increasing the ultimate cost of the finished article. Then, after the transfer had been correctly positioned, it was necessary to rub it down with soap and a brush to clean the transfer and article surface and to secure an intimate contact. This operation was again entirely manual and was particularly a laborious job where large production was being attempted. Quite often as the transfer was being cleaned and pressed down under considerable pressure into the adhesive, minute wrinkles and air pockets were formed in the transfer and between the transfer and the adhesive without the operator being aware of their formation and, consequently, the design was improperly fused to the article, and bore surface imperfections.

After the transfer was so positioned over the adhesive, the decalcomania paper was then removed by the application of water to dissolve the water soluble adhesive. This was accomplished commercially by immersing the entire article of ware in a tub of water after which the paper backing separated therefrom. However, upon separation minute vitreous particles separated themselves from the design layer so as to destroy its overall appearance and attached themselves to other portions of the article surface where no design was desired. Thus, upon firing, these

minute particles were fused into the surface which should have remained clear, causing noticeable specks or discolorations and rendering the finished article commercially unacceptable.

A further inherent disadvantage of the adhesive method of application resulted from the necessity of permitting the adhesive to dry before firing. This not only was time consuming but required a manufacturer to maintain a large area for storage purposes.

For many years workers in the ceramic and decalcomania arts have been attempting by various proposed means and methods to overcome the above-mentioned difficulties and disadvantages, but for one reason or another and in spite of the claims made in the patented art covering such means and methods, they have proven relatively unsatisfactory and commercially unacceptable. The trade, therefore, for lack of any satisfactory solutions, has thus continued to tolerate the old methods and the old type of decalcomanias above described and has assumed as inevitable the burden of a great percentage of spoilage and loss running as high as twenty-five per cent in many instances.

It is, therefore, one of the objects of the present invention to provide an improved form of vitreous decalcomania for application to chinaware, pottery or the like and an improved method of forming and applying the same.

Another object of the invention is to provide a ceramic decalcomania which may be merely slid off the paper backing and applied to a surface to be decorated without the use of a special sticky adhesive and without requiring a waiting period to permit drying of the special adhesive, thus eliminating factory storage space, permitting proper positioning and immediate firing and eliminating the damage caused by the escape of the adhesive gases during firing.

Still another object is to provide a ceramic decalcomania comprising a design layer, composite or single in form, supported on a flexible film and comprising vitrifiable material, the design layer being formed directly on the soluble adhesive coating of the decalcomania paper and adapted to be released therefrom and applied directly against the surface to be decorated, the remaining thin film of water soluble adhesive serving to adhere the transfer to the article surface.

A further object is to provide a ceramic decalcomania having a design layer and a supporting layer or film on the top surface thereof, the top layer or film being comprised of two incompatible or immiscible materials which penetrate down into the design layer upon application thereto, thereby forming a design and outer supporting film which is heterogeneous in nature and minutely granular or open, thus permitting the gases generated during firing in the design and supporting film to readily escape without causing surface imperfections.

A further object of the invention is to provide a method of applying a design to a ceramic article which comprises forming a design layer directly on the soluble adhesive coating of decalcomania paper, forming a flexible supporting film over said design layer, separating the design layer and supporting film from the paper backing by dissolving the adhesive coating, applying the design layer directly against the ceramic article with the supporting film on the outer surface thereof, the remaining soluble adhesive serving to adhere the transfer to the article surface, and then firing the same.

Another further object is to provide a method of applying ceramic decalcomania of the simplex or duplex type which comprises aligning a multiplicity of finished decalcomanias in stacks and securing the same together, immersing the entire stack in water and removing the same, sliding the transfer from the paper backing as they are required for application to chinaware or the like, applying the same to the chinaware without the use of a special adhesive, and then immediately firing the same.

Another object is to provide a decalcomania of the foregoing character in which the supporting film is on the top surface of the design layer so that upon firing the gases of the tough supporting film need not pass up through the design layer to disturb the same.

Other and further objects and advantages of the invention will become apparent hereinafter from the description which follows and by reference to the accompanying drawing in which:

Figure 1 is a diagrammatic, vertical sectional view of a ceramic decalcomania of the simplex type comprising a preferred embodiment of the present invention;

Fig. 2 is a diagrammatic, vertical sectional view of the transfer portion of the decalcomania prior to firing after it has been slid off the paper backing and applied to the surface of an article of chinaware to be decorated;

Fig. 3 is a diagrammatic, vertical sectional view showing the design layer of the decalcomania after it has been fired and fused into the upper surface of the article of chinaware;

Fig. 4 is a diagrammatic, vertical sectional view of a duplex type of decalcomania embodying the present invention; and

Fig. 5 is a diagrammatic, vertical sectional view of the manner in which a plurality of decalcomanias may be arranged in stacks for rapid handling and application.

The decalcomania illustrated in Fig. 1 of the drawing and comprising a preferred embodiment of the present invention is of the simplex type. It comprises an absorbent paper backing 10 having a coating 11 of chemically pure hydrolized starch which is water soluble and permits the transfer portion, presently to be described, to be separated from the paper backing 10. The design layer 12 is illustrated diagrammatically in the drawing as a single layer applied onto the releasable coating 11 but it is to be understood that it more frequently may be arranged as a composite layer with overlapping strata and areas and perhaps with a background film, and may comprise a plurality of colors formed adjacent to each other in the desired outline and design. The design layer for the purposes of the present invention comprises the design that is finally fused onto the article to be decorated.

The design film 12 may be applied to the soluble adhesive coating 11 by various methods, such as screen printing, lithography, rotogravure and the like, although for beauty of design and proper shading and diversity of colors, the lithograph method has been found quite satisfactory. The material of which the design film 12 is composed is a pure resinous varnish and a quantity of pulverized glass of the desired color, and this film may be applied by either of two methods. By one method, the pulverized glass may first be thoroughly mixed in with the varnish prior to

printing and then the mixture may be applied as a vitreous ink to the releasable coating 11. Or, if desired, the varnish may be printed directly onto the coating 11 and then the pulverized glass may be dusted on in the usual manner while the varnish is still wet. Whichever method is employed, the design layer is formed only after a plurality of printings in order to secure the various colors and shadings of colors in the design, each printing being allowed to dry before the next successive printing is applied.

After the design layer 12 has been completed and is dried, then a clear transparent, flexible supporting film or carrier layer 13, which comprises one of the novel features of the present invention, is applied over the top thereof. This supporting carrier film 13 is comprised of at least two incompatible or immiscible substances and a solvent. For example, the material of the film may comprise 124 ounces of ethyl cellulose mixed into paste form with a quantity of anhydrous alcohol. To this paste, is added approximately 4 ounces of polymerized methyl-methacrylate resin and then the entire mixture is dissolved in a quantity of solvent comprising butyl alcohol. The quantity of solvent that is added may vary in accordance with the proper consistency required by the method of printing employed.

The ethyl cellulose and the polymerized methyl-methacrylate resin are incompatible or immiscible with each other, and even after thorough agitation of the mixture, the resultant mass is still heterogeneous rather than homogeneous. The minute droplets of polymerized methyl-methacrylate are separately interspersed between separate minute droplets of ethyl cellulose. The structure of the mass is, therefore, composed substantially of disunited globular units or particles without any bonding medium to hold such units or particles together, and after the flowable mixture has been applied as a covering supporting film 13 and has dried, the disunitel, heterogeneous character as above described is still present. The dried film is, thus, more or less granular or open and still in the form of minute separate units or particles as compared to an impervious surface.

The same characteristic is also imparted to the design layer 12 by the supporting film 13. Although the design layer 12 as applied to the releasable coating 11 and dried, is relatively homogeneous and impervious, nevertheless, when the mixture comprising the supporting film 13 is applied in a wet state thereover, the design layer 12 is softened by the solvent in the later applied film. As a consequence, the ethyl cellulose and the polymerized methyl-methacrylate resin penetrate down and merge to a certain degree into the resinous varnish and the pulverized colored glass so that the incompatible units or particles of ethyl cellulose and polmerized methyl-methacrylate resin each include particles of pulverized glass. Thus, the relatively impervious surface of the design layer 12 is "opened" up in a manner similar to that described with respect to the carrier film 13.

The important result of the relatively open or non-impervious nature of the carrier film 13 and the design film 12 is that when the design and carrier layers have been transferred to the chinaware and are being fired at relatively high temperatures, the gases generated by the burning and decomposition of the binder materials and solvents of each layer 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 up through a relatively impervious surface under great pressure so as to cause blistering, bubbling or pitting of the surface. The gases merely take the easiest avenues of escape which are already provided between the minute divisions or particles.

When the article is fired with the transfer applied thereon, the clear supporting film 13 is burned away as well as the varnish binder in the design layer 12, leaving only the pulverized glass particles which under the high temperature become fused into the outer surface of the article as an integral part thereof. The surface of the design is flat and smooth as shown in Fig. 3, and contains no imperfections therein rendering the final product unacceptable.

The method of application of the transfer to the article is extremely simple but effective and involves none of the disadvantages or poor results of prior methods. No special adhesive or cement is required. The decalcomania illustrated in Fig. 1 of the drawings may be dipped in water for a short period to partially dissolve the hydrolized starch layer 11 and to permit the design layer 12 and its carrier film 13 to be slid therefrom. After being separated from the paper backing 10 the transfer is then applied to the surface of the article to be decorated, the design coating 12 being placed directly against the article surface as shown in Fig. 2. Although most of the hydrolyzed starch is dissolved by the water, a sufficient quantity remains in the under surface of the design layer 12 and serves to adhere the composite transfer film to the article. However, the hydrolyzed starch is not of the extremely sticky nature as the resinous varnishes which have been heretofore employed as the special cement, and consequently the composite transfer film may be readily slid about on the article surface into the desired position prior to firing.

During application of the composite film to the article, the top supporting film 13, which is flexible and tough, serves as a carrier and holds the various projecting parts of the design in their proper relative positions. Positioning of the design is facilitated by the transparency of the supporting film. Also because of the intimate bond which has been established between the carrier film 13 and the design layer 12, no particles of the design are permitted to break away when the transfer is released from the paper backing 10 so that when transferred the design remains intact.

When the composite transfer has been properly positioned on the article surface, it is then rubbed down lightly and gently with a soft rubber squeegee in order to eliminate any air pockets and effect intimate contact with the article surface, care being taken, however, not to disturb the position thereof on the surface. The rubbing pressure that is applied is very slight since it is unnecessary to force the transfer down into intimate contact with any special adhesive or to smooth out any irregularities in the adhesive. Since the hydrolized starch itself serves as the adhesive and is carried by the transfer, it is disposed in a thinner, smoother and more regular film than any special adhesive could ever be applied by a brush or any other method.

Another and greatly important advantage resulting from the elimination of the use of a

special and separately applied adhesive as a means of causing the transfer to adhere to the chinaware prior to and during firing, is the fact that the relatively great volume of gases which were generated therefrom and therein during firing have been eliminated. Heretofore, when special resinous adhesives were employed, a "boiling" action occurred and the gases which were generated by the heat collected in concentrated areas and forced their way up through the design layer to the atmosphere, thus causing imperfections therein. However, the hydrolized starch in comparison to such resinous adhesives is not caused to "boil" or become highly active under heat, but on the contrary quietly decomposes without affecting the design layer in any way.

Furthermore, because the design layer **12** is substantially in direct contact with the surface of the article and is not separated therefrom by a relatively thick layer of special adhesive, or a supporting film, the contact of the fusible material in the design layer with the article surface is more intimate and the layer **12** is not caused to be forced away therefrom by the boiling action of any special adhesive therebeneath. When the temperatures are sufficiently high to liquefy the outer skin of the article of chinaware, the liquified vitrifiable material of the design layer is directly thereagainst and consequently the two substances readily merge as an integral surface without any imperfections therein, as shown in Fig. 3.

The firing of the transfer into perfect fusion with the surface of the article of ware is also facilitated by preconditioning the transfer. This preconditioning comprises the application of a mixture containing a plasticizer and a solvent for the design and carrier layers, to the outer surface of the carrier layer **13** which has the effect of causing the layer **13** and the design layer **12** to become quite soft and to approach their wet or semi-fluid condition as when first applied to the decalcomania paper. By softening these layers, they are further "opened" up so that 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 had been placed in the furnace in a hard dry state. As a result of this preconditioning, the firing period may be reduced to a much shorter time and production may therefore be increased.

Because of the simplicity of structure of the decalcomania and the method of applying the same without the use of any special adhesive, mass production methods of application to articles of ware by relatively unskilled operators is made possible, and the results as evidenced by the finished products are substantially perfect, the percentage of spoilage being reduced to a very low minimum. A rapid method of application of the transfer to an article also comprises an important feature of the present invention as it has enabled the production rate of decorative chinaware to be at least trebled. This rapid method, as shown in Fig. 5, comprises simultaneously cutting the decalcomanias **20** from stacks of large sheets and arranging the cut stacks of decalcomanias in groups of one hundred, for example, each group being held together by adhesive **21** on one side thereof similar to a pad of paper. When the operator then desires to apply a design onto an article of chinaware, the entire pack is merely immersed in water for a suitable period of time to dissolve the soluble adhesive coating **11**; then, after removal from the water, the pack may be placed by the operator on a stand or table adjacent a supply of chinaware to be decorated, and following which the design and carrier films may be progressively removed one by one when application is desired. When the top transfer portion has been removed and applied, its paper backing is turned or torn off the stack thereby exposing the next transfer below, as shown in Fig. 5.

In Fig. 4 of the drawing, the invention is shown as embodied in a decalcomania of the duplex type. This embodiment comprises a heavy paper backing **15**, a layer of adhesive **16** adapted to permit the backing **15** to be separated from the rest of the transfer, a layer of thin tissue paper **17**, a layer **11** of water soluble adhesive such as hydrolized starch, the design layer **12** and the top supporting film **13**. This duplex decalcomania is prepared in a manner similar to that utilized in producing the simplex type of Fig. 1 of the drawing and the application of the transfer to the article of ware is also similar. These duplex decalcomanias may be handled in the usual manner by stripping the thin tissue paper **17** from the paper backing **15** or they also may be arranged in unified stacks of one hundred. If the latter method is followed, the water in which they are immersed may be treated with a wetting agent so as to cause the tissue paper **17** to remain firmly adhered to the paper backing **15**, thus permitting the films **12** and **13** to be readily removed from the tissue paper **17**, this removal action being similar to the simplex type.

It is thus apparent that the novel form of ceramic decalcomania and the method of producing and preparing the same for firing on chinaware and the like have overcome all the difficulties and disadvantages of the prior art decalcomanias and methods. No elaborate preparations or equipment are required and the necessity for skilled help has been eliminated. The manufacturer of chinaware is assured of perfect firing and the great percentage of spoilage and loss has been eliminated, thus reducing the overall cost of production of the finished article.

Although there has been described above and illustrated in the drawing an improved form of ceramic decalcomania and a method of preparing and applying the same, it is to be understood that modifications in the details of structure and composition of materials and in the steps of the methods may be resorted to without departing from the spirit and scope of the appended claim.

I claim:

A decalcomania comprising a water permeable backing coated with a soluble adhesive layer, a vitreous design layer on said adhesive layer containing a pulverized vitrifiable material in a combustible binder, and a flexible supporting film disposed directly over design layer, said design layer and said supporting film being releasable as a unit from said backing to permit said design layer to be adhered to an article to be decorated with said supporting film outermost, said supporting film comprising interspersed discrete particles of ethyl cellulose and a polymerized methyl methacrylate resin with said ethyl cellulose being present in said film in a major proportion, and said supporting film being partially merged with said design layer at the interface therebetween.

HARRY C. RATHKE.

(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
439,536	Maxwell	Oct. 28, 1890
493,449	Schmalz	Mar. 14, 1893
829,131	Wachter	Aug. 21, 1906
1,271,006	Becker	July 2, 1918
1,996,549	McNutt	Apr. 2, 1935
2,088,031	Miller	July 27, 1937
2,154,198	Carr et al.	Apr. 11, 1939
2,220,525	Kauppi et al.	Nov. 5, 1940
2,235,514	Brown	Mar. 18, 1941

Number	Name	Date
2,261,260	Kraus	Nov. 4, 1941
2,267,787	Ciavola	Dec. 30, 1941
2,271,192	Hinz	Jan. 27, 1942
2,294,211	Rothrock	Aug. 25, 1942
2,359,185	Wysong	Sept. 26, 1944
2,359,462	Bricker	Oct. 3, 1944
2,385,920	Jenkins	Oct. 2, 1945
2,445,084	Rehberg et al.	July 13, 1948
2,475,802	Osserman	July 12, 1949

OTHER REFERENCES

Hercules, Ethyl Cellulose for Varnishes, 1939, pages 12, 14, inside page of back cover.