

- [54] **CURABLE DECORATING SYSTEMS FOR GLASS OR METAL CONTAINERS**
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[56]

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[57]

ABSTRACT

A method of and articles for decorating heat resistant surfaces such as glass or metal using a heat transfer decoration comprising in sequence a temporary carrier, a transfer lacquer layer which is removably adhered to the surface of said carrier, at least one design print layer adhered over the lacquer layer and a heat-activatable adhesive layer adhered over said design print layer wherein at least the transfer lacquer and design print layers contain cross-linkable resin means and a cross-linking agent for cross-linking the resin intralayer and interlayer to form a unified adherent decoration resistant to abrasion and chemicals. The metal or glass surface may optionally be coated with a cross-linkable primer composition prior to application of the heat transfer decoration thereto.

16 Claims, No Drawings

CURABLE DECORATING SYSTEMS FOR GLASS OR METAL CONTAINERS

This invention relates to heat transfers for labeling and particularly to high quality, multi-color, chemically resistant decorations for glass, ceramic, metal, or heat stable plastic surfaces.

The art of heat transfer decorating is very old. It is described, for example, in an early U.S. Pat. No. 1,030,908 to McKerrow, which describes a heat transfer label having a paper backing, a transfer layer of resin or wax, and a design of printing and coloring upon the transfer layer. The transfer layers of McKerrow and those who followed, as illustrated by U.S. Pat. Nos. 1,331,581, 1,882,593, 2,219,071 and 2,667,003, have not been entirely satisfactory for a number of reasons.

Improved heat transfer labels based upon the use of oxidized waxes as a release layer are in substantial commercial use and are disclosed in U.S. Pat. No. 2,862,832 to Shepard, which discloses a heat transfer label comprising a wax release layer on a suitable carrier, an ink layer on the wax release layer, and a heat-activatable thermoplastic adhesive layer over the ink layer. Though such a heat transfer label is in considerable commercial use, there are certain disadvantages associated with it. For example, upon transfer to clear, transparent surfaces such as plastic and glass, a portion of the molten wax release layer is transferred along with the label. Upon solidifying, this wax coating, present as a "halo" around the design print, appears cloudy over clear areas and detracts from the appearance of the design print.

Other transfer labeling specifically for glass and for ceramics and of more recent origin include as typical examples the "water slide off" type decal wherein the design print is derived from ceramic type inks ultimately fired into the glass or ceramic article, as described, for example in U.S. Pat. No. 3,015,574 to J. Gobel. Labeling techniques employing direct dry heat transfer and subsequent firing of the ceramic inks are also known, as shown, for example in Canadian Pat. No. 919,521 to R. A. Keeling et al. Similarly, solvent activated types of labels have been described, wherein release assistance is provided by solvent activation through the carrier sheet or web (U.S. Pat. No. 3,298,850, K. J. Reed et al), or by direct activation of the adhesive layer by heat and/or pressure upon micro-encapsulated solvents (U.S. Pat. No. 3,728,210, J. Pi-ron). Finally, as another general type of the decalcomania class is the precision die cut design print with a pressure sensitive adhesive transfer layer, as shown for example in U.S. Pat. No. 3,297,508.

All of the above techniques for transfer decorations on heat resistant bases such as glass, ceramics, or metal suffer from a variety of disadvantages, most notable of which are the lack of chemical, abrasion, and rub resistance when the design print and adhesive are plastic, due in part to insufficient adhesion and cohesion between and within the various layers of the transfer label, and, when the design print is based on ceramic inks, which have limited color availability, lack of high quality multi-color designs.

Accordingly, it is an object of the present invention to provide a stable heat transfer label for heat resistant bases.

It is a further object of the invention to provide a chemical, abrasion, and rub resistant transfer label for heat resistant bases.

It is still a further object of the invention to provide a high quality multi-color design print, preferably printable by roto gravure, as part of the heat transfer label.

I have discovered that by employing in one or more of the layers of the transfer label certain polymerizable crosslinking agents which are capable, preferably in response to heat, of crosslinking the resins in adjacent layers to form strong, cohesive interlayer chemical bonds, chemical, abrasion and rub resistance are greatly increased, and highly resistant multicolored transfer labels are obtained. In a preferred embodiment, crosslinking occurs both interlayer and intralayer, resulting in a cured label which is thermoset throughout its thickness from the outer surface of the transfer layer right to and including the surface of the heat resistant base to which it is applied. In that embodiment not only are the cohesion and abrasion resistance of the label much better than previously available, but also the label is rendered essentially temperature insensitive, so that glass, ceramic or metal containers bearing the thermoset label can be subjected to high temperatures without deleterious effects on the label's properties.

The present invention can be used with particular advantage in multilayer decorative transfer labels such as those disclosed in copending U.S. Pat. application Ser. No. 244,292, filed Apr. 14, 1972, by B. Asnes, incorporated herein by reference. In that application a heat transfer label system is described which comprises an adhesive layer, laid down and adhered to a design print, which has been laid down and adhered to a transfer lacquer layer, (first down lacquer), which has been laid down and releasably adhered to a release layer, which layer may or may not have a backing sheet or layer adhered to it. The transfer lacquer layer is preferably a clear cellulosic resin, such as a cellulosic ester, having a softening point well above 300°F to 450°F, i.e. a cellulosic resin which does not appreciably soften or tackify at transfer temperatures. The design print layer is made up of one of more colors of conventional heat transfer inks such as nitrocellulose and/or polyamide inks, containing dispersed or dissolved therein pigments and/or dyes of the colors desired. The last down adhesive layer is made up of a conventional heat-activatable adhesive, suitable adhesives being disclosed therein.

The term "crosslinking agent" is used to designate a material which chemically reacts, e.g. polymerizes, with crosslinkable polymerizable material to form chemical bonds, i.e. crosslinkages, between the polymer molecular chains of that material or between the polymer molecular chains of that material and a different material. The "different" material may include polymer chains or parts of chains of the crosslinking agent itself, i.e., during polymerization the crosslinking agent itself may form polymer chains which may be themselves crosslinked by the crosslinking agent and/or crosslinked with another or other crosslinkable materials by the crosslinking agent. The preferred embodiment utilizes several polymeric crosslinking agents which react with polymeric crosslinkable materials. The term crosslinking as used herein includes the formation of chemical bonds between the chain of the crosslinking agent and/or the chains of one or more

crosslinkable materials. In fact, both the crosslinkable material and the crosslinking agent take an active part in any reaction which occurs between them, and the term "crosslinking agent" is used more or less to conveniently designate the more reactive of the two materials. Indeed, some materials are suitable as both the crosslinkable material and the crosslinking agent, e.g., those polymers which undergo substantial crosslinking with themselves at elevated temperatures.

Crosslinking agents suitable for use in accordance with the invention are well known in the art. Choice of a particular crosslinking agent depends upon which layer it is to be used in, and the nature of the material in the adjacent layer, or layers, it is desired to crosslink. If the crosslinking agent is used in the first down or transfer lacquer layer, it must not reduce the release properties of the lacquer/release layer interface. Accordingly it should have a sufficiently high melting point to keep from becoming soft or tacky at the temperatures at which the label will be transferred, lest it adhere to the release layer and interfere with release. Also, it should not crosslink or otherwise be reactive with the material in the release sheet, which would also prevent good release. If the crosslinking agent is used in the adhesive layer, it must not interfere with the necessary adhesive properties of that layer.

Where the layer with which crosslinking is desired contains polymeric materials with available reactive groups, such as carboxyl or hydroxyl groups, for example the cellulosic materials, suitable crosslinking agents include those having blocked isocyanate groups, epoxy groups, urea formaldehyde groups, including substituted urea formaldehyde groups, primary and secondary amines and polyamines, and other materials known in the art. Crosslinking will also occur between materials having available urea formaldehyde groups and materials having available epoxy groups; between materials having available urea formaldehyde groups and materials having available carboxyl groups; between "blocked" isocyanates and materials containing epoxide groups; etc. Generally, crosslinking agents suitable for crosslinking particular polymeric materials are known to those skilled in the art, those dealt with herein being only exemplary.

By "blocked" isocyanates is meant reaction products of isocyanates with active hydrogen containing compounds which result in an addition product having only limited thermal stability. These compounds are stable at room temperature, but react at elevated temperatures as if an isocyanate were present. Suitable blocked isocyanates are known in the art, as disclosed for example in Sanders & Frisch, *Polyurethanes, Chemistry & Technology*, Vol. 1, pp. 118-21 (1962). Suitable blocking agents include those disclosed therein, such as the phenols, substituted phenols, alkyl and aryl mercaptans, and other compounds having reactive hydrogen, such as the alcohols. Commercially available blocked isocyanates suitable for use in the present invention include a variety of Aminimides available from Ashland Chemical Co., especially Ashland Aminimide 21001 (bis (trimethylamine) sebacimide) and Ashland Aminimide 20603 (Bis (dimethyl-2-hydroxypropylamine) adipimide), and a caprolactam blocked polymeric isocyanate available under the mark Isonate 123P from the Upjohn Company.

In a preferred embodiment, material containing blocked isocyanate groups is used as a crosslinking

agent in the transfer lacquer layer of a multi-layer decorative label, and the adjacent design print layer contains a polymeric material containing available hydroxyl groups. Preferably, the transfer lacquer layer also contains a polymeric material having available hydroxyl groups. Use of the blocked isocyanate crosslinking agents in the transfer lacquer layer is especially advantageous because their reactivity is generally low enough to minimize the likelihood of reaction with the release layer, yet at elevated temperatures they readily crosslink with materials having available hydroxyl groups.

Suitable polymers having available hydroxyl groups include known polyols, such as cellulose and modified cellulosic materials such as cellulose esters, including cellulose acetate, cellulose propionate, cellulose acetate butyrate, etc., substituted cellulosic materials such as hydroxyalkyl cellulose; starches, both unmodified and modified; polymeric resins based on alcohols, such as polyvinyl alcohol, or on monomers having a plurality of hydroxyl groups, such as diols and glycols; and other polyols well known in the art. It is preferred to use a cellulosic material as the source of hydroxyl substituents in the transfer lacquer layer, preferably cellulose esters such as cellulose acetate.

The amounts of the reactive components included in the various layers can vary considerably, depending upon the particular types of materials used and the properties desired of them in use. The transfer lacquer layer, for example, may be predominantly made up of crosslinkable material, such as the cellulose ester, and contain a relatively small amount of a crosslinking agent, such as the blocked isocyanates. Thus it may contain from about 80 to about 99 percent by weight cellulose acetate or other cellulosic material and from about 0.5 to about 20 percent by weight blocked isocyanates. Preferably that layer contains about 85 to 95 percent by weight cellulose acetate or other cellulose ester and between about 5 to about 15 percent polyisocyanate material. Other materials may also be incorporated in the transfer lacquer layer, such as a small amount of a tracer compound which is normally colorless but fluoresces under the influence of ultraviolet radiation. The tracer compound is useful in the printing process to facilitate the registration of clear lacquers.

In those layers which are separated from the release layer by the transfer lacquer layer or other layers, the reactivity and physical characteristics are not as critical as they are in the transfer layer, since adherence to the release layer is not a problem. Thus, those layers may be formulated with a view to optimizing both intralayer cohesion and interlayer adhesion. The adhesive bond between layers in the decoration of the present invention may be referred to as a cohesive bond or cohesion, since the crosslinking which occurs between the materials in adjacent layers in effect creates an interlayer blend of chemically linked material. Thus, in layers other than the transfer lacquer layer, materials can be used which are much more reactive than those used in the transfer lacquer layer. For example, more reactive crosslinking agents such as urea formaldehydes or epoxy materials can be used in the design print and adhesive layers. In a preferred embodiment the design print layers contain both a crosslinkable material, such as a material having available hydroxyl groups, and a crosslinking agent, such as a urea-formaldehyde resinous material. The relative amounts of each can be

about the same, or either may predominate. Preferably the design print layers contain from about 30 to 55 percent by weight polyol and from about 40 to 65 percent by weight heat reactive urea formaldehyde binder. The preferred urea formaldehyde polymers or pre-polymers are substituted ureaformaldehydes, such as butylated urea formaldehyde material. The polyol in the design print layers is preferably a hydroxyl modified vinyl resin, a hydroxyl modified vinyl chloride-vinylacetate copolymer being most preferred. The design print layers will also contain the pigments necessary for the desired color, and minor amounts of other additives known in the art may be added.

Where the adhesive layer is crosslinked with its adjacent print layer, in accordance with the invention, it must both act as an adhesive to bind the decoration to the glass, ceramic, metal or other substrate, and serve as a crosslinked, integrated layer in the finished decoration. Preferably it is a heat activatable adhesive, and the same materials which make it a heat activatable adhesive also participate in the crosslinking between the adhesive layer and the adjacent design print layers. Again, these may comprise one or more crosslinkable materials and one or more crosslinking agents. In a preferred embodiment, the crosslinkable material in the adhesive layer comprises a carboxyl modified vinyl resin, and the adhesive layer further comprises two epoxy type crosslinking agents: an epoxy modified vinyl resin and a highly reactive diglycidyl ether-bisphenol A type of polyepoxide. Other additives may also be included, such as a small amount of an ultraviolet radiation absorber, which permits the adhesive layer to be easily distinguished from the transfer lacquer layer during printing. Again, the amounts required of the various ingredients depend upon the particular ingredients used in the system. The preferred embodiment contains between about 35 - 60 percent of the epoxy modified vinyl resin, from 1 to 15 percent of the diglycidyl ether-bisphenol A polyepoxide, and from 35 - 60 percent of the carboxyl modified vinyl resin.

In practice, the decorative label is made by forming a suitable release layer, as, for example, in the manner described in the above mentioned co-pending U.S. Pat. application Ser. No. 244,292 by B. Asnes. Once the release layer is formed, the transfer lacquer layer is applied onto the release layer, preferably by roto gravure printing. The design print and adhesive layers are thereafter laid down sequentially over the transfer lacquer layer, also preferably by printing techniques.

In applying the finished decorative label to the substrate it is greatly preferred if the substrate is first treated with any of the well known silane adhesion promoters. Such materials include epoxy silanes (e.g., A-187, from Union Carbide) mercapto silanes (e.g., A-189, also from Union Carbide), and others. It is generally preferred to pre-heat the substrate before application of the decorative label. Generally, pre-heating temperatures from about 150°F to about 250°F have been found to be advantageous. After pre-heating, the decorative label is put in contact with the heated substrate and heat and pressure are applied to the temporary backing which supports the release layer, to effect pressing of the adhesive layer against the substrate surface. This is accomplished in a heat transfer decorating machine, preferably the Dennison TD1B Decorating Machine, described in several U.S. Patents including U.S. Pat. Nos. 2,862,832, 3,064,714, 3,231,448 and

3,261,754, or its equivalent. After transfer, the decorated substrate is heat cured, e.g. for 10 to 20 minutes at about 200°-300°F, and then it may be further heat cured, e.g., for 10 to 20 minutes at about 350°-450°F.

Upon curing, a very attractive, clear and precise decorative label which is very strongly bonded to the substrate and has excellent abrasion resistance is produced.

The benefits provided by the present invention are outstanding. The applied decorative labels are far superior in durability, abrasion and mar resistance, ease of application and appearance to heat transfer labels previously known. One of the most important advantages obtained through the present invention is the increase in decorating speed. With even the most efficient of comparable previous systems, the labeling speeds were limited to about 20 or, at most, about 30 bottles per minute. Speeds of between 60 and 100 bottles per minute have been achieved using the present invention, with the decorated bottles having the improved appearance, chemical and abrasion resistance previously mentioned.

While it is preferred that a number of crosslinking and/or crosslinkable materials be used to obtain the reactions between adjacent layers, benefits can be derived from much simpler systems in accordance with this invention. Thus, for example, a two component reactive system might be used in which the same crosslinking agent, for example, a blocked isocyanate material, is contained in both the transfer lacquer layer and in the adhesive layer, and reacts from both directions with a single crosslinkable material in the design print layer, e.g., a polyol. The same agents would also work if the crosslinking agent were in the design print layer and the crosslinkable materials are in the transfer lacquer and adhesive layers.

It is also preferred that each layer contain both a crosslinkable material and a crosslinking agent. In this way the intralayer cohesion is improved by crosslinking between the materials within each layer; and the interlayer cohesion, and thus the overall cohesion of the label, is improved by the action of the crosslinking agents in both adjacent layers. In effect, the decoration becomes thermoset, both throughout each layer and between layers, as discussed above. However, some benefit is obtained even when one or more of the layers contains only one of the reactive materials, whether it be a crosslinkable material or a crosslinking agent.

To summarize the most preferred embodiment, all of the transfer lacquer layer, the design print layer or layers and the adhesive layer contain both crosslinkable and crosslinking materials. In the transfer lacquer layer the preferred crosslinkable material is cellulose acetate, and the preferred crosslinking agent is Isonate 123P, a caprolactam blocked polymeric isocyanate available from the Upjohn Company. In the design print layer or layers the preferred crosslinkable material is a hydroxyl modified vinyl chloride-vinylacetate resin and the preferred crosslinking agent is butylated urea-formaldehyde polymeric material. In the adhesive layer the preferred crosslinkable material is a carboxyl modified vinylchloride-vinylacetate resin, and two epoxy crosslinking agents are preferably used, namely, an epoxy modified vinylchloride-vinylacetate copolymer resin and a diglycidyl ether-bisphenol A type of polyepoxide. At curing temperatures (200°-450°F), it is believed that the polyisocyanate in the transfer lac-

quer layer becomes unblocked and reacts both with the hydroxyl groups of the cellulose acetate in the transfer lacquer layer and the hydroxyl groups of the hydroxyl modified resin in the design print layer. It is similarly believed that the butylated urea-formaldehyde in the design print layer reacts with the same hydroxyl groups in the transfer lacquer and design print layers, and also with both of the epoxides and also the carboxyl groups in the adhesive layer. To complete the picture, the hydroxyl groups of the hydroxyl modified resin in the design print layer reacts with the now unblocked polyisocyanate in the transfer lacquer layer, with the butylated ureaformaldehyde in its own design print layer and with both of the epoxy compounds in the adhesive layer. This system, involving various crosslinking agents and crosslinkable materials gives a particularly strong, cohesive, mar resistant, decorative label.

The invention will be further clarified with reference to the following illustrative embodiments.

EXAMPLE 1

A heat transfer decoration was prepared by printing on a suitable release surface as described in the above-mentioned U.S. Pat. application, Ser. No. 244,292 by B. Asnes, a multiple layer print applied by roto gravure, comprising a clear lacquer composed of cellulose acetate, 9.8 parts, (E-398-3, made by Eastman Chemical Products, Inc.) dissolved in 80 parts of methyl ethyl ketone and 8.9 parts acetone, and containing 0.4 parts of a fluorescent dye (a substituted phenyl benzotriazole sold under the name Intrawite OB by Intracolor Corporation) and 1.0 parts of blocked polymeric isocyanate, (Isonate 123P, by Upjohn Co.). Inside the periphery of the first printed dried clear lacquer there is printed the design print using a reactive yellow ink consisting of 15.3 parts butylated urea-formaldehyde resin solution (Resimene U-920, by Monsanto), 11.5 parts hydroxyl modified vinylchloride-vinylacetate copolymer resin (VAGD, by Union Carbide) dissolved in 22.5 parts ethyl acetate, 34.2 parts n-propyl acetate, 16.6 parts toluol, and 3.2 parts isopropanol, and containing 0.1 parts silicone resin (S-10, Union Carbide). Sumatra Yellow pigment by Hercules, 6.5 parts, is dispersed into this solution with a Cowles Dissolver and the mixture is ground to No. 8 Hegman in a ball or sand mill. Over the design print, but inside the periphery of the first clear lacquer, a clear, curable, heat activatable adhesive layer is printed, consisting of 13.9 parts epoxy modified vinylchloride-vinylacetate copolymer resin (VERR, Union Carbide), 13.9 parts carboxyl modified vinylchloride-vinylacetate copolymer resin (VMCA, Union Carbide) dissolved in 34.6 parts ethyl acetate and 34.6 parts toluol, and containing 2.8 parts diglycidyl ether-bisphenol A epoxy resin (ERL-2774, Union Carbide) and 0.2 parts ultraviolet absorber (Uvinul D-50, General Aniline and Film). The applied heat-activatable adhesive over-print was dried to a non-tacky but heat-activatable state. The final print is monitored after the last press station under ultraviolet light which fluoresced the dye in the clear transfer layer (first down lacquer) to make it clearly visible, and was absorbed by the ultraviolet absorber in the overprinted clear adhesive layer (last down lacquer) so it appeared to be darker than the first down lacquer, whereby it is possible to keep the two clear lacquers and the ink print in perfect printing registration.

The resulting decorative label is transferred to a glass bottle in the manner discussed above. Before decoration, an amino alkoxy silane, i.e., a solution of gamma-aminopropyltriethoxysilane (0.05% in Toluene-ethanol) (A-1100, Union Carbide) is applied to the surface to be decorated. Application of the silane to the ware imparts significant hydrolytic resistance to the cured decoration on the ware. The container is then heated to 150°-250°F before the decoration is applied in a Dennison TD1B heat transfer decorating machine at a speed of about 60 bottles per minute. Thereafter the decoration on the container is cured in an oven for 10 to 20 minutes at 200° to 300°F and then further cured for 10 to 20 minutes in an oven at 350°F to 450°F. After curing is complete, the lacquer layer which surrounds the ink print, and protects it, is observed to be water-white and nearly invisible.

The cured decoration will withstand 40 rubs with methyl ethyl ketone with nothing removed, and a 30 minute immersion in boiling water with very little removed by scotch tape after cross-hatching with a razor.

EXAMPLE 2

A reactive white ink may be printed on top of the yellow ink in Example 1 before application of the adhesive to provide opacity to the transparent yellow color when the decoration is transferred to the container. The reactive white ink consists of 10.1 parts Resimene U-920, 7.7 parts VAGD, dissolved in 8.3 parts ethyl acetate, 22.6 parts n-propyl acetate 11.0 parts toluol, 2.1 parts isopropanol, and containing 0.05 parts S-10 silicone resin. Titanium dioxide (OR-580, Cyanamid), 38 parts, is dispersed and ground into the above formulation as in Example 1. Printing, decorating and curing are the same as in Example 1.

EXAMPLE 3

A reactive transparent blue ink may be printed in addition to and in line with the yellow ink in Example 1, over all of which a white ink may be printed as in Example 2. The reactive blue ink consists of 14.2 parts Resimene U-920, 10.8 parts VAGD, dissolved in 11.6 parts ethyl acetate, 31.9 parts n-propyl acetate, 15.5 parts toluol, 3.0 parts isopropanol, and containing 0.1 parts S-10. Monarch Blue pigment CFR X-3367 (Hercules), 12.9 parts is dispersed and ground into the above formulation as in Example 1. Printing, decorating, and curing are the same as in Example 1. The test results are also similar to those in Example 1.

EXAMPLE 4

A reactive transparent red ink may be printed in addition to and in line with the yellow ink in Example 1, the blue ink in Example 3, over all of which a white ink may be printed as in Example 2. The reactive red ink consists of 14.5 parts Resimene U-920, 10.9 parts VAGD, dissolved in 11.9 parts ethyl acetate, 32.5 parts n-propyl acetate, 15.8 parts toluol, 3.1 parts isopropanol, and containing 0.1 parts S-10. Sparta Red pigment (Hercules), 10.9 parts, is dispersed and ground into the above formulation as in Example 1. Printing, decorating, and curing are the same as in Example 1, with similar test results.

While particular embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from this inven-

tion in its broader aspects. Therefore, it is intended that the specification be interpreted as illustrative only, and not in any limiting sense.

I claim:

1. A stable heat transfer decoration comprising in combination a temporary carrier having a release surface from which the transfer is readily releaseable at elevated transfer temperature, and removably adhered to said surface in sequence a transfer lacquer layer, at least one design print layer, and a heat-activatable adhesive layer, wherein at least said transfer lacquer and design print layers adjacent to and in contact with each other contain cross-linkable resin means for forming cross-linked polymers, at least one of said two adjacent layers containing cross-linking agent means for cross-linking with said resin means in both layers, said agent means being stable at room temperature and activatable at elevated temperature to cross-link with said resin means within said one layer and between the two contacting layers, said resin and agent means being present in amounts effective to increase the abrasion and chemical resistance of the transfer decoration after application to a receiving surface and activation at elevated temperature.

2. The heat transfer of claim 1, in which said agent means reacts to form cross-links at a temperature between about 200°F and 450°F.

3. A heat transfer according to claim 2 wherein said one layer containing the cross-linking agent means is the design print layer.

4. A heat transfer according to claim 3 wherein all three layers including the heat-activatable adhesive layer contain cross-linkable resin means with which said agent means reacts at elevated temperature to form crosslinks.

5. A heat transfer according to claim 2 wherein each of said layers contains cross-linkable resin means, and the transfer lacquer and heat-activatable adhesive layers each contain cross-linking agent means activatable to form cross-links at elevated temperature with the resin means in the design print layer.

6. A heat transfer according to claim 4 wherein each of said layers contains cross-linkable resin means and cross-linking agent means activatable to form cross-links within the layer and interlayer at the interface with the adjacent layer, whereby all layers are cross-linked together upon transfer and activation at elevated temperature.

7. A heat transfer according to claim 6 wherein said agent means are selected from the group consisting of blocked polyisocyanates, urea-formaldehyde resins and polyepoxide resins.

8. A heat transfer according to claim 2 wherein the cross-linkable resin means in the transfer lacquer layer is a cellulosic material containing sufficient hydroxyl substituents for cross-linking, and said transfer layer also contains a blocked polyisocyanate as said cross-linking agent means.

9. A heat transfer according to claim 6 wherein said release surface is the surface of an inert thermoset resin, said cross-linkable resin means in the transfer lacquer layer is a cellulosic material having sufficient hydroxyl substituents for cross-linking, said cross-linking agent means in the transfer lacquer layer is a blocked polyisocyanate, said resin means in said design print layer has sufficient hydroxyl substituents for cross-linking, said cross-linking agent means in the de-

sign print layer is a urea-formaldehyde resin, said resin means in the adhesive layer contains sufficient carboxyl substituents for cross-linking, and said cross-linking agent means in the adhesive layer is a polyepoxide resin.

10. A heat transfer according to claim 9 wherein said cellulosic material is cellulose acetate.

11. A heat transfer according to claim 9 wherein said cellulosic material is a cellulose ester, said resin means in the design print layer is a hydroxyl modified copolymer of vinyl chloride-vinyl acetate and said resin means in the adhesive layer is a carboxyl modified copolymer of vinyl chloride-vinyl acetate.

12. The method of decorating a heat resistant surface of glass or metal comprising the steps of transferring to said surface from a release surface of a temporary carrier, under and heat and pressure, a decoration comprising in sequence a transfer lacquer layer, at least one design print layer, and a heat-activatable adhesive layer which is non-tacky at room temperature, wherein at least said transfer lacquer and design print layers adjacent to and in contact with each other contain cross-linkable resin means for forming cross-linked polymers, at least one of said two adjacent layers containing cross-linking agent means for cross-linking with said resin means in both layers, said agent means being stable at room temperature and activatable at elevated temperature to cross-link with said resin means within said one layer and between the two contacting layers, immediately stripping the temporary carrier from said layers, and curing said resin and agent means in said layers at a temperature between about 200°F and about 450°F to form a cross-linked structure within and between said layers, whereby an adherent cross-linked decoration is provided with improved resistance to abrasion and chemicals.

13. The method according to claim 12 wherein each of said layers contains both said resin means and agent means and wherein said heat-resistant surface of said metal or glass is coated with primer means having cross-linkable substituents reactive at elevated temperature with the agent means in said adhesive layer, whereby all of said layers, after curing, are cross-linked together and to said primer.

14. The method according to claim 13 wherein said primer is a silane, said release surface is an inert thermoset resin, said resin means in the transfer lacquer layer is a cellulose ester having sufficient hydroxyl substituents for cross-linking, the agent means in said transfer layer is a blocked polyisocyanate, said resin means in the design print layer has sufficient hydroxyl substituents for cross-linking, said agents means in the design print layer is a urea-formaldehyde resin, said resin means in the adhesive layer has sufficient hydroxyl or carboxyl substituents for cross-linking, and said agent means in the adhesive layer is a polyepoxide resin.

15. A decorated article of glass or metal comprising primer means on a surface of said article and a heat-transferred organic decoration comprising an adhesive layer over said primer means, at least one design print layer over said adhesive layer, and a protective transfer lacquer layer over said design print layer, all of said layers comprising polymeric resin means, all of said resin means and primer means being cross-linked intralayer and interlayer to form a unified adherent decoration resistant to abrasion and chemicals.

16. A decorated article according to claim 15 wherein said primer is a silane, said resin means in the transfer lacquer layer is a cellulose ester having cross-linked hydroxyl substituents, said resin means in the design print layer has crosslinked hydroxyl substituents, 5

and said resin means in the adhesive layer has hydroxyl or carboxyl substituents cross-linked to said primer means by means of a polyepoxide resin.

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