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[54] **DECORATION OF SUBSTRATES BY THERMAL TRANSFER OF PHOTOSENSITIVE, THERMOPLASTIC, DYE-IMAGED FILM**

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[56] **References Cited**

UNITED STATES PATENTS

2,409,564	10/1946	Heinecke et al.	96/83
2,510,750	6/1950	Marquardt	156/219
3,536,490	10/1970	Hochberg	96/15
3,565,618	2/1971	Marechal	96/28

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[57] **ABSTRACT**

A process for decorating substrates comprises coating a film of photosensitive composition in a thermoplastic binder onto a less adherent carrier, photoimaging the film, heating the film until adhesive and contacting the film surface with a more adherent support, and then separating the carrier and support whereby the film adheres to the support. This process is useful in color decoration of wear fabrics such as leather, vinyls, and textiles. Tipping and valley printing effects are obtained by embossing while transferring.

1 Claim, No Drawings

DECORATION OF SUBSTRATES BY THERMAL TRANSFER OF PHOTOSENSITIVE, THERMOPLASTIC, DYE-IMAGED FILM

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a decoration process by surface bonding wherein direct contact transfer of a film from carrier to base is employed. More particularly, it is directed to a decoration process wherein photosensitive, dye-forming components in a thermoplastic binder are thermally transferred to a substrate.

2. Prior Art

The demands of fashion have led to the coating of leather, and other sheet materials of a porous and absorbent nature, with solid polymeric finishes which add color and improve the appearance substantially. Commerial dyes are available for addition to the finishes to impart overall coloration. However, the interface between the coating and sheet material such as a wear fabric, is subject to high shear stress and delaminating forces when worn, aggravated by chemical attack of perspiration and migrating chemical components of the sheet material. The leather industry, in particular, is subject to problems arising out of delamination.

Such concern about delamination has made transfer of colored designs from a carrier support to wear fabrics like leather impractical. Most multilayer transfer sheets now used in decorating static surfaces are unable to withstand high shear stresses and delaminating forces that would develop at interfaces between layers of a multilayer structure coated on a flexible substrate subject to flexing and bending in use, e.g., on a wear fabric. A typical multilayer transfer sheet is disclosed in U.S. Pat. No. 2,528,395 and comprises a carrier support bearing a plurality of layers, one being a photographic image or colorant pattern-containing layer, another being an adhesive layer for establishing adherence to a receiving substrate. Generally, the binder for the image layer is selected for photographic quality to keep image definition unchanged during the transfer step. The adhesives used are meant to establish a rigid bond. As a result, an interface between the image and adhesive layer is easily delaminated on continued mechanical flexing.

Other layers present increase the probability of delamination by introducing additional interfaces. In the improved transfer sheet of U.S. Pat. No. 2,409,564 another layer is introduced between a photographic image layer and the adhesive layer just to keep one layer from floating off the other during image development, washing, and fixing steps. Transfer sheets also may contain stripping or release layers and additional colorant-containing layers. It would be highly desirable to avoid so many layers, yet still achieve full color decoration, such as by subtractive colors of molecular dyes in overlay. Thermal transfer processes, such as that of U.S. Pat. No. 3,060,023, which minimize layers face other problems such as transferring with uniform adhesion both the imaged and unimaged areas of film.

Decoration of leather and leather-like fabrics by embossing is a desirable supplement for color decoration, but embossing generally requires heat and pressure. Embossing pressures applied after transfer of a multilayer decoration tend to delaminate the decoration at internal interfaces just like the high shear stresses met in fabric wear. Heat further increases stress through differences in thermal expansion between layers.

It is an object of this invention to provide a decoration process which avoids the delamination problem associated with the use of multilayer transfer systems.

Another object is to provide a convenient process in which designs can be inspected for definition before transfer and which can be changed rapidly to give access to changing fashion.

Still another object is to provide a process wherein the composition that is to be transferred is photoimagable.

A further object of this invention is to provide in a transfer composition a plurality of photosensitive components which, upon suitable exposure to activating light and subsequent color development, form a multiplicity of subtractive dye colors, each transparent to different selected wavelengths of visible light.

Still another object of this invention is to provide a process in which a transfer film is made to conform to a regularly contoured or irregular receiving surface, and to provide for integral binding of the transferred film to leather, woven fabrics, and other porous, open surfaces, offering stabilization against delamination and peel strength in adhesion testing.

A further object of this invention is to provide a decoration process by which contours are embossed on a receiving surface and color decoration of the same surface is carried out in one operation during film transfer.

SUMMARY OF THE INVENTION

In summary, this invention is directed to a decoration process comprising

1. coating a layer of photosensitive dye-forming composition in a film-forming thermoplastic binder onto a less adherent carrier support forming thereon a film with an outer surface;

2. imparting an image to the film by photoimaging the film with activating light;

3. heating the film to a temperature of between 40° and 220°C. at which its outer surface is adhesive and contacting the outer film surface with a more adherent receiving support; and

4. separating the two supports; whereby the photoimaged film layer adheres to and is transferred to the receiving support and is released from the carrier support.

DESCRIPTION OF THE INVENTION

As stated above, this invention is directed to a process for forming and photoimaging a photosensitive film on a first support and thermally transferring such film after photoimaging to a second support for the purpose of decorating the surface of a second support such as leather, woven, or textile fabric surface, said photosensitive film comprising a photosensitive, dye-forming component and a film-forming, thermoplastic binder component. The binder must have an adhesive or stick temperature in the range 40°–220°C. and greater adhesion to the second surface than to the first surface at a temperature at or below the stick temperature and the film must have substantially the same thermal transfer characteristics before and after exposure to imaging light. The process comprises:

1. applying a coating composition comprised of the dye-forming component and the binder component to a less-adherent carrier support to form a film thereon,

2. exposing the film to activating light in a desired pattern to produce photoimage;

3. heating the film to a temperature sufficient to raise the outer film surface to a stick temperature, contacting the outer film surface with a more adherent receiving support and maintaining sufficient contact to cause the film surface to stick to the surface of the receiving support; and

4. separating the two supports at a temperature at which the film adheres more strongly to the receiving support than the carrier support, whereby the photoimaged film adheres to and is transferred as a unit to the second surface, releasing the carrier support.

A preferred embodiment of the process of this invention is one that imparts improved laminar peel strength to the transferred film. This is accomplished when:

1. the receiving support presents an open surface which the film composition can enter under thermoplastic flow,

2. both supports are heated to a temperature sufficient to raise a substantial thickness of the film to a stick temperature, and

3. the film composition has sufficient pressure applied to move into said open surface.

Other preferred embodiments of the process of this invention impart an embossed surface to the transferred film. In one such embodiment:

1. the less adherent carrier support presents an embossed surface,

2. the coating applied thereon in step (1) above assumes a surface configuration necessary to conform to said embossed surface of the carrier support, and

3. the surface of the film contacting the carrier support is kept below a temperature at which that surface would deform appreciably during separating step (4) of the decoration process,

whereby the film surface separated from the carrier support essentially retains the surface configuration it assumed during coating of the carrier support.

Another preferred embodiment is suitable for embossing the transferred film and the receiving support in a single operation during transfer. It comprises the process of this invention wherein:

1. sufficient heat is supplied to the film in step (3) to cause thermoplastic flow of the film as a unit, and

2. sufficient heat and pressure is applied to the receiving support during heating and contacting (step 3) to form contours therein to receive a conforming, thermoplastic flow of film composition,

whereby decoration and embossing are combined in a single step during transfer.

The term "surface-conforming" as used hereinafter means capable of changing from a coated film form on a transfer sheet, which coated film usually has a planar outer surface, to a form wherein the outer surface assumes essentially the same configuration as a receiving surface, whether that be planar, regularly contoured, or irregular. Conformity of the exposed surface of the film to the receiving surface generally requires local displacement of binder component and dye component, attainable herein by pressurized flow of heat-softened, thermoplastic film composition, into open areas of a receiving surface, such as the spaces between fibers in fibrous material or into contours embossed in the receiving surface. Such displacement usually reduces the definition of the dye-colored design, but, for the purposes of this invention, image fidelity on the carrier support need not be preserved to a high degree in the decoration transferred to the receiving support, provided the appearance of the decoration is acceptable.

The process of this invention offers distinct advantages. First, because the image that is to appear on the receiving substrate is produced before it is applied to the receiving substrate, an expensive substrate need not be committed until after the quality of the image is seen. Thus coating and photoimaging can be done in different locations under subdued light and under clean conditions, free of lint from fabrics. Second, use of a thermoplastic, photoimaging composition that flows when heated and subjected to pressure enables nonuniformity of a substrate to be overcome. Third, the process enables one-step application of a final topcoat, imaged and embossed, to save processing steps.

A major advantage of adhesive, surface-conforming transfer, attributable to use of imaging and transfer compositions which can be applied and transferred as a single layer, is outstanding stabilization against abrasion and delamination. Use in a single layer of a heat-flowable, thermoplastic binder applied under pressure to achieve a tight, adhesive bond over a maximum conforming surface area locks in the decoration for the useful life of articles of wear.

Still other advantages are derived from use of versatile color-forming systems that produce subtractive color dyes that are transparent to light in at least one region of the visible spectrum, in binders of appropriate light transparency to suit or modify such dye colors. Different visual effects become possible through dye use, particularly full color decoration from overlay of differently colored images.

The practice of this invention requires forming a film with two key properties, each being derived from one of two essential components of the film-forming composition. As the first property, the film must be photosensitive, capable of undergoing local image-forming reaction when exposed to patterns of activating wavelengths of light. The exposure can be through a stencil, line, halftone, or continuous tone negative or positive, a cutout stencil in contact with the layer or by reflectographic or projection exposure. As the second property, the film must be thermoplastic both before and after exposure to light and localized image formation so that at temperatures between 40°C. and 220°C., the entire photoimaged film as a unit sticks or adheres within 10 seconds under slight pressure (i.e., the applied weight of a heated iron) to a receiving support and releases its carrier support.

The film-forming composition is comprised of a photosensitive, dye-forming component and a film-forming thermoplastic, binder component transparent to activating wavelengths of light for the image-forming reaction. In order for the film formed from this composition to transfer from a carrier support to a receiving support at the specified stick or transfer temperature, the binder component in the film-forming composition must have greater adhesion to the second surface than to the first surface at at least one temperature, usually lower than the stick temperature, as is well known in the art. Other materials that can be present should not produce a significant difference between the thermoplastic nature of the film-forming composition and the thermoplastic nature of the binder at the stick temperature selected for transfer — nor should other materials present interfere with the image-forming reaction; nor

with subsequent dye-producing reactions that may be necessary to produce color of an image that is latent or invisible when first formed.

Generally, the two essential components are chosen to form a substantially homogeneous composition, i.e., a uniformly responsive, photosensitive, image-forming mixture. Still other materials may be present to fix the dye image against further color development, for example, chemical, thermal, or light-activated (photofix) agents, but these generally are not an integral part of the photosensitive, dye-forming component. A suitable composition can be an intimate admixture of a film-forming, thermoplastic binder having such relative adhesion to the two surfaces with photosensitive dye-forming materials like those used in a variety of known photoimaging systems. Such systems are well-known and the particular system used in the process of the invention is not critical, although some are preferred to others and will be described more fully below.

Suitable color-forming systems are those that permit convenient color stabilization or fixation of the design after it is generated by activating light. Typical is the heat-developable, heat-fixable photographic system described in U.S. Pat. Nos. 3,394,391; 3,394,392; 3,394,393; 3,394,394; 3,394,395; 3,410,687; and 3,413,121. Heat development or heat fixation can be carried out concurrently with the heat trasnfer of this invention. Particularly preferred as photosensitive coatings are the light-sensitive leuco dye compositions containing a photooxidant component as described in U.S. Pat. Nos. 3,445,234; 3,585,038; and 3,598,592.

Other systems from which suitable photosensitive color-forming components can be chosen are the well known diazo systems which require moist ammonia development; dry diazo systems; fast print-out dye imaging systems based on the light sensitivity of halocarbons; leuco dye systems; and "bleach-out" systems. These and other non-silver dye systems suitable for use in this invention can be found in Jaromin Kosar's book *Light-Sensitive Systems*, John Wiley & Sons, Inc. 1965, Chapters 6 and 8.

Expedients that can be used for the deactivation of imaging systems in the unexposed areas, thereby fixing the image include:

1. Removing one or more of the imaging components, as by volatilization; see U.S. Pat. No. 3,042,516 and U.S. Pat. No. 3,413,121;

2. Volatilizing or otherwise removing a plasticizing solvent; see U.S. Pat. No. 3,445,234;

3. Incorporating a deactivating agent into the unexposed area to be fixed, as by spraying, dipping or coating; see U.S. Pat. No. 3,445,234 and U.S. Pat. No. 3,533,797; and

4. Generating a deactivating agent in situ, including photochemically; see U.S. Pat. No. 3,390,996, U.S. Pat. No. 3,445,233, and thermally; U.S. Pat. No. 3,390,995.

These patents describe suitable photosensitive compositions. Normally for photodecoration use, such compositions contain one or more imaging components in a polymeric binder which can contain a plasticizer and which serves to thicken or adhere the composition to a sheet material. The binder can also serve as a matrix so that the mixture can be cast, extruded or otherwise formed into an imageable coating. Binders mentioned are light-transparent, i.e., transparent to activating wavelengths of light as well as some visible light for viewing, but overall dye color may be present to provide a desirable background color for viewing photodecoration. Binder or matrix amounts vary from about 0.5 part to about 200 parts, preferably 3 to 15 parts, by weight per part of combined weight of the imaging component or components.

Certain classes of polymeric binders cited in these patents and elsewhere exhibit properties described above as necessary for use as film-forming, light-transparent binder component in the present invention. Such classes include vinylidene chloride copolymers such as vinylidene chloride/acrylonitrile, vinylidene chloride/methacrylate and vinylidene chloride/vinyl acetate copolymers; ethylene/vinyl acetate copolymers; cellulosic ethers such as methyl cellulose, ethyl cellulose and benzyl cellulose; cellulose esters such as cellulose acetate, cellulose acetate succinate and cellulose acetate butyrate; synthetic rubbers such as butadiene/acrylonitrile copolymers, and chloro-2-butadiene-1,3polymers; polyvinyl esters such as polyvinyl acetate/acrylate, polyvinyl acetate/methacrylate and polyvinyl acetate; polyvinyl chloride and copolymers such as polyvinyl chloride/acetate; polyvinyl acetals such as polyvinyl butyral and polyvinyl formal; polyurethanes; and polyacrylate and alpha-alkyl polyacrylate esters such as polymethyl methacrylate and polyethyl methacrylate.

Preferred polymer classes combine toughness with flexibility. These properties are usually combined in sheet polymers which are difficult to cut with a knife or scissors. Flexible, clear polyurethane polymer is especially preferred for leather, whereas vinyl resin topcoats are especially preferred for coating vinyl automobile seat covers.

Certain binders containing special agents or fillers can be used in order to improve such properties as abrasion resistance or surface gloss of the final article in which the pieces of photodecorated sheet material are incorporated. Binders of this sort are currently in use in the leather industry. They are broadly classified as urethane clears and vinyl clears and they can be used as the binder components in photosensitive compositions suitable for this invention providing the binder ingredients do not interfere with image-forming, image fixing, or transfer characteristics of the photoimaged film.

Representative of suitable commercially available leather binders or top finishes are General Tire and Rubber Co.'s CV 270, CV 940 and CVX 3040; United Finish Co.'s U-6366 Urethane Clear and KC-10-925 Vinyl Clear; Fleming-Joffe Ltd.'s U-5573 and 8925 CAB 10% + SC; United Finish Co.'s Permalon KC-10-662 Vinyl Clear, Permuthane U-5900 Clear Urethane, Permuthane U-5057 Clear Urethane, and Permuthane U-4849 Clear Urethane; and Du Pont Co.'s 56060 Laminating Adhesive, 46960 Adhesive and C-1924-2 Non-yellowing Urethane.

Preferred commercially available binders include polyurethane polymers based on aliphatic isocyanate monomers which are lightfast. These can be formed from commercially available solutions which form films by simple evaporation of their solvent contents. "Permuthane" U-4934 forms films that exhibit excellent adhesion and flexibility. "Permuthane" U-4818 forms films that exhibit excellent wet and dry rub resistance. Other solutions of aliphatic polyurethane resins favor properties such as gloss, and cold crack resistance.

Thus, within this preferred class of polymers, one can usually be selected to suit a particular receiving substrate and its use when decorated.

In practicing this invention there can be used imaging systems which permit convenient fixation of the colored design in situ, i.e., processes wherein a deactivating agent is generated in situ by photochemical or thermal means. Such systems can be stabilized or fixed prior to color development, and can also be fixed simultaneously with photoactivation.

One preferred system of this type is disclosed in U.S. Pat. No. 3,390,996 wherein the composition has a suitable dual response to light. It consists essentially of (1) an organic color-generator, (2) a photo-oxidant, and (3) a redox couple which consists of (a) a reductant component capable of undergoing a photo-initiated redox reaction with the oxidant component, and (b) an oxidant component which, when photo-activated, undergoes with the reductant component a photo-initiated redox reaction which produces a reducing agent. When irradiated with a pattern of light at one wavelength, normally in the ultraviolet range, the organic color-generator and the photo-oxidant react to form a visible image in a design corresponding to the pattern of light. The unexposed areas remain uncolored or have a light color characteristic of the unexposed coating. The unexposed areas of the coating are color-stabilized or fixed by exposure to light of a second wavelength, normally in the visible range, which causes the redox couple to produce a reducing agent which reacts with the photo-oxidant, thereby blocking further reaction of the photo-oxidant with the color generator.

A preferred composition of the above type for use in this invention is disclosed in U.S. Pat. No. 3,390,994 wherein the photo-oxidant is a hexaarylbiimidazole, which absorbs light in the range of about 250 to 370 mμ in the ultraviolet. The redox couple consists of pyrenequinone or 9,10-phenanthrenequinone as oxidant and a lower alkyl ester of nitrilotriacetic acid or nitrilotripropionic acid as reductant. In combination, the quinone is reduced to a hydroquinone when irradiated with visible light in the range of 380 and 500 mμ. U.S. Pat. No. 3,658,543 discloses as preferred reductant in improved photosensitive compositions an acyl ester of triethanolamine such as triethanolamine triacetate optionally mixed with a lower alkyl ester as in U.S. Pat. No. 3,390,994.

More specifically, the above U.S. Pat. No. 3,658,543 discloses preferred photosensitive compositions suitable for use in the present invention containing one or more of the following:

a. A reductant portion of the redox couple which is 10–100% triethanolamine tripropionate or triethanolamine triacetate (with the latter more preferred) and 90–0% 3,3′,3″-nitrilotripropionic acid, trimethyl ester.

b. Aminotriarylmethanes containing at least two p-dialkylamino-substituted phenyl groups having ortho to the methane carbon atoms a substituent which is alkyl, alkoxy or halogen.

c. A hexaarylbiimidazole of the class 2,2′-bis(o-substituted phenyl)-4,4′-5,5′-tetraarylbiimidazole.

d. As the oxidant portion of the redox couple 9,10-phenanthrenequinone in combination with a mixture of 1,6-pyrenequinone and 1,8-pyrenequinone.

e. Binders, with cellulose acetate butyrate the preferred binder.

f. Plasticizers, with alkyl arenesulfonamides preferably present and a mixture of N-ethyl-p-toluenesulfonamide and o-phenylphenol condensed with ethylene oxide, a particularly preferred mixture.

Other leuco dye types suitable for the generation of a variety of colors according to this invention are described in U.S. Pat. Nos. 3,395,018, 3,390,997 and 3,445,234. Mixtures of leuco dyes may be used herein.

Normally, the practice of this invention requires making up a coating formulation to be applied to the carrier sheet material. In addition to the active imaging and fixing components and the binder component, there are usually present, as may be required, solvents for the photo-imaging components, plasticizers, and such other components as are present. Such solvents are volatile at ordinary pressures and temperatures. Representative of suitable solvents are alcohols such as methanol, ethanol, 1-propanol, 2-propanol, and butanol; esters such as methyl acetate and ethyl acetate; aromatics such as benzene and toluene; ketones such as acetone, methyl ethyl ketone and 3-pentanone; aliphatic halocarbons such as methylene chloride, chloroform, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethylene; miscellaneous solvents such as dimethylsulfoxide and dioxane; and mixtures of these solvents in various proportions as may be required to attain solutions. With color-forming components that depend on poly-molecular reactions for color formation it is often beneficial to leave a small residue of solvent in the dried composition so that the desired degree of imaging can be obtained upon subsequent irradiation. Ordinary drying such as that employed in film casting results in the retention of ample solvent to give a composition with good photosensitivity. The compositions so produced are dry to the touch and stable on storage at room temperature. Moisture of the air is absorbed by many of the compositions, particularly those comprising an acid salt of an aminotriarylmethane on cellulosic substrates, and serves as a suitable solvent.

Sometimes, however, it is more convenient to impregnate the surface of a film comprising a binder layer with certain photosensitive dye-forming materials such as diazonium salts. One way to so impregnate is to merely wet the surface of the binder layer with a solution of the photosensitive material in a carrier solvent capable of penetrating the binder and carrying the photosensitive material with it. Such carrier solvents may be removed by volatilization, if desired, after impregnation.

More than one photosensitive component can be introduced into a single or common binder by a combination of methods, such as admixture followed by impregnation as above thereby allowing the formation of multicolored images using appropriate activating wavelengths of light for each of the photosensitive components used.

Suitable carrier support materials include paper; cloth; cellulose esters such as cellulose acetate, cellulose propionate and cellulose butyrate; and other plastic compositions. The support may have in or on its surface subcoatings designed to facilitate release of the film from the carrier support at the time of transfer. Representative of such subcoatings is a silica coating as a roughening agent.

Carrier supports need not be planar or smoothsurfaced. They can be embossed on the coating surface.

Coatings then acquire such embossing which can be preserved during transfer by proper control of pressure and temperature to provide unusual 3-dimensional effects in surface decoration of the receiving support.

Preferred substrates are materials commonly used in the graphic arts and in decorative applications and include paper ranging from tissue paper to heavy cardboard; films or sheets of polyester of glycol and terephthalic acid; vinyl polymers and copolymers, polyethylene, polypropylene, polyvinyl acetate, polymethyl methacrylate and polyvinyl chloride. Opaque as well as transparent substrates can be used. Carrier supports that are transparent to activating wavelengths of light for the color-forming reaction are especially preferred because exposure of the photosensitive film through them results in a right-reading decoration after transfer, although image reversal can be overcome by proper use of photographic negatives when the coating is exposed directly. The carrier support should be inert to the contacting photosensitive component and binder component of the coating formulation as well as other materials such as solvents and plasticizers that may be present.

Suitable methods of application of the film-forming coating formulation include typical devices for continuously laying down wet films from a fraction to several mils thick. Typical dry film thickness ranges from 0.05 to 1.5 mils. Drying (solvent removal) can be at room temperature, under vacuum at room temperature, by forced air solvent evaporation, or at elevated temperatures as by radiant heating, under atmospheric or reduced pressures, provided the heat is not detectably harmful to the sensitivity of the photosensitive component and to the composition as a whole.

Prior to transfer, the photosensitive film coated in a single layer on the carrier support is exposed to activating wavelengths of light to form a photoimage in the desired pattern through an appropriate light-modulating means. Since the photosensitive component of each image-forming system normally contains one or more characteristic light absorbing groups, the activating wavelengths of light vary from system to system and must be adjusted accordingly. For example, leuco dye-photooxidant systems are generally activatable by actinic light in the ultraviolet and visible light ranges. Appropriate light sources include sunlight, carbon arcs, mercury vapor arcs, fluorescent lamps with ultraviolet light-emitting phosphors, argon glow lamps and electronic flash units containing gases such as xenon; diazo sensitizer/coupler systems are activatable by actinic light from the same kinds of sources. Preferably a visible photoimage is produced while the photosensitive coating is still on the carrier support, either directly upon exposure to activating light or indirectly by first forming a latent dye image and subsequently developing visible color as desired in situ. Visible dye image formation in the carrier-supported film allows designs to be inspected for definition before transfer, and permits rapid change to give easy access to current fashion. If desired, however, a latent dye image can be produced on the carrier support and developed later as a visible image, for example, during transfer, or after transfer to the receiving support.

Typical examples of latent images that can be formed on a carrier support include residual unexposed diazonium salt of a typical diazo sensitizer/coupler photoimaging system and heat-developable photographic images formed by a system such as that disclosed in U.S. Pat. Nos. 3,394,391; 3,394,392; 3,394,393; 3,394;394; 3,394;395; 3,410,687; and 3,413,121 referred to earlier. The latter can be heat-developed during transfer and heat-fixed either then or later on the receiving support. Latent diazo images formed by light-induced decomposition of diazonium salt require the presence of a coupler that can react with residual, unexposed diazonium salt to form an azc dye. Or, if the coupler is present, the latent image can require a pH adjustment to basic conditions, if stabilized by acid initially. A coupler can be provided in the original admixture with the thermoplastic binder in making up the film-forming composition (two component diazo system), or it can be provided at a later time (one component diazo system). The coupler can also be provided as a chemical fixing agent (reducing) for another photosensitive, dye-forming system that can be present, for example, for fixing hexaarylbiimidazole photooxidant for leuco dye according to U.S. Pat. No. 3,445,234 and introduced in sufficient excess to also serve as coupler for diazonium salt subsequently introduced by impregnation. In still another approach, a diazo image can remain latent with coupler present until subsequent exposure to ammonia vapors generated by heating ammonium hydroxide solution develops color, thereby developing a visible decoration while the coating is on either carrier support or the receiving support.

Just as there are many permutations possible in the development of a visible dye image, there are many permutations possible in fixing the image, again on the carrier support, or during transfer, or after transfer to the receiving support.

The fixing system employed will, of course, be compatible with the imaging-forming component and is readily chosen according to the teaching of the art on these systems. With respect to preferred light-sensitive leuco dye compositions containing a photooxidant component other considerations contribute to the choice of a fixing method. More depth of color is attainable using photosensitive formulations that contain no photofix agent. Thermal fixation cannot always be carried out to completion under the transfer temperature and time conditions. Therefore, chemical fixation is preferred.

Chemical fixation by incorporating a deactivating agent into the unexposed area to be fixed, as by spraying, dipping or coating usually involves introducing a solution containing the agent into contact with the photoimaged film on the carrier support or the receiving support. U.S. Pat. No. 3,445,234 discloses the use of hydroquinone solution to fix, i.e., react with any activated biimidazole-leuco dye color forming systems. U.S. Pat. Nos. 3,390,995 and 3,533,797 describe another type of fixing agent for such system which is an organic progenitor of a reducing agent such as hydroquinone. Heat is necessary to transform the progenitor to the reducing agent at temperatures between 80°C. and 160°C. Such progenitors which include acetals, orthoesters, carbonates and orthocarbonates of hydroquinone and of a host of other phenols are suitable for incorporation in the film-forming composition, and will form a chemical fixing agent when heated with the film during the transfer step. They can also be heated on the receiving support to produce a chemical fixing agent. Alternatively, they can be introduced by impregnation in solution form, if desired, rather than being part of

the film-forming composition at the outset of the process.

A preferred chemical fixing method involves no wet processing steps. The fixing agent is incorporated in a tie-coat on the receiving support, said tie-coat having thermoplastic binder similar to that employed in a subsequently transferred photoimaged film. By similar is meant the binders should be the same, or at least miscible with each other. Conditions for transfer are adjusted to a pressure, temperature, and time for thermoplastic flow which permits the fixing agent from the coat layer to diffuse with the transferred layer and thereby fix the previously unfixed image. Alternatively, the two layers may be placed in a dark oven for sufficient time to allow the fixing agent to migrate into the photoimage and fix the system. Suitable time and temperature for migration of the fixing agent can readily be determined.

After photoimaging in the desired pattern with activating light the outer surface of the image-bearing film is placed in contact with the receiving support and is heated. However, it is equally satisfactory to heat the film before, after, or before and after contacting the receiving support. Heating can be direct, such as by dielectric or infrared heating, but it is usually more convenient to heat indirectly, such as by heating either the receiving support or both the receiving support and the carrier support. By heating just the receiving support the surface of the film can be raised to a stick temperature while the surface of the film contacting the carrier support is at a lower temperature. Stick temperatures normally range from 40°C. to 220°C. depending on fabric and transfer film composition, especially the binder. If the adhesive bond of the film to the carrier support is weak, as is true when the carrier support is a commercial release paper treated with release agents, the adhesion of the film to the receiving support develops as the thermoplastic binder softens to a depth just sufficient to result in a good bond to the receiving substrate. Transfer to the receiving support with release of the carrier support can take place at the stick temperature or thereafter upon cooling to a lower temperature. Since only the one surface of the film is preferentially softened, the opposite surface of the film that was in contact with the carrier support tends to retain the surface configuration it assumed when coated on the carrier support. This can be very smooth or it can be regularly contoured, irregular, or take on a variety of desirable shapes depending on the choice of the release paper. For example, use of an embossed release paper as the carrier support will result in the outer surface of the transferred film on the receiving support having an embossed surface in addition to being photodecorated. The two forms of decoration together can more satisfactorily simulate more desirable, expensive fabric surfaces or provide interesting interplay between the color decoration and the embossment to resemble coloration by intricate mechanical procedures such as tipping or valley printing, two effects that are difficult to obtain in the leather industry.

The pressure required for contact transfer of this kind need be only the pressure transmitted by the weight of a heated iron, for example, about 0.1 to 2.0 pounds per square inch (psi), provided the transfer temperature is sufficiently high to rapidly soften the film surface and the contact time is short, that is, less than about 5 seconds. Alternatively, the transfer temperature can be reduced to barely produce softening of the film surface and contact pressures can range as high as 1,000 psi. Those versed in the transfer art can adjust pressure, time, and transfer temperature to suit the film composition and the surfaces involved. Examples which follow illustrate conditions suitable for polyurethane binders popular in the leather industry and other binders such as cellulose acetate butyrate useful with fabrics. With such binders temperatures for contact transfer are in the range of 100°C. to 140°C. and temperatures for release of the film from the carrier support can be the same as the stick temperature or lower just so long as separation of the carrier support from the transferred film is complete. Release may even be conducted below room temperature, depending again on film composition and the choice of supports.

Separating the two supports after placing the outer surface of said film into contact with the receiving support is done manually, usually, but can be vacuum-assisted. In the case of a continuous transfer process wherein the supporting surfaces are continuously fed into contact from feed rolls, separating the supports can be accomplished by an automatic wind-up on separate rolls of the support materials, the receiving support already decorated, the carrier support roll being essentially ready for re-use. Whether manual or automatic, separating the two supports results in the transfer of the photoimaged film as a unit to the receiving support and releasing the carrier support, provided process conditions are satisfactory. If the transfer temperature is not high enough, only partial transfer of the decoration may sometimes occur. At still lower temperatures some of the components of the film may transfer, e.g., just the dye component may leave the film and enter the contacting receiving support, if it should be sufficiently migratory at the temperature employed.

In another embodiment heat is supplied to the film in a manner to cause thermoplastic flow of the film composition to a substantially greater depth of the film than required for just contact binding. Preferably this is accomplished by heat being conducted to the film by or through the receiving support and/or the carrier support, for example, by placing the carrier-supported film and the receiving support face-to-face between heated platens of a press. The heating need not be perfectly balanced between platens as long as the film is raised to a stick temperature. In fact, when transferring to a heat-sensitive receiving support such as leather, it is preferred to conduct most or all of the heat through the carrier support. Whereas the pressure needed to contact transfer is minimal, the pressure reuqired to cause thermoplastic flow of the film is normally 50 to 5,000 psi; preferably, about 500 to 1,000 pis is used. At such pressures the film becomes fluid or plastic enough to change from its coated form on the carrier support to a form wherein the outer surface assumes the same configuration as the receiving surface, whether that be planar, regularly contoured, or irregular. Local displacement of binder component and dye component then accompanies pressurized flow of heat-softened, thermoplastic film composition into open areas of a receiving surface, for example, into spaces between fibers in the case of woven fabrics, into pores of leather and leather-like fabrics, or into contours embossed in the receiving surface. The heated platens may themselves serve as embossing plates or an embossing surface may be placed in contact with the transfer film and the re-

ceiving support and heated along with the film. In this way decoration and embossing may be carried out at one time in one operation during transfer.

Separating the two supports after surface-conforming contact is done manually or automatically just as has been described above for contact transfer. As before, separation is usually conducted at a temperature lower than the stick temperature.

The effects that can be achieved are attractive, especially when the color pattern of the transferred decoration is related spacially to the embossed pattern. Both tipping and valley printing effects are obtained making the color pattern more concentrated at the hills or the valleys of the embossed receiving surface. Three dimensional appearance is enhanced by certain shadings of color in the valleys. Some of the effects are new in appearance and can be the basis of new fashions.

Surface-conforming transfer decoration of this kind stabilizes against abrasion and delamination, achieving an adhesive bonding over a maximum conforming surface area. Bonding can be enhanced further by mechanical adhesion to filled pores. This can be examined microscopically and adhesive test methods employed to quantify resistance to delamination. Different materials have different tests that have become standared in a particular industry, but peel strength tests are common using a self-adhesive cellulose tape about ½ inch wide, pressing it onto the test surface to obtain the maximum amount of contact between the adhesive on the tape and the surface coating to which it is taped, and then pulling the tape off quickly at an angle of peel rather greater than 90°. If none of the coating or only a very small area (usually from the cut corners) peels off, the adhesion is normally classed as satisfactory or good; if about half of the coating peels off, the adhesion is partial and probably unsatisfactory; if all or most of the surface decoration peels off, the adhesion is poor and definitely unsatisfactory. Normally at least three samples are tested. The average standard of adhesion is reported along with any marked variability in the standard which is used.

Surface-conforming decorations transferred to leather and leather-like substrates according to the process of this invention are generally satisfactory or good. Transfer to fabrics, woven and non-woven also results in satisfactory or good adhesion. Transfer to smooth vinyl surfaces that are untreated is sometimes partial, but generally poor in adhesion. However, when vinyl surface is pretreated with special urethane finishes having great adhesion for vinyl, subsequent transfer of decorative films by the process of this invention results in generally satisfactory or good adhesion in peel strength tests, provided the film composition contains a polyurethane binder or has a polyurethane-containing binder such as a polyurethane/cellulose acetate butyrate mixed binder.

In order to build up a full color decoration, it is convenient to transfer a design to a receiving surface already bearing color decoration. The decoration already on and comprising the receiving surface of a receiving support should contain a binder compatible with the binders of this invention. It may be a decorative film previously transferred according to this invention, preferably surface conforming by thermoplastic flow of a tough, flexible binder and containing more than one image-forming component in a common binder component, as above, so as to form a plurality of colors. Multicolored or full color decorations built up on a receiving support as an integral film having a common binder then, if desired, can be conveniently inspected and thermally transferred as a unit to a final receiving surface by repeating steps (3) and (4) of the instant invention.

To add on to preformed color decoration the process of this invention is carried out using the same binder or a miscible binder capable of joining or adding onto the first mentioned binder. Contact transfer is then sufficient to at least join the heated surfaces of the transfer film and the color decoration, forming essentially one continuous film having a common binder and an appropriate combination of subtractive dye colors for full color decoration. This add-on capability based on a common binder can also be used between tie-on coats and topcoats, or decorative coats and topcoats.

The process of this invention provides a heat transfer system for multicolor decoration of all important wear fabrics. More than one color can be combined in each transferred film by incorporating more than one photosensitive component in a common binder. Furthermore, the transfer can be repeated to build up full-color decorations on the receiving support again using a compatible binder in adjacent films. Furthermore, the fabric can be embossed (even at the same time it is decorated) to simulate effects that have been difficult to achieve such as tipping and valley printing. Fabrics that are inexpensive can be significantly upgraded to resemble more expensive fabrics, and will resist delamination and abrasive wear because the color is locked into the fabric. Other fabrics, used briefly to present logo, such as game shirts, convention banners, etc. can be contact-decorated attractively then cleanly stripped later from the fabric surface as in a peel test so that the fabric can be re-used. It can be redecorated by contact transfer with different numerals, dates, colors, or other identifying logo.

The following examples illustrate this invention. Parts and percentages recited in the examples are by weight unless otherwise specified.

EXAMPLE 1

A near ultraviolet light sensitive imaging formulation was prepared as an acetone solution from the following ingredients:

Ingredient	Composition Parts	Role
Acetone	58.5	solvent
Cellulose acetate butyrate	6.0	binder
p-Phenyl phenol-ethylene oxide adduct[1]	4.0	plasticizer
tris(N,N-diethylamino-o-tolyl)methane	0.30	leuco dye
2,2′-bis(o-chlorophenyl)-4,4′,5,5′-tetrakis (m-methoxyphenyl)-1,2′-biimidazole	0.624	photooxidant
p-Toluenesulfonic acid monohydrate	0.3424	acid stabilizer for leuco dye
7-diethylamino-4-methyl-coumarin	0.0924	energy transfer agent to shift activating wavelength towards the visible

[1]Produced from 1 mole of the phenol and 5.9 moles ethylene oxide

The solution was coated on a high-holdout, calendered, bleached, sulfite paper and the acetone allowed to evaporate to give a coating about 0.5 mil thick. The

coated paper was then photographically imaged by (1) placing a blocktype negative bearing a flower design in contact with the coating composition, (2) covering the negative with a heat-absorbing glass plate, and 93) irradiating the coated paper through the glass plate and negative bearing the design by contact flashing with one flash from a xenon flash lamp having an input of 200 watt-seconds (HiCo Lite, emitting ultraviolet light above 200 nm and approximating ordinary unfiltered sunlight).

This produced a blue-colored, positive image, flower design on the coated paper. To fix the image against further color formation by inadvertent exposure to near ultraviolet light, the coating was wet with 2.2% acetone solution of resorcinol. The amount of resorcinol in solution taken up by the coating was sufficient to (1) act as a fixing agent according to U.S. Pat. No. 3,533,797, and (2) provide an excess of resorcinol to serve as a color-forming coupling component for subsequently applied photo-sensitive diazonium salt, as follows.

A stock 1.3% solution of p-diethylaminophenyl diazonium borofluoride in acetone was stabilized against coupling on contact with resorcinol by addition of 2.5% citric acid. The stabilized solution was then sprayed uniformly over the coating bearing the blue flower design, and the acetone was allowed to evaporate. The coating thus impregnated with ultraviolet light-sensitive diazonium salt was then exposed to a single, unfiltered flash of the above xenon lamp through the same negative bearing a flower design but displaced slightly so as not to be in exact register with the blue flower image. Subsequent exposure of the coating on the paper carrier support to moist ammonia vapor (generated by heating ammonium hydroxide solution) raised the pH sufficiently to permit the diazonium salt unaffected by the xenon flash to couple with the excess resorcinol in the coating. This produced an attractive multicolor design in blue and brownish tones and overlap areas of black comprised of a triarylmethane dye image and an azo dye image in a single layer containing cellulose acetate butyrate as a thermoplast binder.

The multicolor flower design was then placed in contact with the surface of a piece of woven "Dacron" polyester cotton blend cloth and placed between the heated platen surfaces of a Carver laboratory press held at a temperature of about 180°C. and subjected to a pressure of about 1,000 psi for a time of 30 seconds. Upon release of the pressure, removal from the press, and cooling to permit handling, the paper backing of the flower design was easily stripped away leaving the cloth with an inverted multicolor flower design as a decoration.

In subsequent testing of peel strength of the transferred flower decoration a piece of ½-inch wide, self-adhesive, cellulose tape was pressed firmly onto the decorated surface and then peeled off quickly at an angle of peel rather greater than 90°. The flower decoration remained firmly adhered to the surface of the cloth and suffered no delamination visible to the eye.

In wash tests repeated application of soap and hot 160°F. water removed practically no dye after many washings.

EXAMPLE 2

The process of coating a paper support with photosensitive hexaarylbiimidazole-coumarin-leuco dye composition, imaging, and then impregnating with diazonium salt and imaging to form a multicolor design was repeated as in Example 1. Then, transfer of the design to the surface of Dacron polyester/cotton blend cloth was made at 1,000 psi in the Carver press, but at a lower temperature of 130°C. for a time of only 10 seconds. As before, the paper carrier support separated easily, leaving a complete surface decoration on the cloth. In a subsequent peel test as in Example 1, the adhesive tape pulled the decoration away from the surface of the cloth. Microscopic examination of the remaining transferred decoration showed that the transferred decoration contacted the surface of the cloth without conforming to the irregular, woven texture of the cloth. As a surface decoration it was suitable for temporary decoration of a game shirt with a numeral identifying a team member; also for contact transferring a strippable lift pass decoration, good for a 5-day ski week, to the sleeve of a ski jacket.

EXAMPLE 3

A dual response photosensitive composition capable of yielding positive blue images when exposed to ultraviolet light or negative blue images by exposure to 400–550 nm wavelength visible light followed by overall exposure to ultraviolet light was prepared from the following ingredients in intimate admixture.

Ingredient	Amount
Acetone	300 ml.
2,2′-Bis(o-chlorophenyl)-4,4′,5,5′-tetrakis (m-methoxyphenyl)-1,2′-biimidazole	2.09 g.
Tris(N,N-diethylamino-o-tolyl)methane	0.45 g.
Dodecylbenzenesulfonic acid (Richardson Company Richonic Acid B)	3.5 g.
Triethanolamine triacetate	2.0 ml.
Trimethyl 3,3′,3″-nitrilotripropionate	3.0 ml.
9,10-Phenanthrenequinone	0.243 g.
Polyethyleneoxide adduct of o-phenylphenol average formula $C_6H_5—C_6H_4—O(CH_2CH_2O)_{\sim 2.23}H$	5.7 g.
Pyrenequinone (1:1 mixture of 1,6- and 1,8-isomers)	0.015 g.
N-ethyl-p-toluenesulfonamide (Monsanto Chemical Company's Santicizer-3)	6.5 g.
Permuthane U-5057 Clear urethane (as binder)	30.0 g.

Under darkroom conditions a pre-embossed sheet of commercial, silica-coated, Warren release paper Transkote Patent BV Chevreau bearing a pebbly pattern like leather was coated on one side with the dual response solution applied from a conventional aerosol dispersing canister, and the acetone was allowed to evaporate to form a smooth-surfaced coating about 0.5 mil thick. A photographic negative bearing a finely detailed image of a grainy leather surface was then placed in contact with the coated side of the carrier support and covered with a Corning 7–54 filter which transmits ultraviolet light. A single flash of the xenon lamp of Example 1 produced a clear, sharp grainy blue image. The coating was then covered with a Corning 0–51 filter which transmits light of wavelengths above 390 nm and subjected to another xenon flash to photofix the image immediately. Optionally, the image could have been fixed over a longer time by exposure to room room-light.

Thermal transfer was made to urethane, vinyl, and "Corfam" poromeric receiving surfaces as follows. A Carver press was heated to about 100°C. which is sufficiently high temperature to raise the U-5057 Clear ure-

thane thermoplastic binder to a stick temperature for the carrier and receiving surfaces involved in these transfers. Then, in turn, the three imaged pieces cut from carrier sheet were placed in contact with each of the three receiving surfaces and subjected to 1,000 psi pressure in the Carver press for about ten seconds. In each case the release from the Warren paper was complete, and a leather-simulating decoration bearing both the pebbly embossed surface of the Warren paper and the grainy color decoration of the photo-formed image was transferred to the receiving surface. The effect given was that of attractive printed, embossed leather. Peel strength tests and examination of the transferred decorations indicated adhesive conformity of the transferred layer to the Corfam poromer and the urethane surface. The decoration peeled from the smooth vinyl surface in the tape test. Upon repeating the transfer as above to a vinyl surface pre-treated with a commercial urethane finish, the peel strength was found to be greater and no delamination was observed as a benefit of the common binder effect.

EXAMPLE 4

The following diazonium salt/coupler combinations were prepared to establish conditions of transfer from commercially available Dalbert transfer paper, silica-coated both sides (Dalbert Chemical Co., Chicago), "Mylar" polyester film, and the bleached, sulfited paper of Example 1 to leather flexible enough for use in shoe uppers or garments, ready for application of a tie-coat and/or a topcoat finish.

A stock diazo sensitizer solution was prepared as a methyl ethyl ketone solution from the following ingredients.

Ingredients	Amounts
Methyl ethyl ketone	100 ml.
p-Diethylaminophenyl diazonium borofluoride	2.6 g.
Bay State binder 8925, cellulose acetate butyrate based, 10% solids (Bay State Lacquer Co., Peabody, Mass.)	100 ml.
Isopropyl alcohol	10 ml.
Citric acid	5.0 g.

Additional stock solutions containing developers (couplers) were prepared as similar methyl ethyl ketone solutions from the following ingredients.

Stock Coupler Solution A

Ingredients	Amounts
Methyl ethyl ketone	100 ml.
Acetone	80 ml.
Isopropyl alcohol	30 ml.
Acetoacetanilide (Fairmount Chemical Co. Developer, diazo grade, orange)	3.54 g.
Citric acid	5.0 g.
Thiourea	5.0 g.

Stock Coupler Solution B

Ingredients	Amounts
Methyl ethyl ketone	100 ml.
Isopropyl alcohol	10 ml.
Betaoxynaphthoicmorpholinopropylamide (Fairmount Chemical Co. Developer, MO-4 blue-black)	6.28 g.
Citric acid	5.0 g.
Thiourea	5.0 g.

and

Stock Coupler Solution C

-Continued

Stock Coupler Solution A

Ingredients	Amounts
Methyl ethyl ketone	100 ml.
Isopropyl alcohol	10 ml.
Resorcinol	2.2 g.
Citric acid	5.0 g.
Thiourea	5.0 g.

The stock diazo sensitizer solution was then combined in turn in 1:2 volume ratio with each of the three coupler solutions A, B, and C, and coated on separate pieces of Mylar polyester film and Dalbert transfer paper using a conventional aerosol dispensing canister to form films about 0.5 mil thick. After solvent removal by evaporation each coated carrier support was irradiated through a design-bearing negative for 180 seconds in a commercial Canon "Kalfile" Model 340VC printer (eight blacklight-blue lamps spaced ¼ inch apart and delivering 2.6 milliwatts/cm² to the coating peaked at about 370 nm), thereafter subjected to ammonia vapor as in Example 1 bring up an azo dye image.

Transfers to pieces of flexible calf skin leather were made in a Carver press heated to various temperatures maintaining a constant dwell time in the press of 5 seconds at 1,000 psi, with the following tabular results.

Coupler Solution	Carrier Support	Completeness of Transfer at Temperature °C. 70	100	120	150
A	Transfer paper	none	good	good	good
A	"Mylar" polyester	none	dye only	partial	good
B	Transfer paper	partial	good	good	good
B	"Mylar" polyester	dye only	dye only	good	good
C	Transfer paper	none	partial	good	good
C	"Mylar" polyester	none	dye only	partial	good

On the basis of these results it was shown that transfer from the release paper to leather requires heating to a temperature of at least 100°C. and from Mylar polyester at least 120°C. At a temperature of 150°C. there was observed a curling of the calf skin leather but no apparent permanent degradation at the short 5 second dwell time employed in the thermal transfer.

EXAMPLE 5

A thermoplastic binder component formulation was prepared as a 1:1 toluene:isopropyl alcohol solution from the following ingredients by first mixing the solvents, then adding the resins.

Ingredients	Composition Parts by Volume
Toluene	1.0
Isopropyl alcohol	1.0
Permuthane Resin A (Beatrice Chemical Co.)	2.0
Permuthane Resin B (Beatrice Chemical Co.)	1.0

A chemical fixing agent solution was prepared by adding 8.5 parts of 2,2'-methylenebis-(6-t-butyl-4-ethylphenol) available commercially as Plastanox 425 (American Cyanamid Company) to 90.0 parts of the binder component formulation.

An ultraviolet light-sensitive imaging solution was prepared by combining 200 parts of the above binder component formulation with the following ingredients which together formed a photosensitive, dye-forming component.

Ingredients	Amounts parts
2,2'-Bis(o-chlorophenyl)-4,4',5,5'-tetrakis(m-methoxyphenyl)biimidazole	3.75
2,2'-Bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-biimidazole	3.75
p-Toluenesulfonic acid monohydrate	4.10
Tris (4-diethylamino-o-tolyl)methane	3.60

Both solutions were coated and air-dried on release paper (Dalbert Chemical Co., Chicago). The coating containing the chemical fixing agent was then transferred to a piece of leather in a Carver press heated to 140°C., maintaining a dwell time of 5 seconds at 1,000 psi. The photosensitive film still on release paper was then imaged by exposure for one minute to ultraviolet light in the commercial Cannon "Kalfile" Model 340VC printer described in Example 3. The photoimaged film was then transferred to the leather surface on top of the film containing chemical fixing agent, using the same transfer conditions as for the film. The composite film on the leather was then reexposed to the printer light. The background optical density as measured with a Macbeth Densitometer increased by stayed well below the maximum optical density obtained in the image area, showing that some fixation of the unexposed areas had occurred during the transfer of the photoimaged film at 140°C. The film was then placed in the dark at ambient temperature for two and a half days. Exposure of background area then resulted in no increase in optical density and indicated that complete fixation had occurred during the oven treatment.

We claim:

1. A decorative process comprising

1. photoimaging with activating light a composite consisting essentially of a film coated onto a carrier support, the film comprising a first photosensitive dye-forming composition in a film-forming thermoplastic binder;
2. impregnating the film with a second photosensitive dye-forming system which is compatible with the first dye-forming system;
3. fixing the photoimage resulting from step (1) prior to photoimaging the second dye-forming system;
4. photoimaaging with activating light the coated film impregnated with the second photosensitive dye-forming system;
5. heating the film to a temperature of between 40 and 220°C. at which its outer surface is adhesive and contacting the outer film surface with a receiving support more adherent to the film than the carrier support; and
6. separating the two supports, whereby the photoimaged film adheres to and is transferred to the receiving support and is released from the carrier support.

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