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3,752,692

**DIFFUSION TRANSFER IMAGE RECEIVING ELEMENT**

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21 Claims

**ABSTRACT OF THE DISCLOSURE**

This invention relates to photographic elements for use in diffusion transfer processes performed outside of the camera wherein exposure of said photographic elements was affected, and particularly relates to an image-receiving element which is opaque to avoid exposure of the photosensitive element after removal from the camera and which is further adapted to prevent distortion or curling of the image-receiving element subsequent to separation from the photosensitive element.

**BACKGROUND OF THE INVENTION**

The present invention is particularly related to color diffusion transfer processes. In such processes, a sheet of photosensitive material is exposed to create therein a latent image is developed, and, concurrent with and under the control of this development, an imagewise distribution of color providing materials is formed. At least a portion of these color providing materials is transferred by means of an alkaline aqueous processing liquid to a superposed image-receiving element to form a color positive image thereon. As examples of such processes, mention may be made of the processes claimed and disclosed in U.S. Pat. No. 2,983,606 wherein dye developers (i.e., dyes containing a silver halide developing function and capable of developing a latent silver halide image) are the color providing materials; the processes claimed and disclosed in U.S. Pat. No. 2,647,049 wherein color developers are employed to develop the latent image and color couplers are the color providing materials; and the processes disclosed in U.S. Pat. No. 2,774,668 wherein complete preformed dyes are used as the color providing substances.

The image-receiving elements employed in such processes generally comprise a support carrying thereon an image-receiving layer of a dyeable material which is permeable to the alkaline aqueous processing solution. Film-forming materials such as polyvinyl alcohol, mixtures of polyvinyl alcohol and poly-N-vinylpyrrolidone or a copolymer of vinyl alcohol and N-vinylpyrrolidone such as those disclosed and claimed in U.S. Pat. No. 3,003,872 are particularly suitable for use in such processes. As additional examples of materials for use as the image-receiving layer, mention may be made of nylons such as N-methoxymethylpolyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; cellulose acetate; gelatin; nitrocarboxymethyl cellulose as disclosed in U.S. Pat. No. 2,992,104; and acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl- $\alpha,\beta$ -unsaturated carboxamides and copolymers thereof with N-alkyl- $\alpha,\beta$ -carboxamides as disclosed in U.S. Pat. No. 3,069,263; copolymers of vinyl phthalimide and  $\alpha,\beta$ -unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and  $\alpha,\beta$ -unsaturated carboxylic acids and terpolymers of N-vinylpyrrolidones,  $\alpha,\beta$ -unsaturated carboxylic acids and alkyl esters of  $\alpha,\beta$ -unsaturated carboxylic acids as disclosed in U.S. Pat. No. 3,044,873; copolymers of N,N-dialkyl- $\alpha,\beta$ -unsaturated carboxamides with  $\alpha,\beta$ -unsaturated carboxylic acids, the corresponding amides of such acids and copolymers of

N-aryl and N-cycloalkyl,  $\alpha,\beta$ -unsaturated carboxamides with  $\alpha,\beta$ -unsaturated carboxylic acids as disclosed in U.S. Pat. No. 3,069,264; and the like.

Image-receiving elements of the type herein contemplated preferably contain, in addition to the above-described layer adapted to receive an image by diffusion transfer, a layer of a polymeric acid positioned between said image-receiving layer and the support. In the most preferred embodiments, a timing layer of an inert polymer is positioned between said image-receiving layer and said polymeric acid layer in order to provide a timed control for the alkali neutralizing action of said polymeric acid. The nature of such image-receiving elements and materials useful in providing said polymers is described in detail in U.S. Pat. Nos. 3,362,819; 3,362,821 and 3,376,133.

An extensive compilation of specific dye developers particularly adapted for employment in photographic diffusion transfer processes is set forth in the aforementioned U.S. Pat. No. 2,983,606 and in the various copending U.S. applications referred to in that patent, especially in the table of U.S. applications incorporated by reference into the patent as detailed in column 27. As examples of additional U.S. patents detailing specific dye developers for photographic transfer processes, mention may be made of U.S. Pats. Nos. 2,983,606; 2,992,106; 3,047,386; 3,076,808; 3,076,820; 3,077,402; 3,126,280; 3,131,061; 3,134,762; 3,134,765; 3,135,604; 3,135,605; 3,135,606; 3,135,734; 3,141,772; 3,142,565; and the like.

The support for the image-receiving layer may comprise any suitable dimensionally stable layers including conventional rigid or flexible materials such as paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Such materials include alkaline solution impermeable materials such as paper, polymethacrylate acid, methyl and ethyl esters; vinyl chloride polymers, polyvinyl acetal; polyamides such as nylon; polyesters such as polymeric films derived from ethylene glycol terephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate. The preferred material, however, is paper and more particularly baryta paper.

U.S. Pat. No. 3,080,805, among others, describes film units for forming diffusion transfer images wherein said film units, after being exposed within a camera, are designed to be removed from the camera to complete the processing. The diffusion transfer process is initiated by the application of a processing composition as the film unit is withdrawn from the camera. Since the photosensitive element remains light-sensitive during the processing operation, the photosensitive element and the image-receiving element have been provided with opaque layers which are generally employed as coatings on or incorporated into the above-described support layers. A suitable opaque layer may be formed of dispersed carbon black; the particular composition of this opaque layer is not critical and may be varied among many available materials capable of providing the desired opacity. The photosensitive element may be provided with a suitable opaque layer by dispersing carbon black or some other opacifying material in or on the support at the time it is cast.

It has been found, however, that in many instances, particularly upon the elapse of weeks or months after the separation of the image-receiving element from the photo-sensitive element, that a distortion or curl occurs in the image-receiving element. While it is not known for certain the cause of the above-mentioned distortion, it is believed that the aqueous processing composition releases in the image-receiving element and in the support as well as the other layers of the structure, stresses which are

imparted to the element during its manufacture. Efforts have been made to diminish the above-mentioned distortion by applying to the side of the support opposite from the side carrying the image-receiving layer a polymer, particularly a polymer of the same class and properties as that employed as the image-receiving layer. One method of applying this layer has been to incorporate therein the opacifying agent, for example, carbon black, and coating this layer on said surface. However, such attempts have failed to correct the problem of curl upon storage of the processed image-receiving element.

#### SUMMARY OF THE INVENTION

A novel film structure has now been found which is not susceptible to the deficiencies of the prior art.

The present invention is directed to an image-receiving element, particularly suited for use in diffusion transfer processing wherein development and image formation on an image-receiving layer of said image-receiving element is carried out outside of the camera and wherein said image-receiving element is adapted to be removed from superposed relationship with the photosensitive element subsequent to transfer image formation on said image-receiving element.

The novel image-receiving element of the present invention is composed of a base carrying on a first side a layer adapted to receive a diffusion transfer image and on a second side a first and second polymeric layer adapted to provide opacity, anticurl properties and water impermeability to the image-receiving element structure.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to an image-receiving element suitable for use in diffusion transfer photography, particularly color diffusion transfer photography, wherein the base or support carries on one side a layer adapted to receive the diffusion transfer image, preferably a hydrophilic polymer, and on the opposite side carries at least a first and second polymeric layer adapted to provide anticurl properties, opacity and water impermeability. The polymeric composition applied to the support is a water-soluble, i.e., hydratable, polymeric composition and is generally referred to for convenience as the anticurl coat. The outermost polymeric composition which is applied over the above-mentioned anticurl coat and which is thus located furthest from the support layer is composed of a water-insoluble, water vapor permeable polymeric material and is designated as the seal coat. As stated above, the function of the combined anticurl coat and seal coat also includes opacification, that is, the prevention of actinic radiation from passing through the image-receiving element to interfere with the image formation and image transfer from the photosensitive element during processing. The opacifying materials may be employed in either the anticurl coat or the seal coat but preferably are distributed between both of the layers.

The anticurl coat may be employed of any suitable polymeric materials. Preferably the polymer employed is the same polymer as that employed in the image-receiving layer and is hydrophilic. A particularly preferred polymer is polyvinyl alcohol. Other suitable polymers include the cellulose, i.e., cellulose acetate and cellulose acetate butyrate, polyethylene oxide polymers, hydroxyethyl cellulose, carboxymethyl cellulose and gelatin. In order to avoid imparting undue embrittlement to the anticurl coat, it may be desired to modify the anticurl coat to impart a flexibilizing property, for example, by the introduction of plasticizers for the polymer or by modifying the polymer itself; in the case of polyvinyl alcohol by employing partially hydrolyzed polyvinyl alcohol or substituted polyvinyl alcohol, such as a polyvinyl alcohol internally plasticized with ethylene oxide.

As stated above, it is preferred that the opacification be accomplished by distributing between the anticurl coat and the seal coat the means for opacification. Preferably

carbon black is employed in the anticurl coat. In addition to the polymeric material and the opacifying agent, the composition employed for the anticurl coat may also include other additives such as wetting agents, thickeners, antifoamers, and the like. While the composition may be employed at any solids, it is preferred that solids of approximately 30-40% be employed in order to minimize the number of coating layers that have to be applied and to minimize drying problems associated with the casting of the layer. Preferably, the layer is applied from an aqueous medium although solvent solutions and dispersions may also be employed.

The seal coat comprises a water-insoluble, moisture permeable polymer. In a particularly preferred embodiment, the water-insoluble polymer employed in a carboxylated vinyl acetate/crotonic acid copolymer. Such a polymer is preferably laid down from a water solution employing, for example, ammonium hydroxide, in order to solubilize the polymer. Evaporation of the water and ammonium hydroxide provides an insoluble polymeric layer, resistant to alkali. Other suitable materials include vinyl acetate/acrylic acid copolymer and latices of polymers such as acrylics, ethylene/vinyl acetate copolymers, styrene/butadiene copolymers and other water-insoluble polymers known in the art. It has been found, unexpectedly, that the seal coat minimizes the tendency to embrittlement of the anticurl coat.

As stated above, it is preferred that a portion of the opacifying agent be incorporated into the seal coat. It is preferred that the opacifying agent employed be titanium dioxide for aesthetic purposes, however, silica gel, calcium carbonate, barium sulfate, talc and clays may also be suitably employed. Preferably, such opacifying agents will provide an optical reflection density of less than about 1.0 density units with respect to incident radiation. Other optional materials may be employed in the seal coat, for example, wetting agents, thickeners and antifoamers. The seal coat may be employed at varying levels of solids; preferably, a solids level of 24-36% will be employed. While the anti-curl coat has provided a portion of the opacification and corrects the tendency of the image-receiving element to curl, the seal coat will prevent rub-off of the polymer or opacifying agent employed in the anticurl coat and will also provide for slippage of the image-receiving element as it passes through the various exposure and developing functions.

It is preferred that the support and opacifying agents together provide an optical transmission density in excess of 6.0 density units with respect to visible radiation.

Any suitable support may be employed for the novel photographic film unit of the present invention. For example, natural and synthetic polymers conventionally employed as supports for positive photographic prints are suitable for use in the present invention. Particularly preferred is paper, and more particularly, baryta paper which may possess various degrees of aqueous permeability or sensitivity. Preferably, a paper having a Cobb Size Test Level of 1% or less (TAPPI T41 os 69) is preferred in order to minimize the absorption of water by the paper from the aqueous anticurl layer applied thereto.

Optionally, the anticurl coat may be cross-linked to provide a greater degree of dimensional stability and to permit the use of a thinner seal coat than would normally be necessary. In other words, some degree of water insolubility can be provided to the anticurl coat by means of cross-linking. Employing a cross-linking agent renders the edges less susceptible to damage by moisture contact at the film edges where the layer is exposed. The particular cross-linking agents will be selected with regard to the specific polymer employed and will be well known to the art. For example, in the case of polyvinyl alcohol, suitable cross-linking agents include glyoxal, sodium dichromate, zirconium nitrate, stearato chromic chloride, sodium borate, aluminum nitrate, chromium acetate and dimethylol urea.

The present invention will be illustrated in greater detail in conjunction with the following specific example which sets forth a representative fabrication of the film unit of the present invention which, however, is not limited to the detailed description herein set forth but is intended to be illustrative only.

#### Example I

To one side of a cellulose nitrate subcoated baryta paper was applied a layer composed of a mixture of polyvinyl alcohol and poly-4-vinylpyridine. To the opposite side was applied as an anticurl coat, an aqueous solution of a 2:1 ratio of polyvinyl alcohol (99% hydrolyzed) and carbon black at an 18% solids level. The anticurl coat was dried and a seal coat composed of a 2:1 ratio of titanium dioxide and carboxylated vinyl acetate/crotonic acid copolymer in water was coated thereon. Ammonium hydroxide was employed to solubilize the polymer and the composition was applied at a level of 24% solids. The two polymer layers together provide a thickness of about 1.5 mils.

The thus-prepared photographic element may be contacted with an aqueous alkaline processing composition on the surface containing the polyvinyl alcohol and poly-4-vinylpyridine layer and pressed into contact with an exposed photosensitive sheet of the type used in Type 108 Polaroid Polacolor film to affect the processing of the latter and the formation of a dye transfer image in the image-receiving sheet. Sufficient pressure was applied to the combined elements to insure good wet contact between the superposed sheets. After an imbibition period of approximately one minute, the image-receiving element may be separated and contain a positive multicolor transfer image. The thus-processed image-receiving element was maintained at 0% relative humidity for 72 hours. At the end of the test period, the element was examined and substantially no curl was observed.

The polymer suitable for the anticurl coat and the seal coat have been described above primarily in terms of employing different polymers for each of said coats. It should be understood, however, that the same polymer may be employed for both coats but possessing differing characteristics in separate layers of the single polymer. For example an anticurl coat may be applied and then a cross-linking agent may be applied to the outer surface to cross-link the layer to a given depth, sufficient to impart the properties desired for the seal coat while at the same time retaining the properties for the anticurl coat.

For example, any of the suitable anticurl coats may be applied, e.g., a layer 0.5 to 1.5 mils in thickness and dried. The thus-formed layer may then be given a wash coat of a cross-linking agent to provide the desired degree and depth of cross-linking to the layer. Alternatively, a cross-linking agent may be incorporated therein and activated by, e.g., heat to provide the desired degree and depth of cross-linking. It is essential, however, that the cross-linking be limited to a depth less than the total thickness of the layer. Cross-linking the entire thickness of the layer is detrimental to the anticurl properties.

The following non-limiting example illustrates the formation of anticurl and seal coats employing the same polymer.

#### Example II

To one side of a cellulose nitrate subcoated baryta paper was applied a layer composed of a mixture of polyvinyl alcohol and poly-4-vinylpyridine. To the opposite side was applied, as a aqueous solution of a 2:1 ratio of polyvinyl alcohol and carbon black at an 18% solids level to provide a layer 0.8 mil thick. The thus-formed coat was dried and a wash coat of 2% solution of glyoxal in water was applied thereto.

The thus-prepared photographic element may be contacted with an aqueous alkaline processing composition

on the surface containing the polyvinyl alcohol and poly-4-vinylpyridine layer and pressed into contact with an exposed photosensitive sheet of the type used in Type 108 Polaroid Polacolor film to affect the processing of the latter and the formation of a dye transfer image in the image-receiving sheet. Sufficient pressure was applied to the combined elements to insure good wet contact between the superposed sheets. After an imbibition period of approximately one minute, the image-receiving element may be separated and contain a positive multicolor transfer image. The thus-processed image-receiving element was maintained at 0% relative humidity for 72 hours. At the end of the test period, the element was examined and substantially no curl was observed.

It should be understood that both the anticurl coat and the seal coat may be applied at a relatively wide range of solids. The solids may range from 15-45%, preferably 24%.

As stated above, opacifying means may be provided to either or both of the layers. In a preferred embodiment, they are provided to both layers with a light-colored material, such as titanium dioxide, incorporated in the seal coat for aesthetic purposes. It should be understood that in addition to the pigments designated, dyes may be employed either alone or in conjunction with pigments in either one or in both the anticurl and seal coats to provide the desired level of opacification.

Although the invention has been discussed in detail throughout employing dye developers, the preferred image-providing materials, it will be readily recognized that other, less preferred, image-providing materials may be substituted in replacement of the preferred dye developers in the practice of the invention. For example, there may be employed dye image-forming materials such as those disclosed in U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294; 3,330,655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,443,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. No. 2,774,668 and 3,087,817, wherein color diffusion transfer processes are described which employ the image-wise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

What is claimed is:

1. An image-receiving element adapted to be used in processing an exposed photosensitive silver halide element by diffusion transfer processing outside of the camera in which exposure occurs, which comprises a support carrying on a first side a layer of a dyeable hydrophilic polymeric material which is permeable to alkaline processing composition adapted to receive a diffusion transfer image and, on a second side, in order, a first and second polymeric layer, said first layer consisting essentially of a hydrophilic polymeric composition and said second layer consisting essentially of a water-insoluble, moisture vapor permeable, polymeric composition, and a material for providing opacity to said element associated with said first and second layers.

2. An element as defined in claim 1 wherein said support comprises paper.

3. An element as defined in claim 1 wherein said first polymeric layer is cellulose acetate.

4. An element as defined in claim 1 wherein said second polymeric layer is applied from an alkaline composition.

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5. An element as defined in claim 1 wherein said second polymeric layer is applied from an aqueous latex.

6. An element as defined in claim 1 wherein said second polymeric layer is carboxylated vinyl acetate/crotonic acid copolymer.

7. An element as defined in claim 1 wherein said layer adapted to receive a diffusion transfer image is polyvinyl alcohol and poly-4-vinylpyridine.

8. An element as defined in claim 1 which includes a polymeric acid layer intermediate said support and said layer adapted to receive a diffusion transfer image.

9. An element as defined in claim 1 wherein said support is flexible.

10. An element as defined in claim 1 wherein said first and second polymeric layers taken together are present at a coverage per unit area effective to provide a substantially planar configuration to said image-receiving element subsequent to processing.

11. An element as defined in claim 1 wherein said material for providing opacity is associated with both of said first and second polymeric layers.

12. An element as defined in claim 11 wherein said material for providing opacity comprises carbon black.

13. An element as defined in claim 12 wherein said material for providing opacity includes titanium dioxide.

14. An element as defined in claim 12 wherein said carbon black is disposed in said first polymeric layer.

15. An element as defined in claim 13 wherein said opacifying material and said support provide an optical transmission density of greater than about 6.0 density units.

16. An element as defined in claim 13 wherein said titanium dioxide provides an optical reflection density less than about 1.0 density units.

17. An element as defined in claim 13 wherein said

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titanium dioxide is disposed in said second polymeric layer.

18. An element as defined in claim 1 wherein said first polymeric layer is polyvinyl alcohol.

19. An element as defined in claim 18 wherein said second polymeric layer is cross-linked polyvinyl alcohol.

20. An element as defined in claim 1 wherein said first polymeric layer is cross-linked.

21. An element as defined in claim 20 wherein said first polymeric layer is polyvinyl alcohol and is cross-linked with glyoxal.

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