United States Patent [19]
Chiklis
[11] B 3,925,081
[45] Dec. 9, 1975

[54] PHOTOGRAPHIC PRODUCTS CONTAINING ANTI-REFLECTION LAYER

[75] Inventor: **Charles K. Chiklis,** Lexington, Mass.

[73] Assignee: **Polaroid Corporation,** Cambridge, Mass.

[22] Filed: **Apr. 24, 1973**

[21] Appl. No.: **354,008**

[44] Published under the Trial Voluntary Protest Program on January 28, 1975 as document no. B 354,008.

[52] **U.S. Cl.** .... **96/72;** 96/3; 96/29 R; 96/29 D; 96/67; 96/50 PL; 96/76 R; 96/76 C; 96/77; 96/84 R; 96/87 R; 96/119 R; 428/421; 428/422; 428/480; 428/483

[51] **Int. Cl.²** .. **G03C 1/76;** G03C 3/00; G03C 1/40; G03C 1/84

[58] **Field of Search** .... 96/77, 76 R, 76 C, 87 R, 96/84 R, 3, 29 D, 50 PL, 29 R, 67, 119 R, 72; 117/76 F, 76 P, DIG. 7, 72 R, 138.8 F, 138.8 A, 161 R, 161 UH, 161 UF; 428/421, 422, 489, 483

[56] **References Cited**

UNITED STATES PATENTS

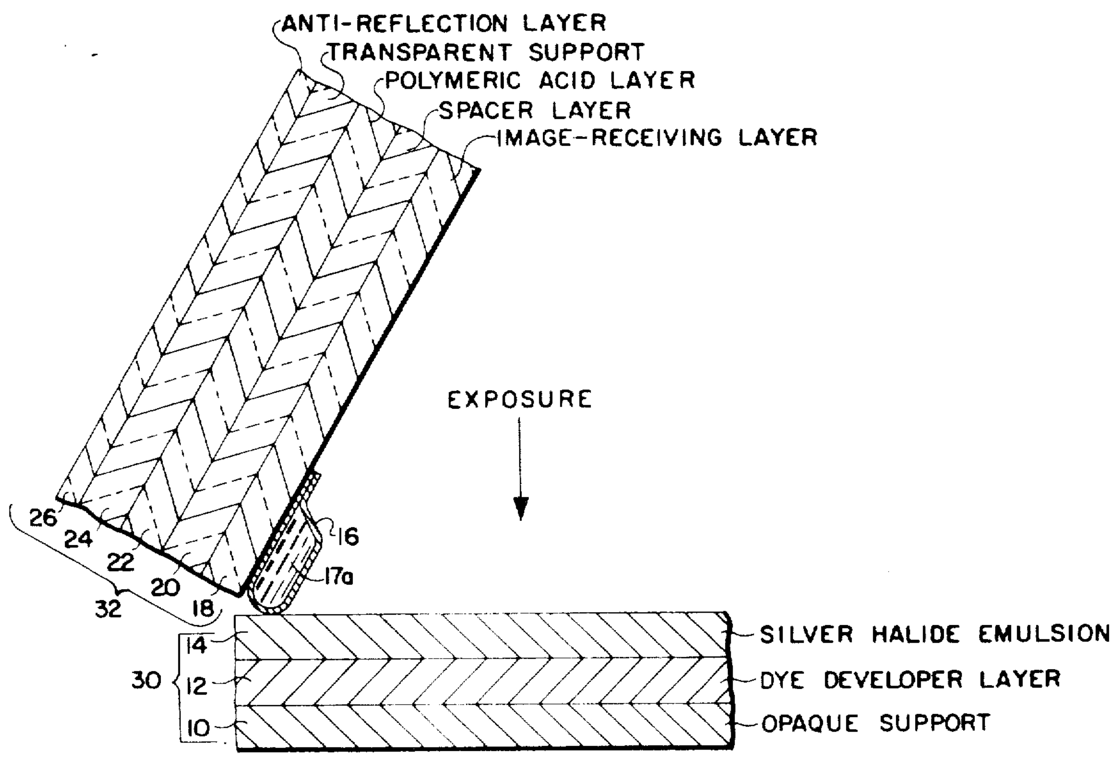
2,331,716	10/1943	Nadeau et al.	96/87 R
2,376,428	5/1945	Hansell	96/84 R
2,430,479	11/1947	Pratt et al.	117/DIG. 7
2,698,242	12/1954	Saner	96/87 R
3,023,126	2/1962	Underwood et al.	117/76 F
3,198,692	8/1965	Bridgeford	117/76 F
3,617,354	11/1971	Carnahan	117/76 P
3,703,426	11/1972	Larson et al.	117/76 F

Primary Examiner—Ronald H. Smith
Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—Stanley H. Mervis

[57] **ABSTRACT**

Photographic images, particularly multicolor images, viewed through a transparent support, have an anti-reflection coating on the outer surface of said support. The anti-reflection coating comprises a quarterwave layer of a fluorinated polymer. The images may be formed by multicolor diffusion transfer processes using dye developers or other image dye-providing materials. In the preferred embodiments, the photographic image is an integral negative-positive reflection print. Abrasion resistance of the anti-reflection coating carried by polyester transparent support is improved by surprisingly low levels of an isocyanate.

53 Claims, 4 Drawing Figures



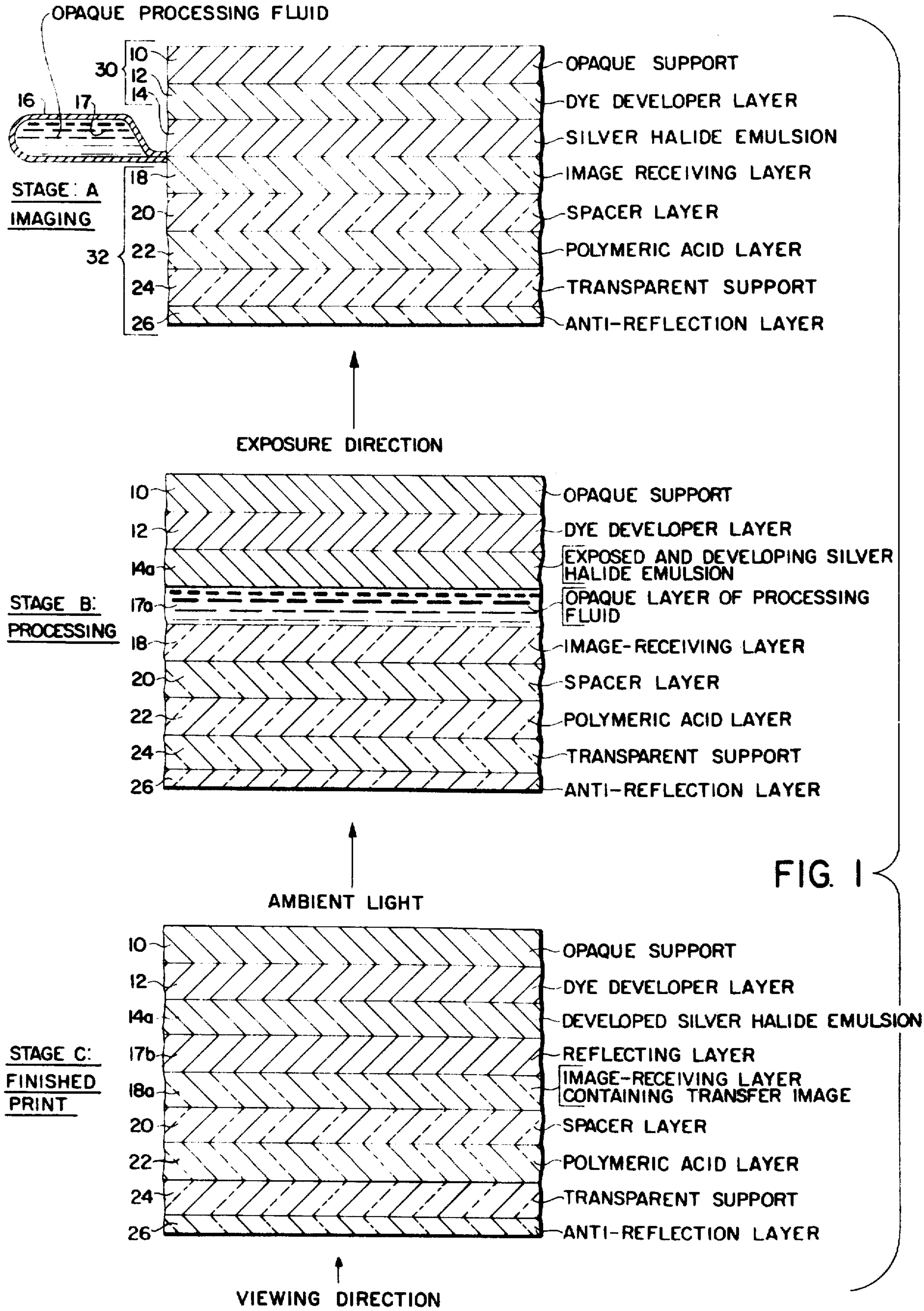

OPAQUE PROCESSING FLUID
30
10
12
14
16
17
OPAQUE SUPPORT
DYE DEVELOPER LAYER
SILVER HALIDE EMULSION
IMAGE RECEIVING LAYER
SPACER LAYER
POLYMERIC ACID LAYER
TRANSPARENT SUPPORT
ANTI-REFLECTION LAYER
STAGE: A
IMAGING
32
18
20
22
24
26
EXPOSURE DIRECTION
10
12
14a
17a
18
20
22
24
26
STAGE B:
PROCESSING
OPAQUE SUPPORT
DYE DEVELOPER LAYER
EXPOSED AND DEVELOPING SILVER HALIDE EMULSION
OPAQUE LAYER OF PROCESSING FLUID
IMAGE-RECEIVING LAYER
SPACER LAYER
POLYMERIC ACID LAYER
TRANSPARENT SUPPORT
ANTI-REFLECTION LAYER
AMBIENT LIGHT
10
12
14a
17b
18a
20
22
24
26
STAGE C:
FINISHED PRINT
OPAQUE SUPPORT
DYE DEVELOPER LAYER
DEVELOPED SILVER HALIDE EMULSION
REFLECTING LAYER
IMAGE-RECEIVING LAYER CONTAINING TRANSFER IMAGE
SPACER LAYER
POLYMERIC ACID LAYER
TRANSPARENT SUPPORT
ANTI-REFLECTION LAYER
VIEWING DIRECTION

FIG. 1

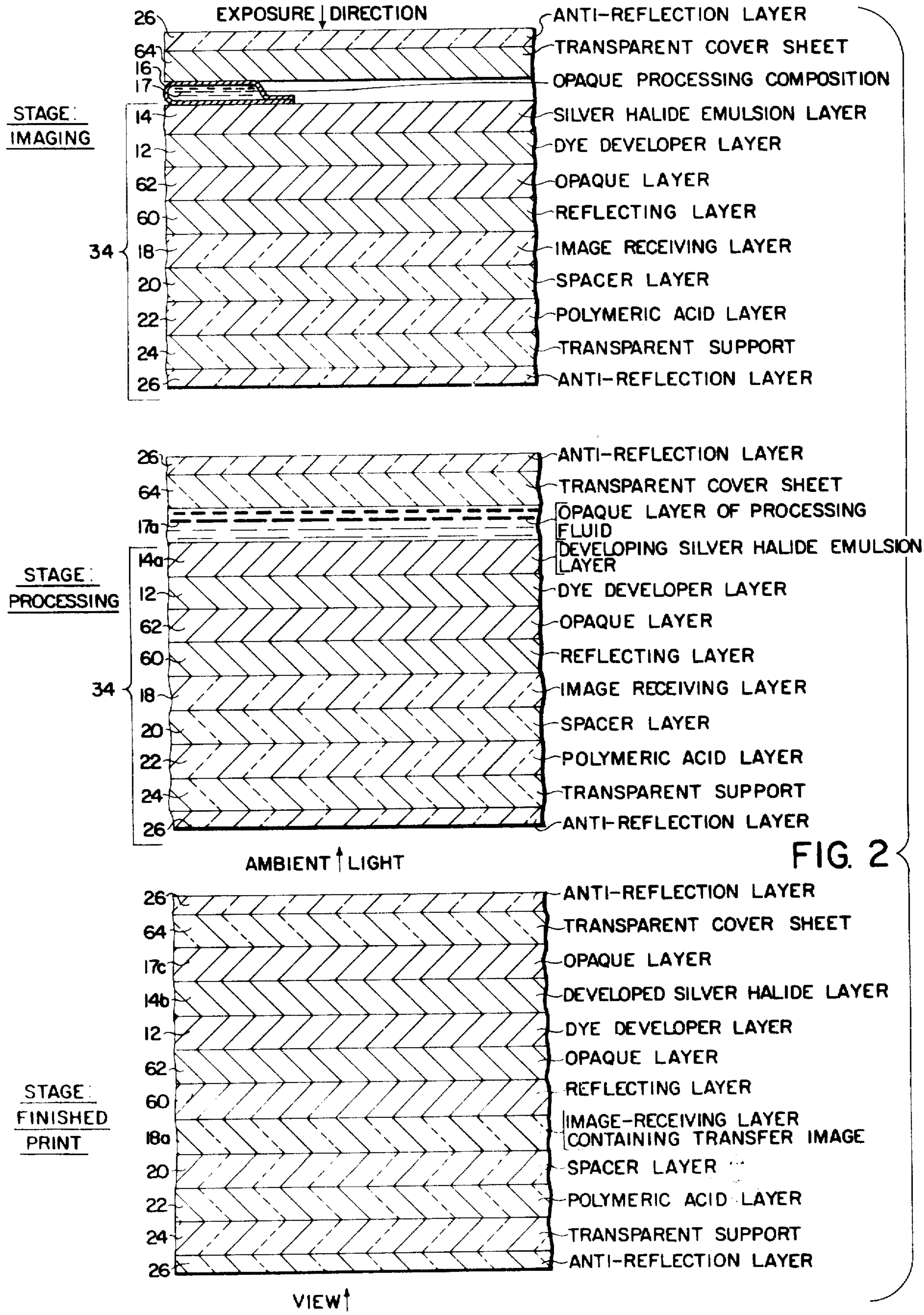

EXPOSURE DIRECTION
STAGE: IMAGING
26
64
16
17
14
12
62
60
34
18
20
22
24
26
ANTI-REFLECTION LAYER
TRANSPARENT COVER SHEET
OPAQUE PROCESSING COMPOSITION
SILVER HALIDE EMULSION LAYER
DYE DEVELOPER LAYER
OPAQUE LAYER
REFLECTING LAYER
IMAGE RECEIVING LAYER
SPACER LAYER
POLYMERIC ACID LAYER
TRANSPARENT SUPPORT
ANTI-REFLECTION LAYER
STAGE: PROCESSING
26
64
17a
14a
12
62
60
34
18
20
22
24
26
ANTI-REFLECTION LAYER
TRANSPARENT COVER SHEET
OPAQUE LAYER OF PROCESSING FLUID
DEVELOPING SILVER HALIDE EMULSION LAYER
DYE DEVELOPER LAYER
OPAQUE LAYER
REFLECTING LAYER
IMAGE RECEIVING LAYER
SPACER LAYER
POLYMERIC ACID LAYER
TRANSPARENT SUPPORT
ANTI-REFLECTION LAYER
AMBIENT LIGHT
STAGE: FINISHED PRINT
26
64
17c
14b
12
62
60
18a
20
22
24
26
ANTI-REFLECTION LAYER
TRANSPARENT COVER SHEET
OPAQUE LAYER
DEVELOPED SILVER HALIDE LAYER
DYE DEVELOPER LAYER
OPAQUE LAYER
REFLECTING LAYER
IMAGE-RECEIVING LAYER CONTAINING TRANSFER IMAGE
SPACER LAYER
POLYMERIC ACID LAYER
TRANSPARENT SUPPORT
ANTI-REFLECTION LAYER
VIEW

FIG. 2

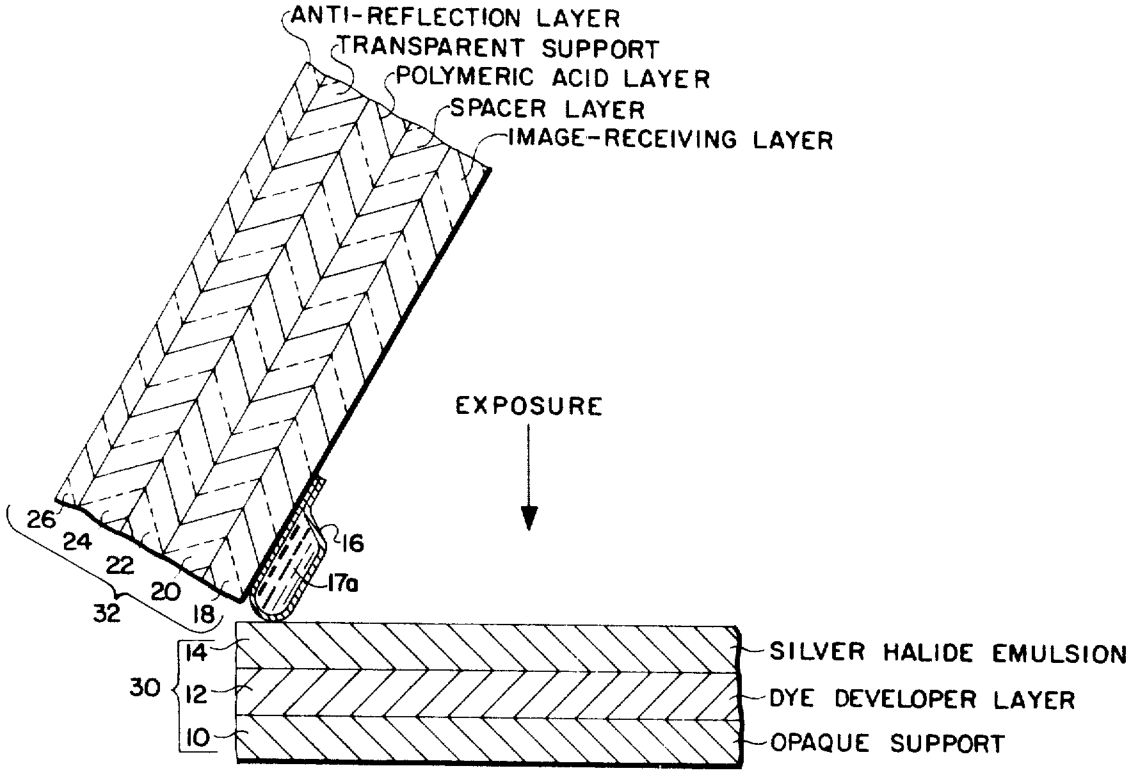

ANTI-REFLECTION LAYER
TRANSPARENT SUPPORT
POLYMERIC ACID LAYER
SPACER LAYER
IMAGE-RECEIVING LAYER
EXPOSURE
26
24
22
20
18
32
16
17a
14
12
10
30
SILVER HALIDE EMULSION
DYE DEVELOPER LAYER
OPAQUE SUPPORT

FIG. 3

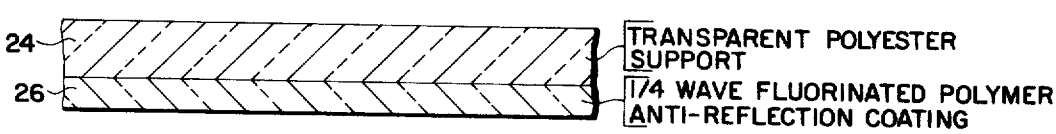

24
26
TRANSPARENT POLYESTER SUPPORT
1/4 WAVE FLUORINATED POLYMER ANTI-REFLECTION COATING

FIG. 4

PHOTOGRAPHIC PRODUCTS CONTAINING ANTI-REFLECTION LAYER

This invention is concerned with photography and, more particularly, with the formation of images in color or black-and-white by diffusion transfer processing.

A number of photographic processes have been proposed wherein the resulting photograph comprises the developed silver halide emulsion(s) retained as part of a permanent laminate, with the desired image being viewed through a transparent support. Of particular significance are those processes where the image is in color and is formed by a diffusion transfer process. If the image is to be viewed as a reflection print, the image-carrying layer is separated from the developed silver halide emulsion(s) in said laminate by a light-reflecting layer, preferably a layer containing titanium dioxide. Illustrative of patents describing such products and processes are U.S. Pat. No. 2,983,606 issued Mar. 9, 1961 to Howard G. Rogers, U.S. Pats. No. 3,415,644, 3,415,645 and 3,415,646 issued Dec. 10, 1968 to Edwin H. Land, U.S. Pats. Nos. 3,594,164 and 3,594,165 issued July 20, 1971 to Howard G. Rogers, and U.S. Pat. No. 3,647,437 issued Mar. 7, 1972 to Edwin H. Land.

Referring more specifically to the aforementioned U.S. Pat. No. 3,415,644, said patent discloses photographic products and processes employing dye developers wherein a photosensitive element and an image-receiving layer are maintained in fixed relationship prior to photoexposure and this fixed relationship is maintained after processing and image formation to provide a laminate including the processed silver halide emulsions and the image-receiving layer. Photoexposure is made through a transparent (support) element and application of a processing composition provides a layer of light-relecting material to provide a white background for viewing the image and to mask the developed silver halide emulsions. The desired color transfer image is viewed through said transparent support against said white background.

While such processes provide very useful and good quality images, it has been found that the full potential quality of the image is not obtained because the transparent support through which the image is viewed in fact reflects "white" light to the viewer's eyes. Furthermore, this property of reflecting some of the light incident on the surface of the transparent support adversely affects the ability of the film to record a subject when photoexposure is effected through such a transparent support.

In accordance with the copending application of Edwin H. Land, Stanley M. Bloom and Howard G. Rogers, Ser. No. 276,979 filed Aug. 1, 1972, now U.S. Pat. No. 3,793,022 issued Feb. 19, 1974 the above-noted problems are substantially, if not completely, eliminated by the provision of an anti-reflection layer through which the image is viewed and/or photoexposure is effected. The present invention is directed toward improvements in the products and processes disclosed and claimed in said Ser. No. 276,979, and, in its more specific embodiments, provides novel anti-reflection coatings.

It is, therefore, a primary object of this invention to provide novel photographic products and processes which provide color or black-and-white images as part

of a permanent laminate, said laminate exhibiting substantially less surface reflection of incident light.

It is a further object of this invention to provide diffusion transfer images, particularly multicolor transfer images, which are viewed through a transparent element the outer surface of which carries an improved anti-reflection coating.

Yet another object of this invention is to provide diffusion transfer films which are exposed through a transparent support, the outer surface of which carries an anti-reflection coating of improved scratch resistance.

Further objects of this invention include the provision of novel anti-reflection coatings and of transparent supports carrying said anti-reflection coatings, such supports being particularly useful for carrying photographically useful layers.

Other objects of this invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and relation of components and the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description of the invention taken in conjunction with the accompanying drawings wherein:

FIGS. 1 and 2 are diagrammatic, enlarged cross-sectional views of two embodiments of film units embodying the present invention, illustrating the arrangement of layers during the three illustrated stages of a monochrome diffusion transfer process, i.e., exposure, processing and final image;

FIG. 3 is a diagrammatic, enlarged cross-sectional view of another film unit embodying the present invention;

FIG. 4 is a diagrammatic, enlarged cross-sectional view of a transparent sheet, adapted for use as a support for an image-carrying element, including an anti-reflection coating in accordance with the present invention.

As noted above, this invention is particularly concerned with color diffusion transfer processes wherein the layer containing the diffusion transfer image, i.e., the image-receiving layer, is not separated from the developed photosensitive layers after processing but both components are retained together as part of a permanent laminate. Film units particularly adapted to provide such diffusion transfer images have frequently been referred to as "integral negative-positive" film units. The resulting image may be referred to as an "integral negative-positive reflection print" and as so used this expression is intended to refer to a reflection print wherein the developed photosensitive layers have not been separated from the image layer, i.e., the layer containing the transfer dye image. A light-reflecting layer between the developed photosensitive layer(s) and the image layer provides a white background for the dye image and masks the developed photosensitive layer(s). These layers are part of a permanent laminate which usually includes dimensionally stable outer or support layers, the transfer dye image being viewable through one of said supports. This invention is particularly concerned with improving the aesthetic qualities of such integral negative-positive reflection prints.

The present invention is applicable to a wide variety of diffusion transfer processes. The arrangement and order of the individual layers of the film used in such processes may vary in many ways as is known in the art, provided the final photograph is a laminate wherein the desired image is viewed through a transparent support, e.g., an integral negative-positive reflection print as described above. For convenience, however, the more specific descriptions of the invention hereinafter set forth will be by use of dye developer diffusion transfer color processes and of integral negative-positive film units of the type contemplated in the previously mentioned patents, particularly U.S. Pats. Nos. 3,415,644 and 3,594,164. It will be readily apparent from such descriptions that other image-forming reagents may be used, e.g., color couplers, coupling dyes or dyes (couplers) which release a dye or dye intermediate as a result of coupling or oxidation.

When such integral negative-positive reflection prints are viewed under ordinary lighting conditions, a small but significant amount of light is reflected from the external surface of the transparent support. The effect of this reflection of incident light is to limit the clarity with which the image may be seen except when the viewer's eyes are "just right", i.e., good viewing may be highly directional, in that the print may have to be "tilted" with respect to the viewer's line of vision to avoid obscuring image detail. This problem becomes more acute when several persons try to view the same image, as those not directly in front of the print will experience substantial glare, with the amount of glare increasing as the angle of view becomes more oblique. In addition, the color(s) of a color image may appear less saturated.

If photoexposure is effected through such a transparent support, reflection of light from the surface of the transparent support has been found to have several undesirable results. One result is a reduction in the exposure index or "speed" of the film, due to the fact that some of the light which has passed through the camera lens will be reflected before it can reach the photosensitive layer(s) and the thus reflected light will not participate in the recording of the photographed subject matter. Furthermore, such reflected light has a tendency to "bounce" within the camera, and may cause flare and reduced contrast and resolution in the final image. If photoexposure is effected through the transparent support in a camera which includes an image-reversing mirror in the optical path, light reflected from the surface may cause a "ghost" image of a particularly bright object within the scene to be superposed on another portion of the scene in the resulting photograph.

As noted earlier, the copending application of Land, et al., Ser. No. 276,979 teaches that such undesirable reflection from the transparent support may be substantially reduced, if not completely eliminated, by modifying the external surface of such transparent supports so as to provide a controlled change in the index of refraction to which incident light is subjected as it passes from air into the transparent support.

The present invention is directed towards perfecting the advantages provided by the teachings of Ser. No. 276,979 by providing improved anti-reflection coatings for use, e.g., on the external surface of the transparent support of a photographic element. In accordance with the present invention, the adhesion of an anti-reflection coating comprising a quarter-wave stratum of a fluorinated polymer, i.e., a stratum having an optical thickness of one-quarter (¼) of substantially the same, predetermined wavelength of light, carried by a high refractive index, transparent synthetic polyester sheet or support, is improved by the presence of an isocyanate.

The principles of physics by which anti-reflection coatings function are well known and may be used to special advantage in the present invention. Thus, it is well known that application of a single layer transparent coating will reduce surface reflection from a transparent layer (support) if the refractive index of said coating is less than that of the transparent layer to which it is applied and the coating is of appropriate optical thickness. In the photographic products with which this invention is concerned, the anti-reflection coating will normally be in optical contact with air. Under these circumstances, and because the index of refraction of air is 1, the applicable principles of physics give the following rule: if the index of refraction of the coating material (anti-reflection layer) is exactly equal to the square root of the index of refraction of the substrate (transparent support), then all surface reflection of light will be eliminated for that wavelength at which the product of the refractive index times thickness is equal to one-quarter of that wavelength. At other wavelengths the destructive interference between light reflected from the top and bottom surfaces of the anti-reflection coating is not complete but a substantial reduction in overall reflectivity is obtained. By selecting the optical thickness of the anti-reflection coating to be one-quarter of a wavelength for approximately the midpoint of the visible light wavelength range (i.e., one-quarter of 5500 Angstroms or about 1400 Angstroms), the reduction in reflectivity is optimized. The term "optical thickness" as used herein refers to the product of the physical thickness of the coating times the refractive index of the coating material. Unless otherwise indicated, as used herein the expression "quarter-wave" refers to coatings having an optical thickness of one-quarter of a predetermined wavelength of light, said wavelength being 5500 Angstroms.

The anti-reflection coating should be optically clear and provide an essentially uniform layer.

The anti-reflection coatings of this invention are used with polyester art known polymeric film base materials. Such film bases typically have a thickness of about 3 to 10 mils (0.003 to 0.010 inch). Particularly useful polyester film bases have a thickness of about 3 to 6 mils. Polyester films have higher refractive indices than cellulose acetate, and the resultant greater incidence of surface reflected light as compared with cellulose acetate would normally be considered to be a disadvantage of using such materials in integral negative-positive reflection or other prints in which the image is viewed through a transparent base. (Indeed, the greater surface reflection resulting in greater glare, and the resultant need for more directional viewing, exhibited by polyester films as compared with cellulose acetate is well known from the commonly used protective transparent covers for notebook pages.) These higher indices of refraction make it much more possible to provide anti-reflection coatings which practically eliminate all reflectivity, whereas reflectivity can only be reduced when using cellulose acetate.

Particularly useful transparent supports are films of polyethylene terephthalate, such as those commercially available under the trademarks "Mylar" (E.I.DuPont de Nemours & Co.) and "Ester" (Eastman Kodak Co.) Such polyester films have an index of refraction on the order of about 1.66. A number of materials suitable for anti-reflection coatings, e.g. fluorinated polymers, have indices of refraction of about 1.35 to 1.40 which is close to the 1.29 ideal index of refraction, i.e., the geometric mean of the indices of refraction of the polyethylene terephthalate and the surrounding air, or, because the index of refraction of air is 1, the square root of the 1.66 index of refraction of polyethylene terephthalate. Furthermore, the fact that the difference of about 0.3 in the indices of refraction between air and the anti-reflection coating is close to the approximate 0.3 difference in the indices of refraction of the anti-reflection coating and the polyethylene terephthalate support means that maximum benefit will be obtained from the anti-reflection coating; the amplitude of the light entering the anti-reflection coating will more closely match the amplitude of the light reflected back from the interface of the polyethylene phthalate and the anti-reflection coating, and more effectively cancel out the thus reflected light.

Reference is now made to the accompanying drawings wherein a plurality of embodiments of this invention are illustrated and wherein like numbers, appearing in the various figures, refer to like components. For ease of understanding, these embodiments illustrate the formation of a monochrome image using a single dye developer. The illustrated embodiments include appropriate means of opacification to permit the processing of the film unit outside of a dark chamber, i.e., the film unit is intended to be removed from the camera prior to image completion and while the film is still photosensitive. Opacifying systems are described in the previously noted patents and per se form no part of the present invention which is equally applicable to film units intended to be processed within a dark chamber.

In the discussion of FIGS. **1**,**2** and **3**, reference to the anti-reflection coating **26** is to be understood as referring to the anti-reflection coating provided by stratum **26** of FIG. **4**.

A particularly useful opacifying system for film units of the type shown in FIGS. **1** and **3** utilizes a color dischargeable reagent, preferably a pH-sensitive optical filter agent or dye, sometimes referred to as an indicator dye, as is described in detail in the aforementioned U.S. Pat. No. 3,647,437. In film units of the type shown in FIG. **2**, photoexposure is effected from the side opposite the side from which the image is viewed. An opague layer to protect the exposed silver halide from further exposure may be provided by including a light-absorbing opacifying agent, e.g., carbon black, in the processing composition which is distributed between the photosensitive layer(s) and a transparent support or spreader sheet. In such film units, it may be desirable to include a preformed opaque layer, e.g., a dispersion of carbon black in a polymer permeable to the processing composition, between a preformed light-reflecting layer and the silver halide emulsion(s). Such opacifying systems are shown and described in the aforementioned U.S. Pats. Nos. 3,594,164 and 3,594,165.

Referring to FIG. **1**, Stages A,B and C show in diagrammatic cross-section, respectively, imaging, processing, and the finished print in one embodiment of this invention. In Stage A, there is shown a photosensitive element **30** in superposed relationship with an image-receiving element **32**, with a rupturable container **16** (holding an opaque processing composition **17**) so positioned as to discharge its contents between said elements upon suitable application of pressure, as by passing through a pair of pressure applying rolls or other pressure means (not shown). Photosensitive element **30** comprises an opaque support **10** carrying a layer **12** of a dye developer over which has been coated a silver halide emulsion layer **14**. The image-receiving element **32** comprises a transparent support **24** carrying, in turn, a polymeric acid layer **22**, a spacer layer **20** and an image-receiving layer **18**. An anti-reflection coating **26** is present on the outer surface of the transparent support **24**. Photoexposure of the silver halide emulsion layer is effected through the anti-reflection coating **26** and the transparent support **24** and the layers carried thereon, i.e., the polymeric acid layer **22**, the spacer layer **20** and the image-receiving layer **18** which layers are also transparent, the film unit being so positioned within the camera that light admitted through the camera exposure or lens system is incident upon the outer surface of the anti-reflection coating **26**. After exposure the film unit is advanced between suitable pressure-applying members, rupturing the container **16**, thereby releasing and distributing a layer **17***a* of the opaque processing composition between the photosensitive element **30** and the image-receiving element **32**. The opaque processing composition contains a film-forming polymer, a white pigment and has an initial pH at which one or more optical filter agents contained therein are colored; the optical filter agent (agents) is (are) selected to exhibit light absorption over at least a portion of the wavelength range of light actinic to the silver halide emulsion. As a result, ambient or environmental light within that wavelength range incident upon transparent support **24** and transmitted through said transparent support and the transparent layers carried thereon in the direction of the photoexposed silver halide emulsion **14***a* is absorbed thereby avoiding further exposure of the photoexposed and developing silver halide emulsion **14***a*. In exposed and developed areas, the dye developer is oxidized as a function of the silver halide development and immobilized. Unoxidized dye devoloper associated with undeveloped and partially developed areas remains mobile and is transferred imagewise to the image-receiving layer **18** to provide the desired positive image therein. Permeation of the alkaline processing composition through the image-receiving layer **18** and the spacer layer **20** to the polymeric acid layer **22** is so controlled that the process pH is maintained at a high enough level to effect the requisite development and image transfer and to retain the optical filter agent (agents) in colored form, after which pH reduction effected as a result of alkali permeation into the polymeric acid layer **22** is effective to reduce the pH to a level which "discharges" the optical filter agent, i.e., changes it to a colorless form. Absorption of the water from the applied layer **17***a* of the processing composition results in a solidified film composed of the film-forming polymer and the white pigment dispersed therein, thus providing the reflecting layer **17***b* which also serves to laminate together the photosensitive element **30** and the image-receiving element **32** to provide the final laminate (Stage C). The positive transfer image in dye developer present in the image-receiving layer **18***a* is viewed through the transparent support **24** and the intermediate transparent layers against the reflecting layer **17***b* which provides an essentially white background for the dye image and also effectively masks from view the developed silver halide emulsion **14***b* and dye developer immobilized therein or remaining in the dye developer layer **12**.

The optical filter agent is retained within the final film unit laminate and is preferably colorless in its final form, i.e., exhibiting no visible absorption to degrade the transfer image or the white background therefor provided by the reflecting layer **17b**. The optical filter agent may be retained in the reflecting layer under these conditions, and it may contain a suitable "anchor" or "ballast" group to prevent its diffusion into adjacent layers. Alternatively, if the optical filter agent is initially diffusible, it may be selectively immobilized on the silver halide emulsion side of the reflecting layer **17b**, e.g., by a mordant coated on the surface of the silver halide emulsion layer **14**; in this embodiment the optical filter in its final state may be colorless or colored so long as any color exhibited by it is effectively masked by the reflecting layer **17b**.

The reflecting layer provided in the embodiment of this invention shown in FIG. **1** is formed by solidification of a stratum of pigmented processing composition distributed after exposure. It is also within the scope of this invention to provide a preformed pigmented layer, e.g., coated over the image-receiving layer **18**, and to effect photoexposure therethrough, in accordance with the teachings of U.S. Pat. No. 3,615,421 issued Oct. 26, 1971 to Edwin H. Land.

In the embodiment illustrated in FIG. **1**, photo-exposure is effected through the image-receiving element. While this is a particularly useful and preferred embodiment, it will be understood that the image-receiving element may be initially positioned out of the exposure path as illustrated in FIG. **3** and superposed upon the photosensitive element after photoexposure, in which event the processing and final image stages would be the same as in FIG. **1**.

In the embodiment illustrated in FIG. **1**, photo-exposure and viewing of the final image both are effected through the transparent support **24**. Accordingly, the advantages of the anti-reflection coating **26** are obtained twice, i.e., first, by minimizing failure of the film unit to record light passed by the camera lens and second, by minimizing glare during viewing.

It will be noted in the embodiment illustrated in FIG. **1** that the image-viewing layer **18** is temporarily bonded to the silver halide emulsion layer **14** prior to exposure. The rupturable container or pod **16** is so positioned that upon its rupture the processing composition **17** will delaminate the film unit and distribute itself between the image-receiving layer **18** and the silver halide emulsion layer **14**. The distributed layer of processing composition **17a** upon solidification forms a layer **17b** which bonds the elements together to form the desired permanent laminate. Procedures for forming such prelaminated film units, i.e., film units in which the several elements are temporarily laminated together prior to exposure, are described, for example, in U.S. Pat. No. 3,625,281 issued to Albert J. Bachelder and Frederick J. Binda and in U.S. Pat. No. 3,652,282 to Edwin H. Land, both issued Mar. 28, 1972. A particularly useful and preferred prelamination utilizes a water-soluble polyethylene glycol as described and claimed in the copending application of Edwin H. Land, Ser. No. 247,023 filed Apr. 24, 1972 (now U.S. Pat. No. 3,793,023 issued Feb. 19, 1974).

The use of such temporarily laminated film units maximizes the beneficial effects obtained in the photoexposure stage from having the exposure effected through the anti-reflection coating **26**, since the preclamination eliminates any other layer-to-air interface which could also reflect light and thus reduce the amount of light recorded by the photosensitive layer(s).

It will be recognized that the transfer image formed following exposure and processing of film units of the type illustrated in FIG. **1** will be a geometrically reversed image of the subject. Accordingly, to provide geometrically nonreversed transfer images, exposure of such film units should be accomplished through an image reversing optical system, such as in a camera possessing an image reversing optical system utilizing mirror optics, e.g., as described in U.S. Pat. No. 3,447,437 issued June 3, 1969 to Douglas B. Tiffany. As noted above, when photoexposure is effected in such an image reversing optical system, photoexposure through an anti-reflection layer provides additional advantages in preventing the reflection of light which might cause the formation in the final image of a reflected or ghost image of one part of the photographed scene superposed upon another part of the scene.

If desired, the photosensitive element **30** may utilize a transparent support instead of the opaque support **10** shown in FIG. **1**. In this alternative embodiment, the film unit should be processed in a dark chamber or an opaque layer, e.g., pressure-sensitive, should be superposed over said transparent support to avoid further exposure through the back of the film unit during processing outside of the camera.

FIG. **2** illustrates another film structure adapted to provide an integral negative-positive reflection print and wherein photoexposure and viewing are effected from opposite sides. In this embodiment, a photosensitive element **34** comprises a transparent support **24** carrying a layer **22** of a polymeric acid, a spacer **20**, an image-receiving layer **18**, a light-reflecting layer **60** (e.g., of titanium dioxide), an opaque layer **62** (e.g., of carbon black), a dye developer layer **12**, and a silver halide emulsion layer **14**. After photoexposure, a processing composition **17** is applied by rupturing a pod **16** and distributing the processing composition between a cover or spreader sheet **64** and silver halide emulsion layer **14**. The cover sheet **64** may be transparent as illustrated in FIG. **2** and described in detail in the above noted U.S. Pat. No. 3,594,165, in which event photoexposure may be effected through it while it is held in place, e.g., by a binder tape around the edges of the film unit or by temporary lamination prior to photoexposure, as discussed above. In this embodiment, an anti-reflection coating **26** is provided on the outer or exposure surface of the transparent cover sheet **64**. (Alternatively, cover sheet **64** may be opaque in which event it is positioned out of the exposure path prior to photoexposure, as described in detail in the above noted U.S. Pat. No. 3,594,164.) The opaque processing composition **17** contains suitable opacifying agents, e.g., carbon black, titanium dioxide, etc. The light-reflecting layer **60** preferably includes a white pigment, such as titanium dioxide, to provide a white background against which the transfer image may be viewed. The opaque layer **62**, e.g., a layer of carbon black in gelatin, provides the requisite light protection while assuring an aesthically pleasing white background for the final image.

Processing of film units of the types described above is initiated by distributing the processing composition between predetermined layers of the film unit. In exposed and developed areas, the dye developer will be immobilized as a function of development. In unexposed and undeveloped areas, the dye developer is unreacted and diffusible, and this provides an imagewise distribution of unoxidized dye developer, diffusible in the processing composition, as a function of the point-to-point degree of exposure of the silver halide layer. The desired transfer image is obtained by the diffusion transfer to the image-receiving layer of at least part of this imagewise distribution of unoxidized dye developer. In the illustrated embodiments, the pH of the photographic system is controlled and reduced by the neutralization of alkali after a predetermined interval, in accordance with the teachings of the above noted U.S. Pat. No. 3,615,644, to reduce the alkalinity to a pH at which the unoxidized dye developer is substantially insoluble and non-diffusible. As will be readily recognized, the details of such processes form no part of the present invention but are well known; the previously noted U.S. patents may be referred to for more specific discussion of such processes.

The film units illustrated in FIGS. **1**,**2**, and **3** have, for convenience, been shown as monochrome films. Multicolor images may be obtained by providing the requisite number of differentially exposable silver halide emulsions, and said silver halide emulsions are most commonly provided as individual layers coated in superposed relationship. Film units intended to provide multicolor images comprise two or more selectively sensitized silver halide layers each having associated therewith an appropriate image dye-providing material providing an image dye having spectral absorption characteristics substantially complementary to the light by which the associated silver halide is exposed. The most commonly employed negative components for forming multicolor images are of the "tripack" structure and contain blue-, green-, and red-sensitive silver halide layers each having associated therewith in the same or in a contiguous layer a yellow, a magenta and a cyan image dye-providing material, respectively. Interlayers or spacer layers may, if desired, be provided between the respective silver halide layers and associated image dye-providing materials or between other layers. Integral multicolor photosensitive elements of this general type are disclosed in U.S. Pat. No. 3,345,163 issued Oct. 3, 1967 to Edwin H. Land and Howard G. Rogers as well as in the previously noted U.S. patents, e.g., in FIG. **9** of the aforementioned U.S. Pat. No. 2,983,606.

A number of modifications to the structures described in connection with the figures will readily suggest themselves to one skilled in the art. Thus, for example, the mulitcolor multilayer negative may be replaced by a screen-type negative as illustrated in U.S. Pat. No. 2,968,554 issued Jan. 17, 1961 to Edwin H. Land and in the aforementioned U.S. Pat. No. 2,983,606 particularly with respect to FIG. **3** thereof.

The image dye-providing materials which may be employed in such processes generally may be characterized as either (1) initially soluble or diffusible in the processing composition but are selectively rendered non-diffusible in an imagewise pattern as a function of development; or (2) initially insoluble or non-diffusible in the processing composition but which are selectively rendered diffusible or provide a diffusible product in an imagewise pattern as a function of development. These materials may be complete dyes or dye intermediates, e.g., color couplers. The requisite differential in mobility or solubility may, for example, be obtained by a chemical action such as a redox reaction or a coupling reaction.

As examples of initially soluble or diffusible materials and their application in color diffusion transfer, mention may be made of those disclosed, for example, in U.S. Pat. Nos. 2,774,668; 2,968,554; 2,983,606; 2,087,817; 3,185,567; 3,230,082; 3,345,163; and 3,443,943. As examples of initially non-diffusible materials and their use in color transfer systems, mention may be made of the materials and systems disclosed in U.S. Pat. Nos. 3,185,567; 3,443,939; 3,443,940; 3,227,550; and 3,227,552. Both types of image dye-providing substances and film units useful therewith also are discussed in the aforementioned U.S. Pat. No. 3,647,437 to which reference may be made.

It will be understood that dye transfer images which are neutral or black-and-white instead of monochrome or multicolor may be obtained by use of a single dye or a mixture of dyes of the appropriate colors in proper proportions, the transfer of which may be controlled by a single layer of silver halide, in accordance with known techniques. It is also to be understood that "direct positive" silver halide emulsions may also be used, depending upon the particular image dye-providing substances employed and whether a positive or negative color transfer image is desired.

It will also be understood that the present invention may be utilized with films wherein the final image is in silver, and photoexposure and/or viewing is effected through a transparent support which is provided with an anti-reflection coating in accordance with the teachings of this disclosure. Indeed, the transfer of silver may be utilized to provide a silver image or to provide a dye image by silver dye bleach processing.

In the preferred embodiments, the layers comprising the individual film units are secured in fixed relationship prior to, during, and after photoexposure and processing to provide the desired integral negative-positive image. Film units of this type are well known in the art and are illustrated, for example, in the above cited U.S. Pat. Nos. 3,415,644; 3,467,437; and 3,594,165, as well as in other patents. In general, a binding member is provided extending around, for example, the edges of the composite structure and securing the elements thereof in fixed relationship. The binding member may comprise a pressure-sensitive tape securing and/or maintaining the layers of the structure together at its respective edges. If the edge tapes are also opaque, edge leakage of actinic radiation incident on the film unit will be prevented. The edge tapes also will act to prevent leakage of the processing composition from the laminate during and after processing. The rupturable pod is so positioned as to discharge its contents between predetermined layers; e.g., between the image-receiving layer **18** and the silver halide emulsion layer **14** of FIG. **1**; these layers may be temporarily bonded to each other with a bond strength less than that exhibited by the interface between the opposed surfaces of the remaining layers, as described above. The binding member may also serve to provide a white mask or border for the final image. The manufacture of such film units or packets is well described in the above-noted and other patents and need not be set forth in any detail here.

Rupturable container **16** may be of the type shown and described in any of U.S. Pats. Nos. 2,543,181; 2,634,886; 3,653,732; 2,723,051; 3,056,492; 3,056,491; 3,152,515; and the like. In general, such containers will comprise a rectangular blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls which are sealed to one another along their longitudinal and end margins to form a cavity in which processing composition **17** is retained. The longitudinal marginal seal is made weaker than the end seals so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **17** of the container by the application of compressive pressure to the walls of the container, e.g., by passing the film unit between opposed pressure applying rollers.

The rupturable container **16** is so positioned as to effect unidirectional discharge of the processing composition **17** between predetermined layers, e.g., the image-receiving layer **18** and the silver halide layer **14** next adjacent thereto, upon application of compressive force to the rupturable container **16.** Thus, the rupturable container **16,** as illustrated in **FIG. 1,** is fixedly positioned and extends transverse a leading edge of the prelaminated film unit with its longitudinal margin seal directed toward the interface between the image-receiving layer **18** and the silver halide emulsion layer **14.** The rupturable container **16** is fixedly secured to this laminate by a tape extending over a portion of one wall of the container, in combination with a separate retaining member or tape extending over a portion of the laminate's surface generally equal in area to about that covered by said tape.

A preferred opacification system to be contained in the processing composition **17** to effect processing outside of a camera is that described in the above-mentioned U.S. Pat. No. 3,647,437, and comprises a dispersion of an inorganic light-reflecting pigment which also contains at least one light-absorbing agent, i.e., optical filter agent, at a pH above pKa of the optical filter agent in a concentration effective when the processing composition is applied, to provide a layer exhibiting optical transmission density > than about 6.0 density units with respect to incident radiation actinic to the photosensitive silver halide and optical reflection density < than about 1.0 density units with respect to incident visible radiation.

In lieu of having the light-reflecting pigment in the processing composition, the light-reflecting pigment used to mask the photosensitive strata and to provide the background for viewing the color transfer image formed in the receiving layer may be present initially in whole or in part as a preformed layer in the film unit. As an example of such a preformed layer, mention may be made of that disclosed in U.S. Pat. No. 3,615,421 issued Oct. 26, 1971 and in U.S. Pat. No. 3,620,724 issued Nov. 16, 1971, both in the name of Edwin H. Land. The reflecting agent may be generated in situ as is disclosed in U.S. Pats. Nos. 3,647,434 and 3,647,435, both issued Mar. 7, 1972 to Edwin H. Land.

The dye developers (or other image dye-providing substances) are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, that is, the previously mentioned cyan, magenta and yellow. They may be incorporated in the respective silver halide emulsion or, in the preferred embodiment, in a separate layer behind the respective silver halide emulsion. Thus a dye developer may, for example, be in a coating or layer behind the respective silver halide emulsion and such a layer of dye developer may be applied by use of a coating solution containing the respective dye developer distributed, in a concentration calculated to give the desired coverage, of dye developer per unit area, in a film-forming natural, or synthetic, polymer, for example, gelatin, polyvinyl alcohol, and the like, adapted to be permeated by the processing composition.

Dye developers, as noted above, are compounds which contain the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho-and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

The image-receiving layer may comprise one of the materials known in the art, such as polyvinyl alcohol, gelatin, etc. It may contain agents adapted to mordant or otherwise fix the transferred images dye(s). Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061, issued Sept. 8, 1964 to Howard C. Haas.

In the various color diffusion transfer systems which have previously been described, and which employ an aqueous alkaline processing fluid, it is well know to employ an acid-reacting reagent in a layer of the film unit to lower the environmental pH following substantial dye transfer in order to increase the image stability and/or to adjust the pH from the first pH at which the image dyes are diffusible to a second (lower) pH at which they are not. For example, the previously mentioned U.S. Pat. No. 3,415,644 discloses systems wherein the desired pH reduction may be effected by providing a polymeric acid layer adjacent the dyeable stratum. These polymeric acids may be polymers which contain acid groups, e.g., carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals or with organic bases; or potentially acid-yielding groups such as anhydrides or lactones. Preferably the acid polymer contains free carboxyl groups. Alternatively, or in addition, an acid-reacting reagent may be provided in a layer adjacent to the silver halide layer most distant from the image-receiving layer, as disclosed in U.S. Pat. No. 3,573,043 issued Mar. 30, 1971 to Edwin H. Land. Another system for providing an acid-reacting reagent is disclosed in U.S. Pat. No. 3,576,625 issued Apr. 27, 1971 to Edwin H. Land.

An inert interlayer or spacer layer may be and is preferably disposed between the polymeric acid layer and the dyeable stratum in order to control or "time" the pH reduction so that it is not premature and thus interfere with the development process. Suitable spacer or "timing" layers for this purpose are described with particularity in U.S. Pat. Nos. 3,362,819; 3,419,389; 3,421,893; 3,455,686; and 3,575,701.

While the acid layer and associated spacer layer are preferably contained in the positive component employed in systems wherein the dyeable stratum and photosensitive strata are contained on separate supports, e.g., between the support for the receiving element and the dyeable stratum; or associated with the dyeable stratum in those integral film units, e.g., on the side of the dyeable stratum opposed from the negative components, they may, if desired, be associated with the photosensitive strata, as is disclosed, for example, in U.S. Pats. Nos. 3,362,821 and 3,573,043. In film units such as those described in the aforementioned U.S. Pats. Nos. 3,594,164 and 3,594,165, they also may be contained on the spreader sheet employed to facilitate application of the processing fluid.

As is now well known and illustrated, for example, in the previously cited patents, the liquid processing composition referred to for effecting multicolor diffusion transfer processes comprises at least an aqueous solution of an alkaline material, for example sodium hydroxide, potassium hydroxide, and the like, and preferably possessing a pH in excess of 12, and most preferably includes a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. The preferred film-forming materials comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Additionally, other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time are capable of utilization. The film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 100 cps, at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature.

In particularly useful embodiments of this invention, the transparent support contains a small quantity of a pigment, e.g., carbon black, to prevent fog formation due to light-piping by internal reflection within the transparent support of actinic light incident upon an edge thereof; such elements are described and claimed in the copending application of Edwin H. Land Ser. No. 194,407 filed Nov. 1, 1971 now abandoned in favor of a continuation-in-part application, Ser. No. 419,808 filed Nov. 28, 1973. Similarly, fog from such light-piping may be avoided by incorporating an alkali-dischargeable dye in a suitable layer, e.g., the image-receiving layer, in accordance with the disclosure of the copending application of Howard G. Rogers, Ser. No. 194,406 filed Nov. 1, 1971 now abandoned in favor of a continuation-in-part application, Ser. No. 408,052 filed Oct. 19, 1973. The transparent support advantageously may include an ultraviolet light absorber, as taught in the copending application of Ronald F. Cieciuch and Herbert N. Schlein, Ser. No. 214,600 filed Jan. 3, 1972 now abandoned in favor of a continuation-in-part application, Ser. No. 300,277 filed Oct. 24, 1972.

While it is generally desirable to provide the anti-reflection coating as part of the transparent support prior to applying the photographically used layers and subsequent assembly of the film unit, it is within the scope of this invention to apply the anti-reflection coating at any stage of the manufacture process that is best suited for the particular materials and components.

As discussed above, the anti-reflection coating or stratum should comprise a material having an index of refraction less than that of the transparent support. The optimum index of refraction to be exhibited by the anti-reflection coating may be readily calculated by the principles of physics previously discussed, but it is not essential that such optimum value be used in order to obtain very beneficial results. In the preferred embodiments of this invention, the transparent support is formed of a polyester having a high index of refraction, e.g., of about 1.6 or higher. The anti-reflection coating preferably has an index of refraction at least 0.20 less than, and more preferably at least 0.20 to 0.3 less than, the index of refraction of the transparent support. Since the polyester transparent supports will have an index of refraction of about 1.6 or higher, the preferred anti-reflection coatings will exhibit an index of refraction of about 1.3 to 1.45.

The fluorinated polymer may be selected from among the many well-known and readily synthesizable fluorinated polymers. The index of refraction typically decreases as the degree of fluorination is increased. Fluorinated polymers having indices of refraction of about 1.3 to 1.45 are preferred.

As stated above, the specific anti-reflection coatings with which this invention is concerned comprises one-quarter wave strata of a fluorinated polymer or blends of the same on a polyester transparent support. It has now been found that is possible to improve the abrasion resistance and/or adhesion of such fluorinated polymer layers carried by polyester supports by having an isocyanate included in the fluorinated polymer layer or disposed between the fluorinated polymer layer and the polyester support. The isocyanate has been found to be effective in quite small quantities, and to be effective with fluorinated polymers which are not crosslinked by the isocyanate. The suitability of any given isocyanate for use with any given fluorinated polymer, and the amount of isocyanate which will give useful improvements in abrasion resistance and/or adhesion to a polyester support may be determined by routine testing. Some isocyanates, particularly at a given level, may provide improved abrasion resistance with limited or no increase in the adhesion to the polyester support.

Generally speaking, the quarter-wave anti-reflection coating **26** will have an optical thickness of about 0.08 to about 0.2 micron and more preferably from about 0.12 to about 0.15 micron, or a preferred physical thickness of about 0.09 to about 0.11 micron.

The following examples are illustrative of the preparation of an element of the type shown in FIG. **4**.

EXAMPLE 1

A transparent 4 mil polyethylene terephthalate film base was coated with a 0.2 weight percent solution of Hylene M-50 (trademark of E. I. du Pont de Nemours for a 50% by weight solution of undistilled methylene-bis-(4-phenyl-isocyanate) in monochlorobenzene in dry (less than 0.1% water) methyl ethyl ketone to provide a dry coverage of about 1 mg./ft.^{2} of the isocyanate. Drying was effected at about 250° F. a quarter-wave fluorinated polymer coating was applied over this "subcoat" by applying a solution comprising, by weight, 112 parts of methyl ethyl ketone (dry), 28 parts of methyl isobutyl ketone (dry), 2.25 parts of Kynar 7201 (tradename of Pennwalt Chemical Co. for a copolymer of vinylidene fluoride and tetrafluoroethylene) and 0.4 parts of polymethyl methacrylate to give a dry coverage of about 15 mg./ft.^{2}. This coating also was dried at about 250° F. The resultant anti-reflection coating exhibited markedly greater resistance to abrasion, as compared with a similar control coating which did not have the isocyanate subcoat, when rubbed vigorously with a dry tissue, such as a Kleenex brand facial tissue. (This abrasion test procedure has been found to be severe enough to cause scratching of uncoated polyethylene terephthalate.) The fluorinated polymer coating also exhibited no separation from the polyester base, as compared with the control coating which did separate, in a cellophane tape adhesion test. (In this test, a cellophane tape such as that sold by 3M Company under the tradename "Scotch" tape is placed on the subject coating, rubbed about 20 to 30 times to insure uniform contact with the coating and then pulled off. This is considered to be a rather rigorous test of adhesion.) While isocyanates are known to be useful as cross-linking agents and adhesion aids, it was surprising to discover that the Hylene M-50 was effective to increase abrasion resistance and adhesion at such low levels. Solubility tests showed that no cross-linking had occurred.

EXAMPLE 2

The procedure described in Example 1 was repeated except that the quantity of the Hylene M-50 was 0.4 weight percent. The abrasion resistance also was greater than the control and the fluorinated polymer coating was not removed in the adhesion test.

EXAMPLE 3

The procedure described in Example 1 was repeated omitting the isocyanate subcoat and adding the Hylene M-50 (approximately 2 weight percent based upon polymer content) to the fluorinated polymer coating solution. The abrasion resistance was not quite as good as that obtained in Examples 1 to 2 but still much greater than a control in which no isocyanate was present. Adhesion of the fluorinated polymer coating to the polyester film base was comparable to that obtained in Examples 1 and 2. Use of dry methyl propyl ketone as the solvent was found to give even better results.

EXAMPLE 4

The procedure described in Example 3 was repeated using dry methyl propyl ketone and a mixture of Kynar 7201, Kel F Elastomer 3700, and polymethyl methacrylate in a weight ratio of about 51 to 21 to 28. (Kel F Elastomer 3700 is a tradename of 3M Company for a 50/50 copolymer of chlorotrifluoroethylene and vinylidene fluoride.) The coating solution contained about 5% Hylene M-50 based on polymer solids. Excellent resistance to abrasion and excellent adhesion were observed in the previously stated tests.

EXAMPLE 5

The procedure described in Example 4 was repeated using each of the following in the same weight percent as the isocyanate in the Hylene M-50: phenyl isocyanate; phenyl isothiocyanate; 3,3-dimethyoxy-4,4-biphenyl diisocyanate; hexamethylene diisocyanate; hexyl isocyanate; n-butyl isothiocyanate; and butyl isocyanate. In each instance, resistance to scratch resistance was greater than the same coating without the isocyanate. Adhesion, however, was not as good as in Examples 1–4 in that portions of the fluorinated polymer layer were removed by the cellophane tape.

As noted in Example 1, Hylene M-50 is sold as an undistilled methylene p-phenyl diisocyanate dissolved in monochlorobenzene. When a comparable solution prepared from purified methylene p-phenyl diisocyanate was used, the abrasion resistance and adhesion were not as good. It is believed that the greater abrasion resistance may be due to the presence of Hylene M-50 of some isocyanate oligomers and, indeed Hylene M-50 is described by the manufacturer as a polyisocyanate. Coating fluids containing the fluorinated polymer Hylene M-50 showed the same improvements in abrasion resistance and in adhesion even though stored at room temperature for long periods, e.g., a week, before coating.

It will be apparent from the above examples that a variety of isocyanates (aliphatic and aromatic) have been found to be useful, including diisocyanates and isothiocyanates and the term "isocyanates" is used herein to include such compounds. The quantity of isocyanate used should not be so great as to adversely affect the index of refraction of the anti-reflection layer. In general, the isocyanate is used in a ratio of about 2.5 to 7.5 weight percent based upon polymer solids, and the polymer coating solution preferably contains about 1–2% solids. The solvents used in the coating solution should be "dry", i.e., substantially free of water, and otherwise non-reactive to avoid undesirable reactions with the isocyanate. (The methyl propyl ketone used in the above examples contained about 0.02 to 0.08% water, and this minute amount of water was not found to be detrimental.) Ketonic solvents are particularly useful. Coating may be effected using a variety of techniques, including dipping, roller application, slot coating, etc.

The desired effects obtained with the Hylene M-50 do not appear to be dependent upon the presence of cross-linkable groups in the coating.

In some instances, it has been found desirable to include a minor proportion of a non-fluorinated polymer, particularly an acrylic polymer such as polymethyl methacrylate, to improve the adhesion, scratch resistance or other properties of the fluorinated polymer. If such a non-fluorinated polymer is included, its proportion should not be so great as to undesirably increase the index of refraction of the fluorinated polymer coating; if, for example, it is desirable to include polymethyl methacrylate, it has been found that it may be present in up to about 30% weight percent of the polymer blend.

Although the above examples have utilized mixtures or blends of polymers in providing the fluorinated polymer anti-reflection layer, it should be understood that such mixtures are not necessary. Also, it should be understood that the proportions of the blended polymers may vary depending upon the properties desired of the final coating and upon the conditions and method of coating. Thus, for example, the Kynar 7201 may be used alone or in blends with polymethyl methacrylate in ratios, respectively, of 100–70% and 0–30% used in Example 4 may be varied over the range 0–25 parts Kel F Elastomer 3700, 100–45 parts Kynar 7201, and 0–30 parts polymethyl methacrylate.

Other fluorinated polymers whose abrasion resistance and adhesion have been increased by the presence of the Hylene M-50 when used alone or in blends include polyvinylidene fluoride, dehydrofluorinated polyvinylidene fluoride, Fluoropolymer B (tradename of E. I. du Pont de Nemours for a 70/20/10 copolymer of vinylidene fluoride, tetrafluoroethylene and vinylbutyrate), and Vitron A (tradename of E. I. du Pont de Nemours for a 30/70 copolymer of hexafluoro propylene and vinylidene fluoride.

Polyethylene terephthalate film bases coated with anti-reflection fluorinated polymer layers as described in the above examples were used as supports for image-receiving elements of the type shown as element **32** in FIG. **1**, and integral negative-positive multicolor reflection prints was prepared in accordance with the procedure described in Example 2 of the copending application of Edwin H. Land, Stanley M. Bloom, and Howard G. Rogers, Ser. No. 246,669, filed Apr. 24, 1972 now U.S. Pat. No. 3,801,318 issued Apr. 2, 1974. Good anti-reflection properties were obtained. The general format of the resultant integral negative-positive reflection print was similar to that shown in FIG. 1 of the above-mentioned U.S. Pat. No. 3,415,644. Good anti-reflection properties were obtained.

The product shown in FIG. 4 has utility apart from use as a photographic film support. One such use is as a protective sheet laminated, anti-reflection coating outermost, to the surface of a processed photographic image, e.g., a diffusion transfer image, in accordance with the teachings of U.S. Pat. No. 2,798,021 issued July 2, 1957 to Edwin H. Land.

It will be recognized by those of ordinary skill in the art that the solvent of choice for a particular material, and the concentration of the material in the coating solution, may be readily determined by routine experimentation. Obviously the solvent should be one which will not adversely affect, mechanically or optically, the transparent support upon which it is coated.

The transparent support advantageously has a moisture permeability rate adapted to accelerate "drying" of the layers forming the integral negative-positive reflection prints of the preferred embodiments. Reference may be made to U.S. Pat. No. 3,573,044 issued Mar. 30, 1971 to Edwin H. Land for a detailed description of dimensionally stable, transparent polyester supports, e.g., microporous polyesters, having suitable permeability rates, and said description is hereby incorporated herein for convenience. It will be understood that selection of an anti-reflection coating should not adversely affect the desired moisture transmission rate of the transparent support(s).

While the image dye-providing material is generally carried on the same support as the photosensitive silver halide, it will be understood that this initial location is not essential, as in forming monochromes the image dye-providing material may initially be contained in the processing composition or in a layer of the image-receiving element as is taught, for example, in the use of dye developers in the previously mentioned U.S. Pat. No. 2,983,606.

The provision of an anti-reflection coating provides a number of advantages. In the absence of the anti-reflection coating, the optimum angle for viewing an image through the transparent support is very specific and limited, if the viewer is to avoid to the maximum possible extent seeing specular reflection from the surface of the transparent support of light from the illumination source. Such anti-reflection coating have been found to substantially reduce or prevent such specular reflection, thus greatly improving viewing. The resulting images exhibit increased color saturation and density and "cleaner" whites, i.e., reduced minimum densities. The avoidance of light loss during photoexposure is useful also in films wherein exposure is effected through a transparent support but the final image is separated and not viewed through a transparent support. The reduction in surface reflection (glare) simplifies copying prints and aids in obtaining truer copy prints; light polarizers are customarily used to eliminate surface glare during copying.

Where the expression "positive image" has been used, this expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive emulsion layers. As an example of an alternative meaning for positive image, assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive emulsion layers will be a positive and the dye image produced on the image-carrying layer will be a negative. The expression positive image is intended to cover such an image produced on the image-carrying layer.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic product for use in diffusion transfer processes comprising a transparent polyester support carrying on one side thereof an image-receiving layer, the other side of said transparent polyester support carrying an anti-reflection coating, said anti-reflection coating having an index of refraction less than said polyester support and comprising a quarter-wave stratum of a fluorinated polymer and an isocyanate in said stratum or between said stratum and said transparent polyester support, said isocyanate being present in a quantity effective to increase the abrasion resistance of said fluorinated polymer stratum.

2. A photographic product as defined in claim **1**, including at least one layer containing photosensitive silver halide carried on said first side.

3. A photographic product as defined in claim **2**, including an image dye-providing material in a layer contiguous to said silver halide containing layer.

4. A photographic product as defined in claim **1** wherein said image-receiving layer includes a mordant for a dye.

5. A photographic product as defined in claim **1** wherein said image-receiving layer is a silver receptive layer containing a silver precipitant.

6. A photographic product as defined in claim **4** wherein said dye is a dye developer.

7. A photographic product as defined in claim **1** wherein said transparent support has an index of refraction of at least about 1.6.

8. A photographic product as defined in claim **7** wherein said polyester is a polyethylene terephthalate.

9. A photographic product as defined in claim **1** wherein said anti-reflection coating has an index of refraction at least about 0.20 less than said transparent support.

10. A photographic product as defined in claim **7** wherein said anti-reflection coating has an index of refraction of about 1.3 to about 1.45.

11. A photographic product as defined in claim **1** wherein said image dye-providing material is a compound which provides a diffusible dye as a function of oxidation or color coupling.

12. A photographic product as defined in claim **2** including an image-receiving layer, said layer of silver halide being positioned between said support and said image-receiving layer.

13. A photographic product as defined in claim **1** wherein said fluorinated polymer stratum includes a vinylidene fluoride copolymer.

14. A photographic product as defined in claim 1 wherein said fluorinated polymer stratum includes a copolymer of vinylidene fluoride and chlorotrifluoroethylene.

15. A photographic product as defined in claim 1 wherein said fluorinated polymer stratum includes a copolymer of vinylidene fluoride and tetrafluoroethylene.

16. A photographic product as defined in claim 1 wherein said fluorinated polymer stratum includes a copolymer of vinylidene fluoride and hexafluoropropylene.

17. A photographic product as defined in claim 1 wherein said polyester film has a thickness of about 3 to 10 mils.

18. A photographic product as defined in claim 1 wherein said fluorinated polymer stratum includes polymethyl methacrylate.

19. A photographic product as defined in claim 1 wherein said isocyanate is a polyisocyanate.

20. A photographic product as defined in claim 1 wherein said isocyanate is methylene-bis-(4-phenylisocyanate).

21. A photographic product as defined in claim 1 wherein said isocyanate is present in said fluorinated polymer stratum at a concentration of about 0.5 to 8 percent by weight of said polymer stratum.

22. A photographic product as defined in claim 1 wherein said isocyanate is coated at a concentration of about 1 mg./ft.^{2} between said polyester support and said fluorinated polymer stratum.

23. A photographic film product comprising a first support and a second support, at least one of said supports being a transparent polyester support, a photosensitive layer carried on one of said supports, and a rupturable container releasably holding a processing composition adapted, when distributed between predetermined layers carried by said supports, to develop said photosensitive layer and provide an image viewable through said transparent polyester support, the external surface of said transparent polyester support carrying an anti-reflection coating, said anti-reflection coating having an index of refraction less than said polyester support and comprising a quarter-wave stratum of a fluorinated polymer and an isocyanate in said stratum or between said stratum and said transparent polyester support, said isocyanate being present in a quantity effective to increase the abrasion resistance of said fluorinated polymer stratum.

24. A photographic product as defined in claim 22 wherein both of said supports are transparent polyester supports and each carries said anti-reflection coating on the external surface thereof.

25. A photographic product as defined in claim 22 including an image-receiving layer and means adapted to provide a masking layer between said photosensitive layer and said image-receiving layer to mask the developed photosensitive layer when the image in said image-receiving layer is viewed through said transparent polyester support.

26. A photographic product for forming a diffusion transfer image in dye within a permanent laminate including at least one developed silver halide layer, said photographic product comprising, in combination, an image-receiving layer; at least one silver halide emulsion, each said silver halide emulsion having associated therewith an image dye-providing substance selected from the group consisting of image dyes and image dye intermediates; means providing a light-reflecting layer between said image-receiving layer and said silver halide emulsion(s) to mask said silver halide emulsion(s) after development thereof and to provide a white background for viewing a dye image in said image-receiving layer; a transparent polyester support through which image-receiving layer may be viewed; means providing a processing composition for developing said silver halide emulsion(s) after photoexposure and for forming a transfer image in at least one dye in said image-receiving layer; said product including an anti-reflection coating on the outer surface of said transparent polyester support, said anti-reflection coating having an index of refraction less than said polyester support and comprising a quarter-wave stratum of a fluorinated polymer and an isocyanate in said stratum or between said stratum and said transparent polyester support, said isocyanate being present in a quantity effective to increase the abrasion resistance of said fluorinated polymer stratum.

27. A photographic film as defined in claim 26 wherein each said dye is a dye developer.

28. A photographic film as defined in claim 26 wherein each said image dye-providing substance is an intermediate for an image dye.

29. A photographic product as defined in claim 26 wherein said silver halide emulsion(s) are adapted to be exposed through said transparent polyester support.

30. A photographic product as defined in claim 26 wherein said means providing a light-reflecting layer comprise a white pigment dispersed in said processing composition, and said processing composition is contained in a rupturable container positioned to distribute said processing composition containing said pigment between said image-receiving layer and said silver halide emulsion(s).

31. A photographic product as defined in claim 26 comprising a temporary laminate including said layers confined between two dimensionally stable supports, at least one of said supports being a transparent polyester support, the bond between a predetermined pair of layers being weaker then the bond between other pairs of layers, and including a rupturable container releasably holding said processing composition, said rupturable container being so positioned as to distribute said processing composition between said predetermined layers, said processing composition being adapted to provide said permanent laminate following distribution and drying.

32. A photographic product as defined in claim 26 wherein said transparent support has an index of refraction of at least about 1.6.

33. A photographic product as defined in claim 31 wherein said polyester is a polyethylene terephthalate.

34. A photographic product as defined in claim 26 wherein said anti-reflection coating has an index of refraction at least about 0.20 less than said transparent polyester support.

35. A photographic product as defined in claim 32 wherein said anti-reflection coating has an index of refraction of about 1.3 to 1.45.

36. A photographic product comprising a first support; a red-sensitive silver halide emulsion; a green-sensitive silver halide emulsion; and a blue-sensitive silver halide emulsion; said silver halide emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer;

an image-receiving layer for receiving image dyes transferred thereto by diffusion as a function of exposure and development of said silver halide emulsion layers; a second support which is a transparent polyester support through which said image-receiving layer may be viewed; a rupturable container releasably holding a processing composition adapted, upon distribution between predetermined layers of said film to develop said silver halide emulsions and to effect the formation of a transfer image in dye in said image-receiving layer, said processing composition also being adapted to provide a permanent laminate including said developed silver halide emulsions and said image-receiving layer; and means providing a light-reflecting layer between said image-receiving layer and said silver halide emulsions effective to provide a white background for viewing said transfer image and for masking said developed silver halide emulsions; said product including an anti-reflection coating on the outer surface of said transparent polyester support, said anti-reflection coating having an index of refraction less than said polyester support and comprising a quarter-wave stratum of a fluorinated polymer and an isocyanate in said stratum or between said stratum and said transparent polyester support, said isocyanate being present in a quantity effective to increase the abrasion resistance of said fluorinated polymer stratum.

37. A photographic product as defined in claim **36** wherein said first support is opaque.

38. A photographic product as defined in claim **36** wherein said transparent polyester support and said image-receiving layer comprise a separate element adapted to be brought into superposed relationship with said silver halide emulsions.

39. A photographic product as defined in claim **36** wherein said layers are held in fixed relationship between said supports prior to and during exposure.

40. A photographic product as defined in claim **39** wherein said fixed relationship is provided by a binder tape along at least two parallel sides of said product.

41. A photographic product as defined in claim **39** wherein said product is a laminate of said layers between said first and said second supports, the bond between a pair of predetermined layers being weaker than the bonds between the other layers, said rupturable container being so positioned as to release said processing composition for distribution between said pairs of layers.

42. A photographic product as defined in claim **36** wherein said silver halide emulsions are present as separate planar layers.

43. A photographic product as defined in claim **36** wherein said silver halide emulsions are present in the form of minute elements arranged in side-by-side relationship in a photosensitive screen pattern.

44. A photographic product as defined in claim **42** wherein said blue-sensitive silver halide emulsion layer is between said image-receiving layer and said other silver halide emulsion layers.

45. A photographic product as defined in claim **42** wherein said blue-sensitive silver halide emulsion layer is between said first support and said other silver halide emulsion layers, and said first support is a transparent polyester support.

46. A photographic product as defined in claim **45** wherein said transparent polyester first support carries an anti-reflection coating on the outer surface thereof, said anti-reflection coating having an index of refraction less than said polyester first support and comprising a quarter-wave stratum of a fluorinated polymer and an isocyanate in said stratum or between said stratum and said transparent polyester first support, said isocyanate being present in a quantity effective to increase the abrasion resistance of said fluorinated polymer stratum.

47. A photographic laminate comprising (a) at least one exposed and developed silver halide layer, (b) an image-carrying layer containing an image in at least one dye, (c) a light-reflecting, white layer positioned between said silver halide layer or layers and said image-receiving layer and effective to mask said developed silver halide layer or layers, and (d) a transparent polyester layer through which said image may be viewed against said white layer, said layers being permanently laminated together, said transparent polyester layer having an anti-reflection coating on the outer surface thereof, said anti-reflection coating having an index of refraction less than said polyester layer and comprising a quarter-wave stratum of a fluorinated polymer and an isocyanate in said stratum or between said stratum and said transparent polyester support, said isocyanate being present in a quantity effective to increase the abrasion resistance of said fluorinated polymer stratum.

48. A photographic image comprising a transparent polyester support carrying on one side thereof an image-carrying layer containing an image in dye or silver, the other side of said transparent polyester support carrying an anti-reflection coating, said dye image being viewable through said anti-reflection coating and said transparent polyester support, said anti-reflection coating having an index of refraction less than said polyester support and comprising a quarter-wave stratum of a fluorinated polymer and an isocyanate in said stratum or between said stratum and said transparent polyester support, said isocyanate being present in a quantity effective to increase the abrasion resistance of said fluorinated polymer stratum.

49. A photographic image as defined in claim **48** wherein said transparent polyester support has an index of refraction of at least 1.6 and said anti-reflection coating has an index of refraction of at least about 0.20 less than said transparent support.

50. A photographic product as defined in claim **49** wherein said anti-reflection coating has an index of refraction of about 1.3 to about 1.45.

51. A photographic product as defined in claim **1** wherein said isocyanate is present in a quantity of about 1 to 2 mg./ft.^{2}.

52. A photographic product as defined in claim **1** wherein said isocyanate is a polyisocyanate.

53. A photographic product as defined in claim **1** wherein said quantity of said isocyanate is also effective to increase the adhesion of said fluorinated polymer stratum to said polyester film base.

* * * * *